$a_0 = 2$

5/5/2018

Co-ordination Compounds

$$\text{Salt}_{1\,(aq.)} + \text{Salt}_{2\,(aq.)} \xrightarrow[\text{Add}^n\ \text{Rxn}]{\text{cryst.}} \text{Add}^n\ \text{cmpd.}\ (\text{Adduct})$$

- $KCl_{(aq.)} + MgCl_{2\,(aq.)} \xrightarrow[\Delta]{\text{cryst}} \underset{\text{carnellite}}{KCl\cdot MgCl_2\cdot 6H_2O} \xrightarrow{H_2O}$ completely ionize K^+, Cl^-, Mg^{2+}

- $CuSO_4 + 4NH_3 \longrightarrow CuSO_4\cdot 4NH_3$

- $4KCN + Fe(CN)_2 \longrightarrow 4KCN\cdot(Fe(CN)_2) \xrightarrow{H_2O}$ completely ionize

  K^+ ✓, $\cancel{Fe^{2+}, CN^-}$

* Types of Addition compound :

1] Double salt :- which ionise completely in aq. medium. All ions show their presence in aq. medium

	Type of ions in aq.	No. of ions
A) carnellite $KCl\cdot MgCl_2\cdot 6H_2O$	$3\ (K^+, Mg^{2+}, Cl^-)$	5
B) Mohr's salt $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$	$3\ (Fe^{2+}, SO_4^{2-}, NH_4^+)$	5
c) Alums	$3\ (X^+, Y^{3+}, SO_4^{2-})$	8

↓

General formula ⇒ $X_2SO_4\cdot Y_2(SO_4)_3\cdot 24H_2O$

Hg
Cu
Hg
Pb

$\Rightarrow XY(SO_4)_2 \cdot 12H_2O \quad \Rightarrow [X(H_2O)_6]^{+}[Y(H_2O)_6]^{3+}(SO_4)_2$

$X^{+} \Rightarrow$ $^{+}$, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, NH_4^{+}

$Y^{3+} \Rightarrow Cr^{3+}, Fe^{3+}, Al^{3+}$

Q. Find the formula of an Alum which gives following observation :

i) gives ppt with $BaCl_2$
$BaSO_4$

ii) gives a volatile product & coloured ppt when reacted with NaOH
$Y^{3+} = Cr^{3+}, Fe^{3+}$

$NH_4Cr(SO_4)_2 \cdot 12H_2O$

iii) gives a volatile product & coloured solⁿ when reacted with Na_2O_2
$X = NH_4^{+}$

Also find the colour of solⁿ when it reacts with excess Na_2O_2.

→ $NH_4Cr(SO_4)_2 \cdot 12H_2O$; Yellow

2] Complex Salt :- does not ionise completely in aq. medium. some of the ions lose their identity in aq. medium.

	Type of ions in aq. medium	No. of ions in aq. med.
A) $4KCN \cdot Fe(CN)_2$ $= K_4[Fe(CN)_6]$		

theo. $3(K^+, CN^-, Fe^{3+})$ 11

Pract. $2(K^+ [Fe(CN)_6]^{4-})$ 5

- Charge on complex is sum of O.S. of C.M.I & ligands

- Space in 3-D where co-ordinate bond form b/w ligand & C.M.I is called co-ordination sphere.

- Simple ions which ionic bond with complex ion are called counter ions.

- Space in 3-D where complex ion forms ionic bond with opp. charge ions is called ionization sphere.

- species in co-ordin^n sphere is non-ionisable while species in ionisation sphere is ionisable.

- Geometry around C.M.I is called co-ordination polyhedra.
  Eg, tetrahedral (4), Sq. planar (4).

- Species in sq. bracket represent co-ordination entity.

- Co-ordination no. is property of CMI, no. of co-ordinate bond formed by CMI is called its C.No.

+3 O.S. of 3d series = 6 always
+2 O.S. of 3d series = 4/6
Ni^{2+} (OH_2 / NH_3) = 6
(Cl^- / CN^-) = 4

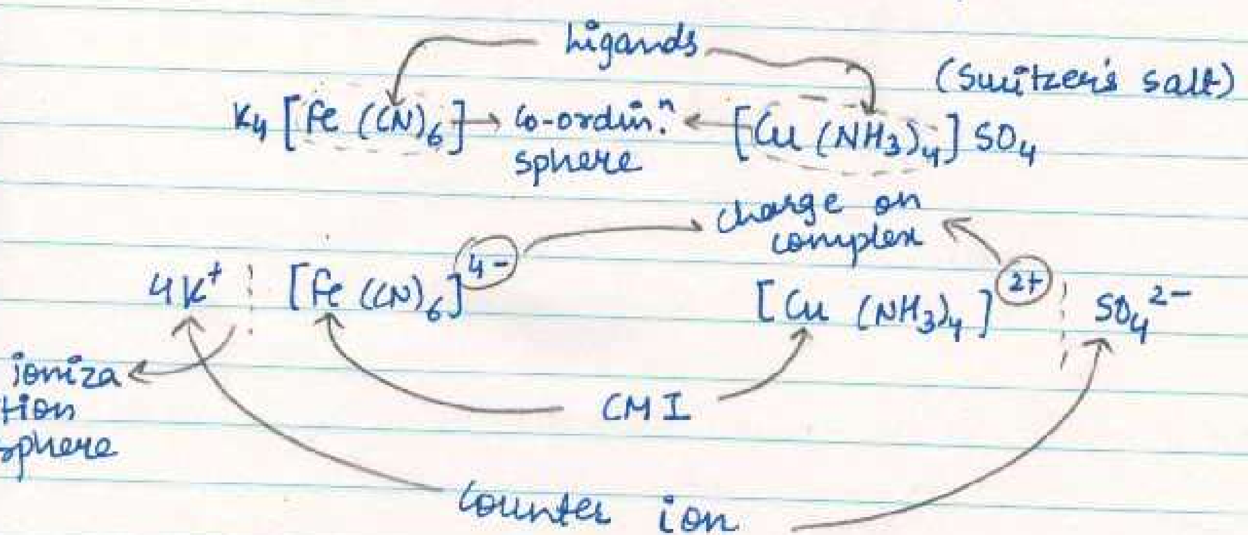
* Basic Terminology :→

- Ions which lose their identity in aq. sol^n are written in square bracket are called complex ions & compound containing such ions are called complex compound.

- In complex ion atleast one metal ion is present which is centre of complex ion, acts as lewis acid is called central metal ion [CMI].

- CMI is surrounded by neutral molecule and ions which act as lewis base and are called ligands.

- Complex formation is a lewis acid-base rxn in which co-ordinate bond is present b/w CMI & ligands, thats why, complex cmpds are also known as co-ordination compounds.



* Classification of Ligands :

1) On the basis of charge :

Cationic	Anionic	Neutral
-ium suffix is used NO^+ → Nitrosylium/ Nitrosonium $N_2H_5^+$ → Hydrazinium	ide → ido ite → ito ate → ato SO_4^{2-} → sulphato O^{2-} → oxido SO_3^{2-} → sulphito $C_6H_5^-$ → phenyl CH_3^- → methyl	- Common name except H_2O → aqua NH_3 → ammine CO → Carbonyl NO → Nitrosyl C_6H_6 → benzene PH_3 → Phosphene

2) On the basis of denticity :

- Having one donor site = monodentate

Eg : H^-, F^-, Cl^-, Br^-, I^-, H_2O, OH^-, NH_3, NH_2^-, NH^{-2}

- Having two donor site

A) form three membered ring with CMI = Monodentate

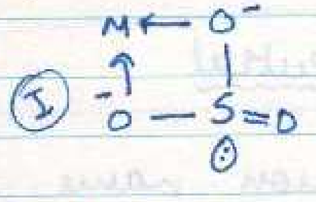
3-membered ring
Angle strain ↑ (Unstable)

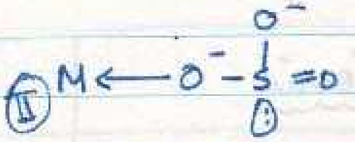
$M \leftarrow O = O$
Stable

Eg : CN^-, SCN^-

B] Form four membered ring with CMI

eg : SO_3^{2-}





comfort

- Stable in comp. of 3-m ring but unstable due to angle strain.
- More stable in comp. of 1st structure.

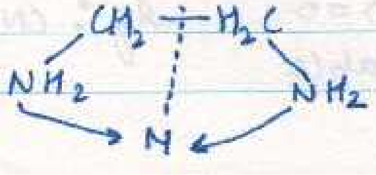
Such ligands are called flexident coz they show variable denticity, as per requirement of C. No. of central metal ion they can act as bidentate ligand.

$[Cr(NH_3)_5 SO_4] Br$ ← Monodentate

$[Cr(NH_3)_4 SO_4]$ ← Bidentate

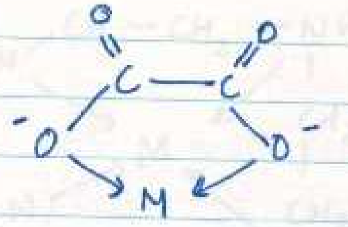
C] Form 5/6/7 membered ring are called bidentate/ didentate

- (en) ethylenediamine (ethane 1-2 diamine)



Symm.

- (ox^{-2}) Oxlato $C_2O_4^{2-}$

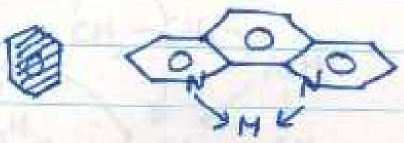


symm.

- dipyridine (dipy)

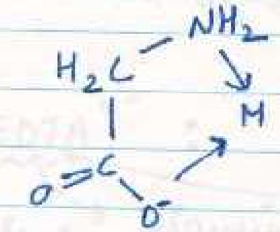
symm.

- Phenanthrolene (Phen)



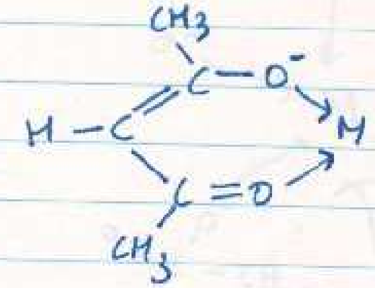
symm.

- glycinato (gly^-)



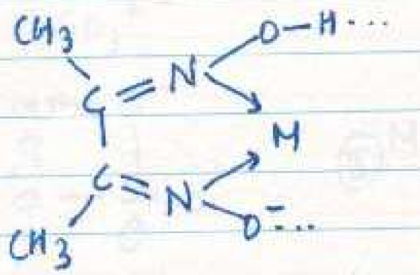
Unsymm.

- Acetylacetonato $(acac^-)$



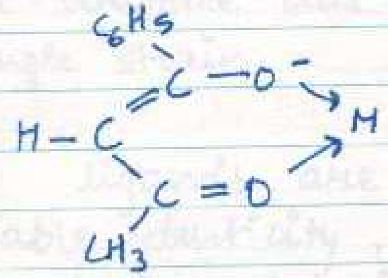
Symm.

- dimethylglyoximato (dmg⁻)



Unsymm.

- benzylacetonato (bcac⁻)



Unsymm.

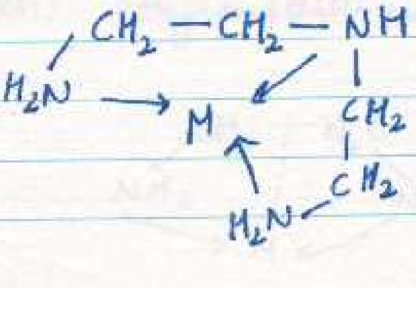
- having,

3 donor site → tridentate
4 donor site → tetradentate
5 donor site → pentadentate
6 donor site → Hexadentate

} Polydentate

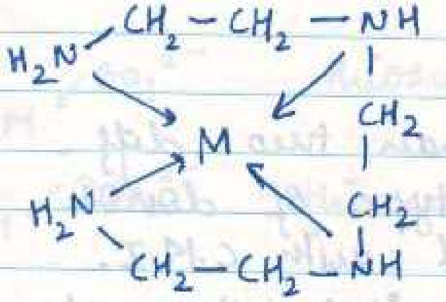
eg,

dien (diethylene tri amine)



tridentate

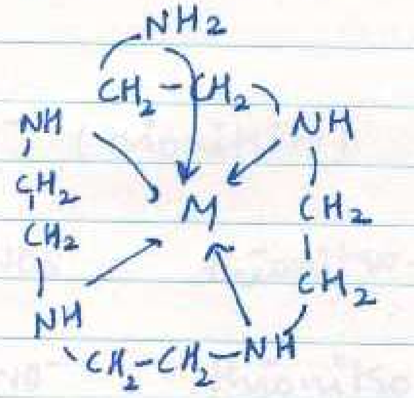
trien (triethylene tetra amine)



tetradentate

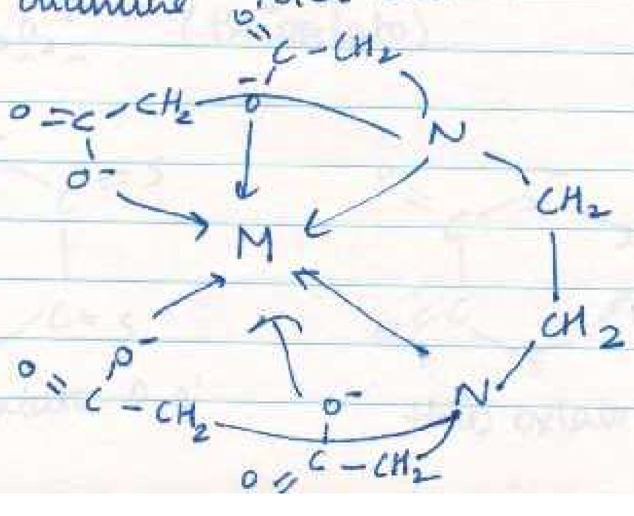
- Pentadentate (teten) :

tetra ethylene penta amine



- $EDTA^{4-}$:

ethylene diamine tetra acetato



$\angle MNO = 8$

• Special case :

1] Ambidentate ligands :

-ve

• Ligands having two or more than two diff. donor site but uses only one type of donor site at a time when co-ordinated with C.M.I.

• In naming of such ligands, capital letter of donor site is written as suffix.

a) CN^- $[:C\equiv N:]^-$

$M \leftarrow C\equiv \bar{N}$ cynido - C

$M \leftarrow N\equiv C^-$ cynido - N

b) SCN^- $[\ddot{\underset{..}{S}} = C = \ddot{\underset{..}{N}}]^-$

$M \leftarrow SCN^-$ Thiocyanato - S

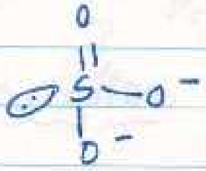
$M \leftarrow NCS^-$ thiocynate - N

c) OCN^-

$M \leftarrow OCN^-$ Cyanato - O

$M \leftarrow NCO^-$ Cyanato - N

d) SO_3^{2-}



$M \leftarrow SO_3^{2-}$ thiosulphato-S

$M \leftarrow OSO_2^{2-}$ thiosulphato-O

e) NO_2^-

$M \leftarrow NO_2^-$ Nitrito-N / Nitro

$M \leftarrow ONO^-$ Nitrito-O / Nitrito

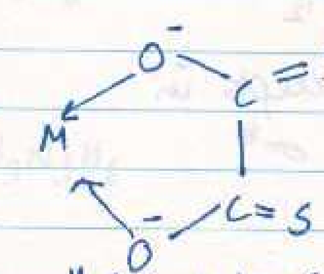
f) NOS^- (thionitrito)

$M \leftarrow NOS^-$ thionitro-N

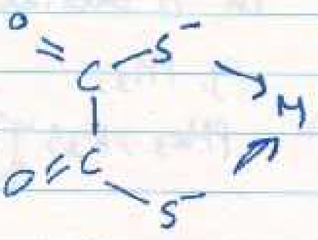
$M \leftarrow SNO^-$ thionitro-S

$M \leftarrow ONS^-$ thionitro-O

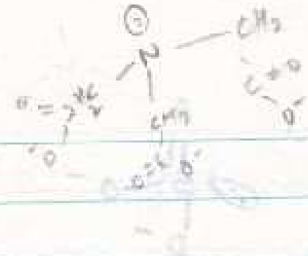
g) $C_2S_2O_2^{2-}$ (thiooxlato)



thio oxlato-O,O'



thio oxlato-S,S'



Q. Calculate dentisity of :

i] $[N(CH_2COO)_3]^{3-}$ 4

NTA^{3-}

ii] $[N(CH_2-CH_2NH_2)_3]$ 4

* Classification of ligands on the basis of bonding pattern :

Classical
- (only donor)

$\boxed{M \leftarrow L}$

H^-, F^-, ~~Cl^-~~, ~~N_2~~, H_2O, OH^-, NH_3, NH_2^-, NH^{-2}, O^{-2}, N^{-3}, en
(2^{nd} pd. donor atom per π bond nahi hona chahiye)

Non-classical
- (donor as well as acceptor)
- π-acid ligands

$\boxed{M \leftarrow L}$ synergic bonding

l.p. / σ-donor
π acceptor

- accepts e^- in π*
(Having π bond on donor atom)
- accepts e^- in d orbital
eg, PH_3, PMe_3, R_2S
- H_2
accepts in σ*

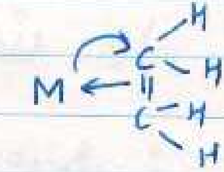
π donor
π acceptor

* π-donor, π-acceptor :

- They are not lewis base but they act as ligand in complex formation coz they share their π-e^- with vacant orbital of metal & accept es^- from filled d-orbital of metal into their vacant π^*. So due to synergy metal ligand B.O. ↑ as a ligand their stability ↑. Such ligands are written with prefix,

η^x where,

$x \rightarrow$ hapticity of ligand (no. of donor atoms participating in donation)

ligand	Bonding Pattern	no. of e^- in do.	name
• C_2H_4		2	η^2-ethylene / π-ethylene
• $CH_2=CH-CH=CH_2$		4	η^4-butadiene / π-butadiene
• C_6H_6		6	η^6-benzene / π-benzene
• $B_3N_3H_6$		6	η^6-borazine / π-borazine

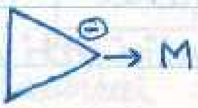
- $C_5H_5^-$ (cyclopentadienyl) (cp)

a)  2 η¹-cp / σ-cp

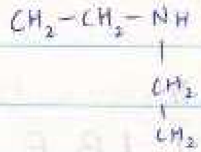
b)  4 η³-cp

c)  6 η⁵-cp / π-cp

- $C_3H_5^-$
  - allyl $CH_2=CH-CH_2^-$
    - a) $M \leftarrow \bar{C}H_2-CH=CH_2$ 2 η¹-allyl / σ-allyl
    - b) $CH_2 \overset{\cdots}{-} \underset{\underset{M}{\downarrow\uparrow}}{CH} \overset{\cdots}{-} CH_2$ 4 η³-allyl / π-allyl
  - cyclopropyl

 η¹-cyclopropyl (2)

Q. Matrix Match



A) gly⁻ i) same donor atoms

B) dipy ii) diff. donor atoms

C) bn iii) optically active

D) pn iv) forms 5-membered ring

v) unsymmetrical bidentate

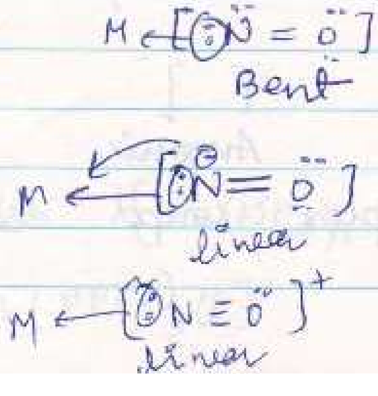
→ C → i ; iii , iv)
A → ii ; iv ; ~~iii~~ v ;
B → i ; iv ;
D → i ; iii ; iv ; v

* <u>On the basis of fixed & variable charge</u> :

1] Innocent Ligand : Having fixed O.S.
eg. Cl^-, OH^-, H_2O, NH_3 , etc.

