QUALITATIVE ANALYSIS (Cations)

PART-II

Analysis of CATIONS (Basic Radicals) : Classificaiton of cation in different groups :

Table : 1

Group	Group reagent	Basic radical	Composition and colour of precipitate
Zero	NaOH or $Ca(OH)_2$, heat if required	NH_4^+, K^+, Na^+	Ammonia gas is evolved.
1.	dil. HCl	Ag^+	AgCl ; White
		Hg_2^{2+}	Hg_2Cl_2 ; White
		Pb^{2+}	$PbCl_2$; White
2.(A)	H_2S in presence of dil. HCl (Insoluble in YAS)	Hg^{2+}	HgS ; Black
		Pb^{2+}	PbS ; Black
		Bi^{3+}	Bi_2S_3 ; Black
		Cu^{2+}	CuS ; Black
		Cd^{2+}	CdS ; Yellow
2.(B)	H_2S in presence of dil. HCl (Soluble in YAS)	As^{3+}	As_2S_3 ; Yellow
		Sb^{3+}	Sb_2S_3 ; Orange
		Sn^{2+}	SnS ; Brown
		Sn^{4+}	SnS_2 ; Yellow
3.	NH_4OH in presence of NH_4Cl	Fe^{3+}	$Fe(OH)_3$; Reddish brown
		Cr^{3+}	$Cr(OH)_3$; Green
		Al^{3+}	$Al(OH)_3$; Gelatinous white
4.	H_2S in presence of NH_4OH and NH_4Cl	Zn^{2+}	ZnS ; White
		Mn^{2+}	MnS ; Buff (or Pink)
		Co^{2+}	CoS ; Black
		Ni^{2+}	NiS ; Black
5.	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+}	$BaCO_3$; White
		Sr^{2+}	$SrCO_3$; White
		Ca^{2+}	$CaCO_3$; White
6.	Na_2HPO_4 in presence of NH_4OH	Mg^{2+}	$Mg(NH_4)PO_4$; White

☞ [YAS = Yellow ammonium sulphide. $(NH_4)_2S_x$].

There are some important points which should be kept in mind while doing the analysis of cations.

1. **Group 1st radicals** (Ag^+, Pb^{2+}, Hg_2^{2+}) are precipitated as chloride because the solubility product of these chlorides (AgCl, $PbCl_2$, Hg_2Cl_2) is less than the solubility products of chlorides of all other metal ions, which remain in solution. Lead chloride is slightly soluble in water and therefore, lead is never completely precipitated by adding dilute hydrochloric acid to a sample; the rest of the lead ions are precipitated with H_2S in acidic medium together with the cations of the second group.
2. **Group 2nd radicals** are precipitated as sulphides because of their low solubility products whereas sulphides of other metals remain in solution because of their high solubility products. HCl acts as a source of H^+ which decreases the concentration of S^{2-} due to common ion effect. Hence, the concentration of S^{2-} ion is too low that it exceeds only the solubility products of the metal sulphides of IInd group.

We can not use H_2SO_4 inplace of HCl because some cations of higher groups i.e. v^{th} group will also precipitate as their sulphates like $BaSO_4$, $SrSO_4$, $CaSO_4$ etc.

HNO_3 can't be used in place of HCl. HNO_3 is a powerful oxidising agent. HNO_3 will oxidize H_2S forming sulphur (yellow precipitate) or colloidal solution causing confusion with CdS, As_2S_3 even though Cd^{2+}, As^{3+} will be absent. The colloidal solution is white-yellow and that cannot be filtered causing unnecessary trouble.

3. **Group 3rd radicals** are precipitated as hydroxides and the addition of NH_4Cl suppresses the ionisation of NH_4OH so that only the group 3 cations are precipitated as hydroxides because of their low solubility products.

(i) Excess of NH_4Cl should not be added, as manganese will precipitate as $MnO_2.H_2O$

(ii) $(NH_4)_2SO_4$ cannot be used in place of NH_4Cl because the SO_4^{2-} will also give the precipitate of $BaSO_4$, $SrSO_4$ etc.

(iii) While proceeding for 3rd group from 2nd group, the filtrate of 2nd group is boiled off to remove the dissolved H_2S and then one drop of concentrated HNO_3 is added and again boil so that if Fe^{2+} is present is oxidised to Fe^{3+}. The K_{sp} of Fe^{2+} is higher than Fe^{3+}, therefore, it is partially precipitated and will thus interfere in the analysis of 4th group radicals. In our scheme Fe^{2+} is not there even if it is present, we shall report only Fe^{3+} (Fe^{2+} needs other special tests).

(iv) If the medium remains acidic the hydroxides do not precipitate and we would think that Fe^{3+}, Al^{3+}, Cr^{3+} are absent even though they may be present.

(v) In place of NH_4OH, NaOH solution can't be used for the precipitation as their hydroxides because in excess of it we get soluble complexes of Al^{3+} and Cr^{3+}.

4. **In 4th group,** ammonium hydroxide increases the ionisation of H_2S by removing H^+ from H_2S as unionised water.

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \ ; \ H^+ + OH^- \longrightarrow H_2O$$

Now the excess of S^{2-} ions is available and hence the ionic products of group 4th group cations exceeds their solubility products and will be precipitated. In case H_2S is passed through a neutral solution, incomplete precipitation will take place due to the formation of HCl, which decreases the ionisation of H_2S. For example

$$MnCl_2 + H_2S \longrightarrow MnS + 2HCl$$

5. **In 5th group** the reagent ammonium carbonate should be added in alkaline or neutral medium. In the absence of ammonia or ammonium ions, magnesium will also be precipitated.

PREPARATION OF ORIGINAL SOLUTION (O.S) :

Original solution is used for the analysis of basic radicals except NH_4^+. It is prepared by dissolving given salt or mixture in a suitable solvent as follows :

- H_2O
- dil HCl
- conc. HCl

$$\text{Salt or Mixt.} + H_2O \xrightarrow{\Delta} \text{soluble (then } H_2O \text{ is suitable solvent)}$$

If given salt or mixture is insoluble in H_2O then it is dissolved in dil HCl.

$$\text{Salt or Mixt.} + \text{dil HCl} \xrightarrow{\Delta} \text{soluble (then dil HCl is taken as solvent)}$$

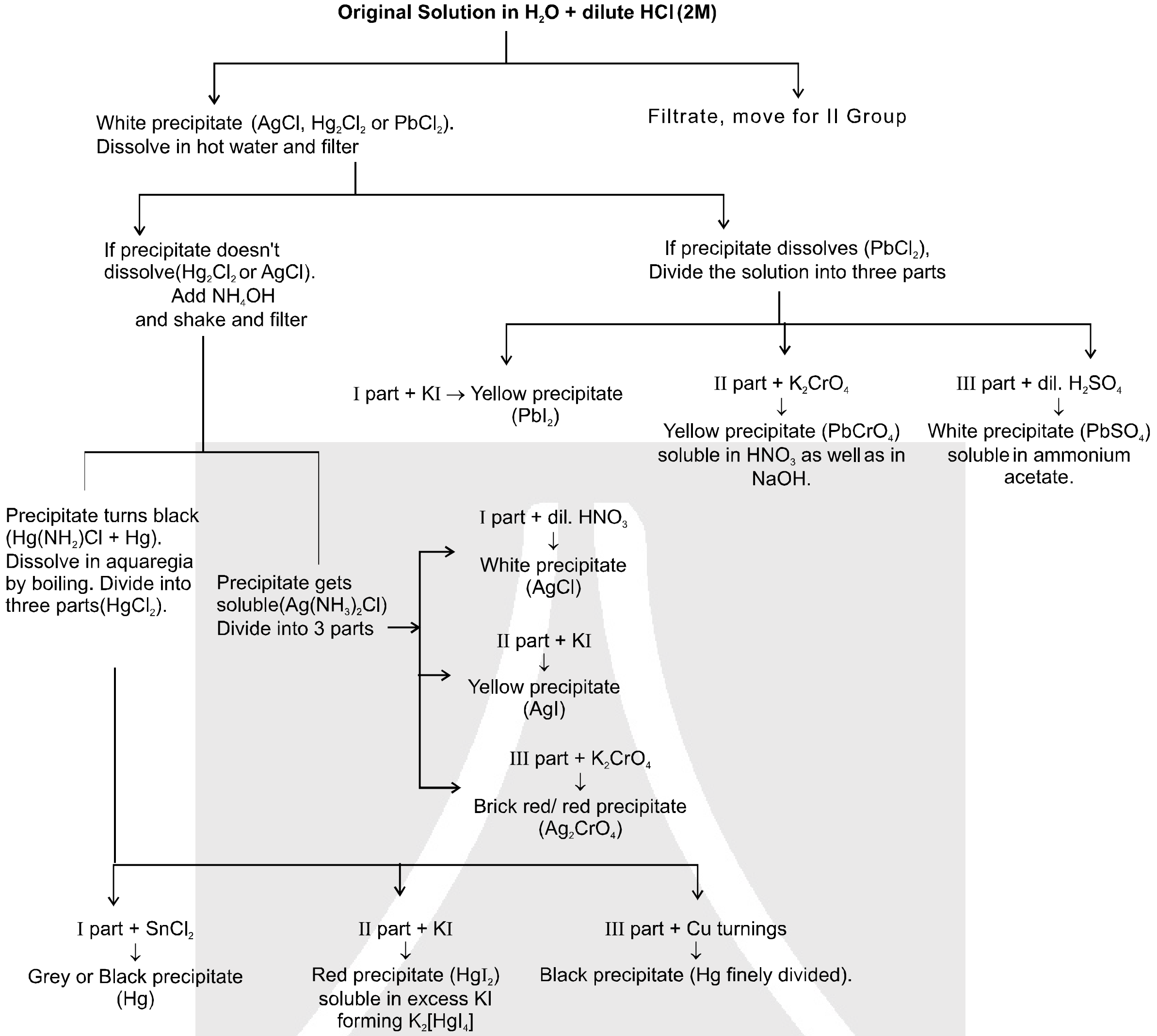
If given salt or mixture is insoluble in dilute HCl then it is dissolved in conc. HCl.

$$\text{Salt or Mixt.} + \text{conc. HCl} \xrightarrow{\Delta} \text{soluble}$$

In this way after selecting suitable solvent, given salt or mixture is dissolved in small quantity in the solvent and filtered. Obtained filtrate is called as original solution (O.S.) and that is used for the detection of basic radicals except NH_4^+.

Section (A) : I^{st} Group

I^{st} GROUP (Pb^{2+}, Hg_2^{2+}, Ag^+) :



1. LEAD ION (Pb^{2+}) :

- **Dilute HCl solution:** White precipitate is formed in cold solution.

$$Pb^{2+} + HCl \longrightarrow PbCl_2 \downarrow \text{(white)} + 2H^+$$

White precipitate is soluble in hot water. White precipitate is also soluble in concentrated HCl or concentrated KCl or excess dil. HCl.

$$PbCl_2 \downarrow + 2Cl^- \longrightarrow [PbCl_4]^{2-} \text{(colourless)}$$

- **Sodium hydroxide solution:** White precipitate is formed which is soluble in excess of the reagent.

$$Pb^{2+} + 2OH^- \longrightarrow Pb(OH)_2 \downarrow ; \qquad Pb(OH)_2 \downarrow + 2OH^- \longrightarrow [Pb(OH)_4]^{2-}$$

$$[Pb(OH)_4]^{2-} + H_2O_2 \longrightarrow PbO_2 \downarrow \text{(black / brownish black)} + 2H_2O + 2OH^-$$

$$[Pb(OH)_4]^{2-} + S_2O_8^{2-} \longrightarrow PbO_2 \downarrow + 2H_2O + 2SO_4^{2-}$$

- **Potassium iodide solution:** A yellow precipitate is formed which is soluble in excess more concentrated (6M) solution of the reagent. Yellow precipitate of PbI_2 is moderately soluble in boiling water to give a colourless solution.

$$PbCl_2 + 2KI \longrightarrow PbI_2 \downarrow + 2KCl ; \qquad PbI_2 + KI \rightleftharpoons K_2[PbI_4] \text{ soluble} \downarrow$$

Yellow precipitate reappears on dilution with water. Yellow precipitate of PbI_2 does not dissolve in excess of dilute solution of KI.

