"CHAPTER NO # 14"

Q:- What are transition elements?

The elements which have partially filled "**d**" or "**f**" orbital either in their atomic states **i-e** "Fe" or in other common oxidation state **i-e** "Fe^{+2}" are called transition elements.

They are also called **d-block** or **f-block** elements.

f-Block elements = Inner transition

d-Block elements = outer transition

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Q:- Why are they called transition Elements?

The word "transition" means **In-between**.
They are called transition elements because, they show such properties, which are transitional between highly reactive and strongly electropositive elements of **s-block** which form ionic bonds and **p-block** which form covalent compounds.

As, they belongs to **d-block** or **f-block** which lies between s-block and p-block that's why they also called transition elements.

→ "Series of Transition Elements:-

There are two series of transition elements:

- → **d-block series.**
- → **f-block series.**

The d-block elements consist of the following Four series of ten elements each:

1): From **Scandium ($Sc=21$)** to **Zinc ($Zn=30$)**
This is 3d-series-

2): From **Yttrium ($Y=39$)** to **Cadmium ($Cd=48$)** This is 4d-series-

3): From **Lanthanum ($La=57$)** to **Mercury ($Hg=80$)** This is 5d-series-

4) From Actinium ($Ac=89$) onwards — 6d-series

The f-block elements constitute two series:

1): From **Cerium ($Ce=58$)** to **Lutetium ($Lu=71$)** This is 4f-series. (Lanthanides)

2): From **Actinium ($Ac=89$)** **Lawrencium ($Lr=103$)** this is 5f-series. (Actinides)

→ "**General outer most configuration**":-

→ For d-block series: $ns^{1-2}, (n-1)d^{1-10}$

→ For f-block series: $ns^{1-2}, (n-1)d^{1-10}, (n-2)f^{1-14}$

→ **Q: Why Zn-group included in Transition elements?**

As; Zn, Cd, Hg they have completely filled d-orbital but they included in transition elements. because, they show the properties of transition elements to form the complex compounds with ammonia, halides and amines.

Also their chemical behaviors are similar to transition elements.

→ "Coinage Metals (IB) Transition elements justify":-

Elements of "group-IB" called coinage elements. It include **Cu, Ag, Au etc.** In atomic form they are stable by complete their outer most shell.

e.g:- $Cu = ----, 4s^1\ 3d^{10}$

But in bonding or ionic form they attain the charge "+2" and electronic-configuration become:-

e.g:- $Cu^{+2} = ----, 4s^0\ 3d^9$

That's why we say that in bonding form coinage metals show the behavior of transition elements. e.g:- $Ag^{+2} = 5s^0, 4d^9$

$Au^{+3} = 6s^0, 5d^8$

→ ":Typical and Non-typical Elements":-

The elements of group-**IIB** and group-**IIIB** are included in non-typical transition elements:

→ "**II-B Elements**":- It's clear that elements of group-IIB include "**Zn**", "**Cd**", and "**Hg**" don't have partially filled d-orbital in the atomic and ionic form:

→ "**For Example**":-

- **$_{30}Zn = -----4s^2 3d^{10}$** → "atomic form"
- **$Zn^{+2} = ----- 4s^0 3d^{10}$** → "ionic form"

$_{48}Cd = ... 5s^2, 4d^{10}$

$Cd^{+2} = ... 5s^0, 4d^{10}$

$_{80}Hg = ...- 6s^2, 5d^{10}$

$Hg^{+2} = ... 6s^0, 5d^{10}$

→ "**IIIB Elements**":- It's clear that the elements of group IIIB include **Sc, Y** and **La** They don't show the properties of typical transition elements- In compound states they are tri-positive **i-e Sc^{+3}, Y^{+3},** and **La^{+3}** etc- In this way they have no electron in their d-orbital-

→ "**For Example**":-

•- $_{21}Sc$ = ----- $4s^2 3d^2$ → "Atomic form"-

•- Sc^{+3} = ----- $4s^0 3d^0$ → "Ionic form"-

For the reason the elements of group **IIB** and **IIIB** are "**Non-typical Transition Elements**"

→ "**Typical Transition Elements**":-

The remaining group elements:
e.g: **IB, IVB, VB, VIB, VIIB** and **VIIIB** etc are included in typical transition elements- They obey the properties of transition elements-

→ "**Properties**":-

→ Transition elements give the colored compounds those containing Partially filled d-orbital-

→ For the complex compounds with amines, ammonia and halide ions etc-

→ They show variable oxidation states

→ "General Features of Transition elements" :-

- They are all metallic in nature.
- Some of transition elements play an important role in industry. These metals include:
  ∴ Ti, Cr, Fe, Ni, Cu etc
- They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
- They form alloys **(mixture of two metals)** with one another or with other elements of periodic table as well.
- With few exceptions **(II-B group)**. They show variable oxidation state.
- Their ions and compounds are colored in the solid state and the solution state.

→ "Electronic Structure" :-

Electronic distribution of d-block elements are as follow:

→ $_{24}Cr$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d_{xy}^{\uparrow}$
$3d_{yz}^{\uparrow}\ 3d_{xz}^{\uparrow}\ 3d_{x^2-y^2}^{\uparrow}\ 3d_{z^2}^{\uparrow}$

→ $_{29}Cu$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d_{xy}^{\uparrow\downarrow}$
$3d_{yz}^{\uparrow\downarrow}\ 3d_{xz}^{\uparrow\downarrow}\ 3d_{x^2-y^2}^{\uparrow\downarrow}\ 3d_{z^2}^{\uparrow\downarrow}$

→ **NOTE** :- stable states of **d-orbital** are as follows: i.e half filled or full filled
, d^5 , d^{10}

→ "Electronic Distribution of "4d" and "5d" series":-

		3dxy	3dyz	3dxz	3dx²-y²	3dz²	4s
$_{21}Sc$	=	↑	-	-	-	-	↑↓
$_{22}Ti$	=	↑	↑	-	-	-	↑↓
⋮			⋮				⋮
$_{24}Cr$	=	↑	↑	↑	↑	↑	↑
⋮			⋮				⋮
$_{29}Cu$	=	↑↓	↑↓	↑↓	↑↓	↑↓	↑

Following table shows the electronic distribution of "4d" and "5d-block" elements. The elements of group "VI-B" i-e "Cr" group shows the same deviation except "$_{74}W$".

Similarly, the elements of group "I-B" that's "Cu-family" also show the deviated distributed. Following table shows the electronic distribution of 3d, 4d, 5d series.

→ "Irregularities in configuration":-

The exactly half filled and completely filled d orbitals possess extra stability. This may explain the stability of Cu ($3d^{10}4s^1$ not $3d^9 4s^2$) and Cr ($3d^5 4s^1$ not $3d^4 4s^2$). There are so many factors which explained the observed configurations of atoms of the "4d" and "5d" transition series:

→ "Binding Energy":-

.- Energy which binds the atoms together called binding energy.

Transition elements are tough, ductile and malleable - The toughness of metals is due to geater binding energies.