2] Non-innocent Ligand : Can show diff. diff. O.S
eg. $(O_2) \rightarrow O_2 , O_2^- , O_2^{2-}$

$(NO) \rightarrow \underbrace{NO , NO^+}_{M} , \underset{2}{NO^-}$



They can be distinguished by,

i) B.O.
ii) B.L. / B.E.
iii) No. of unpaired e^-
iv) Geometry around donor site.

eq. NO_2^- ONO^- { NO_2^- is an innocent ligand }

Tri. Planar

Bent

v) Confⁿ of central metal ion
vi) U.P e^- of CMI
vii) O.S of CMI

Q. $K_2[Zn(CN)_2(O_2^-)_2] \xrightarrow{Reagent} [Zn(CN)_2(O_2^{\circ})_2]$

Find diff in no of π^- b/w I & II

⟶ 1x2 = 2

* Classification of Complexes :

i] On the basis of charge,

$[\;]^+$ cationic $[\;]^-$ Anionic $[\;]^{\circ}$ neutral

So complex cmpd can be

i] simple cation + complex anion

ii] complex cation + simple anion

iii] complex anion + complex anion

iv] Neutral complex

eg of i)

a) Fischer's salt $K_3[Co(NO_2)_6]$
(Yellow ppt)

b) Sodium nitro prusside $Na_2[\overset{+2}{Fe}(CN)_5\overset{+1}{NO}]$

$\longrightarrow [Fe(CN)_5X]^{-n}$

eg of ii)

a) Browning complex $[Fe(H_2O)_5NO]SO_4$

eg of iii)

a) $[Cr(NH_3)_6][Co(NO_2)_6)$

eg of iv)

a) cis-platin (anticancer) cis-$[Pt(NH_3)_2Cl_2]$

b) Wilkinson catalyst $[Rh(PPH_3)_3Cl]$

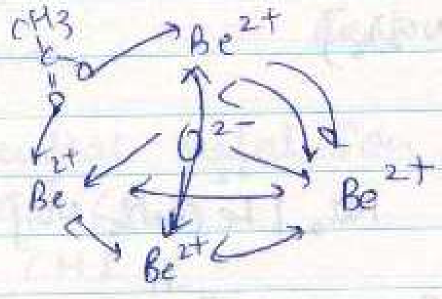
ii] On the basis of no. of CMI

a) Mononuclear : Having one CMI

eq. Cis-platin

b) bi/polynuclear : Having more than one CMI

eq. $[Be_4O(CH_3COO)_6]$



iii] On the basis of types of ligand

a) Homoleptic : only one type of ligand

b) Heteroleptic : more than one type of ligand

iv] On the basis of donation of ligands

A) σ complexes : Having only lone pair donor

Cis-platin

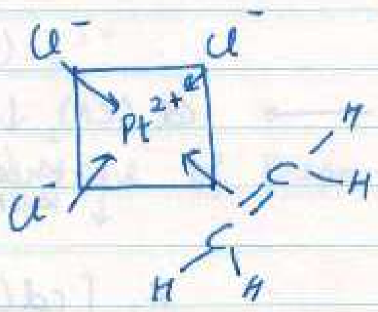
DPP # 6
Q.1→30

B] π- complexes : Having atleast one π donor

eg.
- $Cr(C_6H_6)_2$

- ferrocene
  $Fe(C_5H_5)_2$

- Ziese's salt
  $K[PtCl_3(\eta^2-C_2H_4)]$



C_2H_4 & $PtCl_3$ plane is ⊥er to each other

v] On the basis of Stability :

$$M^{+x} + nL \rightleftharpoons [ML_n]^{+x}$$

$$K_s / K_f = \frac{[ML_n^{+x}]}{[M^{+x}][L]^n}$$

↑
stability constant

K_f ↑ forward rxn ↑
stability of complex ↑
conc. of simple ions ↓

a) Perfect complex : Stable in presence of particular reagent.
Having high value of K_f.

b) Imperfect complex : Unstable in presence of particular reagent.
Having low value of K_f

- $CuSO_4 + KCN \longrightarrow \overset{+2}{Cu}(CN)_2 + K_2SO_4$

$$\overset{+2}{Cu}(CN)_2 \xrightarrow{RT} CuCN\downarrow + (CN)_2$$

$$CuCN \xrightarrow{\text{excess } KCN} K_3[\overset{+1}{Cu}(CN)_4] \xrightarrow{H_2S} \text{no rxn}$$

Perfect w.r.t. H_2S

- $CdSO_4 + KCN \longrightarrow Cd(CN)_2\downarrow$

$$Cd(CN)_2 \xrightarrow{\text{excess } KCN} K_2[Cd(CN)_4] \xrightarrow{H_2S} CdS\downarrow$$

Imperfect w.r.t. H_2S

* Q.

in	AgCl	AgBr	AgI	Ag_2S
H_2O	×	×	×	×
cold NH_3	✓	×	×	×
Hot NH_3	✓	✓	×	×
$S_2O_3^{2-}$	✓	✓	✓	×
CN^-	✓	✓	✓	✓

✓ = soluble
× = insoluble

DPP # 6
Q.1 → 30

Matrix, Imperfect in presence of

A] $[\overset{+}{Ag}(H_2O)_2]^+$ P) Cl^-

B] $[\overset{+}{Ag}(NH_3)_2]^+$ Q) Br^-

C] $[\overset{2+}{Ag}(S_2O_3)_2]^{3-}$ R) I^-

D] $[\overset{+}{Ag}(CN)_2]^-$ S) S^{2-}

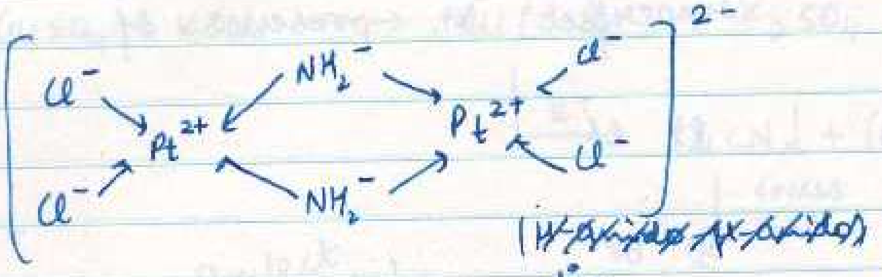
T) None of these

→ A - P, Q, R, S
B - ~~P, Q~~ R, S or Q, R, S
C - ~~P, Q, R, S~~ S
D - [illegible] T

- Chelating ligands :→ those who form ring like structure with CMI (bidentate, polydentate)
Ring formation is called chelation.

- Bridging ligands :→ In polynuclear complexes, ligands joins two or more than two CMI. such ligands are written with μ_n prefix where n = no. of CMI which are directly bonded with a ligand.

Q.



~~(μ-amido μ-amido)~~

→ • dichloridoplatinate (II) - $\overset{\text{di-}}{\wedge}$ μ- amido - dichloridoplatinate (II)
- di-μ-amido bis(dichlorido platinate (II))
- di-μ-amido tetrachlorido diplatinate (II)
- bis-μ-amido dichlorido platinate (II)

* Synergic Bonding :

↖ give & take

$$M \rightleftarrows L$$

↳ π-acid ligands

i] in metal carbonyls ($M(CO)_x$:→

Accⁿ to VBT,

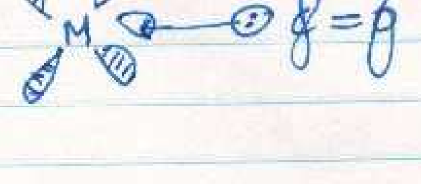
$:C \equiv O:$

BO = 3 EN C < O

donor site 'C'

more EN 'O' donates l.p. to less EN 'C'.

in carbonyl complexes



EN, M < C < O

'c' ko e^- lene mai maja metal se jyada aayega, jaise metal se donation ↑ hoga 'O' apna l.p. withdraw kar lega, metal–c BO ↑

CO BO ↓

CO BE ↓ CO BL ↑

$1 < \text{BO MC} < 2$

$2 < \text{BO CO} < 3$

Acc^n to MOT

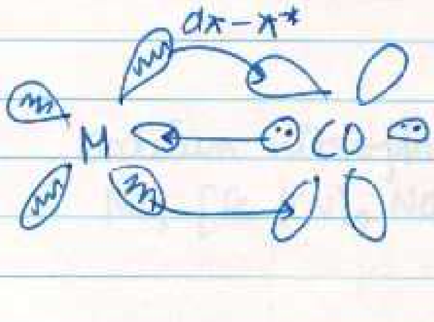
NBMO of 'c' $\longrightarrow$:CO: $\longleftarrow$ NBMO of 'o'

BO = 3, $14e^-$ system

energy of NBMO of 'c' > energy of NBMO of 'o'
So donor atom is 'c'.

HOMO of CO is σ_{NBMO} having slight AB ch^r
LUMO of CO is π^* having 100% AB ch^r

due to donation, BO of CO ↑ slightly
due to acceptance, BO of CO ↓ rapidly
So, due to synergic bonding
Net CO BO ↓ $2 < \text{CO BO} < 3$



Q. If CO BO in $Cr(CO)_6$ is x then comment on CO BO in

A) CO $> x$

B) $BH_3 \leftarrow CO$ $> x$

C) $Cr(CO)_6^+$ $> x$

D) $Cr(CO)_6^-$ $< x$

E) $V(CO)_6^-$ $< x$

F) $Mn(CO)_6^+$ $> x$

G) $[Cr(CO)_5NH_3]$ $< x$ → Classical one l.p. donor b/w 5 CO

H) $[Cr(CO)_5PF_3]$ $> x$

I) $[Cr(CO)_5PCl_3]$ $< x$

Acceptance tendency of
$PF_3 > CO > PCl_3$

Practical evidence of CO BL / Stretching freq. Method :

As strength of spring ↑
to stretch string required energy ↑
$E = h\nu$
Stretching frequency (ν) ↑

As like spring,

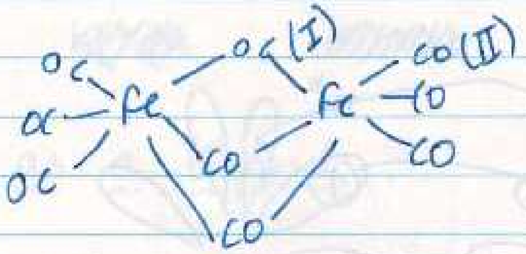
As CO BO ↑
CO BE ↑
Stretching frequency of CO ↑

Q. Compare stretching frequency of CO

A) $Cr(CO)_4 > Cr(CO)_4^-$

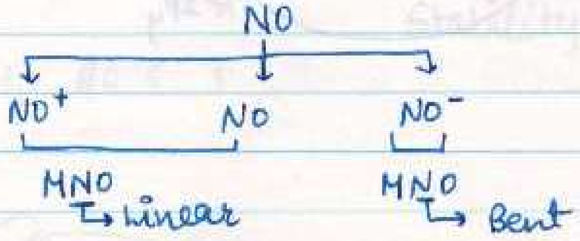
B) $[Cr(CO)_5PF_3] > [Cr(CO)_5PCl_3] > [Cr(CO)_5PMe_3]$

C) $[Cr(CO)_6] > [Cr(CO)_5NH_3] > [Cr(CO)_4(en)]$

D)


II > I

* NO as a ligand :



• How to distinguish b/w NO & NO⁺

eg ⇒ Brown ring complex $[Fe(H_2O)_5NO]SO_4$

- Fe^{2+} NO ≈ 2V (unstable)
- Fe^{+} NO^+ ≈ 0V (stable)

Sodium nitroprusside $Na_2[Fe(CN)_5NO]$

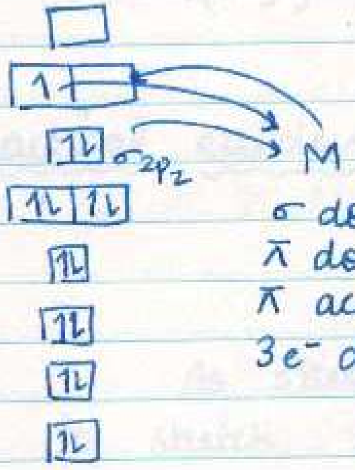
- Fe^{3+} NO 3V (unstable)
- F^{2+} NO^+ 1V (stable)

- $Cr(NO)_4$ — Cr NO ≈ 0V (stable)
  — Cr^{4-} NO^{+} 5V (unstable)

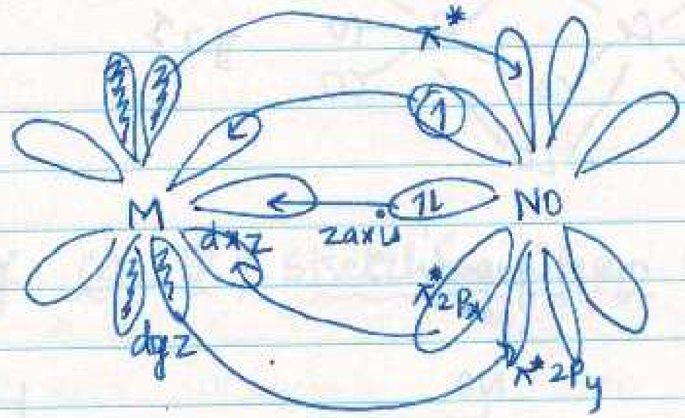
- $Fe(CO)_2(NO)_2$ — Fe^{0} NO 2V (stable)
  — Fe^{2-} NO^{+} 3V (unstable)

→ Synergic bonding in $MNO^{(0)}$

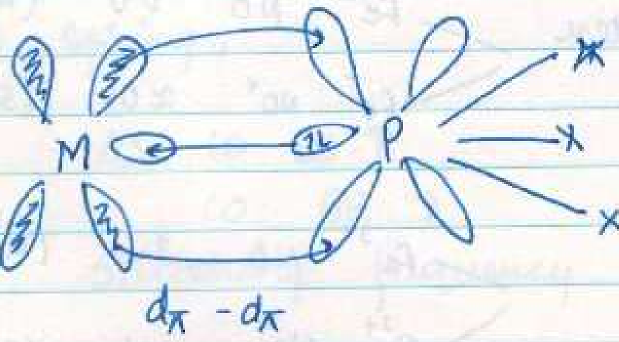
NO <u>15e⁻</u>



σ donor
π donor
π acceptor
3e⁻ donor



→ Synergic bonding in PX_3, SX_2, AsX_3



No change in P−X BO due to synergy because e⁻ from metal ion enters in vacant d-orbital of 'P' not in σ* of P−X bond.

Q. compare stretching frequency of CO

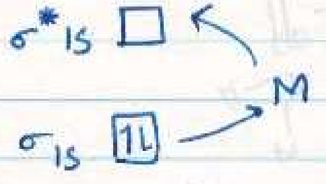
$M(CO)_x$ (cyclopropyl)
(a)

$M(CO)_x$ (π-allyl)
(c)
4 e⁻

$M(CO)_x$ (σ-allyl)
(b)

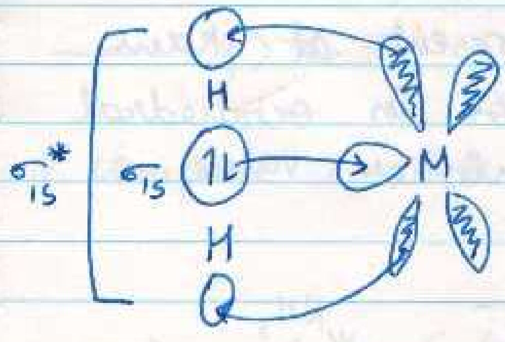
→ c>b>a

→ H_2 as a ligand .



H_2 as a ligand stable when good acceptor present in complex, so e⁻ cloud in σ* of H_2 ↓.
Stability of H_2 ↑

$0 < H_2$ BO < 1

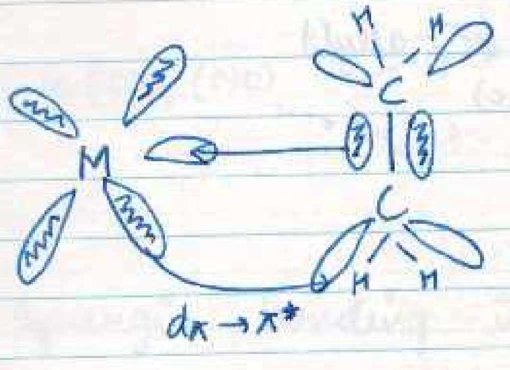


$Mo(CO)_5 H_2 \leftarrow H_2$

$Mo(CO)_2(PMe_3)H_2 \leftarrow H^-$

acceptance tendency of CO > PMe_3

* C_2H_4 as a ligand



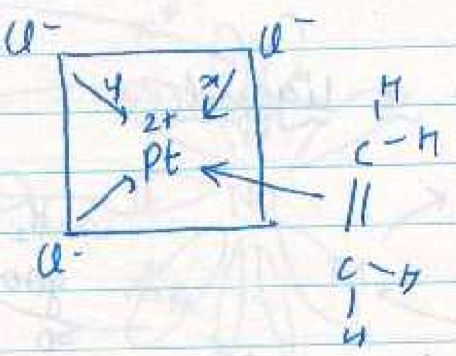
example :→

Zeise's salt

$K[PtCl_3(\eta^2\text{-}C_2H_4)]\cdot H_2O$

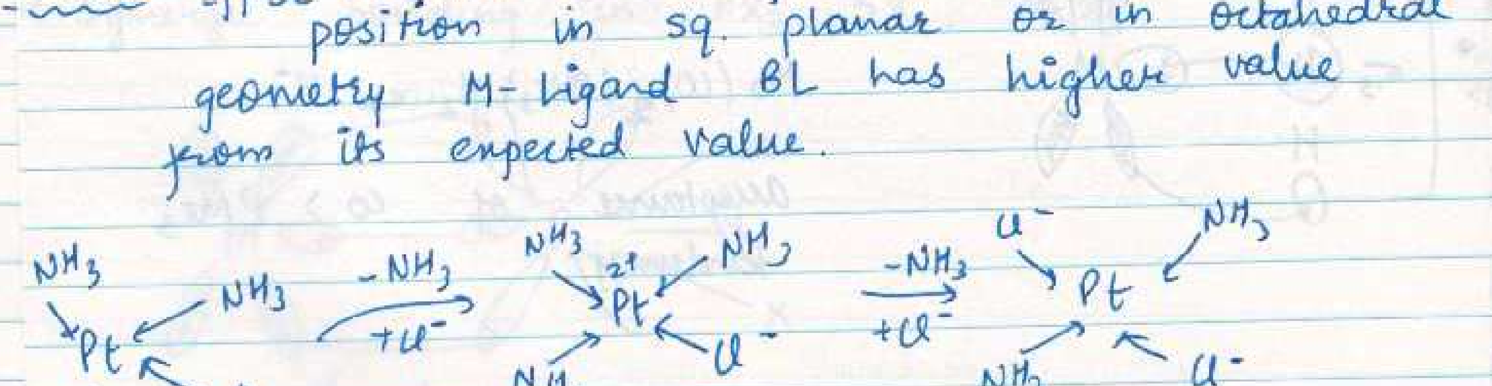
first compound observed which has π-donor ligand.

- $PtCl_3$ & C_2H_4 plane are ⊥er to each other
- C_2H_4 is not planar
- All H atoms are in a plane but not with 'C' atoms due to rep^n b/w dπ → π* & C–H σ bond

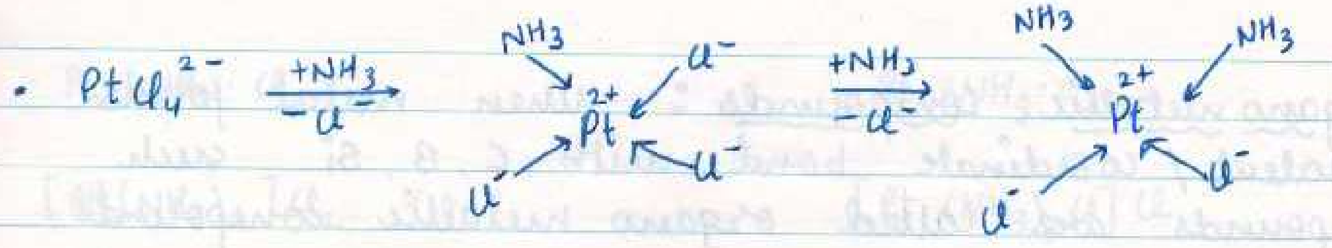


BL $y > x$
due to trans effect

trans effect :→ when strong acc. present at trans position in sq. planar or in octahedral geometry M-Ligand BL has higher value from its expected value.

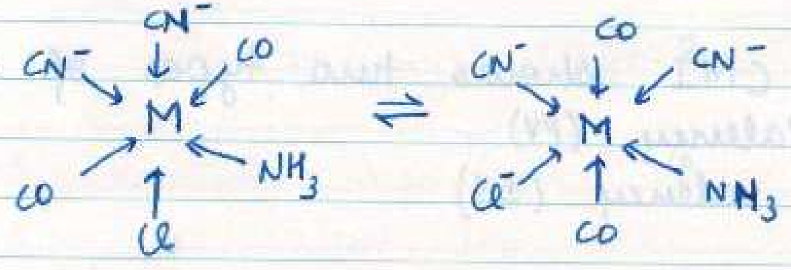


• $PtCl_4^{2-} \xrightarrow[-Cl^-]{+NH_3}$



q. Draw possible correct structure of
$M(CO)_2(CN)_2(NH_3)Cl$
If two type of stretching frequency obtained for CN^- & one type of stretching frequency obtained for CO.

→



q. If difference in C–C BL in C_2H_4 & $K[PtCl_3(C_2H_4)]$ is x & in C_2F_4 & $K[PtCl_3(C_2F_4)]$ is y. then compare x & y

— $y > x$ C_2F_4 is better acceptor than C_2H_4

q. Compare C–C BL in • $C_5H_5^-$ & Ferrocene
• C_6H_6 & $Cr(C_6H_6)_2$

→ $C_6H_6 < Cr(C_6H_6)_2$

$C_5H_5^- <$ Ferrocene

* <u>Organo metallic compounds</u> : When metal forms covalent / coordinate bond with C, B, Si such compounds are called organo metallic compounds.