- **Potassium chromate solution (in neutral, acetic acid or ammonia solution) :** A yellow precipitate is formed.

  $$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2KCl$$

  Yellow precipitate is soluble in sodium hydroxide and HNO_3 (nitric acid).

  $$2PbCrO_4 + 2H^+ \rightleftharpoons 2Pb^{2+} + Cr_2O_7^{2-} + H_2O$$

  $$PbCrO_4 + 4OH^- \rightleftharpoons [Pb(OH)_4]^{2-} + CrO_4^{2-}$$

  Both reversible reactions on buffering the solution with ammonia or acetic acid respectively, $PbCrO_4$ reprecipitates.

- **Ammonia solution:** With ammonia solution, Pb^{2+} gives a white precipitate of lead hydroxide.

  $$Pb^{2+} + 2NH_4OH \longrightarrow Pb(OH)_2 \downarrow + 2NH_4^+$$

- **Dilute H_2SO_4:** White precipitate is formed which is soluble in more concentrated ammonium acetate (6M) solution or ammonium tartrate in the presence of ammonia.

  $$PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 \downarrow + 2HCl$$

  $$PbSO_4 \downarrow + 4CH_3COO^- \longrightarrow [Pb(CH_3COO)_4]^{2-} + SO_4^{2-}$$

2. MERCURY(I) ION (Hg_2^{2+}) :

- **Dilute HCl solution :** White precipitate is formed in cold solution.

  $$Hg_2^{2+} + 2HCl \longrightarrow Hg_2Cl_2 \downarrow \text{(white)} + 2H^+$$

- **Ammonia solution :** A mixture of mercury metal (black precipitate) and basic mercury (II) amido chloride (white precipitate) is formed.

  $$2Hg_2Cl_2 + 4NH_4OH \longrightarrow \underbrace{HgO.Hg(NH_2)Cl \downarrow + Hg \downarrow}_{\text{black}} + 3NH_4Cl + 3H_2O$$

- **Dissolution of white precipitate (Hg_2Cl_2) in aquaregia :**

  $$3Hg_2Cl_2 + 2HNO_3 + 6HCl \longrightarrow 6HgCl_2 + 2NO + 4H_2O$$

- **Potassium iodide solution :** A green precipitate is formed.

  $$Hg_2^{2+} + 2I^- \longrightarrow Hg_2I_2 \downarrow$$

  Green precipitate in excess of reagent undergoes disproportionation reaction and a soluble $[HgI_4]^{2-}$ ions and black mercury are formed.

  $$Hg_2I_2 \downarrow + 2I^- \longrightarrow [HgI_4]^{2-} + Hg \downarrow \text{ (finely divided)}$$

  Boiling the mercury (I) iodide precipitate with water, disproportionation takes place and a mixture of red mercury (II) iodide precipitate and black mercury is formed.

  $$Hg_2I_2 \downarrow \longrightarrow HgI_2 \downarrow + Hg \downarrow$$

- **Potassium chromate solution :** A red crystalline precipitate is formed which turns black when solution of sodium hydroxide is added.

  $$Hg_2^{2+} + CrO_4^{2-} \longrightarrow Hg_2CrO_4 \downarrow \; ; \; Hg_2CrO_4 \downarrow + 2OH^- \longrightarrow Hg_2O \downarrow + CrO_4^{2-} + H_2O$$

- **Potassium cyanide solution :** A black precipitate of mercury is obtained

  $$Hg_2^{2+} + 2CN^- \longrightarrow Hg \downarrow + Hg(CN)_2 \text{ (soluble).}$$

3. SILVER ION (Ag^+) :

- **Dilute hydrochloric acid/soluble chlorides :** White precipitate is formed.

  $Ag^+ + HCl \longrightarrow AgCl\downarrow + H^+$

  The precipitate obtained after filtration is soluble in concentrated HCl.

  $AgCl\downarrow + Cl^- \rightleftharpoons [AgCl_2]^-$

  On dilution with water, the equilibrium shifts back to the left and the precipitate reappears. Dilute ammonia solution dissolves the precipitate forming a soluble complex.

  $AgCl\downarrow + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$

  Dilute nitric acid or hydrochloric acid neutralizes the excess ammonia and the precipitate reappears because the equilibrium is shifted backwards.

  $[Ag(NH_3)_2]Cl + 2HNO_3 \longrightarrow AgCl\downarrow$ (white) $+ 2NH_4NO_3$.

- **Potassium iodide solution:** A bright yellow precipitate is formed which is insoluble in dilute ammonia but partially soluble in concentrated ammonia.

  $Ag^+ + I^- \longrightarrow AgI\downarrow$

  The yellow precipitate is soluble in KCN and in $Na_2S_2O_3$.

  $AgI\downarrow + 2CN^- \longrightarrow [Ag(CN)_2]^- + I^-$; $AgI\downarrow + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + I^-$

- **Potassium chromate solution:** Red precipitate is formed which is soluble in dilute HNO_3 and in ammonia solution.

  $2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4\downarrow$

  $2Ag_2CrO_4\downarrow + 2H^+ \rightleftharpoons 4Ag^+ + Cr_2O_7^{2-} + H_2O$

  $2Ag_2CrO_4\downarrow + 4NH_3 \longrightarrow 2[Ag(NH_3)_2]^+ + CrO_4^{2-}$

- **Disodium hydrogen phosphate solution:** In neutral solution a yellow precipitate is formed with the reagent.

  $3Ag^+ + HPO_4^{2-} \longrightarrow Ag_3PO_4\downarrow + H^+$

  The yellow precipitate is soluble in nitric acid and ammonia solution.

- **Ammonia solution :** Brown precipitate is formed.

  $2Ag^+ + 2NH_3 + H_2O \longrightarrow Ag_2O\downarrow + 2NH_4^+$

  Precipitate dissolves in ammonia.

  $Ag_2O\downarrow + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$

II^nd^ Group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+})

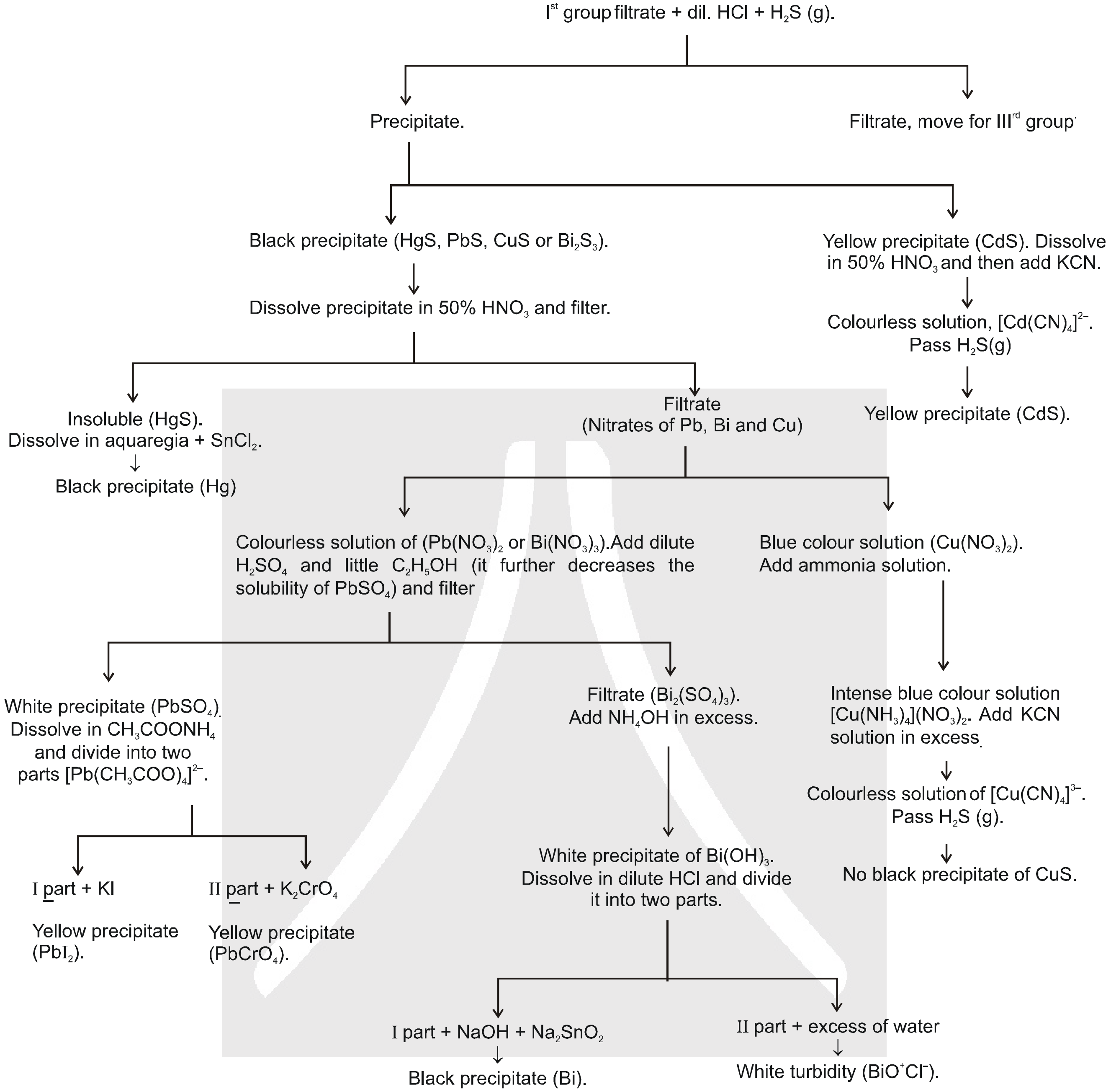
On the basis of the solubility of the precipitates of the sulphides of II group cations in yellow ammonium sulphide, they have been classified into two subgroups as given below :

IIA : HgS, PbS, CuS, Bi_2S_3, all black but CdS is yellow. All insoluble in yellow ammonium sulphide.

IIB : SnS_2, As_2S_3 are yellow, Sb_2S_3 is orange & SnS is dark brown All soluble in yellow ammonium sulphide.

Section (B) : II A Group

IIA Group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, *Cd^{2+})



1. MERCURY (II) ION (Hg^{2+}) :

- **Precipitation with H_2S in acidic medium :** Black precipitate is formed. Precipitate insoluble in water, hot dilute HNO_3 ,alkali hydroxides, or colourless ammonium sulphide.

$$Hg^{2+} + H_2S \xrightarrow{H^+} HgS\downarrow + 2H^+$$

☞ Na_2S (2M) dissolves the precipitate forming soluble complex.

$$HgS + S^{2-} \longrightarrow [HgS_2]^{2-}$$

☞ Aqua regia dissolves the precipitate.

$$3\,HgS + 6\,HCl + 2HNO_3 \longrightarrow 3\,HgCl_2 + 3S\downarrow + 2NO\uparrow + 4\,H_2O$$

Under these circumstance $HgCl_2$ is undissociated. When solution is heated white precipitate of sulphur dissolves forming H_2SO_4.

$$2\,HNO_3 + S\downarrow \longrightarrow SO_4^{2-} + 2\,H^+ + 2NO\uparrow$$

- **Stannous chloride solution :** When added in moderate amounts silky white precipitate is formed.

  $2HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2 \downarrow$

  If more reagent is added, Hg (I) chloride is reduced to black precipitate of mercury.