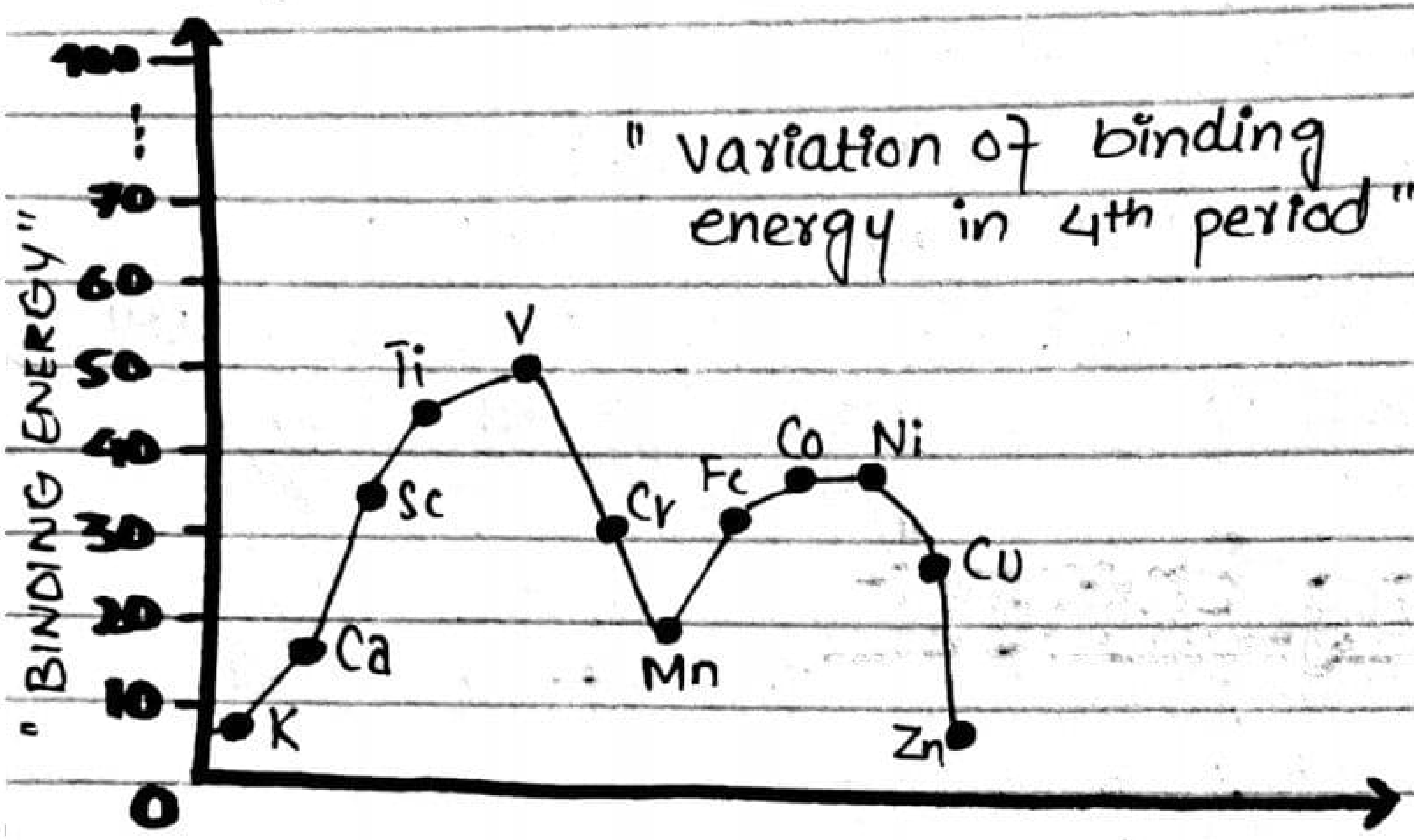
"Reason":- The s-electrons of outer most shell and underlying half filled d-orbital take part in binding.

"Variation in binding energies":-

As we move from left to right in any d-block series, The number of unpaired electrons increases After that the unpaired electrons become decreases and approches to zero. it means that binding forces goes on increasing upto VB and VIB then decreases.

Binding energy ∝ No of unpaired electrons

Variaiton of Binding energy can be showed by graph:



→ "Variable Oxidation State":-

As the transition elements are electropositive so, they have positive oxidation state.

They show variable oxidation states Bcz; they have d- electrons in addition to s- electrons for bonding. These elements have several "**(n-1)d**" aud "**ns**" electrons. The energies of "(n-1)d" and "ns" electrons are very close to each other.

The "(n-1)d" electrons easily lost as "ns" electrons.

The oxidation states increases upto middle of series and after-ward that they decreases.

∴ "Mn" has maximum oxidation states upto "+7"

∴ "All elements of 3d-series shows oxidation state of "+2" and increases by 4s-orbital take part"

→ "Catalytic Activity":-

Most of the transition elements used as a catalysts due to their variable oxidation states.

In this way they form intermediate products with various elements:

They also form interstitial compounds (complex compound) which can absorb an activator to the reacting species:

Some of the examples of catalyst are as follow:

1): A mixture of "ZnO" and "Cr_2O_3" is used for the manufacture of methyl alcohol "**CH_3OH**"

$$CO + 2H_2 \xrightarrow{ZnO+Cr_2O_3} CH_3OH$$

2): "Ni"; "Pt" and "Pd" are used as catalysts for the hydrogenation of vegetable oil and saturation of alkenes and alkynes.

"**Ostwald process**" (preparation of nitric acid) for HNO_3.

3): "MnO_2" is used as catalyst for the decomposition of H_2O_2.

4): "$TiCl_4$" is used as catalyst for the manufacture of plastics.

5): "V_2O_5" is used to oxidize "SO_2" to "SO_3" in manufacture of "H_2SO_4"

6): "Fe" is used as a catalyst for the synthesis of "NH_3" in haber process. about 1% Na_2O and K_2O and about 1% of SiO_2 or Al_2O_3 is used as promoter sometime "Mo" is also used as promoter.

$$N_2 + 3H_2 \xrightarrow{Fe/Mo} 2NH_3$$

→ **"NOTE":-**

Manufacture of H_2SO_4 process called **"Contact Process"**

→ **"NOTE":-**

The substance used to increase the activity of catalyst called "promoter". it also called **"Catalyst For Catalyst"**

→ "Magnetic Behaviour":-

Many transition elements and their compounds are paramagnetic.

"Paramagnetic":- compounds attracted in magnetic field due to unpaired electrons called paramagnetic compounds.

"Diamagnetic":- Some compounds have even number of electrons with paired spin called diamagnetic compounds. They are weakly repeled by magnetic field.

"Ferromagnetic":- The substances which can be magnetized are called ferromagnetic.

Example:- **Fe, Co, Ni etc.**

The magnetic moment **(μ)** is related to the number of unpaired electrons **(n)** by the equation:

$$\mu = \sqrt{n(n+2)} \text{ —— (i)}$$

units of μ (magnetic moment) is "**BM**" which can be called as: "**Bohr Magneton**"

By measuring magnetic moment we are able to calculate the nature of transition metals compound and oxidation state of transition metal can be calculated.

→ "Alloy Formation":-

Mixture of two or more metals called alloy. Transition metals form alloy with each other due to following reasons:

→ Reasons:-

(i) All are almost similar in sizes and atoms of one metal can easily take up position in crystal lattice of the other.

(ii) They form substitutional alloys among themselves.

Example:-

→ Alloy steels are the materials in which the iron atoms are substituted by **Cr, Mn, Ni** steel has more useful properties than iron.

→ Brass, Bronze, and coinage alloys are the best alloys.

Brass	**Bronze**	**Nichrome**
contain Cu = 60–80% Zn = 20–40%	contain Cu = 90–95% Sn = 5–10%	contains Ni = 60% Cr = 15% Fe = 25%
it's strong but flexiable. it's easy to use due to low M.P.	It's strong and long lasting - doesn't corrode.	used in electric heaters and filaments of furnaces.
Used to make key, lock	used to prepare medals, coins etc.	

"Properties of alloys":-

As alloys are made according to requirements so, having different characteristics but few properties are common:

1): Alloy are comparavitely cheap.
2): They are soft and flexiable but hard alloys can also be prepared.
3): They are long lasting Bcz, they don't corrode.
4): They are durable.
5): They have high melting points.
6): They are better conductors but non-conductor alloys are also prepared.

→ "Co-ordination Compounds":-

→ "Definition":- (compounds that retain their geometry after dissociate in water):

compounds which contain complex molecules or complex ions which exist independent called co-ordination or complex compounds.

Such metals can formed by the co-ordination of an electron pair donor (ligand) to metal atom or ion. → (central metal atom)

→ "Explanation":-

The concept of complex compounds can understand by mixing two substances such as "**KCN**" and **$Fe(CN)_2$**. When this mixture is evaporated a new compound is formed. This compound when dissolved in water ionizes $4K^+$ and $[Fe(CN)_6]^{4}$

on this basis the compounds has given formula.

$K_4[Fe(CN)_6]$ (Potassium ferrocyanide)-

$$4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$$

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is called complex ion.

→ "Parts of complex compounds after dissociation in a solvent":-

The complex compounds is mostly made up of two parts.

→ Positively charge ion or cation.

→ Negatively charge ion or anion.

For Example:- in $K_4[Fe(CN)_6]$, "K^+" is a cation and $[Fe(CN)_6]^{-4}$ is the anion.

→ "Complex ion as cation":-

In some complexes the positively charged ion is complex ion.

"Example":-

$$[Cu(NH_3)_4]SO_4 \longrightarrow \underset{\text{"complex cation"}}{[Cu(NH_3)_4]^{+2}} + SO_4^{-2}$$

→ "Complex ion as anion":-

In some complexes the negatively charged ion is complex ion.

"Example":-

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + \underset{\text{complex anion.}}{[Fe(CN)_6]^{-4}}$$

→ "Components of complex compounds:-"

complex compounds consists of three components.

→ Positively or negaiively charged ion which is not complex.

→ A central metal atom or ion which consisted of transition element.

→ Electron pair donor either positive, negaiive or neitral. it actually called as "**Ligand**".

(a) "Central metal atom or ion":-

central metal atom or ion is actually a transition element and can surrounded by number of ligands.

→ "**Example**":-

⇒ In $K_4[Fe(CN)_6]$, Fe^{+2} is the central metal ion, which surrounded by six ligands **(CN^- ions)**.