- Cyanide salts & ionic carbide are not organo metallic compounds.

* WERNER'S THEORY :→

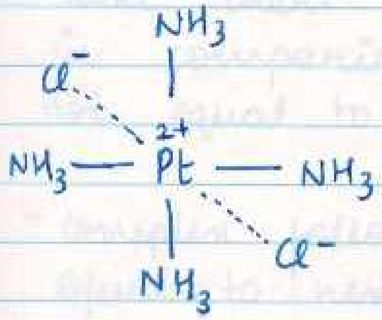
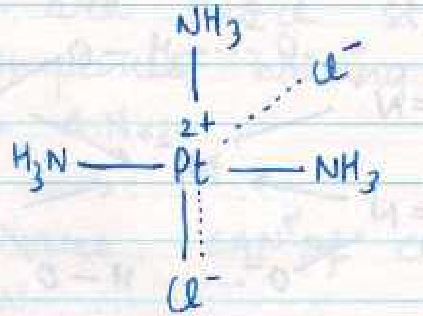
Acc^n to him, CMI shows two types of valency,

i) Primary Valency (PV)
ii) Secondary valency (SV)

PV	SV
· O.S. of CMI	· C.N. of CMI
· Satisfied by anions.	· Satisfied by anions / neutral molecules (ligands)
· Form ionic bond	· Co-ordinate bond
· Generally ionisable	· Non-ionisable
· Non-directional	· Directional
· ~~satisfied by~~ represented by dotted (---) line	· by solid (—) line

<u>Note</u> :

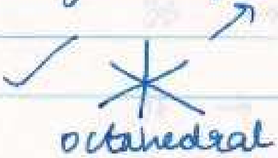
1) Anionic ligands are represented by solid with dotted line. If nothing is specified, always consider neutral ligands inside cordination sphere in conversion of werner's formula into modern formula

	$Pt \cdot 4NH_3 \cdot Cl_2$	$Pt \cdot 3NH_3 \cdot Cl_2$
	$[Pt(NH_3)_4]Cl_2$	$[Pt(NH_3)_3Cl]Cl$
		
PV	2	2
SV	4	4
electrolyte	1:2 (cation : anion)	1:1
cond.	>	
ppt with excess $AgNO_3$	2mol	1mol

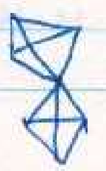
- **Application of Werner's theory:**

i] to predict exact formula of each complex.

ii] to predict the structure of diff. complexes with C.N. 4 & 6.
eg : $[Cr(NH_3)_4Cl_2]Cl$ → 2 isomers

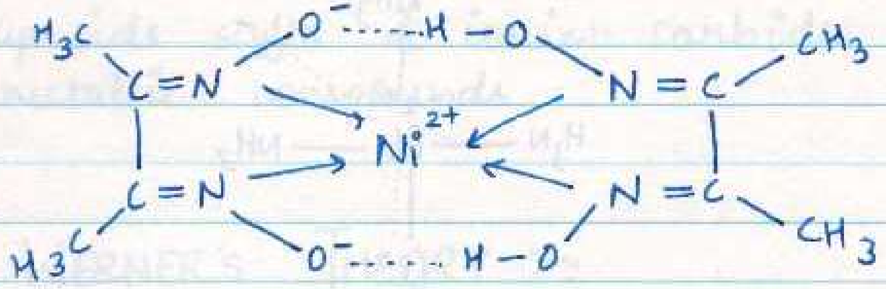

octahedral
2 I


Hexagonal
3 I


trigonal prismatic
3I

* $Ni^{2+} + dmg^- \longrightarrow Ni(dmg)_2 \downarrow$

Rosy red



* E.A.N (Effective Atomic Number) :→

- Total no. of es⁻ in CMI after complex formation.

Q.

1. $[Sc(H_2O)_6]^{3+}$ = 30

2. $[Ti(CO)_6]^{2-}$ = 36

3. $[VO_4]^{3-}$ = 26

4. $[Cr(NH_3)_6]Cl_3$ = 33

5. $[Mn(en)_3]SO_4$ = 29+6

6. $K_3[Fe\overset{12}{(C_2O_4)_3}]$ = 35

7. $\overset{+3}{Co}(gly)_3$ = 36

8. $[Ni\ EDTA]^-$ = 40 -3

9. $[Ag(CN)_2]^-$ = 50

10. $CuCl_4^{2-}$ = 35

11. $[Zn\overset{4}{(acac)_2}]$ = 32+4

12. HgI_4^{2-} = Hg+6 = 86

13. $[Pt\overset{2}{(en)}\overset{3}{(dien)}NH_3]^{4+}$ = Pt+8

Sidgwick EAN Rule (as like octet rule) :

Accⁿ to Sidgwick, complexes having EAN equal to next inert gas atomic no. are more stable in comparison of other complexes having EAN not equal to next inert gas A.N.

- complex follows EAN rule means, EAN of CMI is equal to next inert gas A.N.,

$3d \rightarrow 36$
$4d \rightarrow 54$
$5d \rightarrow 86$

- EAN rule is also called 18e⁻ rule due to 18 valence shell es⁻,

$(n-1)d^{10}\ ns^2\ np^6$

which is confⁿ of next inert gas atomic no.

- This rule is applicable for metal carbonyls & π-complexes.

* Metal Carbonyls :

EAN

Oxidising agent
33 → tetramerize

34 → trimerize

35 → dimerize M–M

36 → stable
37 → Reducing agent

27

Q. find value of x, y, z for

$Fe(CO)_x$ $Cr(CO)_y$ $Ni(CO)_z$

⟶ $x = 5$; $y = 6$; $z = 4$

Q. find the formula of :

$Ni(CO)_4$

a) lightest stable metal carbonyl homoleptic complex

M = $Co(NO)_3$

b) lightest stable metal nitrosyl homoleptic complex.

A = $Cr(NO)_4$

- Nitrosyl complexes are formed by replacement of CO from metal carbonyls.

- $Cr(NO)_4$ is only mononuclear homoleptic nitrosyl complex of 3d series.

Q. Find the value of x+y (x, y are integers)

$x = 3$ $y = 2$

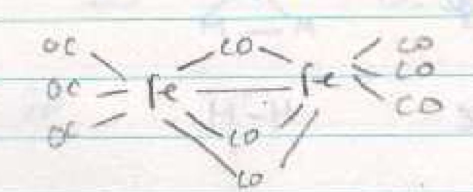
$$Fe(CO)_5 \xrightarrow{-x\,CO} Fe(CO)_{5-x}(NO)_y$$

⑤

- 3 CO are replaced by 2 NO in formation of nitrosyl complex from metal carbonyls.

Q. Find the value of x for $Fe_2(CO)_x$

→ 9.



- $Ti \xrightarrow{36} Ti^{0}\cancel{(C}O)_7$ Steric crowding

  $\xrightarrow{34} Ti^{0}(CO)_6 \xrightarrow{+2e^-} [Ti^{0}(CO)_6]^{2-}$

  $\longrightarrow (Ti^{0}(CO)_6)_3$ unstable

- $V \xrightarrow{35} V(CO)_6 \xrightarrow{+e^-} V(CO)_6^-$

  $\longrightarrow (V(CO)_6)_2$ at very low temp.

- $Cr \xrightarrow{36} Cr(CO)_6$

  $\xrightarrow{34} Cr(CO)_5 \longrightarrow Cr(CO)_5^{2-}$

  $\longrightarrow (Cr(CO)_5)_3$

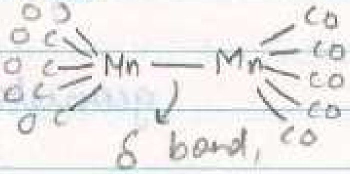
- $Mn \xrightarrow{35} Mn(CO)_5 \longrightarrow Mn(CO)_5^-$

  $\longrightarrow Mn_2(CO)_{10}$

  $\xrightarrow{37} Mn(CO)_6$

  $\downarrow$

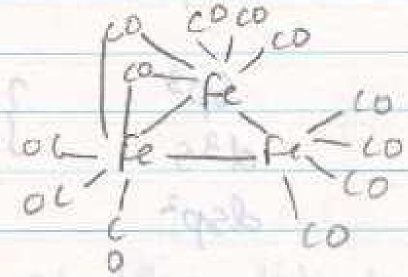
  $[Mn(CO)_6]^+$



- $Fe \xrightarrow{36} Fe(CO)_5$

  $\xrightarrow{34} Fe(CO)_4 \longrightarrow Fe(CO)_4^{2-}$

  $\longrightarrow [Fe(CO)_4]_3$



- $Ni^{0} \longrightarrow Ni^{0}(CO)_4$

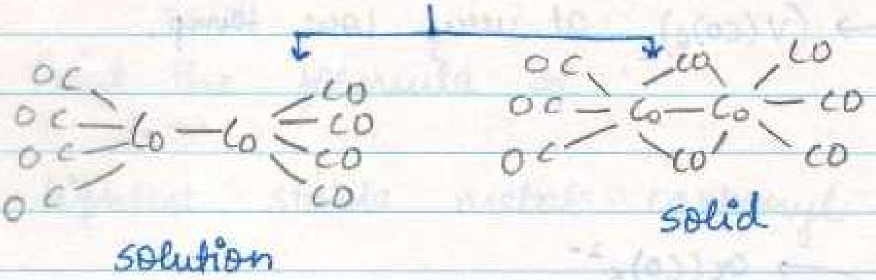
- $Cu \xrightarrow{35} Cu(CO)_3 \longrightarrow Cu(CO)_3^-$

  $\longrightarrow Cu_2(CO)_6$ at very low temp.

- $Co \xrightarrow{37} Co(CO)_5 \longrightarrow [Co(CO)_5]^+$

$Co \xrightarrow{35} Co(CO)_4$

$Co(CO)_4 \rightarrow Co(CO)_4^-$, $Co_2(CO)_8$



solution

solid

* Valence Bond Theory :

No. of hybrid orbital = no. of σ bonds / CN of CMI

CN	hyb.	geometry
2	sp	linear
3	sp^2	trigonal planar
4	sp^3 d^3s	} tetrahedral
	dsp^2	sq. planar
5	$dsp^3 / sp^3d\ (d_{z^2})$	TBP
	$dsp^3 / sp^3d\ (d_{x^2-y^2})$	sq. pyramidal
6	sp^3d^2 / d^2sp^3	Octahedral

- inner orbital complex = $(n-1)d$ orbital participates in hyb.

Outer orbital complex = when nd orbital participate in hyb.

- Classification of ligands on the basis of bond strength :→

SFL (Strong field ligand)	WFL (Weak field ligand)
forms strong bond with CMI	forms weak bond with CMI

Properties of SFL

good donor (lewis B.N. ↑) → Size ↓
→ EN ↓
→ $-ve$ charge ↑

strength

$C > N \mid O > F > Cl > Br > I$

SFL | WFL

* • Spectrochemical Series (Strength of ligands) :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < N_3^-/NO_3^- < F^- < OH^- < CH_3COO^-$

$CO > CN^- > NO_2^- > en \approx dipy > P_y \approx NH_3 > EDTA^{4-} > NCS^- > H_2O > C_2O_4^{2-}$

Trick.

इतना बुरा था कालू श्यामू नाई फुले हाथ ऐसे उसके पानी भरा हो जैसे
नवीन चंद्र स्कसेना इन दिनों अमन पाने के लिए double double नौ सेना कोर्ट के चक्कर लगा रहे हैं।

In presence of SFL, es^- are forced to pair as per requirement of d-orbitals for hybridisation. Due to parining of es^- value of spin only Magnetic moment ↓ such complexes are called low spin complexes, in presence of WFL, no change in no. of unpaired es^- so they have high value of spin only magnetic moment in comparison of low spin complexes such complexes are called high spin complexes. (low spin w.r.t ground state)

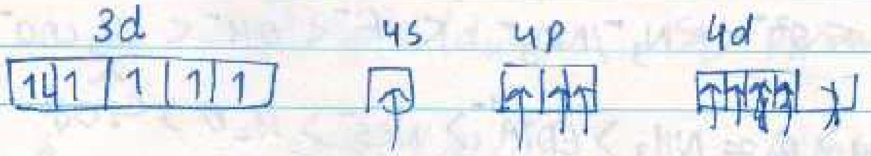
Note : High spin & low spin complexes are defined only when ligand's effect in that configuration occurs.

- $K_4[FeF_6]$

$CN = 6,\ sp^3d^2 / d^2sp^3$

$CMI = Fe^{2+}\ d^6$

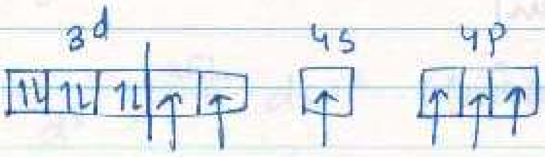
$F^- = WFL$



sp^3d^2 octahedral ↑spin
outer Orbital
para.

• $K_4[Fe(CN)_6]$

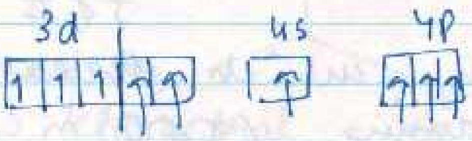
CN = 6 . sp^3d^2 / d^2sp^3
CMI = Fe^{2+} d^6
CN^- = SFL



Inner orbital
d^2sp^3 octahedral
diamagnetic
low spin

• $[Cr(NH_3)_6]Cl_3$

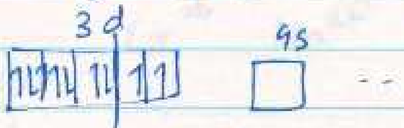
CN = 6
CMI = Cr^{3+} d^3



d^2sp^3 (para.)

• $[Ni(NH_3)_6]Cl_2$

CN = 6
CMI = Ni^{2+} d^8
NH_3 = SFL



sp^3d^2 (para.)

Conclusion,

For CN = 6.

$d^{0,1,2,3}$ — d^2sp^3 — d^0, d^6-SFL, d^{10} diamag.

$d^{4,5,6,7}$ $\xrightarrow{SFL}$ d^2sp^3 (low spin)

$\xrightarrow{WFL}$ sp^3d^2 (high spin)

$d^{8,9,10}$ — sp^3d_2

Q.

	(I)	(II)	(III)	(IV)
d^5	Fe^{3+}	en SFL	low spin, Diama	& ~~Paramagnetic~~
d^3	Cr^{3+}	CN^- SFL	high spin, Para	& diamagnetic
d^6	Co^{3+}	F^- WFL	inner orbital, Dia	&
d^8	Ni^{2+}	SCN^- WFL	outer orbital, Para	

Find total no. of combination in which ~~at least~~ three ~~[illegible]~~ columns/species are used containing (~~II & III~~ I & II) in CN 6.

→ ~~[illegible]~~ 1, 1, 1, 1. 1, 1, 1, 1, 1, 1, 1, 1, 4 $\boxed{16}$.

Q. d^8 $NiCl_4^{2-}$ — sp^3 — para — high spin

d^8 $Ni(CN)_4^{2-}$ — ~~sp^3~~ dsp^2 — di ~~para~~ — low spin

d^{10} $Ni(CO)_4$ — sp^3 — di — $\xrightarrow{4s}$

w.r.t. d^8s^2 { ground state }.

conclusion,

CN = 4

d^7 $\xrightarrow{SFL}$ low spin dsp^2 } para
$\xrightarrow{WFL}$ high spin sp^3

d^8 $\xrightarrow{SFL}$ dsp^2 (low spin) dia
$\xrightarrow{WFL}$ sp^3 (high spin) para

d^9 $\xrightarrow{WFL}$ sp^3 } para
$\xrightarrow{SFL}$ dsp^2

d^{10} $\longrightarrow$ sp^3 diamagnetic.

- $[Ni(PPh)_3Cl_2]$

$\swarrow$ tetrahedral (paramagnetic)

$\searrow$ Sq. planar (diamagnetic)

As the charge on CMI ↑
Or Zeff of CMI ↑
Metal-ligand bond strength ↑

$d\,e^-$ ↑ Zeff ↑ $\longrightarrow$

3d	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
4d				↓ zeff ↑	↓ zeff ↑	
Zeff ↑ 5d ↓				Co^{3+}	Ni^{4+}	

1) generally NH_3 acts as SFL but for Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} it acts as WFL

2) gen. 'O' donor are WFL but act as SFL for Co^{3+}, Cu^{2+}

3) All ligands are SFL for 4d, 5d +4 ions

4) If WFL ≤ SFL
always consider effect of SFL
except $[Co(H_2O)_3F_3]$, $[Co(H_2O)_3Cl_3]$

Q.
If M =
A) $[MCl_6]^{-x}$ WFL — P) Fe^{2+}, Outer orbital d^6
B) $[M(H_2O)_6]^{+x}$ WFL ex (S, T) — Q) Cr^{3+}, Inner orbital d^3
C) $[M(C_2O_4)_3]^{-x}$ WFL (S, T) — R) Fe^{3+}, Paramagnetic d^5
D) $[M(NH_3)_6]^{+x}$ SFL PU — S) Co^{3+}, Diamagnetic d^6
E) $[M(en)_3]^{+x}$ SFL — T) Pt^{4+}, low spin d^6
F) $[M(CN)_6]^{-x}$ SFL — U) Mn^{2+}, high spin d^5

→ A) P, Q, R, T, U
B) P, Q, R, U, T, S
C) P Q R S T U
D) P Q R T U
E) × Q R T S
F) × Q R T S

Q. $[M(C_2O_4)_2]^{-n}$ $M = Cu^{2+}$, Para d^9 Always

$[MCl_4]^{-n}$ $M = Zn^{2+}$, dia. d^{10} Always

$[M(en)_2]^{+n}$ $M = Ni^{2+}$, tetrahedral d^8 sp^3 (WFL)

$[M(NO_2)_4]^{-n}$ $M = Pt^{2+}$, Sq. planar d^8 dsp^2 (SFL)

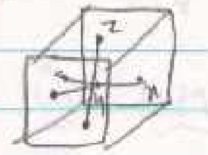
→ A) P Q R S
B) P Q R S
C) P Q S
D) P Q S

Types of d-orbitals

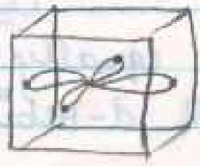
along the axis
$d_{x^2-y^2}$, d_{z^2}
at face centre

b/w the axis
d_{xy}, d_{yz}, d_{xz}
at edge centre

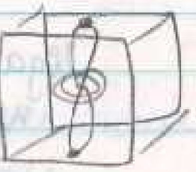
let



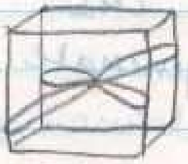
$d_{x^2-y^2}$



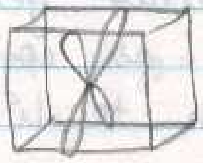
d_{z^2}



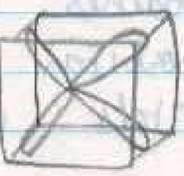
d_{xy}



d_{yz}



d_{xz}



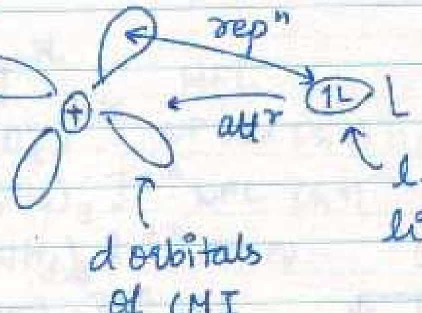
* Crystal Field Theory (CFT) :

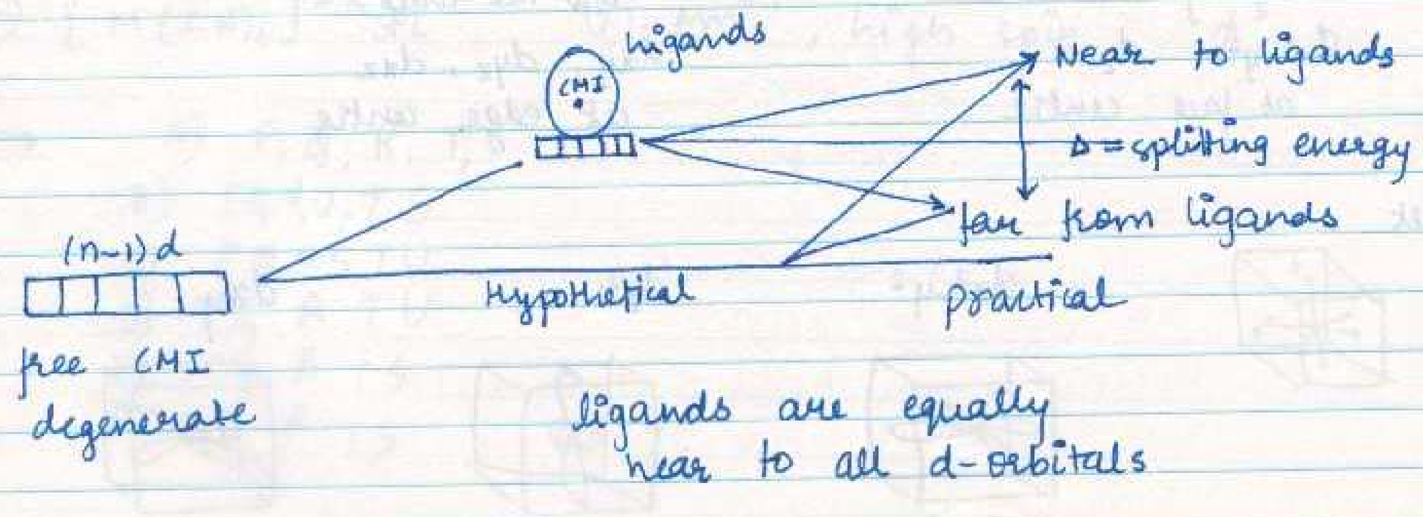
Acc. to CFT,

CMI = point charge

Ligands → Neutral = dipole
→ Anionic = -ve point charge

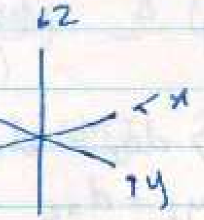
Interaction b/w ligand & CMI = electrostatic





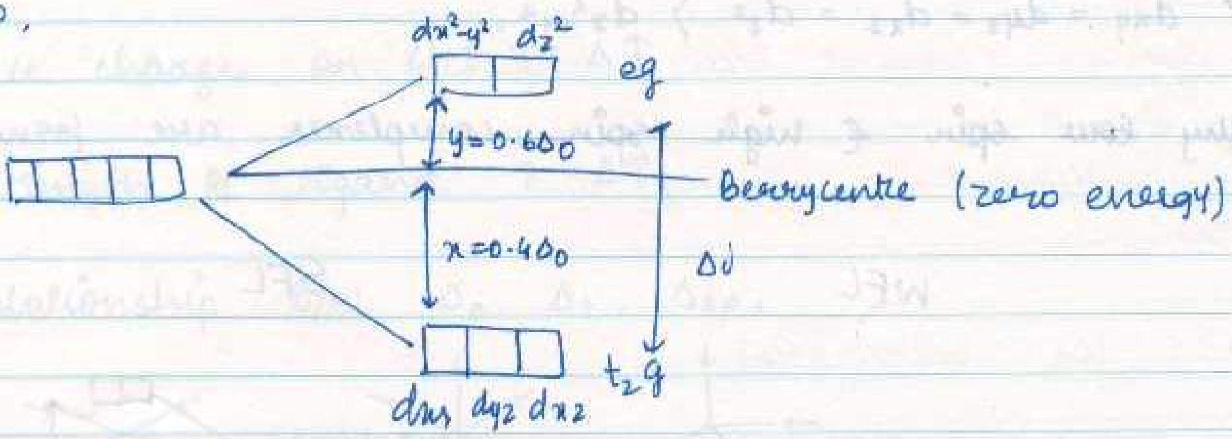
- When ligand approaches CMI in a particular geometry some of the d-orbital exp. more rep^n as compared to other d-orbitals coz they are near to ligands as compared to other d-orbitals. So, d-orbitals are splitted into diff. energy set. loss of degeneracy of d-orbitals is called crystal field splitting & energy diff. b/w them is called splitting energy (Δ).