  $Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + 2Hg \downarrow$

- **Potassium iodide solution :** On slow addition red precipitate is formed.

  $Hg^{2+} + 2I^{-} \longrightarrow HgI_2 \downarrow$

  Precipitate dissolves in excess of KI forming colourless soluble complex.

  $HgI_2 + 2I^{-} \longrightarrow [HgI_4]^{2-}$

  ☞ KCN does not have any effect.

- **Copper chips , sheet or coin :** A black precipitate of mercury is formed.

  $Hg^{2+} + Cu \longrightarrow Hg \downarrow + Cu^{2+}$

- **Sodium hydroxide solution :** When added in small quantity brownish–red precipitate of varying composition is formed and in stoichiometric amounts precipitate turns to yellow when Hg (II) oxide is formed.

  $Hg^{2+} + 2OH^{-} \longrightarrow HgO \downarrow + H_2O$

  Precipitate is insoluble in excess reagent but dissolves readily in acids and this can be used to differentiate Hg (I) from Hg (II).

- **Ammonia solution :** White precipitate of mixed composition (Mercury (II) oxide + Mercury (II) amido nitrate) is formed with metal nitrate.

  $2\,Hg^{2+} + NO_3^{-} + 4NH_3 + H_2O \longrightarrow HgO.Hg\,(NH_2)NO_3 \downarrow + 3\,NH_4^{+}$

- **Cobalt (II) thiocyanate test :** When reagent is added to an aqueous solution of Hg^{2+} ions and the walls of the test tube is stirred with a glass rod, deep–blue crystalline precipitate is formed.

  $Hg^{2+} + Co^{2+} + 4\,SCN^{-} \longrightarrow Co^{+2}\,[Hg(SCN)_4]^{-2} \downarrow$ or $Hg\,[Co(NCS)_4] \downarrow$

  ☞ In place of Cobalt (II) thiocyanate, $Co(CH_3COO)_2$ and NH_4SCN can be added to the aqueous solution of Hg^{2+} ions.

2. COPPER ION (Cu^{2+}) :

- **Precipitation with H_2S in acidic medium :** Black precipitate is formed.

  $Cu^{2+} + H_2S \xrightarrow{H^{+}} CuS \downarrow + 2\,H^{+}$

  Precipitate is insoluble in boiling dilute (M) H_2SO_4 (distinction from cadmium), in NaOH, Na_2S and $(NH_4)_2S$. Precipitate dissolves in hot concentrated HNO_3

  $3\,CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2$ (blue) $+ 2NO + 4H_2O + 3S$

  When boiled for longer S is oxidised to H_2SO_4 and a clear solution of $Cu(NO_3)_2$ is obtained.

  ☞ KCN dissolves the precipitate forming a clear solution.

  $2\,CuS \downarrow + 8\,CN^{-} \longrightarrow 2\,[Cu(CN)_4]^{3-} + S_2^{2-}$ (disulphide ion)

- **Ammonia solution :** When added sparingly a blue precipitate of basic salt (basic copper sulphate) is formed with $CuSO_4$.

  $2Cu^{2+} + SO_4^{2-} + 2\,NH_3 + 2\,H_2O \longrightarrow Cu(OH)_2\,.CuSO_4 \downarrow + 2NH_4^{+}$

  It is soluble in excess of reagent forming a deep blue colouration.

  $Cu(OH)_2\,.CuSO_4\downarrow + 8NH_3 \longrightarrow 2\,[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2\,OH^{-}$

- **Sodium hydroxide in cold solution :** A blue precipitate is formed.

  $Cu^{2+} + 2\,OH^{-} \longrightarrow Cu\,(OH)_2 \downarrow$

  $Cu(OH)_2\downarrow \xrightarrow{Heat} CuO\downarrow$ (black) $+ H_2O$

- **Potassium iodide :** It gives a white precipitate of Cu(I) iodide but the solution is intensely brown because of the formation of tri–iodide ions (or iodine).

  $2\,Cu^{2+} + 5\,I^{-} \longrightarrow CuI \downarrow + I_3^{-}$

  The solution becomes colourless and a white precipitate is visible when excess of sodium thiosulphate solution is added.

  $I_3^{-} + 2\,S_2O_3^{2-} \longrightarrow 3\,I^{-} + S_4O_6^{2-}$

  ☞ These reactions are used in quantitative analysis for the iodometric determination of copper.

- **Potassium ferrocyanide (Potassium hexacyanidoferrate (II)) solution :** Cu^{2+} ions gives brown/chocolate brown precipitate.

  $2Cu^{2+} + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6] \downarrow + 4K^{+}$

  ☞ $2\,[Fe(CN)_6]^{3-} + 3\,Cu^{2+} \longrightarrow Cu_3\,[Fe(CN)_6]_2 \downarrow$ (green)

(vi) Potassium cyanide : When added sparingly forms first a yellow precipitate.

$$Cu^{2+} + 2CN^- \longrightarrow Cu(CN)_2 \downarrow \text{(yellow)}$$

Precipitate quickly decomposes into CuCN and cyanogen.

$$2\,Cu(CN)_2 \downarrow \longrightarrow 2CuCN \downarrow \text{(white)} + (CN)_2 \uparrow \text{(highly poisonous)}$$

Excess reagent dissolves the precipitate forming a colourless soluble complex.

$$CuCN \downarrow + 3\,CN^- \longrightarrow [Cu(CN)_4]^{3-}$$

Complex is so stable that H_2S cannot precipitate Cu (I) sulphide (distinction from cadmium).

- **Potassium thiocyanate solution :** The Cu^{+2} ions solution initially gives a black precipitate which then slowly decomposes to give white precipitate of Cu(I) thiocyanate.

$$Cu^{2+} + 2\,SCN^- \longrightarrow Cu(SCN)_2 \downarrow$$
$$2\,Cu(SCN)_2 \downarrow \longrightarrow 2\,CuSCN \downarrow + (SCN)_2 \uparrow$$

☞ Cu (II) thiocyanate can be immediately converted into Cu(I) thiocyanate by adding a suitable reducing agent like saturated solution of sulphur dioxide.

$$2\,Cu(SCN)_2 \downarrow + SO_2 + 2\,H_2O \longrightarrow 2\,CuSCN \downarrow + 2\,SCN^- + SO_4^{2-} + 4H^+$$

Excess reagent dissolves the precipitate forming a colourless soluble complex.

$$Cu(SCN) + 3SCN^- \longrightarrow [Cu(SCN)_4]^{3-}$$

3. BISMUTH ION (Bi^{3+}) :

- **Precipitation with H_2S in acidic medium :** Black precipitate is formed which is insoluble in cold dilute HNO_3 and yellow ammonium sulphide.

$$2Bi^{3+} + 3H_2S \xrightarrow{H^+} Bi_2S_3 \downarrow \text{(black)} + 6H^+$$
$$Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi\,(NO_3)_3 + 2NO + 3S + 4H_2O$$

☞ $Bi_2S_3\downarrow + 6\,HCl$ (boiling concentrated) $\longrightarrow 2\,Bi^{3+} + 6\,Cl^- + 3\,H_2S$

- **Sodium hydroxide :** White precipitate is formed with the reagent.

$$Bi^{3+} + 3\,OH^- \longrightarrow Bi(OH)_3\downarrow$$

Very slightly soluble in excess reagent in cold solution but soluble in acids.

$$Bi(OH)_3 \downarrow + 3H^+ \longrightarrow Bi^{3+} + H_2O$$

☞ Precipitate on boiling loses water and turns yellowish white which is oxidised to BiO_3^- by H_2O_2.

$$Bi(OH)_3 \longrightarrow BiO.OH\downarrow + H_2O$$
$$BiO.OH + H_2O_2 \longrightarrow BiO_3^- + H^+ + H_2O$$

- **Dilution with water :** Solution of bismuth salts gives white precipitate when water is added in larger quantity.

$$Bi^{3+} + NO_3^- + H_2O \longrightarrow BiO(NO_3) \downarrow + 2H^+$$
$$Bi^{3+} + Cl^- + H_2O \longrightarrow BiOCl \downarrow \text{(bismuth oxychloride or bismuthyl chloride)} + 2H^+$$

Soluble in mineral acids (dilute) but insoluble in tartaric acid (distinction from antimony) and in alkali hydroxide (distinction from tin).

- **Potassium iodide :** When the reagent is added dropwise to a solution containing Bi^{3+} ions, a black precipitate is formed.

$$Bi^{3+} + 3I^- \longrightarrow BiI_3 \downarrow$$

The precipitate dissolves in excess KI forming orange coloured soluble complex.

$$BiI_3 + I^- \rightleftharpoons [BiI_4]^-$$

On dilution the reaction is reversed and black BiI_3 is reprecipitated.

☞ On heating with water black precipitate of BiI_3 turns orange.

$$BiI_3 \downarrow + H_2O \longrightarrow BiOI \downarrow + 2H^+ + 2I^-$$

4. CADMIUM ION (Cd^{2+}) (*Not in JEE advance syllabus) :

- **Precipitation with H_2S in acidic medium :** Yellow precipitate is formed which dissolves in hot dilute HNO_3.

$$Cd^{2+} + H_2S \xrightarrow{H^+} CdS \downarrow + 2H^+$$
$$CdS + 8HNO_3 \longrightarrow 3Cd\,(NO_3)_2 + 4H_2O + 2NO + 3S$$

☞ Precipitate does not dissolve in KCN.

- **Ammonia solution (Dropwise addition) :** Ammonium hydroxide first gives white precipitate of $Cd(OH)_2$ which gets dissolve in excess of reagent forming a soluble complex.

  $Cd^{2+} + 2\,NH_3 + 2\,H_2O \rightleftharpoons Cd(OH)_2\downarrow + 2\,NH_4^+$

  $Cd(OH)_2\downarrow + 4\,NH_3 \longrightarrow [Cd(NH_3)_4]^{2+} + 2\,OH^-$.

- **Potassium cyanide :** Initially a white precipitate of $Cd(CN)_2$ is formed which in excess of reagent dissolves forming a soluble complex.

  $Cd^{2+} + 2\,CN^- \longrightarrow Cd(CN)_2\downarrow$

  $Cd(CN)_2\downarrow + 2\,CN^- \longrightarrow [Cd(CN)_4]^{2-}$

  The colourless soluble complex is not too stable, therefore, reacts with H_2S gas forming a yellow precipitate of CdS.

  $[Cd(CN)_4]^{2-} + H_2S \longrightarrow CdS\downarrow + 2\,H^+ + 4\,CN^-$

  ☞ KI forms no precipitate (distinction from Copper)

5. LEAD ION (Pb^{2+}) :

- **Precipitation with H_2S in acidic medium :** Black precipitate is formed which is soluble in hot dilute HNO_3.

  $Pb^{2+} + H_2S \longrightarrow PbS\downarrow \text{(black)} + 2H^+$

  $3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$

- **Dilute H_2SO_4 :** White precipitate is formed which is soluble in ammonium acetate.

  $Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4\downarrow \text{(white)} + 2HNO_3$

  $PbSO_4 + 2CH_3\,COONH_4 \longrightarrow (CH_3COO)_2\,Pb + (NH_4)_2SO_4(NH_4)_2[Pb(CH_3\,COO)_4]$

- **Potassium iodide :** Yellow precipitate is formed which is soluble in excess more concentrated (6M) solution of the reagent. Yellow precipitate of PbI_2 is moderately soluble in boiling water to give a colourless solution.