⇒ In $[Ag(NH_3)_2]Cl$, Ag^+ is the central metal ion which surrounded by two ligands **(NH_3)**

(b) "Ligand":-

atoms, ions, or neutral molecules which surrounds the central metal atom or ions by donating the electron pair called ligand.

→ "**Example**":-

in $K_4[Fe(CN)_6]$, CN^- is the ligand.

→ "Types of Ligand":-

Depending on the electron pair donating there are many types of ligands.

→ "**Monodentate**":- ligands having only one electron pair to donate which may be negative or neutral. etc

→ **"Example":-**

Negatively charged ligands : $Cl^-, F^-, CN^-, OH^-, I^-, Br^-$

Neutral Ligands : NH_3, H_2O, CO, en etc

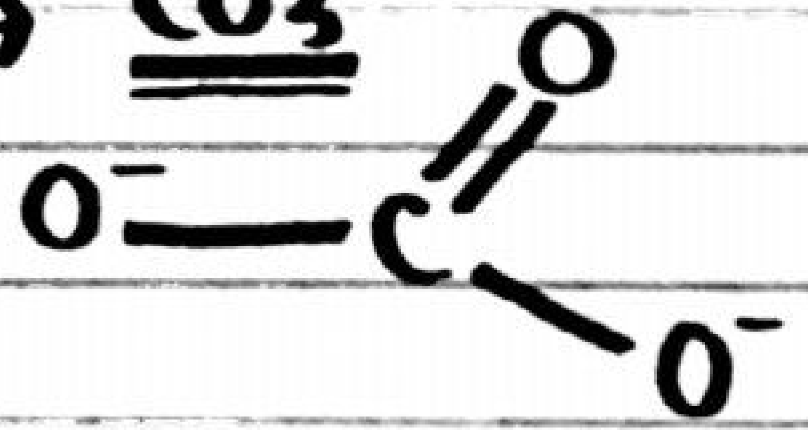
→ **"Bi-dentate":-** Ligands having two donatable electron pairs called bi-dentate ligands.

→ **"Example":-** $CO_3^{-2}, SO_4^{-2}, (COO)_2^{-2}, NH_2-NH_2$ "Hydrazine"

, $\ddot{N}H_2-CH_2-CH_2-\ddot{N}H_2$
"ethylene diamine (en)"

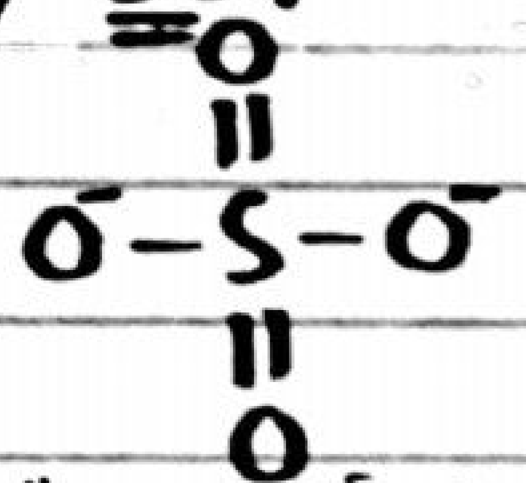
→ **"Structure":-**

→ "CO_3^{-2}"



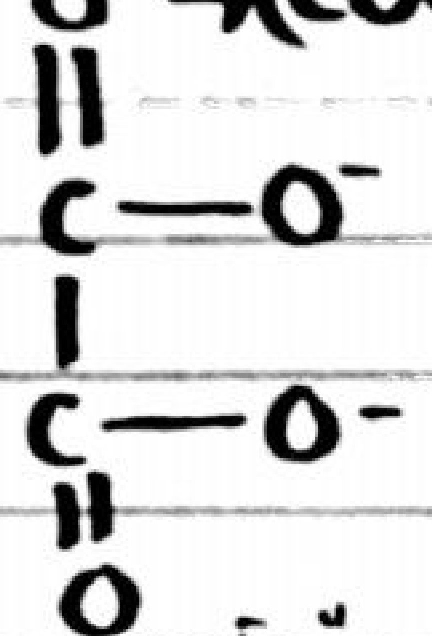
"carbonate" ion

→ "SO_4^{-2}"



"sulphate" ion

→ $(COO)_2^{-2}$



"oxalate" ion

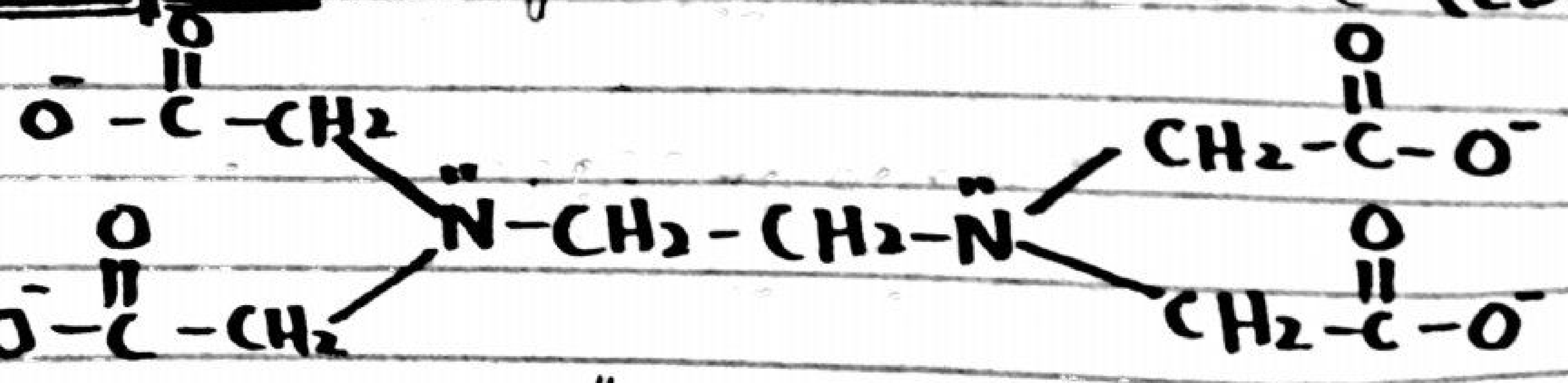
→ **"Tri-dentate":-** Ligands having three donatable electron pairs-

→ **"Example":-** "Diethylene triamine":-

$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\ddot{N}H_2$

→ **"Hexadentate":-** Ligands which have six donatable electron pairs.

→ **Example:-** "Ethylene diamene tetracetate" **(EDTA)**



∴ "The bond between ligand and metal atom or ion

→ **NOTE:-**
"one co-ordination sphere have only one metal atom or ion."

(c) "Co-ordination number of Ligancy":-

Total number of atoms of ligand that co-ordinate with the central metal atom or ion called co-ordination number.

→ **Example:-**

⇨ In $K_4[Fe(CN)_6]$ the co-ordination number of Fe^{+2} is **Six (6)**

⇨ In $[Ni(CO)_4]$ the co-ordination number of Ni^0 is **four (4)**

(d) "Co-ordination sphere":-

The central neutral metal atom or ion along with ligand is called co-ordination sphere. it's usually placed in square brackets. it may be positive, negative or neutral.

→ "**Example:**"

⇨ In $K_4[Fe(CN)_6]$, the $[Fe(CN)_6]^{-4}$ is the co-ordination sphere of complex compound.

⇨ In $[Ni(CO)_4]$, the $[Ni(CO)_4]$ is the co-ordination sphere of complex compound.

(e) "Charge on co-ordination sphere":-

it's the algebric sum of charges present on the central metal atom or ion and charge on the ligand.

→ "**Example:**" in $K_4[Fe(CN)_6]$ the charge on the co-ordination sphere can be calculated:

Charge on Ligand = −6

Charge on Metal = +2

Remaining charge = −4.

So, $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{-4}$

→ "Nomenclature" :-

→ "Rules for assigning name" :-

1) :- "Order of ions" :-

First call cation and then anion.

→ For example :- in $K_4[Fe(CN)_6]$ first call potassium and then $[Fe(CN)_6]$.

2) :- "Naming of Ligands" :-

→ Ligands which are negatively charged end in "**O**"

→ For example :-

→ F^- = Fluoro.
→ CN^- = Cyno.
→ Cl^- = Chloro.
→ $C_2O_4^{-2}$ = Oxalato.
→ CH_3COO^- = Acetato.

→ Neutral ligands are written as such :

→ For Example :-

→ H_2O = Aqua or Aquo.
→ NH_3 = Ammine.
→ CO = Carbonyl.
→ en = Ethylene diammine.