- Splitting in Octahedral :



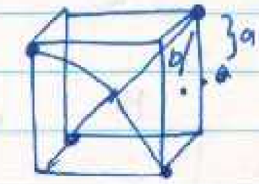
ligands are near to axial d-orbitals and far from non-axial d-orbitas

So,



$d_{z^2} = d_{x^2-y^2} > d_{xy} = d_{yz} = d_{xz}$

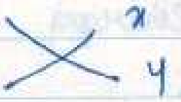
- in tetrahedral :



b>a
ligands are near to non axial d-orbitals

$d_{xy} = d_{yz} = d_{xz} > d_{x^2-y^2} = d_{z^2}$

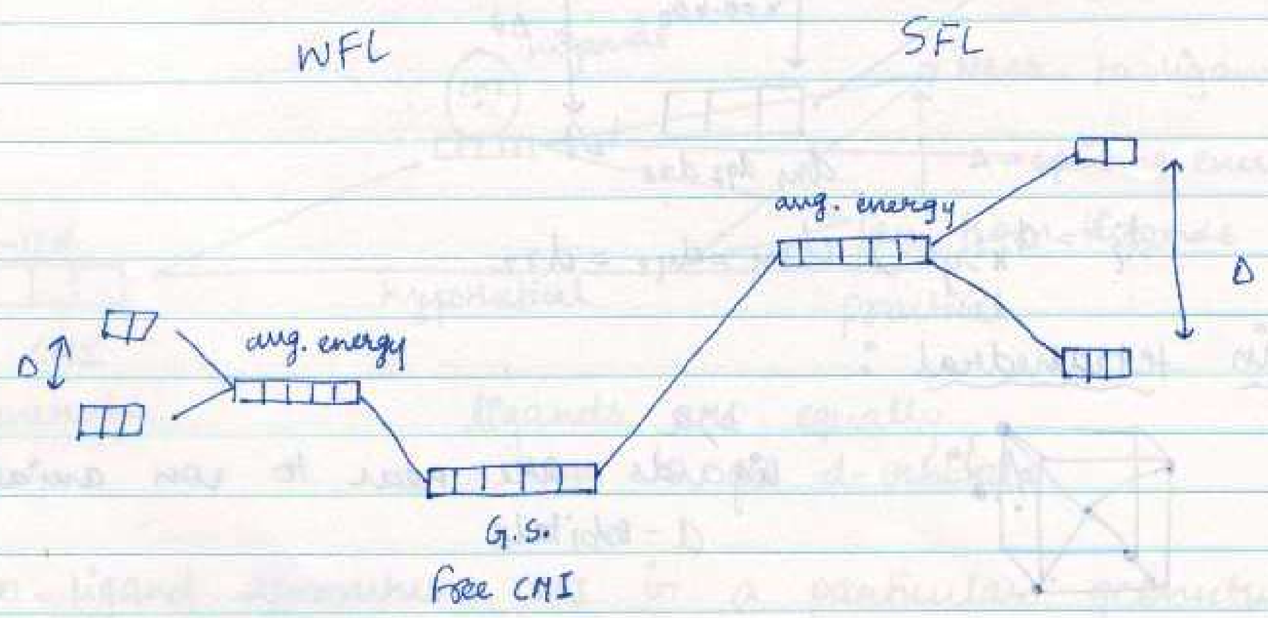
- in Sq. planar :



$$\underbrace{d_{x^2-y^2} > d_{xy}}_{\text{In xy plane}} > d_{z^2} > \underbrace{d_{yz} = d_{xz}}_{\text{equall }\perp}$$

- sp ⇒ $d_{z^2} > d_{yz} = d_{xz} > d_{x^2-y^2} = d_{xy}$ (z axis) (xy Plane)
- sp^2 ⇒ $d_{x^2-y^2} = d_{xy} > d_{z^2} > d_{yz} = d_{xz}$
- dsp^3 (TBP) ⇒ $d_{z^2} > d_{x^2-y^2} = d_{xy} > d_{yz} = d_{xz}$
- dsp^3 (S.P) ⇒ $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} = d_{xz}$
- square antiprismatic ⇒ ~~$d_{z^2} = d_{x^2-y^2} > d_{xy} = d_{yz} = d_{xz}$~~
- Dodecahedron ⇒ ~~$d_{xy} = d_{yz} = d_{xz} > d_{z^2} = d_{x^2-y^2}$~~
  - $d_{xy} = d_{yz} = d_{xz} = d_{x^2-y^2} > d_{z^2}$
  - $d_{xy} = d_{yz} = d_{xz} = d_{z^2} > d_{x^2-y^2}$.

Q. Why low spin & high spin complexes are formed ?



In presence of SFL $\Delta >$ Pairing energy
WFL $\Delta <$ Pairing energy.

from d^4 conf. energy is required to fill e^- either in form of Δ or in form of pairing energy.

- Factors affecting Δ (Splitting Energy) :→

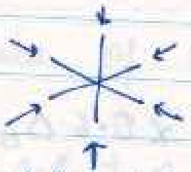
(A) As Z_{eff} of CMI ↑

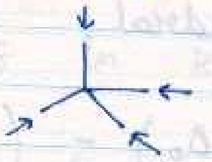
{ distance b/w ligands & CMI ↓
rep^n b/w d-orbitals of CMI & ligands ↑
Δ ↑ }

(B) +ve charge on CMI ↑ Δ ↑

(C) Strength of ligand ↑ Δ ↑

* Relationship b/w Δ_o, Δ_t, Δ_{sp},





	$d_{x^2-y^2}$	d_{z^2} & $d_{x^2-y^2}$	d_{xy}, d_{yz}, d_{xz}
orbital	1	2	3
ligands	4	6	4 (not in direc^n of orbitals)

$\Delta_{sp} > \Delta_o > \Delta_t$

$\Delta_{sp} = \frac{4}{3} \Delta_0$

$\Delta_t \approx \frac{4}{9} \Delta_0$

- Application of CFT :

1] To find stability of complexes :→

$$\Delta G = \underset{\uparrow}{\Delta H} - T \Delta S \xrightarrow{} \text{chelation.}$$

Bond strength

(Δ) / CFSE

* C.F.S.E (Crystal field stabalization Energy) :

Decrement in energy due to crystal field Splitting

CFSE for octahedral,

$$(\eta t_{2g} \times 0.4 \Delta_0) - (\eta_{eg} \times 0.6 \Delta_0) - x \times P.E.$$

↑ e^- in t_{2g} ↑ e^- in eg ↑ no. of extra pair

Q. Find CFSE value & conf^n of (n-1) d orbitals in form of t_{2g} & eg in coordination 6 in presence of SFL as well as WFL.

→

	SFL t_{2g}	SFL eg	WFL t_{2g}	WFL eg	
d^0	0	0	0	0	= 0
d^1	1	0	1	0	$= 0.4\Delta_0$
d^2	2	0	2	0	$= 0.8\Delta_0$
d^3	3	0	3	0	$= 1.2\Delta_0 PE$
d^4	4	0	3	1	$= 1.6\Delta_0^{-PE}, 0.6\Delta_0$
d^5	5	0	3	2	$= 2.0\Delta_0^{-2PE}, 0$
d^6	6	0	~~3~~4	2	$= 2.4\Delta_0^{-3PE}, 0.4\Delta_0^{-P}$
d^7	6	1	5	2	$= 1.8\Delta_0^{-3PE}, 0.8\Delta_0^{-2}$
d^8	6	2	6	2	$= 1.2\Delta_0^{-3PE}, 1.2\Delta^{-3P}$
d^9	6	3	6	3	$= 0.6\Delta_0^{-4PE}, 0.6\Delta^{-}$
d^{10}	6	4	6	4	$= 0\Delta_0^{-5PE}, 0\Delta_0^{-5PE}$

$\Delta_0 = 10\,D_q$
↓
Deciquanta.

Q. Find the formula of CFSE in $\overset{sp^3}{\text{tetrahedral}}$ (filled).

→ $\overset{sp^3}{\boxed{\;|\;|\;|\;}}$ $-\eta\, t_{2g} \times \Delta_t\, 0.4 + \eta_{eg} \times \Delta_t\,(0.6) - x PE$

Q.

Q. Select correct statements for

$[Cr(en)_3]^{3+}$ $\quad$ $[Cr(gly)_3]$

$d^3 \quad 6 \quad +3$ $\qquad$ $6 \quad +3 \quad d^3$

A) Both are inner orbital complex

B) Both are low spin complex

c) Both are paramagnetic

d) Both have same conf^n of CMI

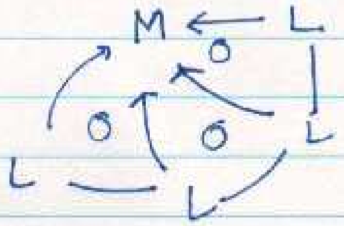
e) Both have same CFSE

* Chelation :

	Δn	no. of rings
$[Ni(NH_3)_6]^{2+} + en \rightarrow [Ni(NH_3)_4 en]^{2+}$	1	1
$+ 2en \rightarrow [Ni(NH_3)_2(en)_2]^{2+}$	2	2
$+ 3en \rightarrow [Ni(en)_3]^{2+}$	3	3
$+ EDTA^{4-} \rightarrow [Ni(EDTA)]^{2-}$	5	5

\# $\Delta n \uparrow$ $\Delta S \uparrow$ $T\Delta S \uparrow$ $\Delta G \downarrow$
Stability $\uparrow$

\# $\Delta n \propto$ no. of rings
no. of rings $\uparrow$ chelation $\uparrow$ stability $\uparrow$



No. of rings formed by a ligand = Denticity − 1

* Priority order for comparison of stability of complexes for same CMI, same C.N. & diff. ligands :

⇒ C-donor > chelation

for same no. of ring(s)

Stability $\propto \Delta$. (CFSE).

Q. Stability order :

1) $PtCl_4^{2-}$ $PdCl_4^{2-}$ $NiCl_4^{2-}$ a>b>c {Zeff}

2) $K_4Fe(CN)_6$ $K_3Fe(CN)_6$ b>a {+ve charge on CMI}

3) $Ni(dmg)_2$ $[Ni(en)_2]^{2+}$ a>b {H-bonding}

4) $Cr(CN)_6^{3-}$, $Cr(C_2O_4)_3^{3-}$
$Cr(en)_3^{3+}$ $[Cr(NH_3)_6]^{3+}$
$[Cr(H_2O)_6]^{3+}$ $a > c > \overset{b}{d} > d > e$ { C > chelati
if no chel
C>N>O>F }

5) $[Fe(C_2O_4)_3]^{3-}$ $[Fe(acac)_3]$ b>a {no. of atoms in a ring}

* Transference of electrons :→

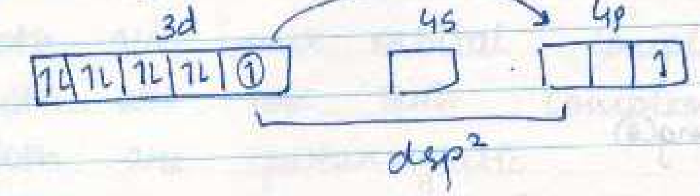
In presence of strong field ligand when single e^- is present in highest energy (n-1) d orbital, excitation of e^- takes place.

eg.

d^7 SFL in CN = 6. $[Co(CN)_6]^{4-}$

d^9 SFL in CN = 4

$[Cu(en)_2]^{+2}$



With the help of transference we can compare reducing nature of Co^{2+} in presence of different diff. ligands.

strength of ligand ↑
rep^n b/w single e⁻ & ligand ↑
energy ↑

$[Co(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)_6]^{+3}$

$NH_3 \longrightarrow$

en $\longrightarrow$

} $E^0 = -ve$

$CN^- \longrightarrow$ } $E^0 = +ve$

Reducing nature ↑

$\Delta G = -nfE$

↑ electrode potential

\# Reducing nature of

$[Cu(en)_2]^{2+} < [Co(en)_3]^{2+}$

(A)

1) Zeff of $Cu^{2+} > Co^{2+}$

removal of e^- is easy in Co^{2+}

2) in complex A outermost e^- present in 4p while in complex B outermost e^- present in 4d
distance from nucleus
$4p < 4d$

* Jahn Teller distortion :→

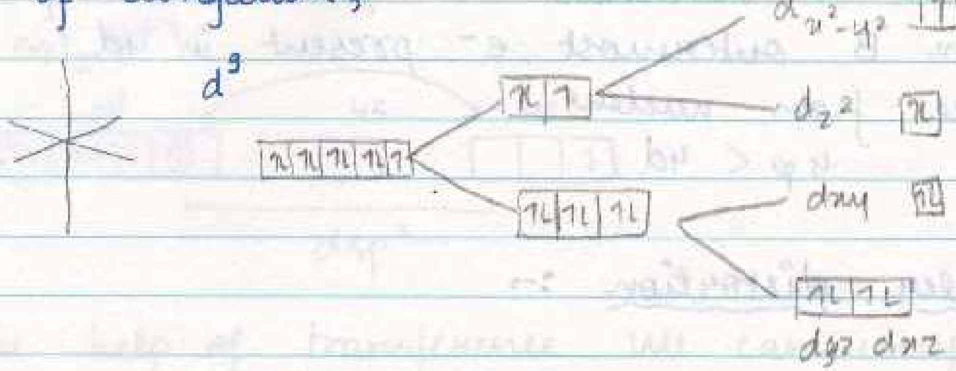
When t_2g & e_g subsets (set of orbitals) are unsymmetrically filled, octahedral complex is no more symmetrical. This is called Jahn teller distortion.

When t_2g set of orbitals are unsymmetrically filled distortion is very weak but when e_g orbitals are unsymmetrically filled, strong distortion is observed.

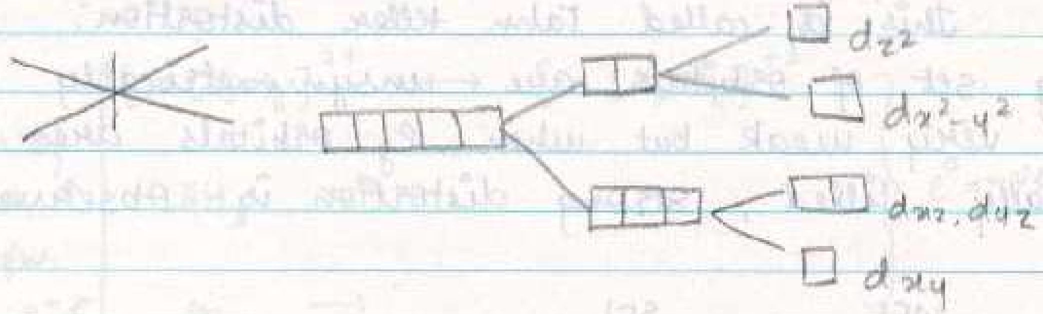
	WFL	SFL
d^0	X	X
d^1	W	W
d^2	W	W
d^3	X	X
d^4	S	W
d^5	X	W
d^6	W	X
d^7	W	S
d^8	X	X
d^9	S	S
d^{10}	X	X

$[Cu(H_2O)_6]^{2+}$
all Cu–O bond length are not identical.

In case of elongation,



In case of compression,



In CN = 5,

In case of SFL (except CO) → sq. pyramidal

In case of WFL & CO → TBP.

* Isomerism :→

Structural

1) ionization
2) hydrate
3) linkage
4) co-ordination
5) co-ordination position
6) ligand
7) polymerisation

Stereo

1) geometrical
2) optical
3) Allogen isomerism.