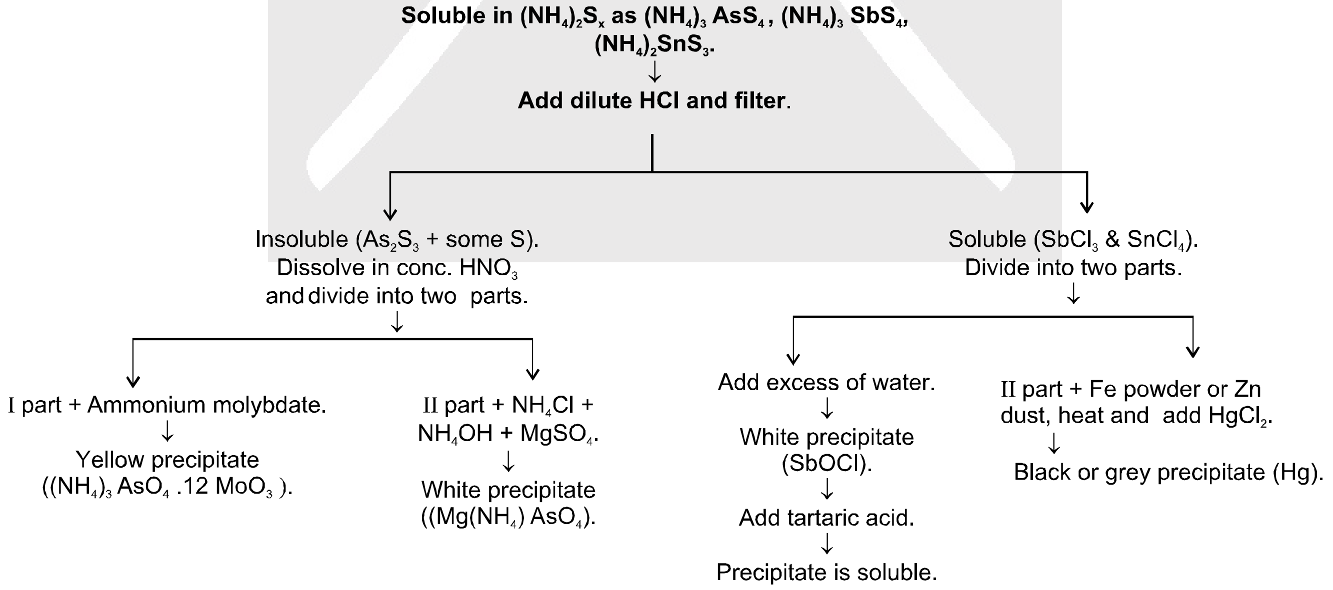
  $(CH_3COO)_2\,Pb + 2KI \longrightarrow 2CH_3\,COOK + PbI_2\downarrow \text{(yellow)}$

- **Potassium chromate :** Yellow precipitate is formed.

  $(CH_3COO)_2\,Pb + K_2CrO_4 \longrightarrow 2CH_3\,COOK + PbCrO_4\downarrow \text{(yellow)}$

Section (C) : IIB Group

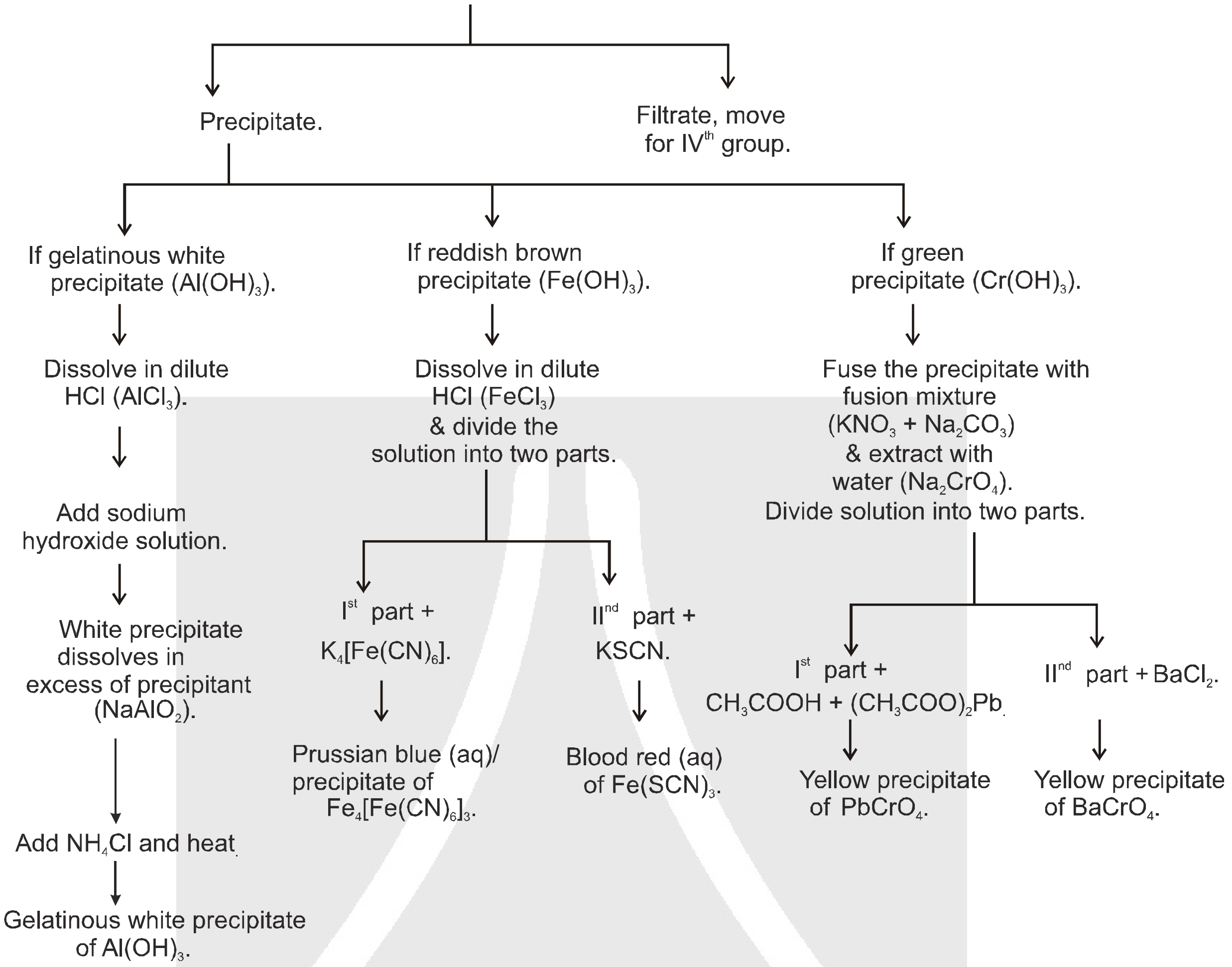
IIB Group (As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}) (Not in JEE advance syllabus)



Section (D) : III^rd^ Group

III^rd^ Group (Al^{3+}, Cr^{3+}, Fe^{3+})

II Group Filtrate $\xrightarrow{\text{Boiloff}}$ **$H_2S\uparrow$ then add conc. HNO_3 (1-2) drops + NH_4Cl (solid) + NH_4OH**



☞ Concentrated HNO_3 is added to oxidise Fe^{2+} to Fe^{3+} if present.

☞ Solid NH_4Cl should be added in excess other wise cations like Zn, Mn, Mg may be precipitated here. To much excess of NH_4Cl should be avoided other wise Cr is not precipitated and Al may form a colloidal solution.

1. ALUMINIUM ION (Al^{3+}) :

- **Precipitation with NH_4OH in presence of NH_4Cl :** White gelatinous precipitate is formed which is slightly soluble in excess reagent. The solubility is decreased in the presence of ammonium salt. A small portion of the precipitate passes into the solution as colloidal $Al(OH)_3$ (Aluminium hydroxide sol), the sol is coagulated on boiling the solution or upon the addition of soluble salt yielding a precipitate of $Al(OH)_3$, known as $Al(OH)_3$ gel. For complete precipitation, add ammonia solution in excess and the mixture is boiled until, the solution has a slight odour of NH_3.

$$Al^{3+} + 3NH_4OH \xrightarrow{NH_4Cl} Al(OH)_3\downarrow + 3NH_4^+$$

- **Sodium hydroxide :** A solution containing Al^{+3} ions give a white precipitate with the reagent.

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3\downarrow$$

White precipitate dissolves in excess sodium hydroxide according to following reaction.

$$Al(OH)_3 + OH^- \rightleftharpoons [Al(OH)_4]^-$$

The reaction is reversible and any reagent, which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration is reduced owing to the formation of the weak base ammonia , which can be readily removed as ammonia gas by heating) or by the addition of acid; in the latter case, a large excess of acid causes the precipitated hydroxide to redissolve.

$$[Al(OH)_4]^- + NH_4^+ \longrightarrow Al(OH)_3 \downarrow + NH_3\uparrow + H_2O$$

$$[Al(OH)_4]^- + H^+ \rightleftharpoons Al(OH)_3 \downarrow + H_2O$$

$$Al(OH)_3 + 3H^+ \text{ (excess)} \rightleftharpoons Al^{3+} + 3\,H_2O$$

- **Dry test :** Aluminium compounds when heated with sodium carbonate upon charcoal gives a white infusible solid, which glows when hot. If the residue is moistened with a little cobalt nitrate solution and again heated, a blue infusible mass is obtained.

$$2\,Al_2O_3 + 2\,Co^{2+} + 4\,NO_3^- \longrightarrow 2\,CoAl_2O_4 \text{ (thenard blue)} + 4NO_2\uparrow + O_2\uparrow$$

Use of excess cobalt nitrate solution should be avoided since this will produce black cobalt oxide (Co_3O_4) upon ignition, which will mask the blue colour.

2. IRON ION (Fe^{3+}) :

- **Precipitation with NH_4OH in presence of NH_4Cl :** Gelatinous reddish brown precipitate is formed which is insoluble in excess reagent but soluble in acids.

$$Fe^{3+} + 3NH_4OH \xrightarrow{NH_4Cl} Fe(OH)_3\downarrow + 3NH_4^+$$

☞ Precipitation of iron(II) hydroxide occurs with ammonia solution. If larger amounts of ammonium ions are present, the dissociation of NH_4OH is suppressed and the concentration of OH^- ions is lowered to such an extent that solubility product of iron (II) hydroxide, $Fe(OH)_2$ is not attained and precipitation does not occur.

- **Sodium hydroxide solution :** Reddish brown precipitate is formed insoluble in excess reagent (distinction from aluminium and chromium).

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3\downarrow$$

- **H_2S gas in acidic solution :** Fe^{3+} reduces to Fe^{2+} .

$$2\,Fe^{3+} + H_2S \longrightarrow 2\,Fe^{2+} + 2H^+ + S\downarrow \text{ (milky-white)}$$

If a neutral solution of iron (III) chloride is added to a freshly prepared saturated solution of H_2S , bluish colouration appears first, followed by precipitation of sulphur. The blue colour is due to a colloidal solution of sulphur of extremely small particle size.

☞ This reaction can be used to test the freshness of H_2S solution.

- **Ammonium sulphide solution :** Black precipitate consisting of Fe(II) sulphide and sulphur is formed.

$$2\,Fe^{3+} + 3\,S^{2-} \longrightarrow 2\,FeS + S\downarrow$$

In HCl, the black precipitate of Fe(II) sulphide dissolves and white precipitate of sulphur becomes visible.

$$FeS\downarrow + 2H^+ \longrightarrow H_2S\uparrow + Fe^{2+}$$

☞ The damp iron (II) sulphide precipitate, when exposed to air, is slowly oxidised to brown iron(III) hydroxide.

$$4\,FeS\downarrow + 6\,H_2O + 3\,O_2 \longrightarrow 4\,Fe(OH)_3\downarrow + 4S\downarrow$$

☞ From alkaline solutions of ammonium sulphide, black iron(III) sulphide is obtained.

$$2\,Fe^{3+} + 3S^{2-} \longrightarrow Fe_2S_3\downarrow$$

On acidification with hydrochloric acid, iron (III) ions are reduced to iron (II) ions and sulphur is formed.

$$Fe_2S_3\downarrow + 4H^+ \longrightarrow 2\,Fe^{2+} + 2\,H_2S\uparrow + S\downarrow$$

- **Potassium ferrocyanide (Potassium hexacyanidoferrate(II)) :** Intense blue precipitate (Prussian blue) of iron(III) hexacyanidoferrate(II) is formed.

$$4Fe^{3+} + 3\,[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow$$

This is insoluble in dilute acids but decomposes in concentrated HCl. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. Sodium hydroxide turns the precipitate red.

$$Fe_4\,[Fe(CN)_6]_3 \downarrow + 12\,OH^- \longrightarrow Fe(OH)_3 \downarrow + 3[Fe(CN)_6]^{4-}$$

☞ Oxalic acid also dissolves Prussian blue forming a blue-solution.