→ Positively charged ligands end in "**ium**"

→ For Example :-

→ $NH_2NH_3^+$ = Hydrazinium.
→ NO^+ = Nitrosylium.
→ NH_4^+ = Ammonium.

3) :- "Order of Ligands" :-

All ligands are arranged alphabetically without any preference order. The prefixes e.g: **di, tri, tetra** are not considered.

4):- "More than one same type of Ligands":-

In order to indicate more than one ligands use the prefixes as:

→ **di** for two.
→ **tri** for three.
→ **tetra** for four etc.

5):- "Termination of Name of Metal":-

If the complex ion is negatively charged then name of metal ends at "**ate**"

⇒ "For example":-

$K_4[Fe(CN)_6]$ the name is: "**Potassium Hexa cyano Ferrate (II)**"

6):- "Oxidation number of Metal ion":-

The oxidation number of metal ion is represented by roman numeral in parenthesis.

7):- "More than one polydentate Ligand":-

If more than one polydentate ligands are there. then in order to indicate their number use:

→ **Bis** for two.
→ **Tris** for three.
→ **Tetra kis** for four.

"NOMENCLATURE" :-

"Exercise : Q3 (iv a)"

→ Write systematic name of following complexes ?

(i) $[Co(NH_3)_6]Cl_3$ Hexaammine cobalt (III) chloride.

(ii) $[Fe(H_2O)_6]^{+2}$ Hexa Aqua Iron (II) ion

(iii) $Na[CoF_6]$ Sodium Hexafluoro cobaltate(V).

(iv) $[Cr(OH)_3(H_2O)_3]$ Triaqua trihydroxo chromium (III)

(v) $K_2[PtCl_6]$ Potassium hexachloro platinate (IV).

(vi) $[Pt(OH)_2(NH_3)_4]SO_4$ Tetra ammine dihydroxo platinum (IV) sulphate

(vii) $K_2[Cu(CN)_4]$ Potassium tetra cyano cupperate(II).

(viii) $Na_2[NiCl_4]$ Sodium tetra chloro Nikelate (II).

(ix) $[Pt(NH_3)_2Cl_4]$ Diammine tetra chloroplatinum (IV)

(x) $[Ag(NH_3)_2]Cl$ Diammine silver (I) chloride.

(xi) $K_4[Fe(CN)_6]$ Potassium Hexacyano Ferrate (II)

(xii) $K_3[Fe(CN)_6]$ Potassium Hexacyano Ferrate (III).

(xiv) $Na[Mn(CO)_5]$ Sodium Pentacarbonyl menganate (-1)

(xv) $Na_2[Ni(CN)_4]$ Sodium tetracyano nikelate (II

(xvi) $[Co(NO_2)_3(NH_3)_3]$ Triammine trinitro cobalt (III)

(xvii) $[PtCl(NO_2)(NH_3)_4]SO_4$ Tetra ammine chloro nitro platinum (IV) sulphate

(xviii) $Ni(CO)_4$ Tetra carbonyl nickel (0)

(xix) $[Co(en)_2Cl_2]Cl$ Dichloro bis ethylen diammine cobalt (III) chloride-

(xx) $[Cr(H_2O)_6]Cl_3$ Hexa aqua chromium (III) chloride-

→ "Question : 04(b)"

(i) **Potassium hexacyano ferrate (II)**

⇒ $K_4[Fe(CN)_6]$

(ii) **Sodium tetra chloro nickelate (II)**

⇒ $Na_2[Ni(Cl)_4]$

(iii) **Tetra ammine copper (II) sulphate**

⇒ $[Cu(NH_3)_4]SO_4$

(iv) **Potassium hexachloro platinate (IV)**

⇒ $K_2[Pt(Cl)_6]$

(v) **Dichloro tetrammine cobalt (III) chloride**

⇒ $[Co(NH_3)_4(Cl)_2]Cl$

→ "Iron":-

We will discussed:-

→ Oxidation state (+2 —— +3)

→ Iron is used as a catalyst in "**Haber's process**" and Reaction between persulphate and iodide ions.

→ Reactions of Hexaaqua iron (II) and (III) with hydroxide, ammonia, carbonate and Thiocyanate ior

→ "**Oxidation State**":- Iron can exist mainly in two oxidation states **+2, +3** etc. In aqueous solution "Fe" readily oxidized from **$Fe^{+2} \rightarrow Fe^{+3}$** this can be shown in reaction:

$$\underset{\text{Ferrous}}{Fe^{+2}_{(aq)}} \longrightarrow \underset{\text{Ferric}}{Fe^{+3}_{(aq)}} + e^-$$

To find the concentration of "Fe^{+3}" in solution we can react the "Fe^{+2}" with an oxidizing agent by the process of titration.

→"As a catalyst in Haber's process":-

Combination of Nitrogen gas and Hydrogen gas produces the Ammonia gas. This process is called Haber's process. For this purpose iron is used as a catalyst.

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$$

N_2 come from air and H_2 is obtain from natural gas (CH_4)

→"As a catalyst in reaction Between Persulphate and iodide ions":-

The reaction Between the persulphate and iodide ions can catalysed either by iron (II) or iron (III) ions.

The reaction take place in two steps :-

"When Fe^{+2} is used":-

$$S_2O_8^{-2} + 2Fe^{+2} \longrightarrow 2SO_4^{-2} + 2Fe^{+3}$$

$$2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$$

"When Fe^{+3} is used":-

In this case the second of these reactions happens First:

$$2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$$

$$S_2O_8^{-2} + 2Fe^{+2} \longrightarrow 2SO_4^{-2} + 2Fe^{+3}$$

Over all reaction (Net) is given as follows:

$$S_2O_8^{-2} + 2I^- \longrightarrow 2SO_4^{-2} + I_2$$

This is a good example to use of transition metal compounds as catalyst because, having ability to change oxidation state.

→"Reaction of Iron ions in sol":-

Simplest ions in solution are as follow:

→ The hexaaquairon (II) ion — $[Fe(H_2O)_6]^{+2}$

→ The hexaaquairon (III) ion — $[Fe(H_2O)_6]^{+3}$

→"Reaction of Ions with -OH ions":-

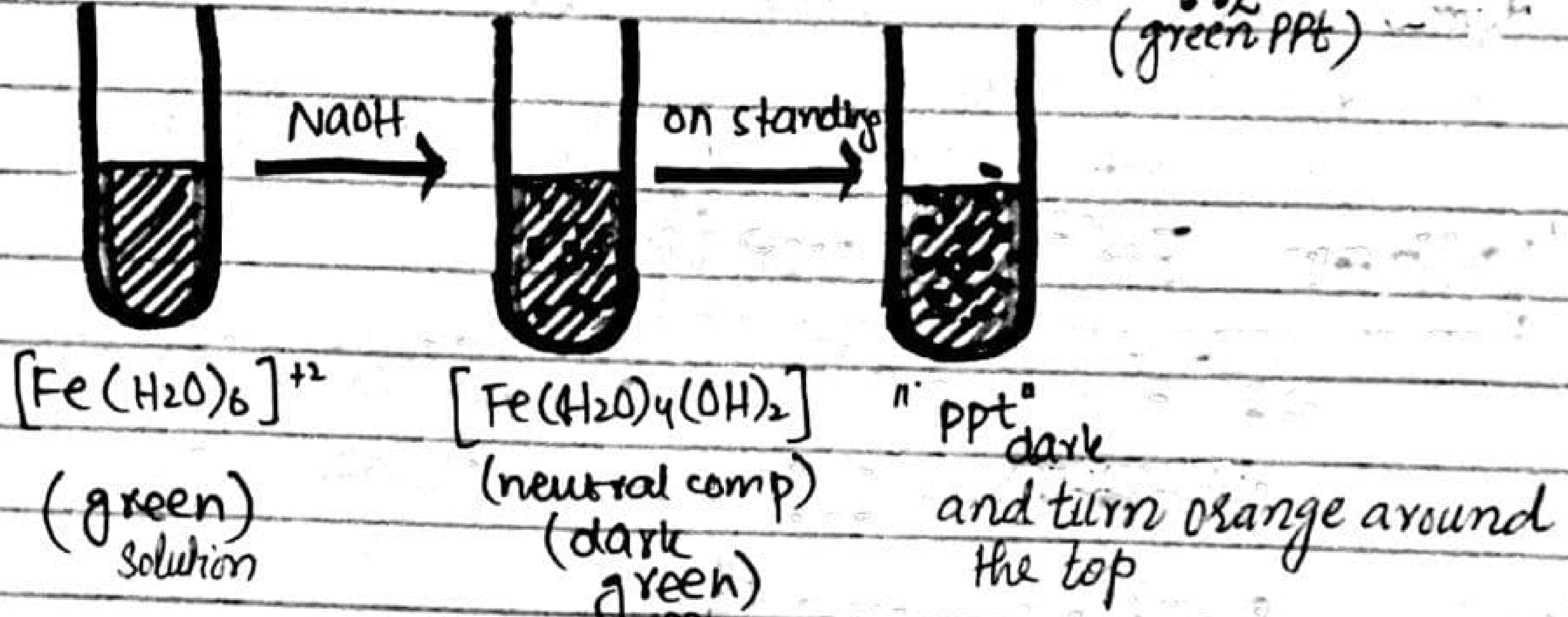
Hydroxide ions remove the hydrogen atoms from H2O (water) ligand and attached them to the iron ions.