· **Stereo :**

CMI = M
Monodentate ligands = a, b, c, d, e, ...
Symm. bidentate = AA, BB, CC, ...
($C_2O_4^{2-}$, en, dipy, $acac^-$)
unsymm. bidentate = AB, AC, BC, ...
(gly^-, $bcac^-$)

$Zn(gly)_2 = M(AB)_2$

$[Pt(NH_3)_2Cl_2] = Ma_2b_2$

$[Cr(NH_3)_3(H_2O)_2Cl]\ SO_4 = Ma_3b_2c$

1. Geometrical : diff. diff. Bond angles

2. Optical : POS ×

CN=2

Linear

Mab

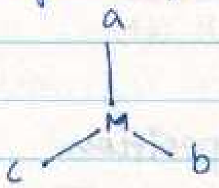
b — M — a

POS ✓ OI×

Only one type GI×
of BA

CN=3

Trigonal planar

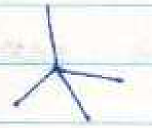


GI ×

POS ✓, OI ×

CN=4

Tetrahedral



Only one type GI ×
of BA
Can show OI

Sq. planar

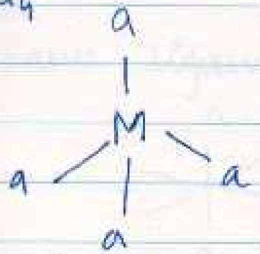
POS ✓ OI×

two types of BA GI ✓

• OI in tetrahedral

Ma_4

*



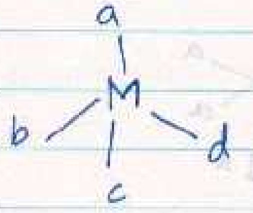
POS ✓

* Ma_3b (POS ✓)

* Ma_2b_2 (POS ✓)

* Ma_2bc (POS ✓)

* M_{abcd}

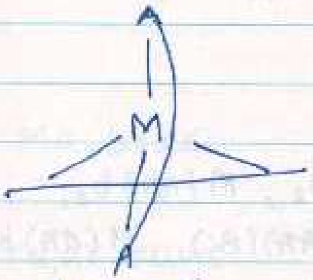


POS × OI ✓

OI = 2

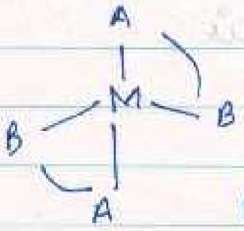
* $M(AA)_2$, $M(AA)b_2$, $M(AA)bc$

$M(AA)(AB)$



POS ✓ OI ×

$M(AB)_2$



POS × OI ✓

OI = 2

M(AB)(CD) OI ✓

$M(AB)c_2$ OI ×

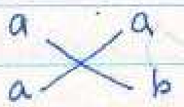
M(AB)cd OI ✓

• GI in sq. planar

Ma$_4$

GI×

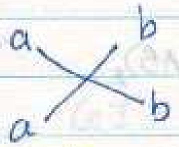
Ma$_3$b



GI×

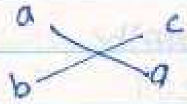
Ma$_2$b$_2$

trans

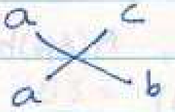


cis

Ma$_2$bc



trans



cis

Mabcd

③ 2 cis, 1 trans

M(AA)$_2$, M(AA)b$_2$, M(AA)(BC), M(AA)bc

identical

M(AB)$_2$ GI=2

cis

trans

M(AB)(CD) GI = 2

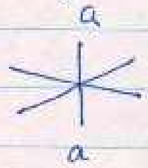
M(AB)cd GI = 2

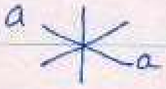
M(AB)c$_2$ GI ×

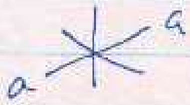
· C.N. = 6

POS

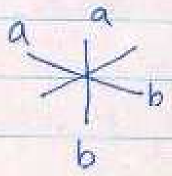
1) same ligands present at trans

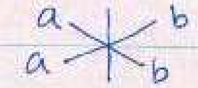


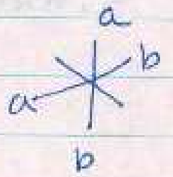


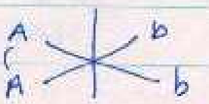


2) two trans are identical



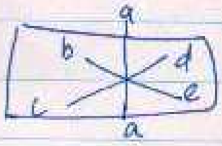






Ma_2bcde

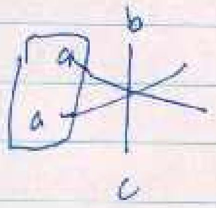
(a,a) trans

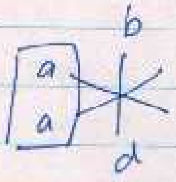


⇒ GI = 3

OA = 0

(a,a) cis





- - -

⇒ GI = 6

OA = 12

GI = 9

OI = 15

SI = 15

$M_{(AA)}bcde$

GI = 6 ; OA = 12, OI = 12 ; SI = 12

consider only (a,a) cis of Ma_2bcde

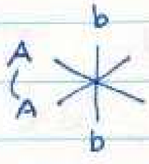
$M_{(AF)}bcde$

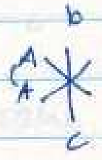
GI = 12 ; OI = 24 ; SI = 24
(24+0)

Mabcdef

GI = 15 ; OI = 30 ; SI = 30

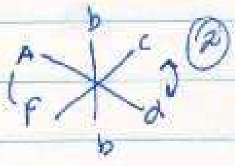
$M_{(AA)}b_2cd$

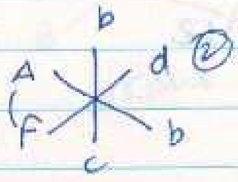


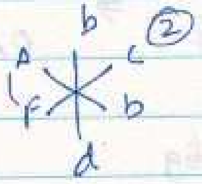


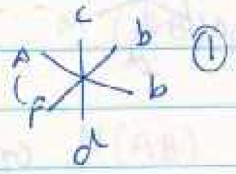
GI = 4 OA = 8

$M_{(AF)}b_2cd$





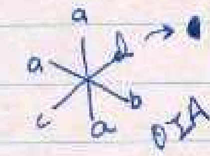




GI = 7
OI = 10

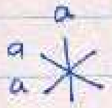
Ma_3bcd

a c
a b
a d
b c
b d
c d

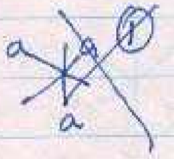


→ ● ③

OIA



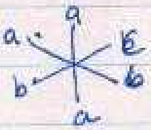
~~③~~①



①

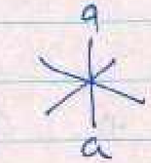
GI = ~~5~~4

Ma_3b_2c



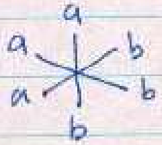
1+② ③

Ma_3b_3

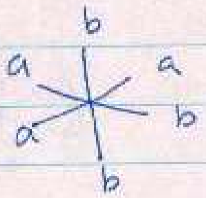


②

fac-mer isomerism



facial

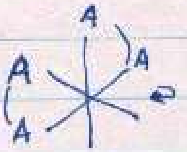


Meridonial

Q $M_{(AA)}b_4 \xrightarrow[+AA]{-b_2}$ compd Z

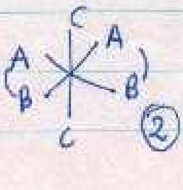
Find total no. of G.I. of x

→ $M_{(AA)_2}b_2$



②

$M(AB)_2C_2$



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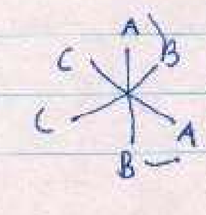

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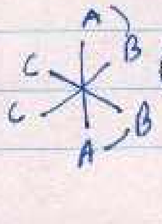

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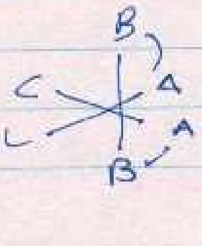
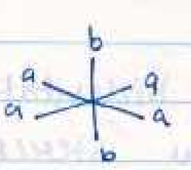
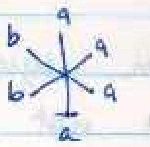


②

Q. Ma_4b_2 $\xrightarrow[+b]{-a}$ Ma_3b_3 two GI

cis/trans ?





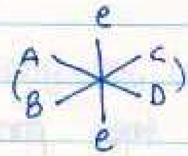
Ma_4b_2 $\xrightarrow[+b]{-a}$ Ma_3b_3

cis/trans ? GI ×

fac/mer ?

Q. $M(AB)(CD)e_2$

→



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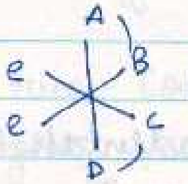
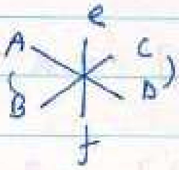


④

Q. M(AB)(CD)ef

→



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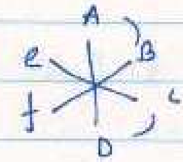


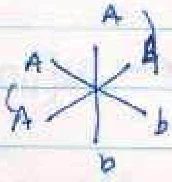
⑧

Q. $M(AA)_2b_2$ $\xrightarrow[+AA]{-b_2}$ $M(AA)_3$

possible compounds

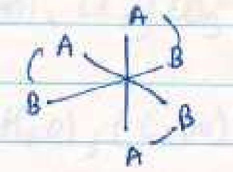
① (OA)

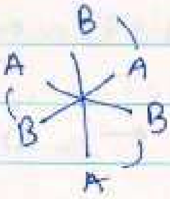
which isomer



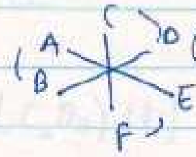
Only cis

Q. $M(AB)_3$

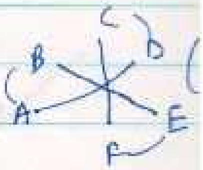




Q. M(AB)(CD)(EF)



④



211-234

- when symm. bidentate ligand present in CN 4 it does not show stereoisomerism. Either it is sq. planar or tetrahedral.

- In CN 6,

  i) when two bidentate ligands are present, cmpd (cis) is always optically active.

  ii) when three bidentate ligands are present cmpd is always OA

  iii) when 3 identical monodentate ligands are present only 1 cis isomer exists.

* Structural Isomerism :→

[Do NOT change CN of CMI]

1] **Ionization** : compounds having same Molecular formula but furnishes different diff. counter ions in aq. medium. In such complexes counter ion can act as ligand and ligand as counter ion.

They can be distinguished by conductivity measurement, qualitative analysis.

$$[ML_x]A \longrightarrow [ML_{x-1}A]L$$

Q.

Cr·5NH$_3$·SO$_4$·Cl has two ionisation isomers A & B. A gives ppt with AgNO$_3$ solⁿ while B gives ppt with BaCl$_2$ solⁿ. Identify A & B & Arrange them in correct order of conductivity.

→ A = $[Cr\cdot 5NH_3\cdot SO_4]Cl$

✓ B > A

B = $[Cr\cdot 5NH_3\cdot Cl]SO_4$

Q. Find the formula of ionisation isomers of given complexes.

*1] $[Cr(NH_3)_4SO_4]Cl \longrightarrow [Cr(NH_3)_4Cl]SO_4$ ✗ No Isomer

2) $[Cr(NH_3)_{4}(bcac)]Br \longrightarrow [Cr(NH_3)_{3}(Br)(bcac)]NH_3$ ✗

3) $[Pt(en)_2Cl_2]CO_3 \longrightarrow [Pt(en)_2(Cl)CO_3]Cl$ ✓

4) $[Pt(H_2O)_3(C_2O_4)CN]Cl \rightarrow [Pt(H_2O)_3(C_2O_4)Cl]CN$ ✓

5) $[Fe(H_2O)_4(O_2N)]Cl \longrightarrow [Fe(H_2O)_4 Cl]NO_2$.

Q. Find the Structural formula of A & B having same M.F. $Pt \cdot 3NH_3 \cdot Cl \cdot Br$. If $\Delta A > \Delta B$

→ A ~~B~~ = $[Pt(NH_3)_3 Cl]Br$

B ~~A~~ B = $[Pt(NH_3)_3 Br]Cl$

Also write down the observation when A & B reacts with excess $AgNO_3$ sol^n.

A ~~B~~ = Pale yellow   B = white

2] Hydrate Isomer :

This type of isomerism arises due to presence of H_2O in complex compound.

When no. of water molecules inside & outside the coordination sphere are different then compounds are hydrate isomers of each other.

- Complex must be complex cation simple anion.
- H_2O ligands are interchanged by -ve counter ions

They can be distinguished by

i) conductivity measurement

ii) Quantitative analysis

iii) Weight loss measurement on ran with conc. H_2SO_4 (removal of uncoordinated water)

iv) Δ splitting / stability of complex

$\times 2, 4$
$6\sqrt{15}$

A) $[Cr(H_2O)_6]Cl_3$

B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

C) $[Cr(H_2O)_4Cl_2]Cl\,2H_2O$

} Hydrate Isomers

~~$[Cr(H_2O)_3Cl_3]\,3H_2O$~~

Conductivity order : A > B > C

Moles of AgCl obt. when 1 mol of each reacts with excess $AgNO_3$: 3 , 2 , 1

Order of M. Wt. of product obt. on rxn with conc. H_2SO_4 : A > B > C

Stability order : A > B > C

3] **Linkage Isomerism :**

Complexes having same MF also having ligands having same MF but co-ordinated by diff. diff. donor site with CMI are linkage isomers of each other. This type of isomerism arises when complex contains ambidentate ligand.

eg,

$[Pt(NH_3)_3CN]Cl \longleftrightarrow [Pt(NH_3)_3NC]Cl$

Q. Find total no. of linkage isomers of $[Pt(CN)_4]^{2-}$.

→ ~~4~~ ⑤

Q. $[Cr(CN)_3(NO_2)_3]^{3-}$ 4×4

→ 16

Q. $[Pt(SCN)_2(NOS)_2]^{2-}$ 3×6

→ 18

Q. Find total no. of isomers of $[Cr(NH_3)_3(CN)_3]$

$2 \times 3 = 6$
$2 \times 2 = 4$

10

→ $\boxed{10}$

Q. Find the isomerism present b/w given pair of complexes

a) $[Cr(H_2O)_5NO_2]Cl_2$

b) $[Cr(H_2O)_4(NO_2)Cl]Cl \cdot H_2O$

c) $[Cr(H_2O)_5ONO]Cl_2$

d) $[Cr(H_2O)_4Cl_2]NO_2 \cdot H_2O$

→ ab → hydrate, ~~ionisation~~
ac → linkage
ad → hydrate, I
bc → linkage, ~~I~~, H
bd → I
cd → H, I

Note : I when counter "ions" get different

7+12+15+15+12
+7

4] Co-ordination Isomerism :

This type of isomerism arises when compound contains complex cation as well as complex anion. Compounds having same MF but ligand or grp of ligands are present in diff. diff. co-ordination sphere, are co-ordination isomers of each other.

eg. $[\overset{+3}{Cr}(NH_3)_6][\overset{+3}{Co}(CN)_6] \longrightarrow [Cr(NH_3)_5CN][Co(CN)_5NH_3]$

⑥

$[Cr(NH_3)_4(CN)_2]\ [Co(CN)_4(NH_3)_2]$

↙

linkage CN

↳ (68)

$[Cr(NH_3)_2(CN)_4]\ [Co(NH_3)_4(CN)_2]$

$[Cr(NH_3)(CN)_5]\ [Co(NH_3)_5(CN)$

+②

Q. Find total no. of C.N. isomers of this $[\overset{+3}{Co}(NH_3)_6]$
$[\underset{+3}{Co}(C_2O_4)_3]$

→ ①

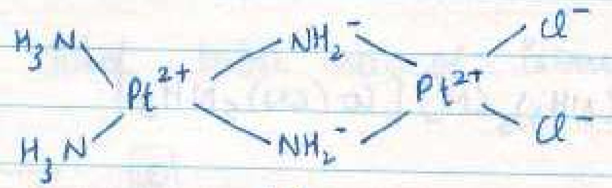
Q. $[\overset{3+}{Pt}(NH_3)_4][\overset{3+}{Pt}(Cl)_4(SCN)_2]$ C.N. isomers.

→ 7

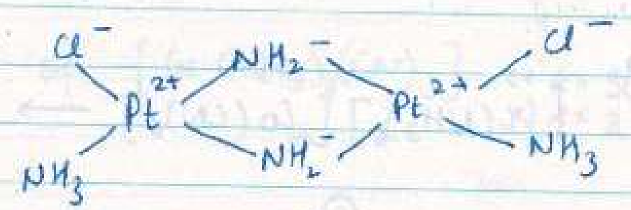
5] Co-ordination position :

This arises in binuclear complexes. Binuclear complexes having same MF but ligand or group of ligands are co-ordinated with diff. diff metal ion are co-ordination position isomers of each other.

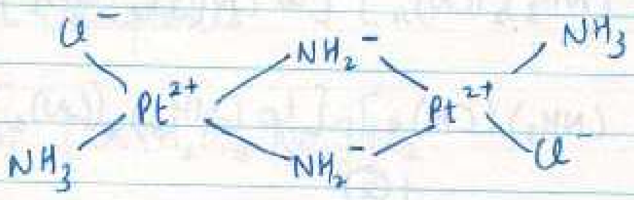
Eg,



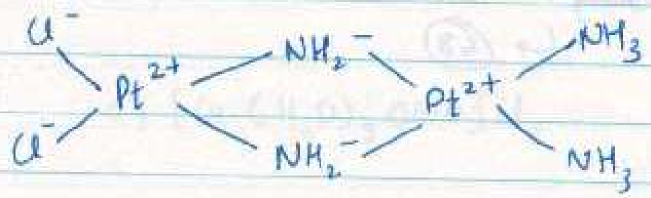
(A)



(B)



(C)



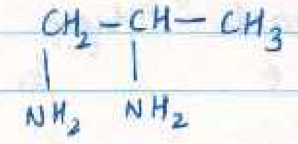
(D)

AB) CPI
AC) CPI
AD) identical
BC) GI
BD) CPI
DC) CPI

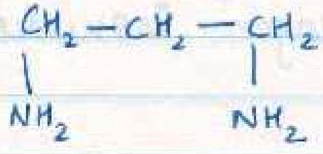
6] Ligand :

When complex contains ligand which can show position isomerism then complex can show ligand isomerism.

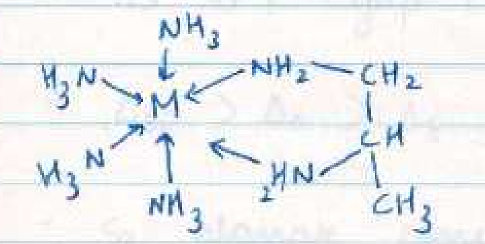
eg,

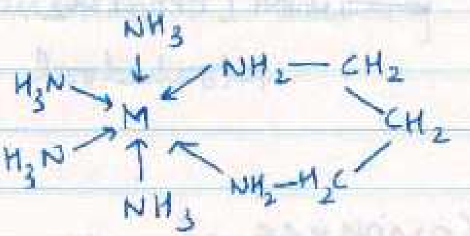


$CH_2(NH_2)-CH(NH_2)-CH_3$



$CH_2(NH_2)-CH_2-CH_2(NH_2)$





Tetraammine -(1,2- diamine propane) M.

7] Polymerisation :

This is not true isomerism. complexes having diff. MF but same empirical formula are polymer isomers of each other.

	Pt	NH_3	Cl	
$[Pt(NH_3)_2Cl_2]$	1	2	2	PI
$[Pt(NH_3)_4][PtCl_4]$	2	4	4	
$[Pt(NH_3)_3Cl]_2[PtCl_4]$	3	6	6	

When a neutral complex contains neutral ligand as well as anionic ligand it can show polymerisation Isomerism.

* Allogen Isomerism :

Complexes having same MF but different geometry around CMI are allogen isomers of each other.

eg,

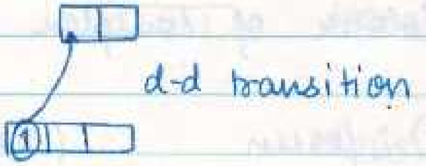
$$\underset{\text{sq. planar}}{Ni(PPh_3)Cl_2} \rightleftharpoons \underset{\text{tetrahedral}}{Ni(PPh_3)Cl_2}$$

* COLOUR OF COMPLEXES :

Colour

- d-d transition
  - due to splitting
  - self emitation
    No. of transition ↓
    Intensity ↓
- Charge Transfer (CT)
  - Ligand to Metal (LMCT)
  - Metal to Ligand (MLCT)
  - Metal to Metal (MMCT)
  - due to potential diff.
    No. of transition ↑
    Intensity ↑

* d-d transition



⇒ d^{10}, d^0, ~~d^5~~ - WFL (d^5-WFL symmetrically filled)

⇒ d^{1-9} ⇒ $\Delta = \frac{hc}{\lambda_{ab.}}$

⇒ As Δ ↑ gap ↑ transition ↓ intensity ↓

⇒ $\Delta_{sp} > \Delta_o > \Delta_t$

- Sq. planar complexes are generally colourless or light yellow.
  Tetrahedral complexes are more intense in compariso of octahedral

* $CoCl_4^{2-}$ → intense blue
$[Co(H_2O)_6]^{2+}$ → Pink

- Octahedral cyano complexes are yellow in colour.

Q. Match them correctly

complex	Colour of complex	
A) $[Ni(H_2O)_6]^{2+}$	P) Green	(R)
B) $[Ni(en)(H_2O)_4]^{2+}$	Q) Blue - Green	
C) $[Ni(en)_2(H_2O)_2]^{2+}$	R) Blue	(B)
D) $[Ni(en)_3]^{2+}$	S) Violet	(Y)

→ A - P, B - Q, C - R D - S VIBGYOR

$\lambda_{ab.} \Rightarrow P > Q > R > S$

Q. Complex . colour

$\Delta\uparrow \quad \lambda_{ab}\downarrow$

$[Cr(NH_3)_5Cl]^{2+} \longrightarrow$ Yellow

$[Cr(NH_3)_5(H_2O)]^{3+} \longrightarrow$ Green

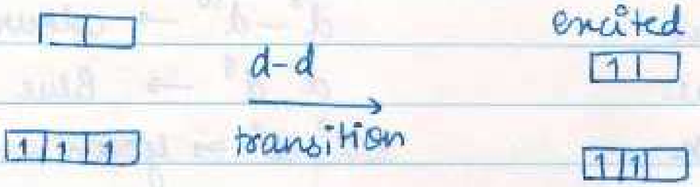
$[Cr(NH_3)_6]^{3+} \longrightarrow$ Blue

$[Cr(CN)_6]^{3-} \longrightarrow$ Violet

→ For abs. colour,

A - S
B - R
C - Q
D - P

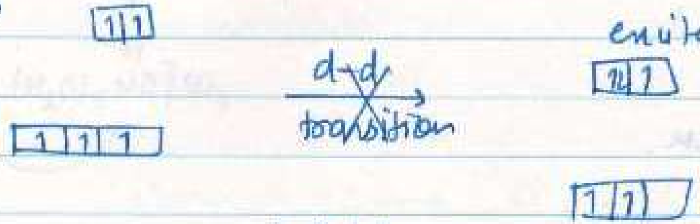
d^3



No change in spin
(extra pairing

Spin allowed

d^5



Change in spin
(extra pairing ✓)

highly unstable

Spin forbidden
(Spin not allowed)

- Emerald green is a mineral beryl - $Be_3Al_2Si_6O_{18}$ cyclic silicate, is coloured due to presence of impurity Cr^{3+} i presence of Al^{3+} at octahedral site.

- Ruby (Red) is an impure Al_2O_3. It contains impurity o Cr^{3+} which is the reason of colour.