Important :

If iron(III) chloride is added to an excess of potassium hexacyanidoferrate (II), a product with the composition of K Fe[Fe(CN)$_6$] is formed. This tends to form colloidal solutions ("soluble Prussian blue") and can not be filtered.

- **Potassium ferricyanide (Potassium hexacyanidoferrate(III)) :** A brown colouration is formed.

$$Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow Fe[Fe(CN)_6]$$

☞ Upon adding hydrogen peroxide or some tin(II) chloride solution, the hexacyanidoferrate(III) part of the compound is reduced and Prussian blue is precipitated.

☞ Fe^{2+} gives dark blue precipitate with potassium ferricyanide. First hexacyanidoferrate(III) ions oxidise iron(II) to iron(III), when hexacyanidoferrate(II) is formed.

$$Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$$

and these ions combine to form a precipitate called Turnbull's blue.

$$4\,Fe^{3+} + 3\,[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$$

Note : Composition of this precipitate is identical to that of Prussian blue. Earlier the composition suggested was $Fe_3[Fe(CN)_6]_2$, hence different name.

$$3Fe^{2+} + 2K_3\,[Fe(CN)_6]\;\; Fe_3 \longrightarrow [Fe\,(CN)_6]_2 \text{ (ferrous ferric cyanide)} + 6K^+$$

Turnbull's blue

☞ Fe(II) in ammonical solution gives red solution with DMG– colouration fades on standing due to the oxidation of the iron(II) complex. Fe (III) does not give such complex.

☞ In complete absence of air, Fe(II) ions produces white precipitate with potassium hexacyanidoferrate(II).

$$Fe^{2+} + 2K^+ + [Fe(CN)_6]^{4-} \longrightarrow K_2Fe\,[Fe(CN)_6] \downarrow$$

Under ordinary atmospheric conditions a pale–blue precipitate is formed.

- **Potassium thiocyanate (Potassium sulphocyanide) :** In slightly acidic medium, a deep red colouration is produced due to the formation of a non-dissociated iron(III) thiocyanate complex.

$$Fe^{3+} + 3\,SCN^- \longrightarrow Fe(SCN)_3$$

This neutral molecule can be extracted by ether or amyl alcohol.

☞ With pure Fe(II) ions no colouration is obtained.

☞ Fluorides and Hg(II) ions bleach the red colour.

$$Fe(SCN)_3 + 6F^- \longrightarrow [FeF_6]^{3-} + 3\,SCN^-$$

$$2\,Fe(SCN)_3 + 3Hg^{2+} \longrightarrow 2\,Fe^{3+} + 3\,Hg\,(SCN)_2$$

- **Sodium acetate solution :** A deep red colouration is obtained owing to the formation of $[Fe_3(OH)_2(CH_3COO)_6]^+$. The reaction becomes complete only if the strong acid which is formed, is removed by the addition of an excess of the reagent, which acts as a buffer.

$$3\,Fe^{3+} + 6\,CH_3COO^- + 2\,H_2O \rightleftharpoons [Fe_3(OH)_2(CH_3COO)_6]^+ + 2H^+$$

This deep red coloured solution on dilution with water and boiling gives reddish brown precipitate of basic ferric acetate.

$$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4\ H_2O \longrightarrow 3\ Fe(OH)_2CH_3COO \downarrow + 3\ CH_3COOH + H^+$$

The excess of acetate ion acts as a buffer and the reaction goes to completion.

- **Disodium hydrogen phosphate solution :** A yellowish–white precipitate is formed.

$$Fe^{3+} + HPO_4^{2-} \longrightarrow FePO_4 \downarrow + H^+$$

The reaction is reversible, because a strong acid is formed which dissolves the precipitate. It is advisable to add small amounts of sodium acetate, which acts as a buffer.

3. CHROMIUM ION (Cr^{3+}) :

- **Precipitation with NH_4OH in presence of NH_4Cl :** A grey-green to green gelatinous precipitate is formed.

$$Cr^{3+} + 3\ NH_3 + 3\ H_2O \longrightarrow Cr(OH)_3 \downarrow + 3\ NH_4^+$$

Precipitate is slightly soluble in excess of reagent in cold forming pink or violet coloured solution. On boiling the solution, chromium hydroxide is reprecipitated.

$$Cr(OH)_3 \downarrow + 6\ NH_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3OH^-$$

- **Sodium hydroxide solution :** A green precipitate is formed.

$$Cr^{3+} + 3\ OH^- \longrightarrow Cr(OH)_3 \downarrow$$

The reaction is reversible. On addition of acids the precipitate dissolves. In excess of reagent the precipitate dissolves readily forming chromites, the solution is green. The reaction is reversible ; on (slight) acidification and also on boiling green precipitate of chromium(III) hydroxide is obtained.

$$Cr(OH)_3 + OH^- \rightleftharpoons [Cr(OH)_4]^-$$

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O\ ;\ NaOBr \longrightarrow NaBr + [O]$$

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2Na_2\,CrO_4 + 5H_2O.$$

The yellow solution of Na_2CrO_4 gave the following reactions with lead acetate, barium chloride and silver nitrate solutions.

(a) Lead acetate solution : Yellow precipitate is formed.

$$CrO_4^{2-} + Pb^{2+} \xrightarrow{CH_3OOH} PbCrO_4 \downarrow$$

(b) Barium chloride solution : Yellow precipitate is formed owing to the formation of barium chromate which is insoluble in acetic acid.

$$CrO_4^{2-} + Ba^{2+} \longrightarrow BaCrO_4 \downarrow$$

(c) Silver nitrate solution : Red/Brick red precipitate is formed owing to the formation of silver chromate which is soluble in ammonia solution and its acidified solution turns to orange because of the formation of dichromate.

$$Na_2CrO_4 + 2AgNO_3 \longrightarrow Ag_2CrO_4 \downarrow + 2NaNO_3\ .$$

- **Acidified H_2O_2 test :** On acidifying the yellow solution with dilute sulphuric acid and adding few drops of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, blue colouration is formed which can be extracted into the organic layer by gently shaking.

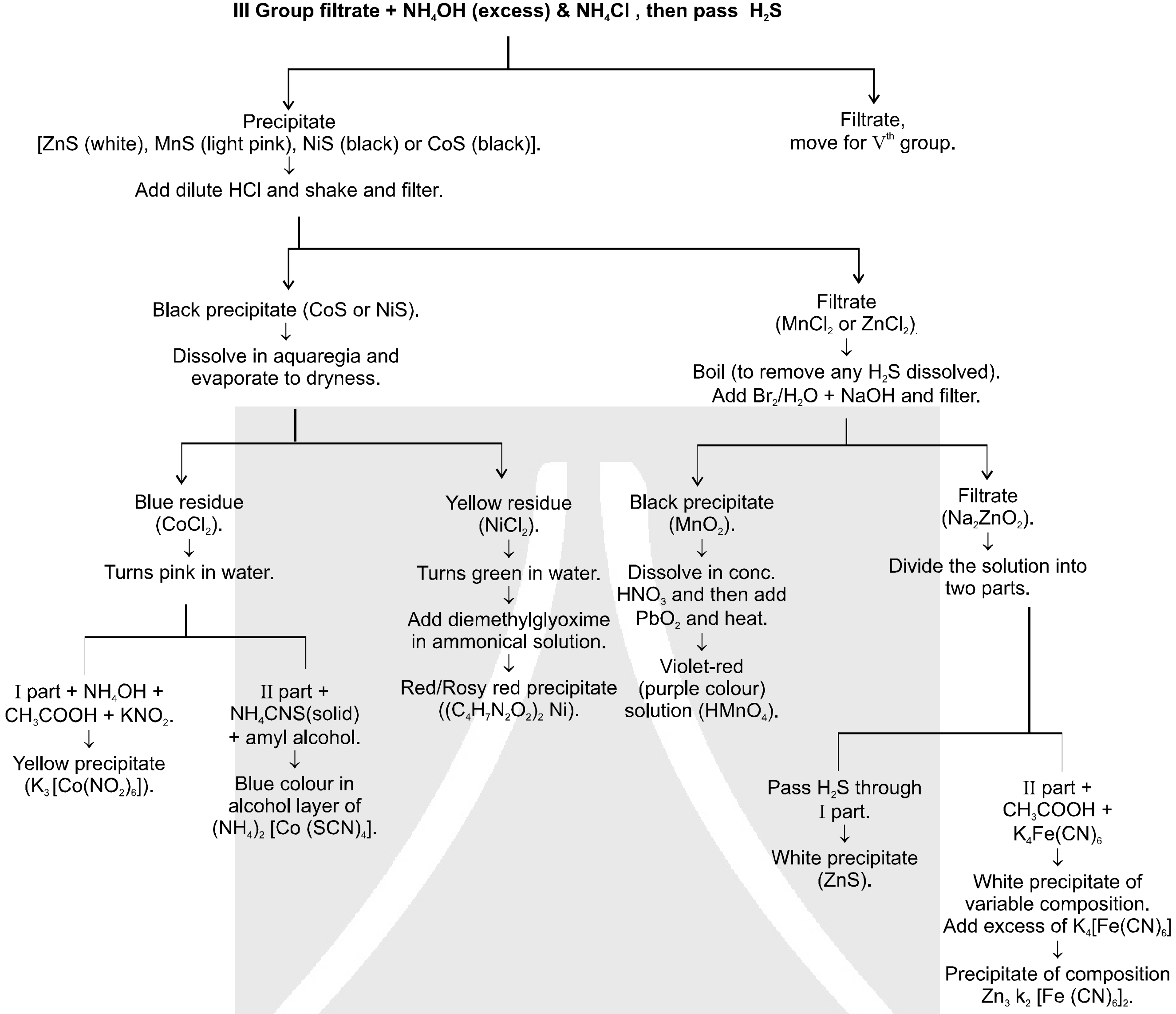
$Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2CrO_4$; $H_2CrO_4 + 2H_2O_2 \xrightarrow{\text{Amyl alcohol}} CrO_5$ (blue colouration) + H_2O

Blue colouration fades slowly due to the decomposition of perchromic acid (or chromium peroxide) with the liberation of oxygen.

$$4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2\,(SO_4)_3 + 7O_2 + 6H_2O$$

Section (E) : IVth Group

IVth GROUP (Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}) :



1. MANGANESE ION (Mn^{2+}) :

- **Precipitation with H_2S in presence of NH_4OH + NH_4Cl :** A buff coloured (light pink) precipitate is formed.

$$Mn^{2+} + S^{2-} \longrightarrow MnS \downarrow$$

It is readily soluble in mineral acids (distinction with Ni and Co) and even in acetic acid (distinction with Ni, Co and Zn).

$$MnS \downarrow + 2H^+ \longrightarrow Mn^{2+} + H_2S\uparrow \; ; \; MnS \downarrow + 2\,CH_3COOH \longrightarrow Mn^{2+} + H_2S \uparrow + 2\,CH_3COO^-$$

- **Ammonia solution :** Partial precipitation of white manganese(II) hydroxide takes place.

$$Mn^{2+} + 2\,NH_3 + 2H_2O \rightleftharpoons Mn(OH)_2 \downarrow + 2\,NH_4^+$$

The precipitate is soluble in ammonium salts when the reaction proceeds towards left.