When enough amount of ehydrogen atoms are removed it form the neutral complex compounds which can be precipitate out as insoluble compound.

In case of iron (II):-

$$[Fe(H_2O)_6]^{+2} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

(green soln) (green ppt)



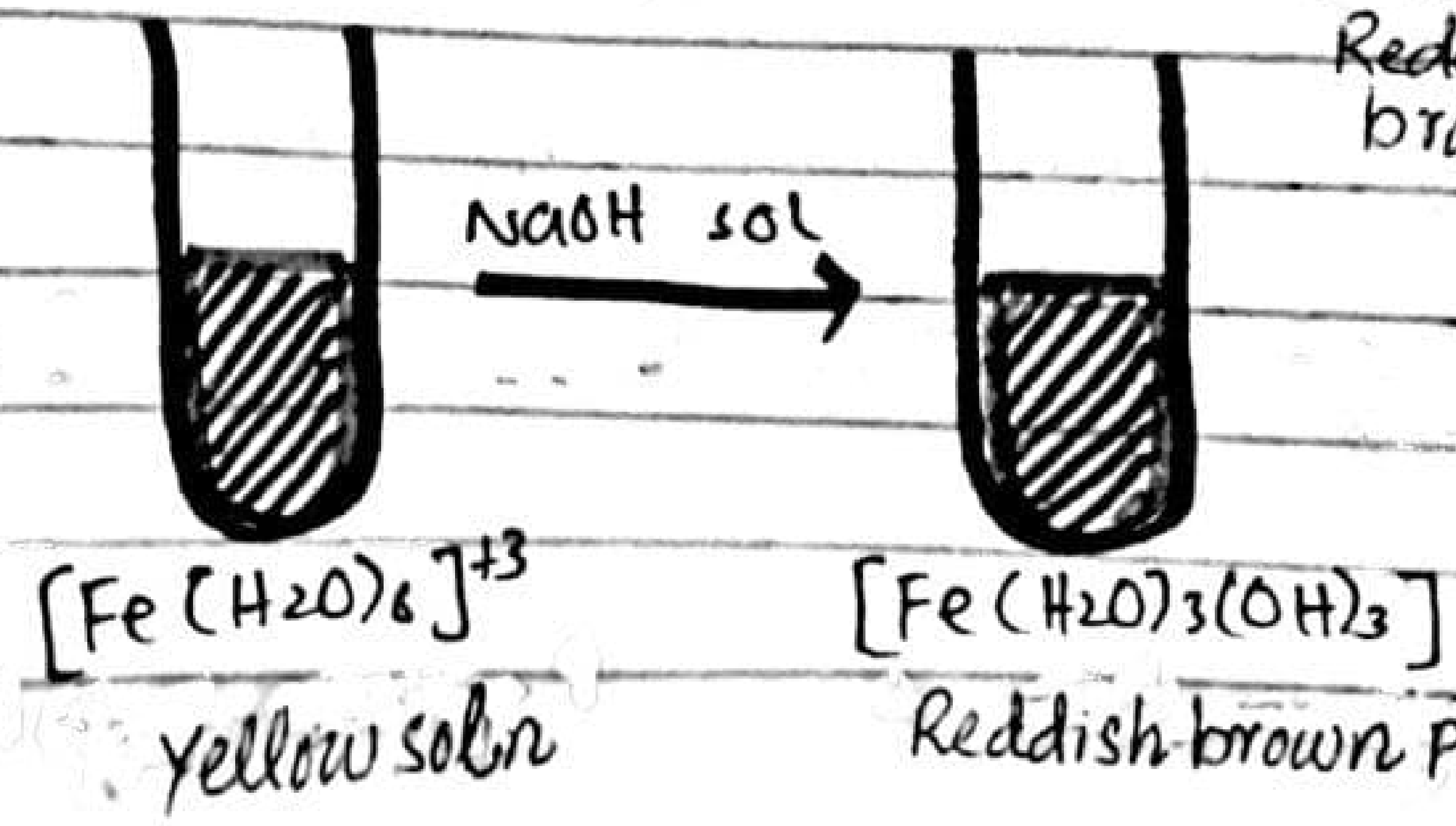
In case of iron (III):-

$$[Fe(H_2O)_6]^{+3} + 3OH^- \longrightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$

Yellow solution

Reddish brown PPt

↓ "neutral comp"



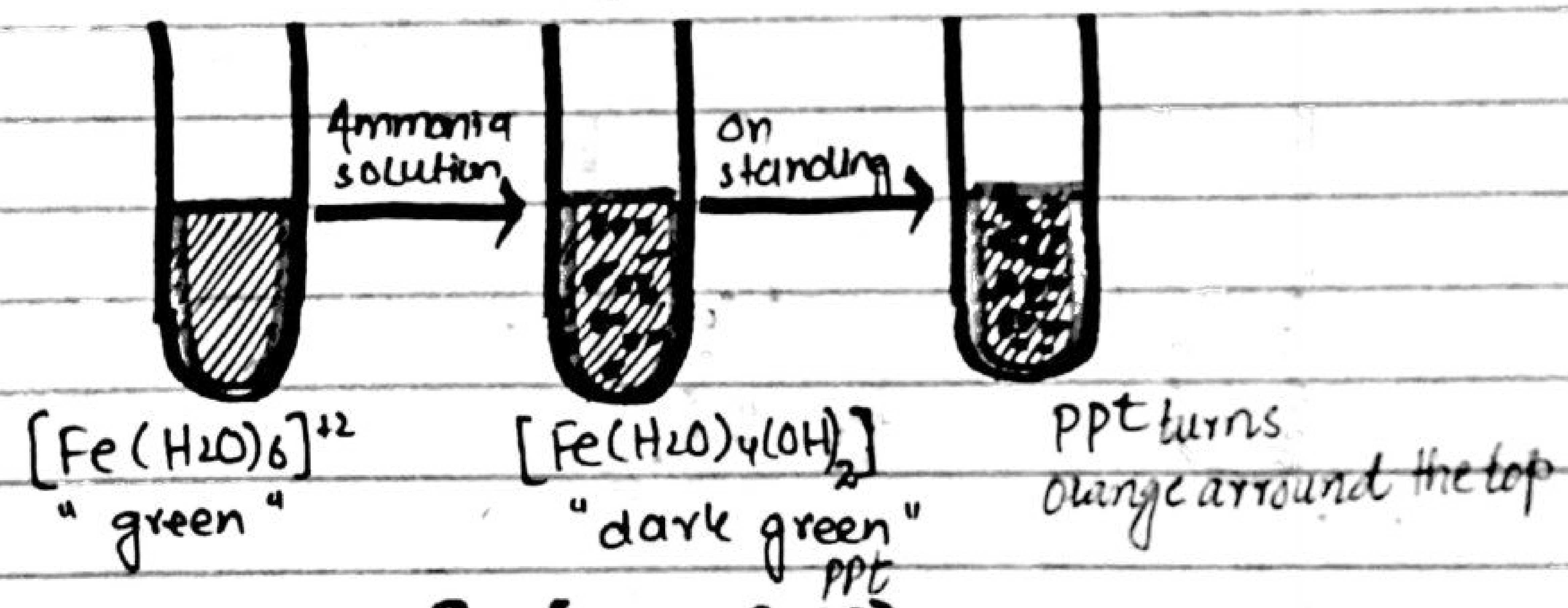
→ "Reaction of ions with Ammonia sol:-"

Ammonia can act as a base as well as a ligand. But when it reacts with iron (II) and (III) ions it acts as a base to remove hydrogen atoms from the Aqua complex.

In case of iron (II):-

The result is same as in case of addition of sodium hydroxide. The ppt again changes color as the iron (II) hydroxide complex is oxidised by air to iron (III) hydroxide.