<u>Colour of transition metal ions in aq. medium</u>:

In presence of water, d-orbitals are splitted, so their solution is coloured due to d-d transition except Fe^{3+} & Mn^{2+}.
$Fe^{3+}_{(aq.)}$ & $Mn^{2+}_{(aq.)}$ are coloured due to [illegible],
LMCT

Fe^{2+} Ni^{2+} → green
Cu^{2+} Cr^{2+} → Blue
Mn^{2+} Co^{2+} → Pink
$Fe^{3+}_{(aq.)}$ → light yellow
$Cr^{3+}_{(aq.)}$ → Violet

$d^0 - d^{10}$ → colourless
d^1, d^9 → Blue (Ti^{3+} → Violet)
d^2, d^8 → green

$[Cr(H_2O)_6]^{3+}$ → Violet

$\left.\begin{matrix}[Cr(H_2O)_5Cl]^{2+} \\ [Cr(H_2O)_5SO_4]^{+} \\ [Cr(H_2O)_5NO_3]^{2+}\end{matrix}\right\}$ green.

- LMCT (Polarisation) :→
d^5 WFL, d^{10}, d^0

FeF_6^{3-}	$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_5OH]^{2+}$	$[Fe(SCN)_6]^{3-}$
colourless	light yellow	Yellow-Brown	Blood red

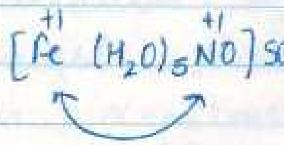
Polarizability $F^- < H_2O < OH^- < SCN^-$
transition ↑ intensity ↑

$\overset{+5}{V}O_4^{3-}$ $\overset{+6}{Cr}O_4^{2-}$ $\overset{+7}{Mn}O_4^-$
intensity ↑
colourless Yellow Purple

* K_2MnO_4 d^1 d-d transition

- MLCT :→

Charge on CMI ≤ ligand
low O.S. of CMI
ligand : CO, NO^+, π donor
eg,
Brown ring complex



$[\overset{+1}{Fe}(H_2O)_5\overset{+1}{NO}]SO_4$

Sodium Nitroprusside
$Na_2[\overset{+2}{Fe}(CN)_5\overset{+}{N}O]$
M~~LC~~T
colourless

- MMCT :→

- At least 2 metal ions should be present, which belongs to d-block (can show variable O.S.)
- P.D. must be present b/w metal ions

$M^{+x} \leftarrow N \equiv C \rightarrow Fe^{2+}$ shows colour when e^- acceptance tendency of $M^{+x} > Fe^{2+}$ or $x > 2$ for $x = 2$, Z_{eff} of $M^{+2} > Fe^{2}$

$M^{+x} \leftarrow N \equiv C \rightarrow Fe^{3+}$ is always coloured

- $\overset{+2}{Fe_2}[\overset{+2}{Fe}(CN)_6]$ (white)
  Ferro Ferrocyanide
  Iron (II) hexacyanido ferrate (II)
  22- complex

  $Fe^{2+} \leftarrow N \equiv \bar{C} \rightarrow Fe^{2+}$
  ~~MMCT~~
  White ppt

- $\overset{+3}{Fe_4}[\overset{+2}{Fe}(CN)_6]_3$
  Ferri Ferrocyanide
  32- complex
  Prussian blue

  $Fe^{2+} \leftarrow C \equiv N \rightarrow Fe^{3+}$
  MMCT ✓
  Blue ppt

- $\overset{+2}{Fe_3}[\overset{+3}{Fe}(CN)_6]_2$
  Ferro Ferric cyanide
  23- complex
  turnbull's blue

  $Fe^{3+} \leftarrow C \equiv N \rightarrow Fe^{2+}$
  MMCT ✓
  Blue ppt

- $Fe[Fe(CN)_6]$
  33 - complex
  Ferric Ferricyanide

  $Fe^{3+} \leftarrow C \equiv N^{-} \rightarrow Fe^{3+}$
  ~~MMCT~~ LMCT ✓
  Red-Brown colouration

eg,

- $Cu_2[Fe(CN)_6]$ $Cu^{2+} \leftarrow N \equiv C \rightarrow Fe^{2+}$ coloured PP $Cu^{2+} > Fe^{2+}$
- $Ag_4[Fe(CN)_6]$ $Ag^{+} \leftarrow N \equiv C \rightarrow Fe^{2+}$ White
- $Zn_2[Fe(CN)_6]$ $Zn^{2+} \leftarrow N \equiv C \rightarrow Fe^{2+}$ White
- $Cd_2[Fe(CN)_6]$ → Bluish white
- $Ag_3[Fe(CN)_6]$ → coloured
- $Cu_3[Fe(CN)_6]_2$ → coloured

• Applications :→

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour rans given by metal ions with a number of ligands, as a result of formation of coordination entities, form the basis for their detection and estimation by classical & instrumental methods of analysis. Examples of such reagents include EDTA, DMG, α-nitroso-β-naphthol, cupron, etc.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium & magnesium complexes.

- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqeous sol^n. Gold can be separated in metallic form from this solution by the addition of zinc.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure ~~impure~~ nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti-pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ & $[Au(CN)_2]^-$ than from a solution of simple metal ions.

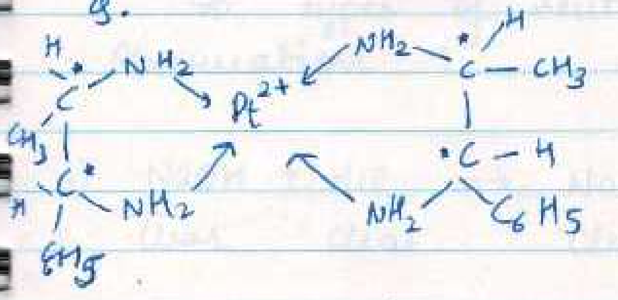
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of

Ex: 3/60 A

metals in toxic proportions in plant / animal systems. Thus, excess of copper and iron are removed by the Chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds. EDTA i used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are : cis platin and related compounds.

9.

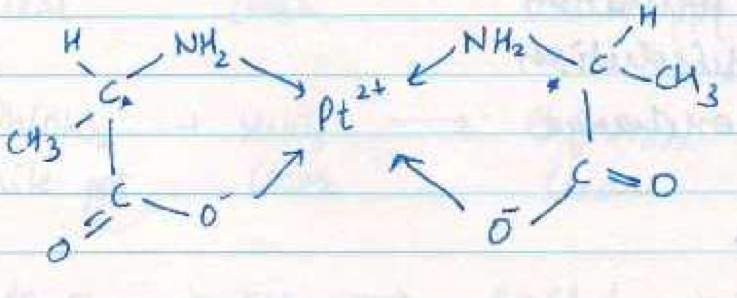


Stereo.

⑥ × ② | 8 + 4 + 2   14.

$\boxed{20}$ cis → 10 (6, 4 OA)
trans → 10 (6, 40A).

9.



⇒ 6

Types of Reaction

1] Acid - Base rxn
- → Neutralisation
- → lewis acid - base
  - → complex formation
  - → Hydrolysis

  (But not exactly lewis acid - base)

2] Thermal decomposition

3] Redox rxn
- → disp^n
- → comp^n
- → displacement
- → decomp.
- → combination

4] Ion exchange
- → ppt formation
- → ppt dissolution
- → ppt exchange

* Neutralisation Rxn :→

In this rxn, formation of H_2O takes place & energy is released so rxn moves in forward direction.

Acid : Compound of NM, generally they are molecules, exist in gaseous / liquid state. When dissolved in water, either ionisable (strong acid) or non-ionisable (weak acid).

Weak acid are present in water in soluble form

due to dipole-dipole interaction / H-bond with H_2O.
No ppt observed in water.

Base : compound of metal, ionic in nature, exists in Solid state, either soluble ~~or~~ (strong base) or insoluble (weak base). Insoluble gives ppt in water

Salt : Ionic cmpd, solid state, either soluble or insoluble.

So, types of neutralisation rxn on the basis of Observation :

1) $NaOH + HCl \longrightarrow NaCl + H_2O$ (simple).
Clear Clear Clear

2) $Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2O$ (ppt formation)
Clear Clear white ppt

3) $Pb(OH)_2 + HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$ (ppt dissolution)
white ppt Clear Clear

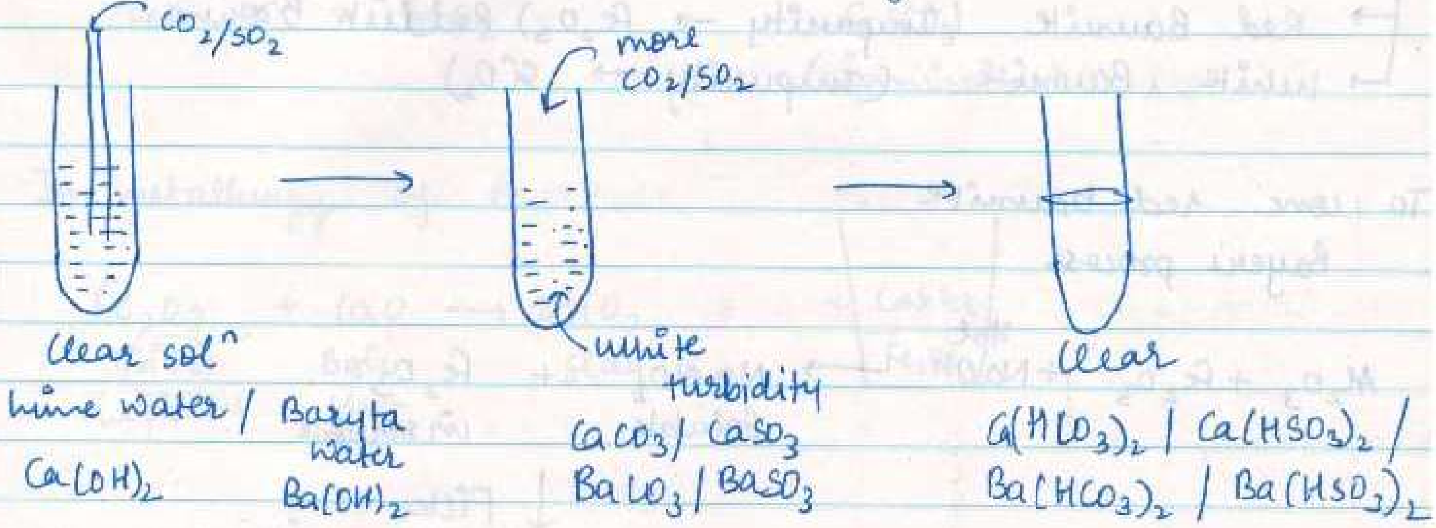
4) $Ag_2O + HCl \longrightarrow AgCl\downarrow + H_2O$ (ppt exchange)
Black-Brown white

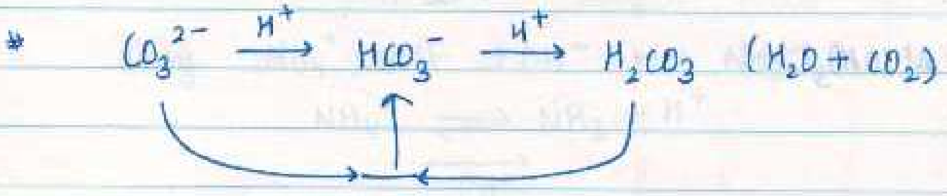
	I	I	I	I	I	I	I	I	I	I	S	S	S	I	S
	Ag_2O	$Pb(OH)_2$	$Cu(OH)_2$	$Cd(OH)_2$	$Fe(OH)_3$	$Fe(OH)_2$	$Al(OH)_3$	$Cr(OH)_3$	$Zn(OH)_2$	$Ni(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$	$Mg(OH)_2$	$NaOH$
CO_2	④	④	④	④	④	④	④	④	④	④	②	②	②	④	①
HCl	④	④	③	③	③	③	③	③	③	③	①	①	①	②	①
HBr	④	④	④	③	③	③	③	③	③	③	①	①	①	②	①
HI	④	④	④	③	③	③	③	③	③	③	①	①	①	②	①
HNO_3	③	③	③	③	③	③	③	③	③	③	①	①	①	③	①
HNO_2	④	③	③	③	③	③	③	③	③	③	①	①	①	③	①
H_2SO_4	③	④	③	③	③	③	③	③	③	③	①	②	②	③	①
$H_2C_2O_4$	④	④	④	④	④	③	④	④	④	④	②	②	②	④	①
H_2S	④	④	④	④	④	④	④	④	④	④	①	①	①	③	①
HCN	④	④	④	④	④	④	④	④	④	④	①	①	①	③	①
H_2SO_3	④	④	④	③	③	③	③	③	③	③	①	①	②	③	①
CH_3COOH	④	③	③	③	③	③	③	③	③	③	①	①	①	③	①

Other Acid - Base Rxns :

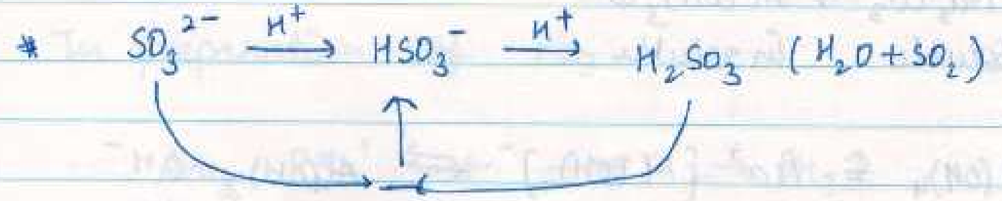
1) Lime water / Baryta water test :

Used to identify CO_2 & SO_2, both give same observation so we can't distinguish them.





$$* \quad CO_3^{2-} \xrightarrow{H^+} HCO_3^- \xrightarrow{H^+} H_2CO_3 \quad (H_2O + CO_2)$$



$$* \quad SO_3^{2-} \xrightarrow{H^+} HSO_3^- \xrightarrow{H^+} H_2SO_3 \quad (H_2O + SO_2)$$

In metallurgy,

Bauxite → Ore of Al
- ↳ $Al_2O_3 \cdot x H_2O$ ($O^{2-} + OH^-$)
  white
- → Red Bauxite (Impurity → Fe_2O_3) Reddish Brown
- ↳ White Bauxite (Impurity → SiO_2)

To conc. red bauxite
Bayer's process

$$Al_2O_3 + Fe_2O_3 \overset{\text{Hot}}{+ NaOH} \longrightarrow \underset{\text{Soluble}}{NaAlO_2} + \underset{\text{insoluble}}{Fe_2O_3}$$

$$\downarrow \text{Filter}$$

$$NaAlO_2$$

Recovery of Al_2O_3 / $Al(OH)_3$ from Filtrate

$$NaAlO_2 \xrightarrow{CO_2} \underset{\text{Soluble}}{Na_2CO_3} + \underset{\text{insoluble}}{Al(OH)_3\downarrow}$$

$$NaAlO_2 = Na\,Al(OH)_4 = Na^+[Al(OH)_4]^- \rightleftharpoons Al(OH)_3 + \underset{\substack{\downarrow CO_2 \\ CO_3^{2-}}}{OH^-}$$

In furnaces

In metallurgy of Cu.

Cu_2S contain impurity of FeO

Basic impurity + acidic flux $\longrightarrow$ slag

$FeO + SiO_2 \longrightarrow FeSiO_3$ (immiscible)

In metallurgy of Fe

$$\underset{\text{impurity}}{Fe_2O_3 + \boxed{SiO_2}} + \underset{\text{Basic flux}}{CaO} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

- In preparation of NH_3

Any NH_4^+ salt $+ OH^- \longrightarrow NH_3\uparrow$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$
$$\xrightarrow[OH^-]{}$$

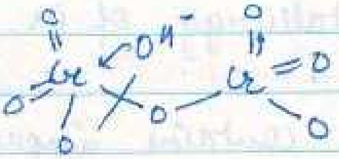
In preparation of PH_3

Any PH_4^+ salt $+ OH^- \longrightarrow PH_3\uparrow$

$$PH_4^+ \rightleftharpoons PH_3 + H^+$$
$$\xrightarrow[OH^-]{}$$

- In preparation of dichromate

$Na_2CrO_4 \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Na_2Cr_2O_7$



- In Salt analysis

To separate Al_2O_3 & Fe_2O_3

$\xrightarrow{NaOH} NaAlO_2 + Fe_2O_3\downarrow$

To separate Cr_2O_3 & Fe_2O_3

$\xrightarrow{NaOH} NaCrO_2 + FeO_3\downarrow$

green

- To distinguish strong acid anion & weak acid anion from soluble salt solution with the help of dilute H_2SO_4.

Stronger the acid weaker the base
Strong acid kaa anion weak base hota hai jiski H^+ lene ki tendency bohot kum hoti hai
Weaker the acid stronger the base weak acid kaa anion strong base hota hai jiski H^+ lene ki tendency bohot jyada hoti hai, H^+ ke liye pagal hota hai

CO_3^{2-} + dil. $H_2SO_4 \longrightarrow CO_2\uparrow$

WA Anion (H_2CO_3)

Cl^- + dil. $H_2SO_4 \longrightarrow X$

SA anion

↑

amt. of H_2O is high dil. H_2SO_4 jo H^+ dega woh H_2O le lega. Cl^- ko H^+ lene ke liye koi pressure nahi hai

CO_3^{2-} + conc. $H_2SO_4 \longrightarrow CO_2\uparrow$

Cl^- + conc. $H_2SO_4 \longrightarrow HCl\uparrow$

↑

amt. of H_2O is very low. conc. H_2SO_4 strong acid hai jo H^+ dega hi dega, abb Cl^- ko H^+ lena hi padega

WA anion

$$\left.\begin{array}{l}CO_3^{2-}\\ SO_3^{2-}\\ S^{2-}\\ S_2O_3^{2-}\\ NO_2^{-}\\ CH_3COO^{-}\end{array}\right\}\xrightarrow[H_2SO_4]{dil.}\text{volatile Product}$$

SA anion

$$\left.\begin{array}{l}F^{-}\\ Cl^{-}\\ Br^{-}\\ I^{-}\\ NO_3^{-}\end{array}\right\}\xrightarrow[H_2SO_4]{dil.}\xcancel{\text{volatile product}}$$

* ION EXCHANGE REACTION :

Soluble (✓) = cation-anion ka alag alag rehna.
cation-anion ke beech mai koi att^r nahi hai, dono ek dusre ko nahi chahte hai.

Insoluble (×) = cation anion ek saath rehna chahte hai, ek dusre ke liye pagal hai

$$Salt_1 + Salt_2 \longrightarrow Salt_3 + Salt_4$$

① ✓ ✓ ✓ ✓ (no rxn)

② ✓ ✓ × ✓ (ppt. formation)

③ ✓ ✓ × × (ppt. formation)

④ × ✓ × ✓ (ppt. exchange)

Solubility $Salt_1 > Salt_3$

$$BaSO_4 \downarrow + Na_2CO_3 \longrightarrow BaCO_3 \downarrow + Na_2SO_4$$

Solubility (K_{sp}) $BaSO_4 > BaCO_3$

$$BaSO_4 \rightleftharpoons Ba^{2+} \; SO_4^{2-}$$

⑤ × ✓ ✓ ✓

ye rxn nahi hogi bina external force ke

This rxn moves in → dir^n when either cation or anion or both disappear from sol^n.

- cation can disappear by,
  i) ppt exchange rxn
  eg, $AgCl + NaI \rightarrow AgI\downarrow + NaCl$
  ii) by complex formation rxn
  coz during complex f. metal ion becomes CMI & loses its identity.

eg, * All Ag salts are soluble in excess KCN
* All Ag salts are soluble in excess hypo except Ag_2S
* All Ag salts are soluble in excess NH_3 except AgI & Ag_2S

Solubility ↓ covalent ↑ →

	$AgCl$	$AgBr$	AgI	Ag_2S	
H_2O	×	×	×	×	$[Ag(H_2O)_2]^+$
Cold NH_3	✓	×	×	×	$[Ag(NH_3)_2]^+$
Hot NH_3	✓	✓	×	×	
$S_2O_3^{2-}$	✓	✓	✓	×	$[Ag(S_2O_3)_2]^{3-}$ CN = 4, chelation
CN^-	✓	✓	✓	✓	$[Ag(CN)_2]^-$

Stability : $[Ag(CN)_2]^- > [Ag(S_2O_3)_2]^{3-} > [Ag(NH_3)_2]^+ > [Ag(H_2O)_2]^+$

As solubility of salt ↓
for dissolution , req. stability of complex ↑ .