- **Sodium hydroxide solution :** Initially white precipitate of $Mn(OH)_2$ is formed which is insoluble in excess reagent and rapidly oxidised on exposure to air, becoming brown.

$$Mn^{2+} + 2\,OH^- \longrightarrow Mn(OH)_2 \downarrow$$

$$Mn(OH)_2 \downarrow + O_2 \longrightarrow 2\,MnO(OH)_2 \downarrow \text{ (hydrated manganese dioxide).}$$

☞ With sodium hydroxide and bromine water initially a white precipitate is formed which immediately turns to black owing to the formation of MnO_2 .

$Mn(OH)_2 \downarrow + Br_2 + 2NaOH \longrightarrow MnO_2\downarrow$ (black) $+ 2NaBr + 2H_2O$

☞ $Mn(OH)_2 \downarrow + H_2O_2 \longrightarrow MnO\,(OH)_2 \downarrow$ (brown) $+ H_2O$

- **Lead dioxide(PbO_2) and concentrated nitric acid :** On boiling a dilute solution of manganese(II) ions with lead dioxide and a little concentrated nitric acid and allowing the suspended solid containing unattacked lead dioxide to settle, the supernatant liquid acquired a violet-red (or purple) colour due to permanganic acid.

$5\,PbO_2 + 2\,Mn^{2+} + 4H^+ \longrightarrow 2\,MnO_4^- + 5Pb^{2+} + 2\,H_2O$

- **Sodium bismuthate ($NaBiO_3$) solution :** When sodium bismuthate ($NaBiO_3$) is added to a cold solution of manganese(II) ions in dilute nitric acid or in dilute sulphuric acid and the mixture stirred and then excess reagent filtered off, a violet–red (or purple) solution of permanganate is produced.

$2\,Mn^{2+} + 5\,NaBiO_3 + 14\,H^+ \longrightarrow 2MnO_4^- + 5\,Bi^{3+} + 5\,Na^+ + 7\,H_2O$

☞ $2Mn(NO_3)_2 + 2Pb_3O_4 + 26HNO_3 \xrightarrow{\Delta} 2HMnO_4$ (violet–red/purple) $+ 15Pb(NO_3)_2 + 12H_2O$

2. ZINC ION (Zn^{2+}) :

- **Precipitation with H_2S in presence of $NH_4OH + NH_4Cl$:** A white precipitate is formed. In neutral solutions, precipitation is partial as H^+ ions concentration produced depressed the ionisation of H_2S .

$Zn^{2+} + H_2S \rightleftharpoons ZnS \downarrow + 2H^+$

The precipitate is soluble in dilute HCl.

$ZnS + 2H^+ \longrightarrow Zn^{2+} + H_2S \uparrow$

- **Sodium hydroxide solution :** A white gelatinous precipitate is formed.

$Zn^{2+} + 2\,OH^- \longrightarrow Zn(OH)_2 \downarrow$

The precipitate is soluble in acids as well as in excess of the reagent.

$Zn(OH)_2 + 2\,H^+ \longrightarrow Zn^{2+} + 2\,H_2O$

$Zn(OH)_2 + 2\,OH^- \longrightarrow [Zn(OH)_4]^{2-}$

☞ Thus, zinc hydroxide is amphoteric in nature.

☞ $[Zn(OH)_4]^{2-} + S^{2-} \longrightarrow ZnS \downarrow$ (white) $+ 4\,OH^-$

- **Ammonia solution :** A white gelatinous precipitate is formed which is readily soluble in excess of the reagent and in solutions of ammonium salts forming the tetraamminezinc(II).

Non–precipitation of $Zn(OH)_2$ by ammonia solution in the presence of NH_4Cl is due to the lowering of OH^- ion concentration to such a value that the K_{sp} of $Zn(OH)_2$ is not attained.

$Zn^{2+} + 2\,NH_3 + 2\,H_2O \rightleftharpoons Zn(OH)_2 \downarrow + 2\,NH_4^+$

$Zn(OH)_2 \downarrow + 4\,NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 2\,OH^-$

- **Potassium ferrocyanide (Potassium hexacyanidoferrate(II)) solution :** A white precipitate of variable composition is formed. If excess reagent is added, the composition of precipitate is $K_2Zn_3[Fe(CN)_6]_2$.

$3\,Zn^{2+} + 2\,K^+ + 2\,[Fe(CN)_6]^{4-} \longrightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow$

The precipitate is insoluble in dilute acids, but dissolves in sodium hydroxide readily.

$K_2Zn_3\,[Fe(CN)_6]_2 + 12\,OH^- \longrightarrow 2\,[Fe(CN)_6]^{4-} + 3\,[Zn(OH)_4]^{2-}$

This reaction can be used to distinguish zinc from aluminium.

$\rightarrow Zn^{2+} + [Hg(SCN)_4]^{2-} \longrightarrow \underset{\text{(white)}}{Zn[Hg(SCN)_4]} \downarrow$

$\rightarrow Cu^{2+} + [Hg(SCN)_4]^{2-} \longrightarrow Cu[Hg(SCN)_4]$

* In the presence of the copper ions, the copper complex Co-precipitated with that of zinc complex and colour become violet.

3. COBALT ION (Co^{2+}) : (Not in JEE advance syllabus)

- **Precipitation with H_2S in presence of $NH_4OH + NH_4Cl$:** A black precipitate is formed. The black precipitate of CoS is insoluble in dilute HCl or acetic acid but hot concentrated HNO_3 or aquaregia dissolves it and white sulphur remains. On longer heating the mixture becomes clear as because sulphur is oxidised to sulphate.

$$2[Co(NH_3)_6]^{3+} + 3S^{2-} \longrightarrow 2CoS\downarrow + 12NH_3 + S$$

or $$CoCl_2 + H_2S \xrightarrow{NH_4OH} CoS\downarrow + 2HCl$$

$$3\ CoS + 2\ HNO_3 + 6\ H^+ \longrightarrow 3\ Co^{2+} + 3\ S\downarrow + 2NO\uparrow + 4\ H_2O$$

$$2CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

☞ Solution on evaporation to dryness gives blue residue ($CoCl_2$) which turns pink on adding water.

- **Potassium nitrite solution :** A yellow precipitate is formed from neutral solution of cobalt(II) ions.

$$CoCl_2 + 7KNO_2 + 2CH_3COOH \longrightarrow K_3[Co(NO_2)_6]\downarrow + H_2O + 2KCl + 2CH_3COOK + NO\uparrow$$

or $$Co^{2+} + 7NO_2^- + 2H^+ + 3K^+ \longrightarrow K_3[Co(NO_2)_6]\downarrow + NO\uparrow + H_2O.$$

- **Ammonium thiocyanate solution :** A neutral or acid solution of cobalt(II) gives a blue colouration in amyl alcohol or ether layer when a few crystals of ammonium thiocyanate are added.

$$Co^{2+} + 4\ SCN^- \longrightarrow [Co(SCN)_4]^{2-}$$

☞ In amyl alcohol or ether, the free acid $H_2[Co(SCN)_4]$ is formed and dissolved by the organic solvent (distinction from nickel)

- **Sodium bicarbonate and bromine water test :** To the test solution sodium bicarbonate is added in excess followed by the bromine water. The mixture is slightly heated, the solution turns apple green.

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4\ NaHCO_3 \longrightarrow Na_4[Co(CO_3)_3] + 3H_2O + 3CO_2$$

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$

$$2Na_4[Co(CO_3)_3] + H_2O + [O] \longrightarrow 2Na_3[Co(CO_3)_3]\text{ (green)} + 2NaOH.$$

☞ Green solution of sodium cobalticarbonate is obtained.

- **Sodium hydroxide solution :** Cobalt(II) nitrate in cold gives a blue basic salt.

$$Co^{2+} + OH^- + NO_3^- \longrightarrow Co(OH)NO_3\downarrow$$

Upon warming with excess alkali, the basic salt is converted into a pink precipitate of Co(II) hydroxide.

$$Co(OH)NO_3\downarrow + OH^- \longrightarrow Co(OH)_2\downarrow + NO_3^-$$

→ $$Co^{2+} + CN^-\text{(excess)} \longrightarrow [Co(CN)_6]^{4-}\text{ (Brown solution)}$$

$$[Co(CN)_6]^{4-} + O_2 + 2H_2O \longrightarrow [Co(CN)_6]^{3-}\text{ (Yellow solution)}$$

4. NICKEL ION (Ni^{2+}) : (Not in JEE advance syllabus)

- **Precipitation with H_2S in presence of $NH_4OH + NH_4Cl$:**
A black precipitate is formed which is insoluble in cold dilute HCl and CH_3COOH but dissolves in hot concentrated HNO_3 and in aquaregia.

$$NiCl_2 + H_2S \xrightarrow{NH_4OH} NiS\downarrow\text{ (Black)} + 2HCl$$

$$3\ NiS\downarrow + 2\ HNO_3 + 6\ H^+ \longrightarrow 3\ Ni^{2+} + 2\ NO\uparrow + 3\ S\downarrow + 4\ H_2O$$

$$NiS + HNO_3 + 3HCl \longrightarrow Ni^{2+} + S\downarrow + NOCl\uparrow + 2Cl^- + 2H_2O.$$

☞ Solution on evaporation to dryness gives yellow residue ($NiCl_2$) which turns green on adding water.

- **Dimethylglyoxime reagent :** A red precipitate is obtained from the solution just made alkaline or acid solutions buffered with sodium acetate.

$$NiCl_2 + 2NH_4OH + 2CH_3 - C = NOH \longrightarrow \underset{\text{(red)}}{(C_4H_7N_2O_2)_2Ni}\downarrow + 2NH_4Cl + 2H_2O \text{ or } [Ni(amg)_2]\downarrow$$

☞ Fe(II) ions give red colouration, bismuth gives yellow precipitate and cobalt gives brown colouration with DMG in ammonical solutions.

☞ Ni^{2+} gives black precipitate (Ni_2O_3) with sodium bicarbonate and bromine water on heating where as Co^{2+} gives green coloured solution, this is the point of difference.

$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O$; $2NiCO_3 + [O] \longrightarrow Ni_2O_3 \downarrow$ (black) $+ 2CO_2$

Section (F) : V^th^, VI^th^ and Zero Group

V^th^ Group (Ba^{2+}, Sr^{2+}, Ca^{2+}) :

IV Group filtrate ⟶ Boil off H_2S then add $(NH_4)_2CO_3$ (aq), NH_4OH & NH_4Cl (s)

↓ White precipitate ($BaCO_3$, $SrCO_3$ or $CaCO_3$).
↓
Dissolve in CH_3COOH and divide into three parts and test in the sequence given below.

↓ Filtrate, move for VI group.

I part + K_2CrO_4. ↓ Yellow precipitate ($BaCrO_4$ insoluble in CH_3COOH).

II Part + $(NH_4)_2SO_4$. ↓ White precipitate ($SrSO_4$).

III part + $(NH_4)_2C_2O_4$. ↓ White precipitate (CaC_2O_4).

1. BARIUM ION (Ba^{2+}) :

- **Precipitation with $(NH_4)_2CO_3$ in presence of $NH_4OH + NH_4Cl$:** A white precipitate is formed which is soluble in acetic acid and dilute mineral acids

$BaCl_2 + (NH_4)_2CO_3 \longrightarrow BaCO_3\downarrow + 2NH_4Cl$

$BaCO_3 + 2CH_3COOH \longrightarrow Ba(CH_3COO)_2 + H_2O + CO_2$

- **Potassium chromate test :** A yellow precipitate is formed, practically insoluble in water

$Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4\downarrow + 2CH_3COOK$

☞ Precipitate is insoluble in dilute acetic acid (distinction from strontium and calcium) but readily soluble in mineral acids.