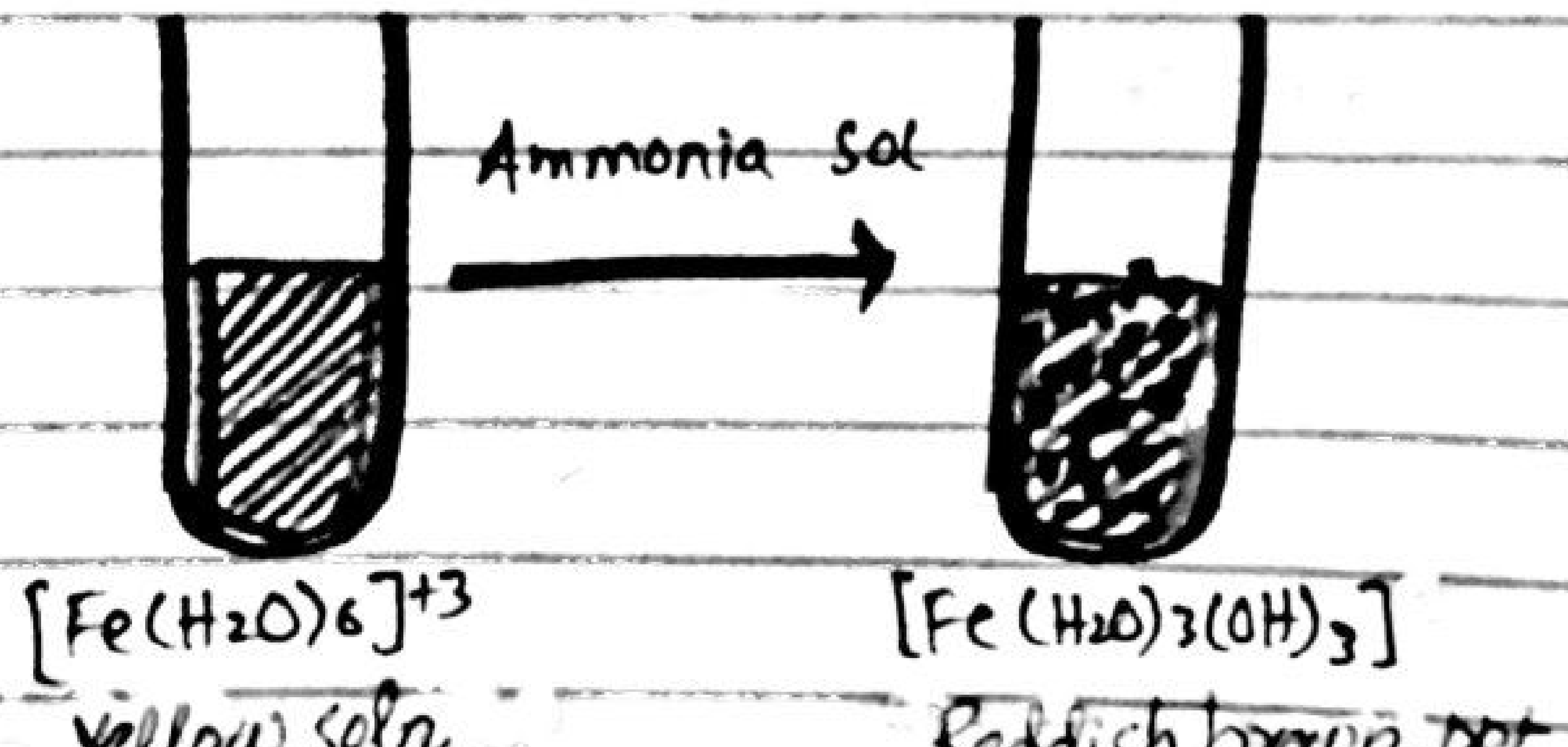
$$[Fe(H_2O)_6]^{+2} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$



In case of iron (III):-

Same results occured same as we add NaOH in a solution.

$$[Fe(H_2O)_6]^{+3} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$



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→ "Reactions with carbonates":-

In case of iron(II) :-

In case of Iron (II) we simply get the ppt (green)

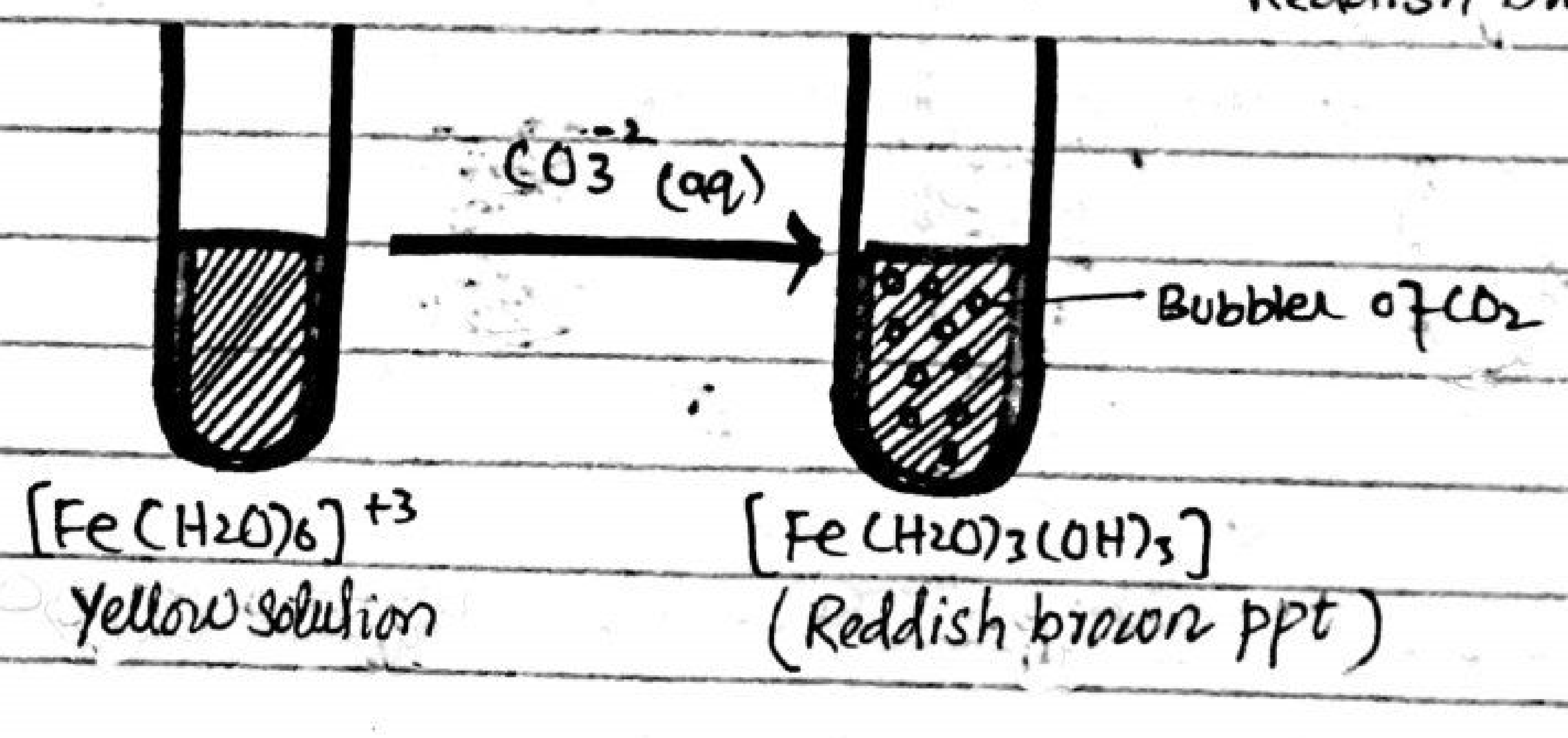
$Fe^{+2} + CO_3^{-2} \longrightarrow FeCO_3$

In case of iron (III) :-

Iron (III) is sufficiently acidic in nature so, it can react with weak basic carbonate ions.
if we add sodium carbonate in iron containing compounds we get the same results as we added ammonia or hydroxal sol.
carbonate ions get hydrogen ions and produced the neutral compound.

$$2[Fe(H_2O)_6]^{+3} + 2CO_3^{-2} \longrightarrow 3CO_2 + 3H_2O + 2[Fe(H_2O)_3(OH)_3]$$