* All Pb(II) salts are soluble in excess NaOH except PbS due to formation of hydroxo complex

$$PbCO_3 + NaOH \longrightarrow \underset{\text{soluble}}{Na_2PbO_2} + Na_2CO_3$$

* All Zn(II) salts are soluble in excess NaOH except ZnS

$$ZnCO_3 + NaOH \longrightarrow \underset{\text{soluble}}{Na_2ZnO_2} + Na_2CO_3$$

- Anion can disappear by ,
  i] On rxn with strong acid

⇒ All carbonate salts are soluble in
dil. HCl, dil. H_2SO_4, dil. HNO_3, CH_3COOH

$$\underset{\text{insoluble}}{Ag_2CO_3} + \text{dil. } HNO_3 \longrightarrow \underset{\text{soluble}}{AgNO_3} + CO_2\uparrow$$

⇒ To Dissolve	Acid which is not used for dissolution
Ag (I) salt	HCl, CH_3COOH
Pb (II) Salt	dil. HCl, dil. H_2SO_4
Ba (II) Salt	dil. H_2SO_4
Ca (II) Salt	×

⇒ All insoluble CrO_4^{2-} are soluble in dil. HCl / dil. HNO_3 / dil. H_2SO_4

Acidic Nature $H_2CrO_4 < \underset{SA}{\underline{HCl / HNO_3 / H_2SO_4}} / \underset{WA}{\underline{CH_3COOH}}$

$SrCrO_4$ is only CrO_4^{2-} which is soluble in CH_3COOH.
H_2CrO_4 is non volatile while H_2CO_3 (CO_2) is volatile.
Weak acid CH_3COOH mai saare CO_3^{2-} soluble hai coz CO_2 volatile hai, ddn ko → le jayega.

WA CH_3COOH mai ek hi CrO_4^{2-} soluble hai $SrCrO_4$ coz saare insoluble CrO_4^{2-} mai uski solubility sabse jyada hai, H_2CrO_4 non volatile hai, solⁿ mai pada rahega.

⇒ All insoluble oxalate are soluble in dil. HCl / dil. HNO_3/ dil. H_2SO_4

Only BaC_2O_4 is soluble in CH_3COOH among insoluble oxalate.

⇒ All insoluble sulphates are insoluble in dil. HCl, dil. H_2SO_4, dil. HNO_3, they are soluble in conc. acid

$$H_2SO_4 \xrightarrow{ka_1} HSO_4^- \xrightarrow{ka_2} SO_4^{2-}$$

$$Ka_1 \gg Ka_2$$

SO_4^{2-} is strong base in comparison of HSO_4^- so SO_4^{2-} can take H^+ ~~from~~ only from conc. acid from soluble HSO_4^-

$$BaSO_4 + \text{dil. } H_2SO_4 \longrightarrow \times$$

H_2O jyada hai woh H^+ le lega

$BaSO_4$ + conc. $H_2SO_4 \longrightarrow Ba(HSO_4)_2$

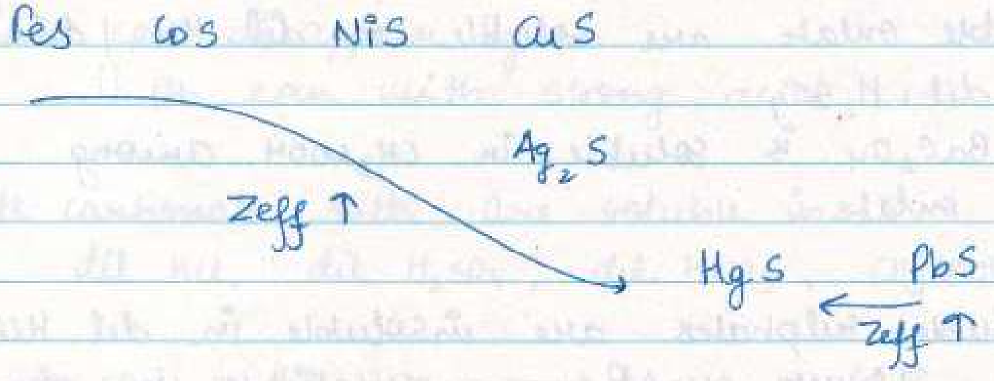
H_2O km hai majburi mai H^+ SO_4^{2-} ko lena padega.

- Sulphide

dissolution tendency coloured > Black

(On the basis of covalent chr)

Black colour sulphide



⇒ only black colour sulphide which insoluble in dil. HCl is FeS

⇒ Only sulphide which is insoluble in dil. HNO_3 is HgS

dil. HCl + $S^{2-} \longrightarrow H_2S$

No change in O.S. of 'S'

rxn can moves in backward dirn

$\text{dil. } HNO_3 + S^{2-} \longrightarrow S\downarrow + NO\uparrow$

change in O.S. of 'S'

Rxn can't move in backward direc^n

So HNO_3 is better reagent for dissolution of black colour sulphide in comparison of dil. HCl.

- **By Redox change :**

$$\underset{\text{(white)}}{AgNO_2\downarrow} + O_3 \longrightarrow \underset{\text{Soluble}}{AgNO_3} + O_2\uparrow$$

* COMPLEX FORMATION REACTION :-

- It is lewis acid - base rxn.
- This rxn is based on hard soft acid base theor
Acc^n to this theory (HSAB), strong lewis acid prefers to form complex with strong lewis base & weak lewis acid prefers to form complex with weak lewis base.

Eg, d-block metal ions form cyano complex, p-bloc & mercury do not form complex with cyanid ion.

- d-block cations except Fe, Mn, Hg form complex with NH_3.
- p-block cation & Hg form iodo complex.
- d-block as well as p-block cations form complex with hypo ($S_2O_3^{2-}$), weak field ligand but forms stable complex due to chelation.

- Reagents of Precipitation :

1] NaOH :→

$$\begin{tikzcd}
 & & \text{Basic} \arrow[r, "NaOH"] & X \\
M^{+x}_{(aq.)} \arrow[r, "NaOH"] & M(OH)_x \arrow[ur] \arrow[dr] & & \\
 & & \text{Amphoteric} \arrow[r, "NaOH"] & \text{soluble sod. Salt}
\end{tikzcd}$$

$M \neq NH_4$, IA, Ba-Sr, Ca

Zn, Be, Al, Ga, Sn, $\overset{+3}{Cr}$, $\overset{+5}{V}$, $\overset{+3}{Sb}$, $\overset{+5}{As}$, Pb

S, p block d^{10} → white

Cr^{3+}, Fe^{2+}, Ni^{2+} → Green

Cu^{2+}, Cr^{2+} → Blue

Mn^{2+}, Co^{2+} → Pink

$Fe(OH)_3$ → Reddish Brown.

$$\begin{tikzcd}
 & Al(OH)_3\downarrow \arrow[r, "NaOH"] & NaAlO_2 \\
Al^{+3} \arrow[ur, "NaOH"] \arrow[r, "\text{excess NaOH}"'] & NaAlO_2 &
\end{tikzcd}$$

$$\begin{tikzcd}
 & Fe(OH)_3\downarrow \arrow[r, "NaOH"] & X \\
Fe^{3+} \arrow[ur, "NaOH"] \arrow[r, "\text{excess NaOH}"'] & Fe(OH)_3\downarrow &
\end{tikzcd}$$

2] NH_3 / NH_4OH :→

- NH_3 is a WB, when it dissolves in water initially it gives OH^- so reacts like NaOH but as it is a weak base, it gives a limited amount of OH^- in water.

On adding excess NH_3 / NH_4OH, NH_3 present in water in molecular form, forms H-bond with H_2O.

So in excess NH_3, main reagent is NH_3 & in limited NH_3 main reagent is OH^-.

In excess NH_3, NH_3 acts as ligand, shows complex formation rxn, it is a SFL so forms complex with d block cation.

$$\begin{tikzcd} & & \text{d block} \arrow[r, "NH_3", "\text{exept Fe, Mn, Hg}"'] & \text{soluble complex} \\ M^{+x} \arrow[r, "NH_4OH/NH_3", "M \neq NH_4^+, IA, Ba, Sr, Ca"'] & M(OH)_x \downarrow \arrow[ur, bend left] \arrow[dr, bend right] & & \\ & & \text{P block} \arrow[r, "NH_3"] & X \end{tikzcd}$$

⇒ Hg shows complex formation as like p block cation due to large size, absence of (n-1)d orbitals

⇒ NH_3 acts as WFL for Mn^{2+}, Fe^{+2}

⇒ K_{sp} of $Fe(OH)_3$ is very very low so it is perfect ppt in presence of NH_3.

d^{10} → colourless

$Cu^{2+}_{(amm.)}$, $Ni^{2+}_{(amm.)}$ → Blue

H.W.

Metal Ion	NaOH	excess NaOH	NH₃ / NH₄OH	excess NH₄OH
Ag^+	$AgOH$ (white) $\xrightarrow{RT}$ Ag_2O (Black brown)		$AgOH$	$[Ag(NH_3)_2]$
Ⓐ Pb^{2+}	$Pb(OH)_2$	Na_2PbO_2	$Pb(OH)_2$	$Pb(OH)_2$
* Hg^{2+}	$Hg(OH)_2$ $\xrightarrow{RT}$ HgO (red)	$Hg(OH)_2$	$Hg(OH)_2$	$HgO.HgNH_2x$
Cu^{2+}	$Cu(OH)_2$ (Blue)	$Cu(OH)_2$	$Cu(OH)_2$	$[Cu(NH_3)_4]^{+2}$ (Blue)
Bi^{3+}	$Bi(OH)_3$	$Bi(OH)_3$	$Bi(OH)_3$	$Bi(OH)_3$
Cd^{2+}	$Cd(OH)_2$	$Cd(OH)_2$	$Cd(OH)_2$	$[Cd(NH_3)_4]^{2+}$ (Clear)
* Fe^{3+}	$Fe(OH)_3$ (Brown)	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3$
Fe^{2+}	$Fe(OH)_2$ (green)	$Fe(OH)_2$	$Fe(OH)_2$	$Fe(OH)_2$
		→ on standing, reddish Brown ($Fe^{2+} \longrightarrow Fe^{+3}$)		
Ⓐ Cr^{3+}	$Cr(OH)_3$ (green)	$NaCrO_2$	$Cr(OH)_3$	$[Cr(NH_3)_6]^{3+}$ (Pink)
Ⓐ Al^{3+}	$Al(OH)_3$	$NaAlO_2$	$Al(OH)_3$	$Al(OH)_3$
Mn^{2+}	$Mn(OH)_2$ (Pink)	$Mn(OH)_2$	$Mn(OH)_2$	$Mn(OH)_2$
Co^{2+}	$Co(OH)_2$ (Pink)	$Co(OH)_2$	$Co(OH)_2$	* $[Co(NH_3)_6]^{2+}$ (Yellow)
Ⓐ Zn^{2+}	$Zn(OH)_2$	Na_2ZnO_2	$Zn(OH)_2$	$[Zn(NH_3)_4]$
Ni^{2+}	$Ni(OH)_2$ (green)	$Ni(OH)_2$	$Ni(OH)_2$	$[Ni(NH_3)_6]$ (Blue)

Ba^{2+}	×	×	×	×
Ca^{2+}	×	×	×	×

3] KI :

⇒ solubility :- All iodide are water soluble except Ag^+, Bi^{3+}, Cu^+, Hg_2^{2+}/Hg^{2+}, Pb^{2+}

⇒ Cu^{2+} & Fe^{3+} show redox rxn with I^-

⇒ In excess of KI :- $I^- \rightarrow$ WFL

p block, Hg insoluble iodide are soluble in excess KI due to formation of iodo complex.

Only iodo complex which is coloured = BiI_4^- (yellow - orange) due to polarization

- $Cu^{2+} + KI \longrightarrow \underset{\text{white}}{CuI\downarrow} + \underset{\text{Brown}}{I_2/KI_3}$

  $\quad \xrightarrow[KI]{} \times$

- $Ag^+ + KI \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} \xrightarrow{KI} \times$

- $Pb^{2+} \xrightarrow{KI} \underset{\text{yellow}}{PbI_2\downarrow} \xrightarrow{KI} \underset{\text{clear}}{PbI_4^{2-}}$

- $Hg^{2+} \xrightarrow{KI} \underset{red}{HgI_2\downarrow} \xrightarrow{KI} \underset{clear}{HgI_4^{2-}}$

  $\downarrow \Delta$

  $\underset{yellow}{HgI_2}$

- $Hg_2^{2+} \xrightarrow{KI} \underset{green}{Hg_2I_2} \longrightarrow \underset{Black}{Hg\downarrow} + \underset{clear}{HgI_4^{2-}}$

  - Hg_2^{2+} disp^n in presence of ligand $\underset{Black\ ppt}{Hg} + Hg^{2+}$

- $Bi^{3+} \xrightarrow{KI} \underset{Black-brown}{BiI_3\downarrow} \xrightarrow{KI} \underset{yellow-orange}{BiI_4^-}$

- $Fe^{3+} + KI \longrightarrow Fe^{2+} + I_2/KI_3$

- $K_4Fe(CN)_6 + KI \longrightarrow \times$

- $K_3Fe(CN)_6 + KI \longrightarrow K_4Fe(CN)_6 + KI_3/I_2$

* **Note** :

- $Ag^+ \xrightarrow[NH_3]{excess} [Ag(NH_3)_2]^+ \xrightarrow[standing]{on} Ag_3N$

  $\downarrow$ explosive rxn

  $Ag + N_2$ $(\Delta G = -ve)$

- $Hg^{2+}X^- \xrightarrow[NH_3]{excess} HgO\cdot HgNH_2^+X^-$

due to high p.p. of Ag^+ & Hg^{2+}

4] KCN :→

- All cyanides are water insoluble except NH_4^+, IA, IIA, $Hg(CN)_2$

- CN^- polyatomic anion, p block, polarizability ↓

- s, p block, d^{10} → white

  d^{1-9} (gen.) → yellow

- excess KCN : All insoluble d-block cyanide are soluble in excess KCN

CN^- → Strongest ligand (Complex of cyano)
d^{10} → clear solution
d^{1-9} (gen.) → Yellow
(Octahedral)

- Cu^{2+} shows redox with CN^-

eg,

- $Ag^+ \xrightarrow{KCN} \underset{white}{AgCN\downarrow} \xrightarrow{KCN} \underset{Clear}{[Ag(CN)_2]^-}$
- $Pb^{2+} \xrightarrow{KCN} \underset{white}{Pb(CN)_2\downarrow} \xrightarrow{KCN} \times$

- $Cu^{2+} \xrightarrow{KCN} \underset{\text{yellow - brown}}{Cu(CN)_2\downarrow} \xrightarrow[\text{Standing}]{\text{On}} \underset{\text{white}}{CuCN\downarrow} + (CN)_2\uparrow$

  $\quad CuCN \xrightarrow{KCN} K_3[Cu(CN)_4]$

- $Cd^{2+}/Zn^{2+} \xrightarrow{KCN}$ White ppt $\downarrow \xrightarrow{KCN}$ Clear sol^n

- $Fe^{3+} \xrightarrow{KCN} \underset{\text{Yellow - brown}}{Fe(CN)_3\downarrow} \xrightarrow{KCN} K_3[Fe(CN)_6]$

- $Fe^{2+} \xrightarrow{KCN} \underset{\text{Yellow}}{Fe(CN)_2\downarrow} \xrightarrow{KCN} K_4[Fe(CN)_6]$

  $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$] Yellow colour

- $Ni^{2+} \xrightarrow{KCN} \underset{\text{greenish-yellow}}{Ni(CN)_2\downarrow} \xrightarrow{KCN} \underset{\text{Clear}}{K_2[Ni(CN)_4]}$

- $Hg_2^{2+} \xrightarrow{KCN} Hg_2(CN)_2\downarrow \xrightarrow{KCN} \underset{\text{Black ppt}}{Hg} + \underset{\text{Clear}}{Hg(CN)_2}$

Q. $M^{+x} \xrightarrow{NaOH}$ Reddish Brown ppt $\xrightarrow{NH_4OH} X$

$$\begin{tikzcd}
M^{+x} \arrow[r, "KCN"] \arrow[d, "KI"'] & A \arrow[r, "KCN"] & C \arrow[r, "M^{+x}"] \arrow[dr, "M^{+y}"'] & E \\
 & & & F \\
M^{+y} \arrow[r, "KCN"] & B \arrow[r, "KCN"] & D \arrow[r, "M^{+x}"] \arrow[dr, "M^{+y}"'] & G \\
 & & & H
\end{tikzcd}$$

Identify A - H & M^{+x}.

$\rightarrow M^{+x} = Fe^{3+}$

$A = Fe(CN)_3$ $\qquad$ $E = Fe[Fe(CN)_6]$

$B = Fe(CN)_2$ $\qquad$ $F = Fe_3[Fe(CN)_6]_2$

$C = K_3[Fe(CN)_6]$ $\qquad$ $G = Fe_4[Fe(CN)_6]_3$

$D = K_4[Fe(CN)_6]$ $\qquad$ $H = Fe_2[Fe(CN)_6]$

Q. Which pair of ions can be separated by NaOH?

A) Pb^{2+} ; Cu^{2+}
B) Al^{3+}, Ca^{2+}
C) Ni^{2+}, Zn^{2+}
D) Cr^{3+}, Fe^{3+}

Q. Which d-block metal ion is soluble in excess NH_3 as well as excess NaOH but when limited NaOH is used it gives white coloured ppt?

→ Zn^{2+}

Q. A metal ion gives ppt & coloured solⁿ when reacts with KI. Find the formula of cmpd when metal ion reacts with excess KCN.

→ $K_3[Cu(CN)_4]$

5] Na_2CO_3 :-

- All CO_3^{2-} water insoluble except NH_4^+, IA

• Colour : s/p block, Zn^{2+} → white
d block → coloured (except Zn^{2+})

• ppt : $M^{+} \longrightarrow M_2CO_3$
$M^{2+} \longrightarrow MCO_3 \cdot M(OH)_2$
except $\underline{Ca^{2+}, Ba^{2+}, Sr^{2+}}$, Fe^{2+} ⟶ value of Ksp is high
↳ soluble OH^-
P.P.T ↓ $M^{+3} \longrightarrow M(OH)_3$

$M^{+n} \leftarrow O \begin{cases} H \rightarrow \\ H \end{cases}$ $H_2O \rightarrow H^+ \; OH^-$ $[OH^-]\uparrow$

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$ $[CO_3^{2-}]\downarrow$

- All CO_3^{2-} are soluble in dil. HCl / dil. H_2SO_4 / dil. HNO_3 as well as in CH_3COOH due to formation of volatile CO_2.

6] Na_2CrO_4 :→

- All CrO_4^{2-} are water soluble except $\underset{Red}{Ag^+, Hg_2^{2+}}$, $\underset{Yellow}{Sr^{2+}, Ba^{2+}, Pb^{2+}}$

- $Hg_2^{2+} \xrightarrow{CrO_4^{2-}}$ Brown ppt (Unknown comp.) $\xrightarrow{\Delta}$ Hg_2CrO_4 (Red)

- CrO_4^{2-} is anion of WA H_2CrO_4 which is non volatile. All insoluble CrO_4^{2-} are soluble in SA (dil. HCl, HNO_3, H_2SO_4) but only one insoluble CrO_4^{2-} is soluble in CH_3COOH which is $SrCrO_4$ due to its high Ksp among insoluble CrO_4^{2-}.

7] $Na_2C_2O_4$:→

- All $C_2O_4^{2-}$ are water insoluble except NH_4^+, SA, FeC_2O_4, BeC_2O_4

Colour : white except $Fe_2(C_2O_4)_3$ (Blue) ⇒ used in blueprints

- $H_2C_2O_4$ is a WA, non volatile in nature, $C_2O_4^{2-}$ is SB so soluble in SA but only one insoluble $C_2O_4^{2-}$ is soluble in CH_3COOH which is BaC_2O_4 due to its high K_{sp} among insoluble oxlate

K_{sp} $\underbrace{Mg < Ca < Sr < Ba}_{insoluble} < \underset{Soluble}{Be}$

8] Na_2SO_4 :-

- All sulphates are water soluble except Hg^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}

Colour : Anhydrous sulphate = white

- SO_4^{2-} is anion of SA so insoluble SO_4^{2-} are not soluble in any dil. acid

$BaSO_4$ + dil. $H_2SO_4 \rightarrow$ ×

Insoluble SO_4^{2-} are soluble in conc. HCl / HNO_3 / H_2SO_4 due to formation of HSO_4^-

$BaSO_4$ + conc. $H_2SO_4 \longrightarrow Ba(HSO_4)_2$

9] $Na_2S_2O_3$:-
(aq. sol^n of Hypo.)