☞ Addition of acid to K_2CrO_4 changes the yellow colour of the solution to reddish–orange due to the formation of dichromate.

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

☞ The solubility products of $SrCrO_4$ and $CaCrO_4$ are much larger than for $BaCrO_4$ and hence they require a larger CrO_4^{2-} ion concentration to precipitate them. The addition of acetic acid to the K_2CrO_4 solution lowers the CrO_4^{2-} ion concentration sufficiently to prevent the precipitation of $SrCrO_4$ and $CaCrO_4$ but it is maintained high enough to precipitate $BaCrO_4$.

2. STRONTIUM ION (Sr^{2+}) :

- **Precipitation with $(NH_4)_2CO_3$ in presence of $NH_4OH + NH_4Cl$:**
A white precipitate is formed which is soluble in acetic acid.

$SrCl_2 + (NH_4)_2CO_3 \longrightarrow SrCO_3\downarrow + 2NH_4Cl$

$SrCO_3 + 2CH_3COOH \longrightarrow Sr(CH_3COO)_2 + H_2O + CO_2$

- **Ammonium sulphate solution :** A white precipitate is formed which is slightly soluble in boiling hydrochloric acid.

$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow SrSO_4\downarrow + 2CH_3COONH_4$

☞ The solubility of the precipitate in water is low but not negligible.

☞ The precipitate is insoluble in ammonium sulphate solution even on boiling (Distinction from calcium–forms a soluble complex $(NH_4)_2[Ca(SO_4)_2]$) and slightly soluble in boiling HCl.

☞ It is almost completely converted into the corresponding carbonates by boiling with a concentrated solution of sodium carbonate.

$$SrSO_4 + CO_3^{2-} \rightleftharpoons SrCO_3 \downarrow + SO_4^{2-}$$

3. CALCIUM ION (Ca^{2+}) :

- **Precipitation with $(NH_4)_2CO_3$ in presence of $NH_4OH + NH_4Cl$:** A white precipitate is formed. The precipitate is soluble in water which contains excess carbonic acid (e.g freshly prepared soda water) because of the formation of soluble hydrogen carbonate. On boiling precipitate reappears again, as CO_2 is removed. The precipitate is also soluble in acetic acid.

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NH_4Cl$$

$$CaCO_3 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + CO_2$$

- **Ammonium oxalate solution (concentrated) :** A white precipitate is formed. The precipitation is facilitated by making the solution alkaline. The precipitate is practically insoluble in water ($K_{sp} = 2.6 \times 10^{-9}$), insoluble in acetic acid but readily soluble in mineral acids.

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 \downarrow + 2CH_3COONH_4$$

- **Potassium hexacyanidoferrate (II) solution :** White precipitate of a mixed salt is produced.

$$Ca^{2+} + 2\,K^+ + [Fe(CN)_6]^{4-} \longrightarrow K_2Ca[Fe(CN)_6] \downarrow$$

In presence of ammonium chloride the test is more sensitive and in this case K^+ is replaced by NH_4^+ ions in the precipitate.

☞ This test can be used to distinguish, calcium from strontium, barium and magnesium ions.

☞ The confirmatory test for the basic radicals of (V) group have to be done in the order of Ba^{2+}, Sr^{2+} then Ca^{2+} (i.e BSC) because Ba^{2+} give positive test with all the reagents used in the confirmatory test of these group radicals, K_2CrO_4, $(NH_4)_2\,SO_4$ & $(NH_4)_2\,C_2O_4$. So performs the test for Sr^{2+} with $(NH_4)_2SO_4$ only when Ba^{2+} is absent. Similarly Sr^{2+} gives the test with both $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$. So proceeds with Ca^{2+} only when Sr^{2+} is absent otherwise it will respond to ammonium oxalate test.

VIth GROUP :

1. MAGNESIUM ION (Mg^{2+}) :

- **Disodium hydrogen phosphate solution :** To the filtrate of V group or Mg^{2+} ions solution add 1 ml $(NH_4)_2C_2O_4$ solution and heat if white precipitate is formed then filter it. Now to filtrate add a solution of disodium hydrogen phosphate. A white crystalline precipitate is formed in the presence of NH_4Cl (prevent precipitation of $Mg(OH)_2$) and ammonia solution.

$$Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow Mg(NH_4)PO_4 \downarrow$$

☞ Precipitate is sparingly soluble in water, soluble in acetic acid and in mineral acids.

☞ The precipitate separates slowly from dilute solutions because of its tendency to form supersaturated solution. This may be overcome by cooling and by rubbing the test tube beneath the surface of the liquid with a glass rod.

A white flocculent precipitate of magnesium hydrogen phosphate is obtained in neutral solutions.

$$Mg^{2+} + HPO_4^{2-} \longrightarrow MgHPO_4 \downarrow$$

☞ Ammonium phosphate can also be used.

- **Ammonia solution :** A white gelatinous precipitate is formed.

$$Mg^{2+} + 2\,NH_4OH \longrightarrow Mg(OH)_2\downarrow + 2\,NH_4^+$$

The precipitate obtained is sparingly soluble in water but readily soluble in ammonium salts.

$$Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2\,OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \;;\; NH_4^+ + OH^- \longrightarrow NH_4OH \text{ (weak base)}$$

NH_4^+ ions 'remove' OH^- causing the hydroxide to dissolve more. Not possible with NaCl.

- **Ammonium carbonate solution :** A white precipitate of basic magnesium carbonate is obtained in the absence of NH_4^+ salts.

  $$5\,Mg^{2+} + 6\,CO_3^{2-} + 7\,H_2O \longrightarrow 2\,MgCO_3.Mg(OH)_2.5\,H_2O \downarrow + 2HCO_3^-$$

  In the presence of NH_4^+ salts no precipitation occurs, because the equilibrium

  $$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$$

  is shifted towards the formation of HCO_3^- ions. K_{sp} of the precipitate being high (K_{sp} of pure $MgCO_3$ is 1×10^{-5}), the concentration of carbonate ions necessary to produce a precipitate is not attained.

- **Titan yellow (a water soluble yellow dyestuff) :** It is adsorbed by $Mg(OH)_2$ producing a deep red colour or precipitate.

  Dissolved the precipitate in dilute HCl (minimum quantity) and to 1 drop of this add 1 drop of NaOH solution

  (2 M) followed by 1 drop of titan yellow solution a deep red colour solution or precipitate is obtained.

☞ Ba^{2+} and Ca^{2+} do not react but intensify the colour.

ZERO GROUP :

1. AMMONIUM ION (NH_4^+) :

Sodium hydroxide solution : Ammonia gas is evolved on warming the solution containing ammonium salt and sodium hydroxide.

$$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$$

☞ The gas can be identified by the following characteristics / reactions.

— Its characteristics smell.

— The evolution of the white fumes of ammonium chloride when a glass rod dipped in dilute HCl is held in the vapour.

$$NH_3 + HCl \longrightarrow NH_4Cl \uparrow \text{ (white fumes)}$$

— Its ability to turn filter paper moistened with $Hg_2(NO_3)_2$ solution black.

$$Ha_2(NO_3)_2 + 2NH_3 \longrightarrow \underbrace{Hg(NH_2)NO_3 + Hg}_{\text{black}} + NH_4NO_3$$

— Its ability to turns filter paper moistened with $CuSO_4$ solution deep blue.

$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

— Filter paper moistened with a solution of manganese (II) chloride and hydrogen peroxide made alkaline with ammonia gives a brown colour due to the oxidation of manganese.

$$2NH_3 + Mn^{2+} + H_2O_2 + H_2O \longrightarrow MnO(OH)_2 \downarrow + 2NH_4^+$$

- **Nessler's reagent (Alkaline solution of potassium tetraiodidomercurate(II) :**

  Brown precipitate or brown or yellow colouration is obtained according to the amount of ammonia or ammonium ions present. The precipitate is a basic mercury (II) amido–iodide. It is also known as "IODIDE of MILLON's base.

  $$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow HgO\,Hg\,(NH_2)I \downarrow + 7I^- + 3H_2O$$

- **Sodium hexanitrito–N–cobaltate (III) solution :**

  NH_4^+ ions gives a yellow precipitate with the reagent.

  $$3NH_4^+ + [Co(NO_2)_6]^{3-} \longrightarrow (NH_4)_3\,[Co(NO_2)_6]\downarrow$$

- **Hexachloridoplatinate (IV) solution (i.e., hexachloroplatinic acid) :**

  NH_4^+ ions gives a yellow precipitate with the reagent.

  $$2NH_4^+ + [PtCl_6]^{2-} \longrightarrow (NH_4)_2\,[PtCl_6]\downarrow \text{ yellow}$$

- **Saturated sodium hydrogen tartrate solution ($NaHC_4H_4O_6$) :**

  NH_4^+ ions gives a white precipitate with the reagent.

  $$NH_4^+ + HC_4H_4O_6^- \longrightarrow NH_4\,HC_4H_4O_6 \downarrow$$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Which of the following precipitate(s) does / do not dissolve in excess of ammonia solution ?
(A) $Zn(OH)_2$ (B) $Ni(OH)_2$ (C) $Al(OH)_3$ (D) (B) and (C) both

Ans. (C)

Sol. (A) $Zn(OH)_2 + 4\,NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$ (colourless solution) + $2OH^-$
(B) $Ni(OH)_2\downarrow + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$ (deep blue solution) + $2OH^-$
(C) $Al(OH)_3 + NH_3 \longrightarrow$ No reaction.

2. Chocolate brown precipitate is formed with :
(A) Cu^{2+} ions and $[Fe (CN)_6]^{3-}$ (B) Cu^{2+} ions and $[Fe(CN)_6]^{4-}$
(C) Fe^{3+} ions and $[Fe (CN)_6]^{4-}$ (D) Fe^{2+} ions and dimethylglyoxime

Ans. (B)

Sol (A) $Cu_3\,[Fe(CN)_6]_2\downarrow$ (green) ; (B) $Cu_2\,[Fe(CN)_6]\downarrow$ (chocolate brown)
(C) $Fe_4[Fe(CN)_6]_3\downarrow$ (Prussian blue) ; (D) red solution of iron(II) dimethylglyoxime.

3. Colour of cobalt chloride solution is :
(A) pink (B) black (C) colourless (D) green

Ans. (A)

Sol. Anhydrous Co(II) salts are blue in colour while hydrated Co(II) salts are pink/red.

4. A red colouration or precipitate is not obtained when :
(A) Fe^{3+} reacts with potassium thiocyanate (B) Fe^{2+} reacts with dimethylglyoxime.
(C) Hg^{2+} reacts with potassium iodide. (D) None

Ans. (D)

Sol. (A) $Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3$ (red solution)
(B) Red solution of iron(II) dimethylglyoxime.
(C) $Hg^{2-} + 2I^- \longrightarrow HgI_2$ (red).

5. **Statement-1 :** Addition of NH_4OH to an aqueous solution of $BaCl_2$ in presence of NH_4Cl (excess) precipitates $Ba(OH)_2$.
Statement-2 : $Ba(OH)_2$ is water soluble.
(A) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(B) Both Statement-1 and Statement-2 are true but Statement-2 is not correct explanation of Statement-1.
(C) Statement-1 is true but Statement-2 is false.
(D) Statement-1 is false but Statement-2 is true

Ans. (D)

Sol. Ba^{2+} ions does not give any precipitate with NH_4OH solution in excess of NH_4Cl because product formed, $Ba(OH)_2$ is soluble in water

6. **Statement-1 :** Sodium meta aluminate on boiling with ammonium chloride produces white gelatinous precipitate.
Statement-2 : Aluminium hydroxide is formed which is not soluble in water
(A) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(B) Both Statement-1 and Statement-2 are true but Statement-2 is not correct explanation of Statement-1.
(C) Statement-1 is true but Statement-2 is false.
(D) Statement-1 is false but Statement-2 is true

Ans. (A)

Sol. $[Al(OH)_4]^- \xrightarrow[\text{boil}]{NH_4Cl} Al(OH)_3\downarrow + OH^-$

7. Which of the following statement(s) is (are) incorrect?

(A) Fe^{2+} ions give a dark blue precipitate with potassium hexacyanidoferrate (III) solution.