Yellow sol. — Reddish brown ppt



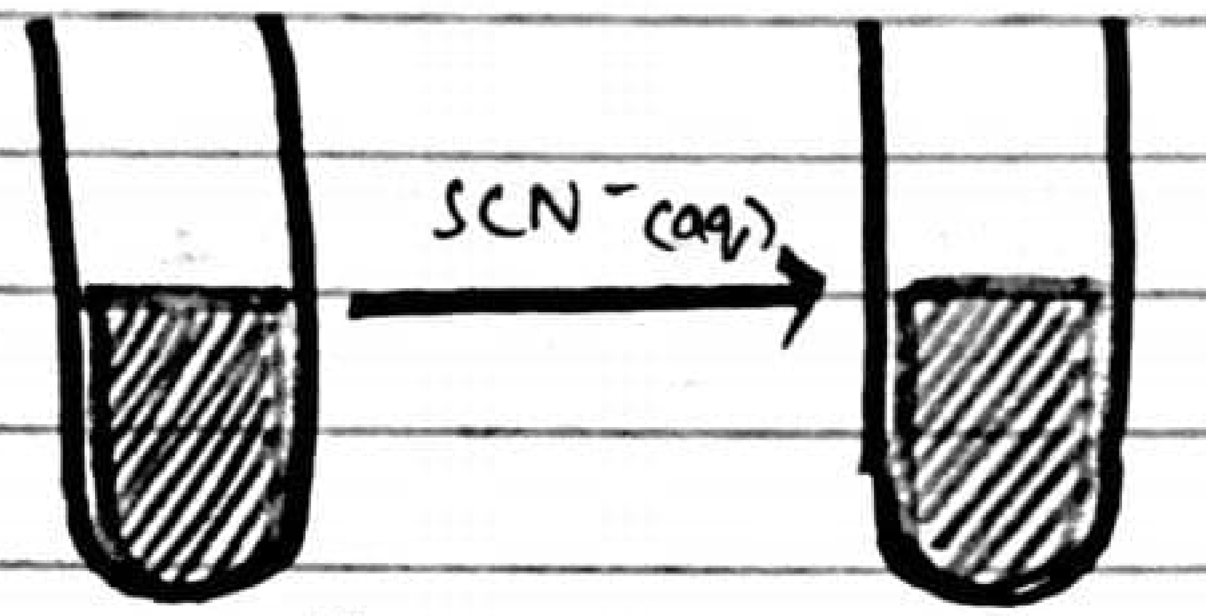
→ "Reaction with Thiocyanate ions":-

In case of iron (III) :-

It provided extremely sensitive test for iron (III) ions in sol.
if we add thiocyanate ions **SCN⁻** in a sol containing iron (III) ions we get blood red sol containing $[Fe(SCN)(H_2O)_5]^{+2}$ ion.

$$[Fe(H_2O)_6]^{+3} + SCN^- \longrightarrow [Fe(SCN)(H_2O)_5]^{+2} + H_2O$$

" Blood red color "



→ "Copper:-"

We will discussed:

→ Oxidation states (+1 — +2)

→ Reactions of Hexaaqua copper (II) ions with hydooxide, Ammonia and carbonate ions.

→ "Oxidation states":-

copper forms two types of compounds.

(i) Copper (+1) / Cuprous compounds in which Cu is monovalent.

(ii) copper (+2) / cupric compounds in which Cu is divalent.

When the cupric / cuprous is not stated in the copper salts then cupic is implied.

e.g:- copper sulphate implies cupric sulphate.

Mostly the "cuprous" compounds are colorless and diamagnetic as **filled 3d-orbital** ($Cu^+ = 3d^{10}$)

Cu_2O, Cu_2S etc are red and black which are exception. They are insoluble in water. Soluble compounds of Cu (+1) are unstable in water that's why disproportionate into **Cu^{+2}, Cu etc.**

•• Disproportionate → element become reduced and oxidized both.

in color-

For example:- $[Cu(H_2O)_4]^{+2}$ etc-

⇒ sol of Cu^{+2} is acidic in nature due to hydrolysis.

$$Cu^{+2} + H_2O \longrightarrow [Cu(OH)]^{+} + H^{+}$$

Cu^{+2} has un-complete out most shell so, it's paramagnetic in nature-

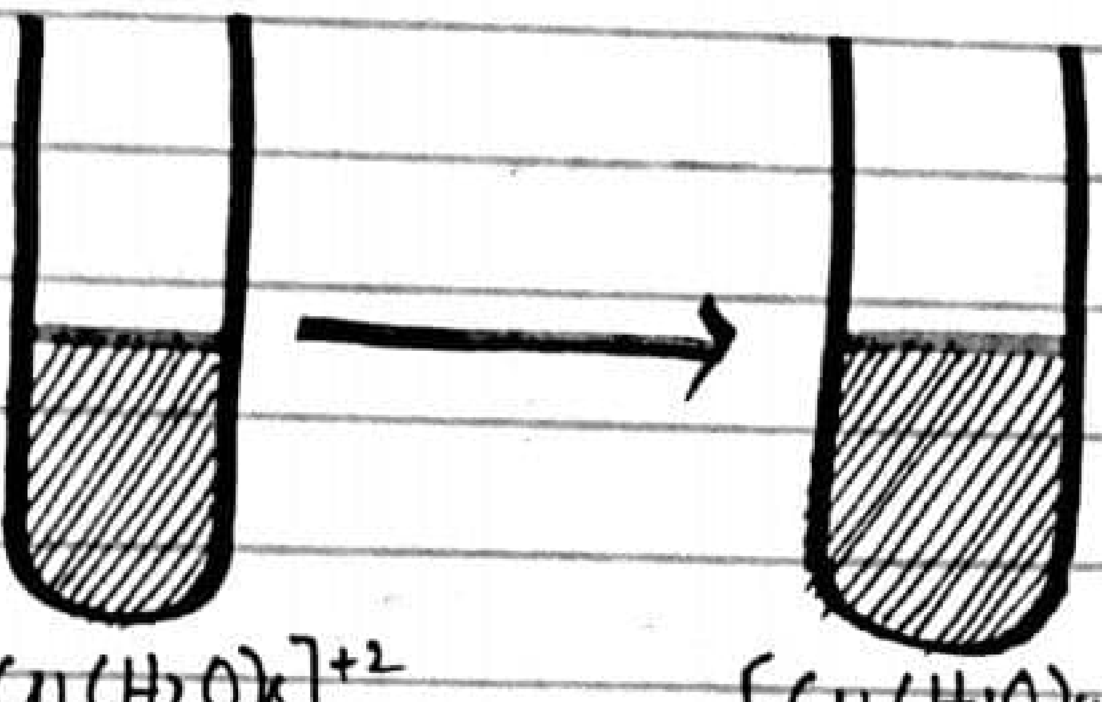
→ "Reaction of Hexaaqua copper (II) with hydroxide ion":-

Hydroxide ions removed the hydrogen atoms from the water ligand.

Removal of two hydrogen atoms from water produces a neutral complex which is shown in reaction:-

$$[Cu(H_2O)_6]^{+2} + 2OH^{-} \longrightarrow \underset{\text{(blue ppt)}}{[Cu(H_2O)_4(OH)_2]^{0}} + 2H_2O$$

change in color is as follows:-



$[Cu(H_2O)_6]^{+2}$ "Blue color"

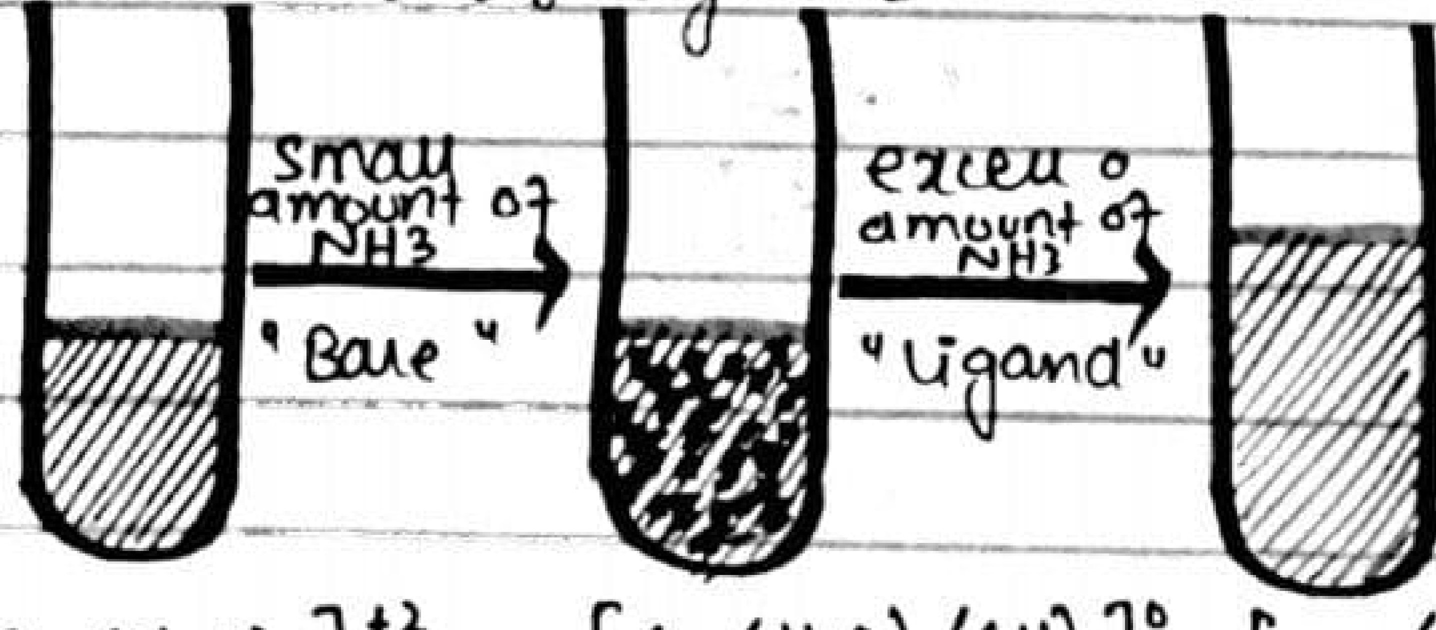
$[Cu(H_2O)_4(OH)_2]^0$ "Deep Blue color"