Solubility : All thio sulphates are water soluble except Ag^+, Bi^{3+}, Cu^+, $[Ni(en)_3]^{2+}$, Hg_2^{2+}/Hg^{2+}, Ba^{2+}, Pb^{2+}

Colour : Simple thiosulphate salts $\longrightarrow$ white

$[Ni(en)_3]S_2O_3 \longrightarrow$ Purple

coloured due to d-d transition (complex cation)

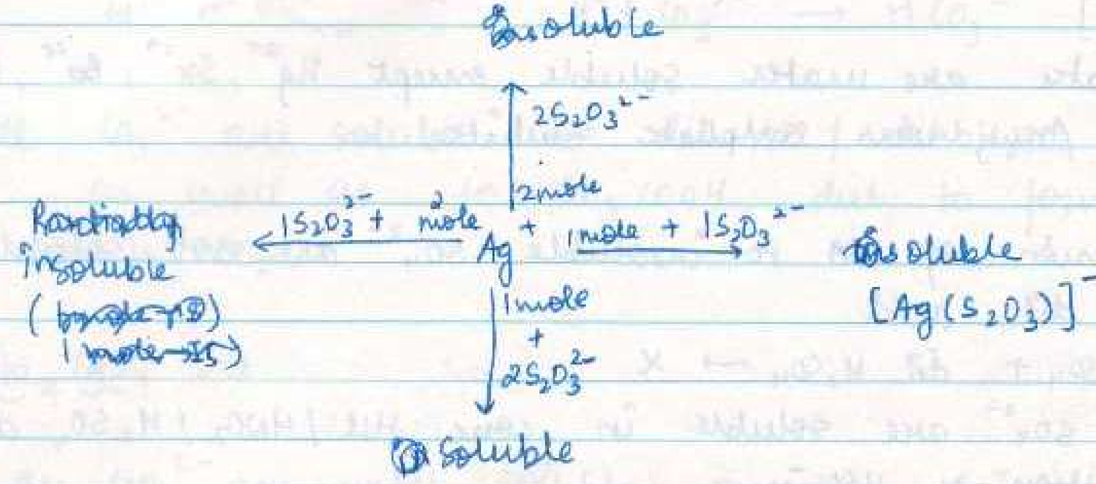
excess $Na_2S_2O_3$:

$S_2O_3^{2-}$ $\xrightarrow{WFL}$ (p block cations are soluble)

$\xrightarrow[\text{chelation}]{SFL}$ (d block cations are soluble)

- All insoluble simple thiosulphates are soluble in excess thiosulphate except BaS_2O_3.

9. soluble / insoluble



10] H_2S :→
(Na_2S, $H_2S + H^+$)

$$\underset{\text{WA}}{H_2S} \rightleftharpoons H^+ \; S^{2-}$$

$$\xleftarrow[H^+]{} [S^{2-}]\downarrow$$

$$\xrightarrow[OH^-]{} [S^{2-}]\uparrow$$

Conc. of S^{2-}

Na_2S or $H_2S + OH^- > H_2S > H_2S + H^+$

- ppt in diff. conc. of S^{2-}

in Na_2S → All are insoluble except NH_4^+, IA, IIA

in H_2S + HCl ⟶ Ag^+ Hg_2^{2+} Pb^{2+}
Pb^{2+}, Cu^{2+}, Bi^{3+}, Hg^{2+}, Cd^{2+}
$Sb^{3+/5+}$, $Sn^{2+/4+}$, $As^{3+/5+}$ } x ⟵ K_{sp} ↓

in H_2S ⟶ x + Zn^{2+}

- colour of insoluble sulphide

Black : PbS, HgS, Ag_2S, FeS, CuS, CoS, NiS
White : ZnS
Pink / buff : MnS
Yellow : Cd^{2+}, $As^{3+/5+}$, Sn^{4+}
Orange : $Sb^{3+/5+}$
Black - Brown : Sn^{2+}, Bi^{3+}

- MgS, Al_2S_3, Cr_2S_3 exist only in solid state in aq. medium they get hydrolysed

$$Al_2S_{3\,(s)} \xrightarrow{H_2O} Al(OH)_3 \downarrow + H_2S \uparrow$$

- Fe^{3+} shows redox with S^{2-}

- <u>Dissolution</u> <u>of</u> <u>insoluble</u> <u>sulphides</u> :

Hot & dil. HNO_3 > HCl > CH_3COOH
SA + OA   SA   WA

- HgS is only sulphide which is insoluble in hot & dil. HNO_3.
- due to its lowest K_{sp} among sulphides.

- MnS is only sulphide which is soluble in CH_3COOH due to very high K_{sp}.

- Among black coloured sulphides, FeS is only sulphide which is soluble in dil. HCl due to high ionic ch^r (low P.P. of Fe^{2+}).

- Those who precipitate in presence of HCl are insoluble in dil. HCl.

- Only ZnS, MnS & FeS are soluble in dil. HCl.

11] $\underbrace{CaCl_2}$

Ca^{2+} $\quad$ Cl^-

All Cl^- are water soluble
except Ag^+, Cu^+, Hg_2^{2+}, Pb^{2+}

$\rightarrow$ Insoluble
(CaF_2, $CaCO_3$, $CaSO_3$, $Ca_3(PO_4)_2$, CaC_2O_4)

All are soluble in dil. HCl.

12] $\underbrace{BaCl_2}$

$\hookrightarrow Ba^{2+}$

Insoluble : $BaCO_3$, BaC_2O_4, $BaSO_3$, $Ba_3(PO_4)_2$,
BaS_2O_3, $BaSO_4$, $BaCrO_4$ → coloured

BaC_2O_4 ← soluble in CH_3COOH

$BaSO_4$ ← Insoluble in dil. HCl

13] $AgNO_3$
↳ Ag^+

Soluble : AgF, Ag_2SO_4, $AgNO_3$, all bi salts

Solubility : - All Ag (I) salts are soluble in hot & dil. HNO_3
except $AgCl$, $AgBr$, AgI
Acidic nature $HCl / HBr / HI > HNO_3$

- All Ag(I) salts are soluble in NH_4OH except
AgI & Ag_2S

- All Ag (I) salts are soluble in hypo except Ag_2S

- All Ag (I) salts are soluble in KCN.

14] $(CH_3COO)_2Pb$
↳ Pb^{2+}

Soluble : $(CH_3COO)_2Pb$, $Pb(NO_2)_2$, $Pb(NO_3)_2$, all bi salts

Solubility : - All Pb (II) salts are soluble in NaOH
except PbS
- All Pb (II) Salts are soluble in hot & dil.
HNO_3 except $PbSO_4$, $PbCl_2$, $PbBr_2$, PbI_2
- Only white ppt which is soluble in
hot water is 6 $PbCl_2$

	$PbCl_2$	$PbBr_2$	PbI_2		
$H_2O(25°C)$	×	×	×	✓	Soluble
Hot water	✓	×	×	×	insoluble
Boiling water	✓	✓	✓		

* REDOX :-

• Oxidising agent & reducing agent :

- Oxidising agent : 1) Halogens

$F_2 \rightarrow F^-$ $Br_2 \rightarrow Br^-$

$Cl_2 \rightarrow Cl^-$ $I_2 \rightarrow I^-$

2) $O_3 \longrightarrow O_2$ / oxide

3) $Pb^{4+} \longrightarrow Pb^{2+}$

4) $Bi^{+5} \longrightarrow Bi^{+3}$

5) $NaOCl / CaOCl_2 \longrightarrow NaCl / CaCl_2$

6) $S_2O_8^{2-} \longrightarrow SO_4^{2-}$

7) $H_2O_2 \longrightarrow H_2O$

8) $KMnO_4 \xrightarrow{H^+} Mn^{2+}$

$\xrightarrow{WB / Neu.} MnO_2$

$\xrightarrow[(KOH)]{SB} Mn^{+6}$

9) $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{+3}$

10) $MnO_2 \longrightarrow Mn^{2+}$

11) $HNO_2 \longrightarrow NO$ (Heating of HNO_2

$\xrightarrow{N^{-3}} N_2$

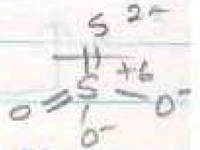
12) $Fe^{3+} \longrightarrow Fe^{2+}$
13) $Ag^{+} \longrightarrow Ag$
14) $Cu^{2+} \longrightarrow Cu^{+}$ (when insoluble compound of Cu^{+} form)

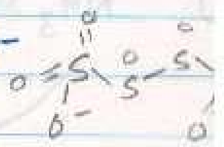
15) conc. $H_2SO_4 \longrightarrow SO_2$
16) conc. $HNO_3 \rightarrow NO_2$
17) dil. $HNO_3 \longrightarrow NO$
$\longrightarrow N_2O$ (when react with metal having reactivity $> H_2$)

- **Reducing agents :**

1) $Cl^{-} \rightarrow Cl_2$ $Br^{-} \rightarrow Br_2$
$I^{-} \rightarrow I_2$
2) $NH_3 \longrightarrow N_2$
3) $PH_3 \longrightarrow P_4 / P_4O_6 / P_4O_{10}$
4) $H_2S \longrightarrow S_8$
5) $HNO_2 \longrightarrow HNO_3$
6) $SO_2 / H_2SO_3 \longrightarrow H_2SO_4$
7) $NO \longrightarrow NO_2$
8) $H_3PO_3 \longrightarrow H_3PO_4$
9) $H_3PO_2 \longrightarrow H_3PO_4$
10) $CO / C_2O_4^{2-} \longrightarrow CO_2$
11) $H_2O_2 \longrightarrow O_2$
12) $Sn^{2+} \rightarrow Sn^{4+}$
13) $Fe^{2+} \rightarrow Fe^{3+}$
14) $Mn^{2+} \rightarrow MnO_2$
15) $Cr^{+3} \rightarrow CrO_4^{2-}$

*16) $S_2O_3^{2-} \xrightarrow{SOA} \overset{0}{S} + SO_4^{2-}$
$S_2O_3^{2-} \xrightarrow[WOA]{} S_4O_6^{2-}$





* Imp. redox series :

1) $Mn^{2+} \rightarrow MnO_2 \rightarrow K_2MnO_4 \rightarrow KMnO_4$

Stable in basic med.

2) $H_2S \rightarrow S \rightarrow SO_2 \rightarrow H_2SO_4$

3) $HI \leftrightarrows I_2 \rightarrow HIO_3$

4) $H_2O \leftrightarrows H_2O_2 \rightarrow O_2$

5)
$$\begin{tikzcd} Cr^{+3} \arrow[r, "O\ (OH^-)"] & CrO_4^{2-} \arrow[d, "H^+"] \\ & Cr_2O_7^{2-} \arrow[ul, "R"] \end{tikzcd}$$

6)
$$\begin{tikzcd} NH_3 \arrow[r] \arrow[r, bend right=60] & N_2 \arrow[r] & NO \arrow[r] & NO_2 \arrow[r] & HNO_2 \arrow[ll, bend left=40, "R"] \arrow[rr, bend right=40, "O"'] \arrow[lll, bend left=60] & + & HNO_3 \end{tikzcd}$$

* Types of Redox Rxn :

1] Intramolecular
- Disp^r
- Thermal decomposition

2] Intermolecular
- Comp^r
- Combination
- Displacement

- Disproportionation :

1) $Cl_2 + H_2O \longrightarrow HCl + HOCl$ (same for Br_2)
2) P_4, S_8, I_2, Cl_2, Br_2 + NaOH → lowest O.S product + hypo ous salt

$$X_2 + \underset{\text{cold \& dil.}}{NaOH} \longrightarrow NaOX + NaX$$

$$\text{hot \& conc.} \longrightarrow NaXO_3 + NaX$$

$$P_4 + NaOH \xrightarrow{\text{atm. } CO_2} PH_3 + NaH_2PO_2$$

$$S_8 + NaOH \longrightarrow Na_2S + Na_2S_2O_3$$

3) Decomposition of H_2O_2

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

4) Heating of -ous acid / oxidation state < max.

$H_3PO_3 \rightarrow H_3PO_4 + PH_3$
$H_3PO_2 \rightarrow H_3PO_4 + PH_3$
$HOCl \rightarrow HO_3Cl + HCl$
$HClO_2 \rightarrow HClO_3 + HCl$
$HClO_3 \rightarrow HClO_4 + HCl$
$HNO_2 \rightarrow HNO_3 + NO$
$H_2C_2O_4 \rightarrow H_2CO_3 + CO$
$H_2SO_3 \longrightarrow H_2SO_4 + S$

5) Hydrolysis of KO_2

$$KO_2 + H_2O \longrightarrow KOH + H_2O_2 + O_2$$

6) K_2MnO_4 in H_2O/H^+

$K_2MnO_4 \longrightarrow KMnO_4$ ~~$+ Mn^{2+}$~~ $+ MnO_2$

7) Cu^+ & Au^+ in aq. medium

$$Cu^+_{(aq.)} \longrightarrow Cu^{2+}_{(aq.)} + Cu$$

$$Au^+_{(aq.)} \longrightarrow Au^{3+}_{(aq.)} + Au$$

HE > IE

Reactivity $H_2 > Cu/Au$

8) Mixed anhydride of p-block + water
gp. 15, 16, 17

$$NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$P_4O_7 / P_4O_8 / P_4O_9 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

$$ClO_3 + H_2O \longrightarrow HClO_3 + HClO_4$$

$ClO_2 + H_2O \longrightarrow$ ~~$HClO_2 + HClO_3$~~

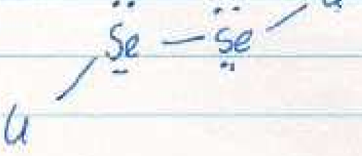
$ClO_2 \cdot xH_2O$

9) Hg_2^{2+} in presence of complexing ligand
(eg: NH_3, I^-, CN^-, S^{2-})

$\hookrightarrow Hg^{2+} + Hg$

10) Heating of mono halide of gp. 16 :→

$$Se_2Cl_2 \xrightarrow{\Delta} SeCl_4 + Se$$



11) Heating of Ozonide / peroxide / superoxide :
(O_3^- , O_2^{2-} , O_2^-)

$KO_2 / K_2O_2 \longrightarrow K_2O + O_2$

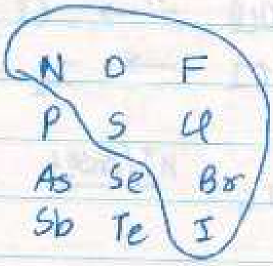
$KO_3 \xrightarrow{\Delta} KO_2 + O_2$
(Red-orange) (Yellow-orange)

12) $\underset{sp^3}{XeO_3} \xrightarrow{OH^-} \overset{+6}{HXeO_4^-} \xrightarrow{OH^-} \overset{+8}{XeO_6^{4-}} + Xe + O_2$
↖ sp^3d

Perxenate ion

- Combination Reaction :→

1) H_2 + Non metal ⟶ XH_n
(gp. 15, 16, 17)
15 → 3 (n)
16 → 2
17 → 1



EXO.

2) $S + O_2 \xrightarrow{RT} X$
$S + O_2 \xrightarrow{\Delta} SO_2$
$N_2 + O_2 \xrightarrow{RT} NO$
$N_2 + O_2 \xrightarrow{\Delta} NO$
$C + \underset{(lim)}{O_2} \xrightarrow{\Delta} CO$

$C + \underset{excess}{O_2} \xrightarrow{\Delta} CO_2$

$P_4 + O_{2(lim)} \longrightarrow P_4O_6$

$P_4 + O_2 (exe) \rightarrow P_4O_{10}$
P_4 + dry air →
$SO_2 (g) + Cl_2 (g) \rightarrow SO_2Cl_2$

$H_2 + O_2 \xrightarrow[quinol]{2\text{-ethylanthra}}$

3) $Li + air \longrightarrow Li_2O + Li_3N$

$Na + air \longrightarrow Na_2O_2$

$K + air \longrightarrow KO_2$

$Mg + air \xrightarrow{RT} X$

$Mg + air \xrightarrow{\Delta} MgO$

- Comproportionation Rxn :-

1] Non metal $+ H_2O/OH^- \underset{\xleftarrow{H^+}}{\xrightarrow{disp^n}}$ Acid / salt (two type)

$Na_2S + Na_2S_2O_3 \xrightarrow{H^+} S\downarrow$

$NaCl + NaOCl \xrightarrow{H^+} Cl_2 \uparrow$

$NaI + NaIO_3 \xrightarrow{H^+} I_2$

$PH_3 + H_3PO_4 \xrightarrow{H^+} X$

~~OX~~

*// $H_2S + SO_2 \longrightarrow S\downarrow + H_2O$

$HCl + HOCl \xrightarrow{H^+} Cl_2 + H_2O$

$HI + HOI \longrightarrow I_2 + H_2O$

2) $Mn^{2+} + KMnO_4 \xrightarrow{H^+/ZnSO_4}$ ~~K_2MnO_4~~ MnO_2

3) $S +$ Conc. $H_2SO_4 \longrightarrow$ ~~H_2S~~ ~~+~~ SO_2

$S +$ dil. $H_2SO_4 \longrightarrow X$

4) $NaH + H_2O \longrightarrow H_2\uparrow + NaOH$

5) $Cu^+_{(aq.)} \longrightarrow Cu^{2+}_{(aq.)} + Cu$

$\longleftarrow$

when

isoluble cmpd of Cu^+ forms

NH_2CONH_2

6) $N^{-3} + N^{+3} \longrightarrow N_2$

$NH_4Cl + HNO_2 \longrightarrow N_2\uparrow + 2H_2O + HCl$

$RNH_2 + HNO_2 \longrightarrow N_2\uparrow + H_2O + ROH$

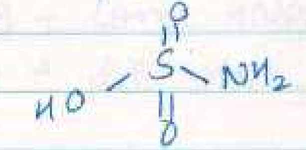
Urea $+ HNO_2 \rightarrow N_2\uparrow + H_2O + CO_2$

Thiourea $+ HNO_2 \rightarrow N_2\uparrow + H_2O + HNCS$

$\downarrow Fe(OH)_3$

Blood red

Sulphamic acid



$HO-S(=O)_2-NH_2$

$+ HNO_2 \rightarrow N_2\uparrow + H_2O + SO_3 \; (H_2SO_4)$.

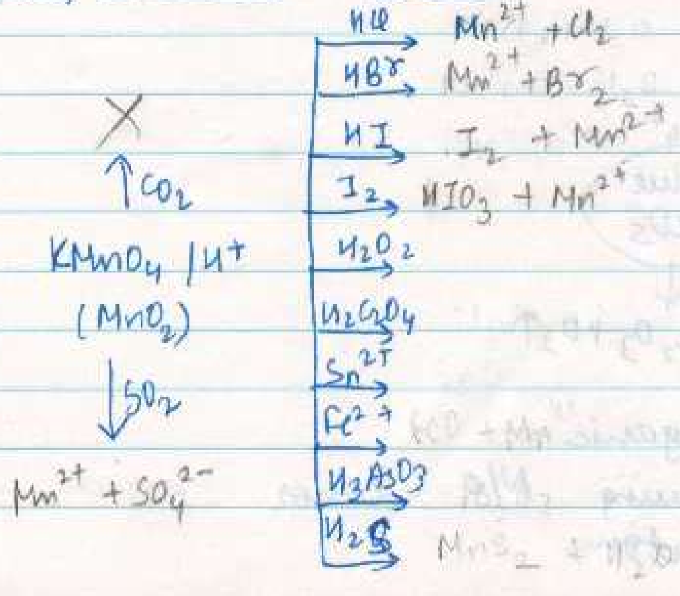
7) Heating of Ammonium salts : (containing anion 'N' atom)

$\overset{-3}{N}H_4\overset{+3}{N}O_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$\overset{-3}{N}H_4\overset{+5}{N}O_3 \xrightarrow{\Delta} N_2O + H_2O$

$\overset{-3}{N}H_4\overset{-1}{N}_3 \xrightarrow{\Delta} N_2H_2$

* Displacement Rxns :→



$$KMnO_4/H^+ \begin{cases} \xrightarrow{S_2O_3^{2-}} S + SO_4^{2-} \\ \xrightarrow[\text{limited}]{S_2O_3^{2-}} HSO_4^- / SO_4^{2-} \end{cases}$$

- $KMnO_4 + I^- \xrightarrow{OH^-} IO_3^- + MnO_2$

- $KMnO_4 + S_2O_3^{2-} \xrightarrow{OH^-} MnO_2 + SO_4^{2-}$

- $K_2Cr_2O_7/H^+$

$HCl \rightarrow Cl_2$

$HBr \rightarrow Br_2$

$HI \rightarrow I_2$

$H_2S \rightarrow S$

$HNO_2 \rightarrow HNO_3$

$H_3AsO_3 \rightarrow AsO_4$

$SO_2 \rightarrow SO_4^{2-}$

$NO_2 \rightarrow HNO_3$

$CO_2 \rightarrow X$

$Sn^{2+} \rightarrow Sn^{4+}$

$Fe^{2+} \rightarrow Fe^{3+}$

$\downarrow Cr^{3+}$

- $Cr^{3+} + H_2O_2 + OH^- \longrightarrow CrO_4^{2-}$

$Cr_2O_7^{2-}/H^+ + H_2O_2 \longrightarrow$ Blue CrO_5 $\downarrow$ $Cr_2O_3 + O_2\uparrow$

Stable in organic solvent having N/O donor atom

- Zn + conc. $HNO_3 \longrightarrow NO_2 + Zn(NO_3)_2$
  Zn + dil. $HNO_3 \longrightarrow N_2O + Zn(NO_3)_2$

Cu + conc. $HNO_3 \longrightarrow NO_2 + Cu(NO_3)_2$
Cu + dil. $HNO_3 \longrightarrow NO + Cu(NO_3)_2$

Cu^+ is formed only when insoluble Product is formed.

- Fe + conc. $HNO_3 \longrightarrow NO_2 + Fe(NO_3)_3$
  Fe + dil. $HNO_3 \longrightarrow N_2O + Fe(NO_3)_2$

Hg + conc. $HNO_3 \longrightarrow NO_2 + Hg(NO_3)_2$
Hg + dil. $HNO_3 \longrightarrow NO + Hg_2(NO_3)_2$

*Q. Cu + 45% $HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + NO$
N_2O_3