(B) Fe^{3+} ions give intense blue precipitate with potassium hexacyanidoferrate (II) solution.

(C) Fe^{3+} ions give a brown colouration with potassium hexacyanidoferrate (III) solution.

(D) Fe^{2+} ions give a deep red colouration with ammonium thiocyanate.

Ans. (D)

Sol. (A) $Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe_3[Fe(CN)_6]_2$

(B) $4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow$ (intense blue)

(C) $Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow Fe[Fe(CN)_6]$ (brown colouration)

(D) $Fe^{3+} + 4SCN^- \longrightarrow Fe(SCN)_3$ (deep red colouration)

$Fe^{2+} + 4\,SCN^- \longrightarrow$ No reaction

8. Consider the following statements :

S_1 : Cu^{2+} ions are reduced to Cu^+ by potassium iodide and potassium cyanide both, when taken in excess

S_2 : H_2S will precipitate the sulphide of all the metals from the solutions of chlorides of Cu, Zn and Cd if the solution are aqueous.

S_3 : The presence of magnesium is confirmed in qualitative analysis by the formation of a white crystalline precipitate of $MgNH_4PO_4$.

S_4 : Calomel on reaction with potassium iodide gives red precipitate.

and arrange in the order of true /false.

(A) TTFF (B) TFTF (C) TTTT (D) TTTF

Ans. (D)

Sol. S_1, S_2 and S_3 are correct statements.

S_4 : $Hg_2^{2+} + 2I^- \longrightarrow Hg_2I_2\downarrow$ (green) [Calomel : Hg_2Cl_2]

9. Which of the following pair (s) of ions would be expected to form precipitate when dilute solutions are mixed?

(A) NH_4^+, $[Co(NO_2)_6]^{3-}$ (B) NH_4^+, CO_3^{2-} (C) Fe^{3+}, OH^- (D) Ba^{2+}, SO_4^{2-}

Ans. (A,C,D)

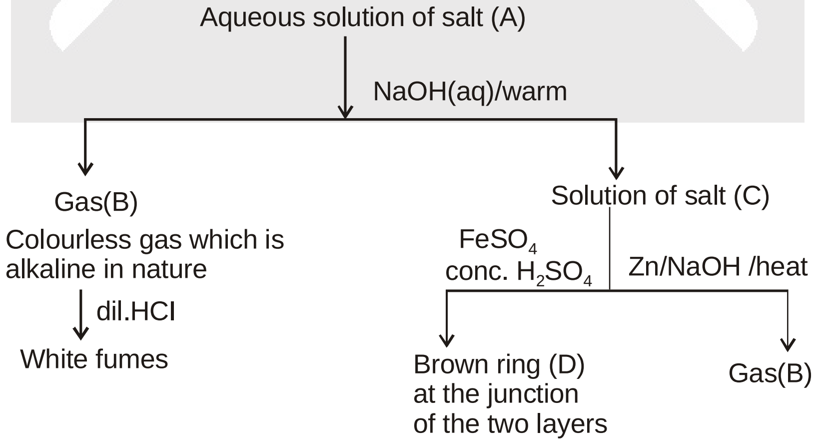
Sol. (A) $NH_4^+ + [Co(NO_2)_6]^{3-} \longrightarrow (NH_4)_3[Co(NO_2)_6]\downarrow$ (yellow)

(B) Ammonium and alkali metal carbonates are water soluble.

(C) $Fe^{3+} + OH^- \longrightarrow Fe(OH)_3\downarrow$ (reddish - brown)

(D) $Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4\downarrow$ (white)

Comprehension (Q.10 to Q.12)



Salt (A) on heating gives a colourless neutral gas which supports combustion.

From the aforesaid, flow diagram, answer the following questions.

10. The compound (A) contains the following acid radical.

(A) NO_2^- (B) NO_3^- (C) Br^- (D) SO_3^{2-}

Ans. (B)

Sol. NO_3^- and NO_2^- both give brown ring test and reduction of NO_3^- and NO_2^- both give ammonia which with dilute HCl gives dense white fumes.

if $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; N_2O supports the combustion

but $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$; Nitrogen does not supports combustion.

Hence, the anion is NO_3^-.

11. The basic radical of salt (A) and gas B both give brown precipitate with Nessler's reagent. The composition of the brown precipitate is :

(A) $(NH_4)_2[HgI_4]$ (B) $Hg(NH_2)NO_3$ (C) $HgO.Hg(NH_2)I$ (D) $(NH_4)_3[Co(NO_2)_6]$

Ans. (C)

Sol. $NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow HgO.\ Hg\ (NH_2)I \downarrow + 7I^- + 3H_2O$

12. Which of the following statement is correct ?

(A) Salt (A) gives yellow precipitate with chloroplatinic acid as well as with sodium cobaltinitrite.

(B) The brown ring is formed due to the formation of nitroso ferrous sulphate $[Fe(NO)]^{2+}SO_4^-$.

(C) Salt 'C' reacts with silver nitrate solution to form white precipitate.

(D) (A) and (B) both.

Ans. (D)

Sol. (A) $2NH_4^+ + [PtCl_6]^{2-} \longrightarrow (NH_4)_2\ [PtCl_6] \downarrow$ (yellow)

$3NH_4^+ + [Co(NO_2)_6]^{3-} \longrightarrow (NH_4)_3\ [Co(NO_2)_6] \downarrow$ (yellow)

(B) $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO \uparrow + 4SO_4^{2-} + 4H_2O$

$SO_4^{2-} + Fe^{2+} + NO \longrightarrow [Fe(NO)]^{2+}\ SO_4^{2-}$

(C) $Ag\ NO_3 + NaNO_3 \longrightarrow$ No reaction.

If the anion is NO_2^- then $Ag^+ + NO_2^- \longrightarrow Ag\ NO_2 \downarrow$ (white)

Reactions :

$NH_4NO_3 + NaOH \longrightarrow NH_3\uparrow + NaNO_3$
(A) (B) (C)

$NH_3 + HCl \longrightarrow NH_4Cl\uparrow$ (White)

$NO_3^- + 4Zn + 7OH^- + 6H_2O \longrightarrow NH_3 + 4[Zn(OH)_4]^{2-}$

True/False :

13. Magnesium is precipitated from its salt solution as only magnesium ammonium phosphate by adding disodium hydrogen phosphate solution in absence of ammonium chloride and aqueous ammonia.

Sol. **(False)** Precipitation is carried out in presence of ammonium chloride and aqueous ammonia as they prevent precipitation of magnesium hydroxide.

$Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow Mg\ (NH_4)\ PO_4 \downarrow$ (white)

14. When a solution of nitrite acidified with dilute hydrochloric acid is treated with solid urea, the nitrite is decomposed, and nitrogen and carbon dioxide are evolved.

Sol. **(True)** $CO(NH_2)_2 + HNO_2 \longrightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O$.

15. Solution of alkali metal cyanide containing freshly prepared iron (II) sulphate solution and dilute H_2SO_4 on exposure to air produces prussian blue precipitate

Sol. **(True)** $Fe^{2+} + 2\ CN^- \longrightarrow Fe(CN)_2 \downarrow$; $Fe(CN)_2 \downarrow + 4CN^- \longrightarrow [Fe(CN)_6]^{4-}$

$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$; $Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow$

Subjective :

16. What happens when ?

(A) Aqueous solution of $CrCl_3$ is added to ammonia solution.

(B) Ammonium carbonates reacts with $MgCl_2$ (i) in absence of ammonium salts and (ii) in presence of ammonium salts :

Sol. (A) $Cr^{3+} + 3NH_3 + 3H_2O \longrightarrow Cr(OH)_3\downarrow$ (green) $+ 3NH_4^+$

$Cr(OH)_3$ precipitate formed becomes slightly soluble in excess of precipitant in cold forming a violet or pink solution containing $[Cr(NH_3)_6]^{3+}$ complex ions.

$Cr(OH)_3\downarrow + 6\,NH_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3OH^-$

(B) (i) $5Mg^{2+} + 6\,CO_3^{2-} + 7H_2O \longrightarrow 4MgCO_3.Mg(OH)_2.5\,H_2O\downarrow + 2HCO_3^-$

White precipitate of basic magnesium carbonate is formed.

(ii) In presence of ammonium salts no precipitation occurs, because the equilibrium

$NH_4^+ + CO_3^{2-} \longrightarrow NH_3 + HCO_3^-$

is shifted towards the formation of HCO_3^- ions.

17. Salts given in column (I) reacts with the excess of reagents given in column (II) and form white /coloured precipitates. Select the correct options for the salts given in column (I) with the reagent(s) given in the column (II)

	Column-I		**Column-II**
(A)	$Zn\ (NO_3)_2$	(p)	Sodium hydroxide
(B)	$Cu\ (NO_3)_2$	(q)	Ammonia solution
(C)	$Fe(NO_3)_3$	(r)	Disodium hydrogen phosphate
(D)	$Ag(NO_3)_2$	(s)	Potassium ferrocyanide

Ans. (A - r, s) ; (B - p, r, s) ; (C - p, q, r) ; (D - p, q, r, s)

Sol. (A) $Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2\downarrow$ (white) ;

$Zn\,(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$ (colourless soluble complex)

$Zn^{2+} + 2NH_3 + 2H_2O \longrightarrow Zn\,(OH)_2\downarrow$ (white) $+ 2NH_4^+$

$Zn(OH)_2\downarrow + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$ (colour less soluble complex) $+ 2OH^-$

$3Zn^{2+} + 2HPO_4^{2-} \longrightarrow Zn_3\,(PO_4)_2\downarrow$ (white) $+ 2H^+$

$3\,Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \longrightarrow K_2\,Zn_3\,[Fe(CN)_6]_2\downarrow$ (bluish white)

(B) $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2\downarrow$ (blue)

$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$ (deep blue soluble complex)

$Cu^{2+} + 2HPO_4^{2-} \longrightarrow Cu_3(PO_4)_2\downarrow$ (blue) $+ 2H^+$

$Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6]\downarrow$ (chocolate brown)

(C) $Fe^{3+} + 3OH^- \longrightarrow Fe\,(OH)_3\downarrow$ (reddish brown)

$Fe^{3+} + 3NH_3 + 3H_2O \longrightarrow Fe(OH)_3\downarrow$ (reddish brown) $+ 3NH_4^+$

$Fe^{3+} + HPO_4^{2-} \longrightarrow FePO_4\downarrow$ (yellowish-white) $+ H^+$

$4Fe^{3+} + 3\,[Fe(CN)_6]^{4-} \longrightarrow Fe_4\,[Fe(CN)_6]_3\downarrow$ (intense blue) $\xrightarrow[K_4[Fe(CN)_6]]{\text{excess}} KFe^{III}[Fe(CN)_6]^{II}$.

(soluble prussian blue)

(D) $2Ag^+ + 2OH^- \longrightarrow Ag_2O\downarrow$ (brown) $+ H_2O$

$2Ag^+ + 2NH_3 + H_2O \longrightarrow Ag_2O\downarrow$ (brown) $+ 2NH_4^+$

$4Ag^+ + HPO_4^{2-} \longrightarrow Ag_3PO_4\downarrow$ (yellow) $+ H^+$

$4Ag^+ + 3\,[Fe(CN)_6]^{4-} \longrightarrow Ag_4[Fe(CN)_6]\downarrow$ (white)