→ "Reaction of Hexaaqua copper(II) with Ammonia solⁿ:-

When $Cu(OH)_2$ dissolved in excess of NH_4OH, a blue soluble cupric ammine hydroxide is obtained: 1) Ammonia as base

$$\underset{\text{blue sol.}}{[Cu(H_2O)_6]^{+2}} + 2NH_3 \longrightarrow \underset{\text{Blue ppt}}{[Cu(H_2O)_4(OH)_2]} + 2NH_4^+$$

color changes are as follows:
2) When ammonia as ligand



$[Cu(H_2O)_6]^{+2}$ "solution" "Blue"

$[Cu(H_2O)_4(OH)_2]^0$ "ppt" "deep blue"

$[Cu(NH_3)_4(H_2O)_2]^{+2}$ "soluble form" "deep blue sol."

→ "Reaction of Hexaaqua copper (II) ions with carbonate ions":-

Normal cuprous carbonate (Cu_2CO_3) and cupric carbonate ($CuCO_3$) have not been isolated but basic cupric carbonates such as:-

→ **Malachite: $Cu(OH)_2 \cdot CuCO_3$ or $CuCO_3 \cdot CuO \cdot H_2O$ (green)**

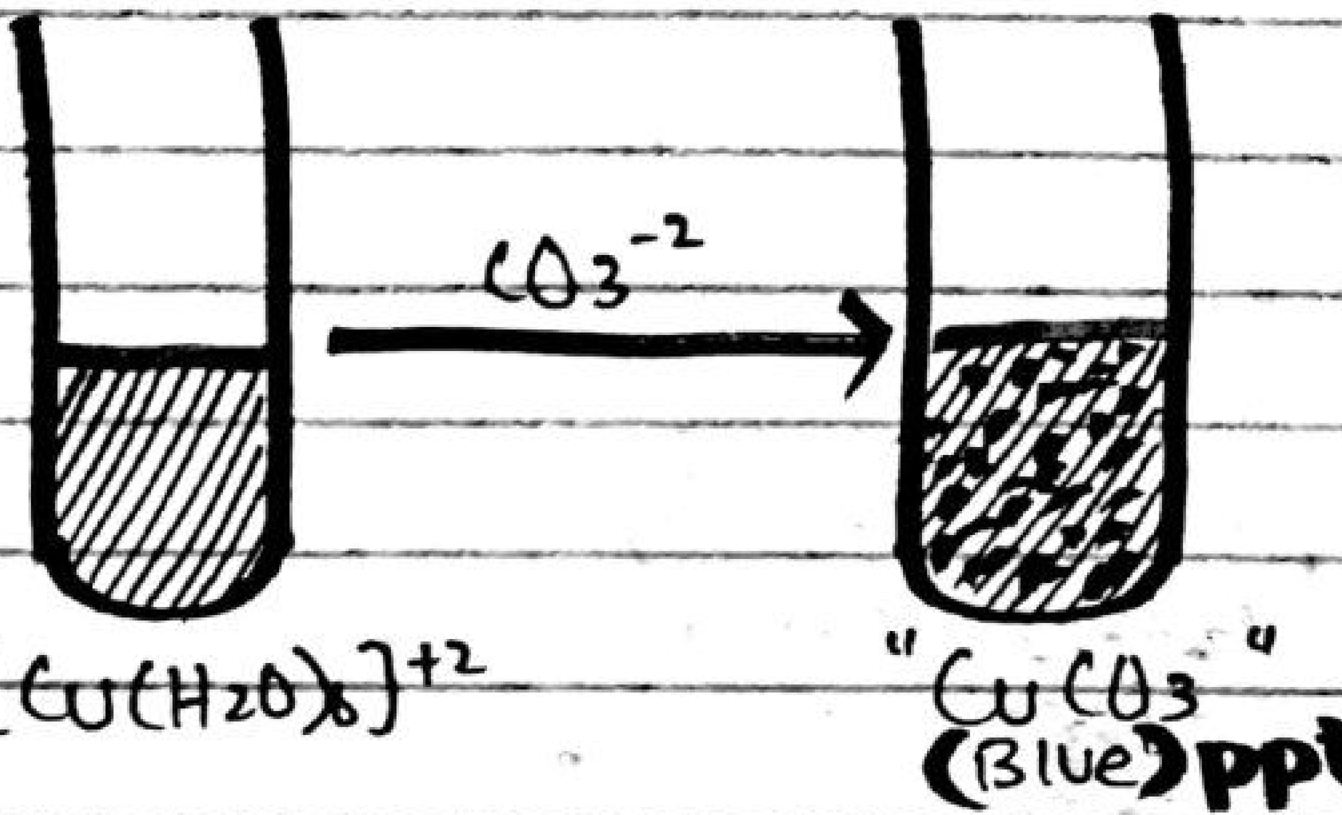
→ **Azurite: $Cu(OH)_2 \cdot 2CuCO_3$ (Blue)**

are known.

Malachite is obtained by passing CO_2 gas thoough the aqueous suspension of $Cu(OH)_2$.

$$2Cu(OH)_2 + CO_2 \longrightarrow \underset{\text{"malachite"}}{Cu(OH)_2 \cdot CuCO_3} + H_2O$$

We simpy get the ppt of what we can think of as copper(II) carbonate.



$$Cu^{+2}_{(aq)} + CO_3^{-2}{}_{(aq)} \longrightarrow CuCO_{3(s)}$$

"Exercise":-

"Question No:-01"

→ **Choose the correct option:-**

(i) transition metals (c)
(ii) It has complete filled d-orbital (c)
(iii) Zn (c)
(iv) Transition elements (d)
(v) Diamagnetic (c)
(vi) Electron (a)
(vii) Bohr Magneton (c)
(viii) Cu and Sn (a)
(ix) Pentacarbonyl Iron(0) (b)
(x) $Na_3[FeCl(CN)_5]$ (c)
(xi) square plane, Tetrahedral, (d)
(xii) Blue ions (a)
(xiii) Vanadium (c)
(xiv) Bright yellow (b)
(xv) oxidizing agent (a)
(xvi) Mn (a)
(xvii) Light pink (c)
(xviii) Fe (c)
(xix) Haber process (c)
(xx) Ligand (a) when Ammonia with 'Cu' or None of these

"Question No:-02"

(i) Why are d-block elements called transition elements?

Ans :- pg (1) → NOTES

(ii) Why do the d-block elements show different oxidation state?

Ans :- pg (8) → NOTES

(iii) Why does "**Mn**" show the max num of O.S in 3d-series?

Ans:- "Mn" has two electrons in 4s-orbital and 5-unpaired electrons in 3d-orbital. On bonding it looses it's 4s-electrons that's why un-paired electrons increases in num.

As we know that;

$$\text{Num of unpaired electrons} \propto \text{Oxidation states}$$

so, "Mn" show max num of O.S in 3d-series.

(iv) What is the difference b/w double salts and co-ordination compound or complex compounds?

→ **"Double salt":-**

Two salts crystallized out in one solid called the double salt.

Example:- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

→ **"Co-ordination compounds":-** pg NO # 12 → NOTES

(v) Explain following terms:-

(i) Ligand :- pg # 14

(ii) Co-ordination sphere :- pg # 16

(iii) Central Metal:- pg #14

(vi) How chromate converted into di-chromate?

ANS:- pg # 29

(vii) What's the difference B/W paramagnetism and dia-magnetism?

ANS:- pg # 10

(viii) What are the advantages of potassium-dichromate in titration?

ANS:- pg # 33

(ix) How does di-chromate is converted into chromate?

ANS:- For this purpose we add base instead of an acid. By this the reaction become reversed. The orange color changes into yellow this indicated the formation of chromates.

$$CrO_4^{-2} + H^+ \underset{\uparrow OH^-}{\rightleftharpoons} Cr_2O_7^{-2} + H_2O$$