Qualitative Analysis

Introduction :

Qualitative analysis involves the detection of cation(s) and anion(s) of a salt or a mixture of salts. The systematic procedure for qualitative analysis of an inorganic salt involves the following steps :

(a) Preliminary tests

- Physical appearance (colour and smell).
- Flame test.
- Dilute sulphuric acid test.
- Concentrated sulphuric acid test.
- Dry heating test.
- Borax bead test.
- Potassium permanganate test.
- Tests for sulphate, phosphate and borate.

(b) Wet tests for acid radicals.

(c) Wet tests (group analysis) for basic radicals.

1. Physical Examination of the Mixture :

The physical examination of the unknown mixture involves the study of colour, smell and density.

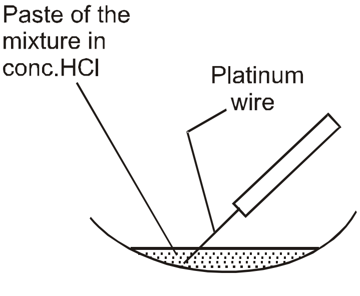
2. Dry Heating Test :

This test is performed by heating a small amount of mixture in a dry test tube. Quite valuable information can be generated by carefully performing and noting the observations here. On heating some salts undergo decomposition thus evolving the gases or may undergo characteristic changes in the colour of residue.

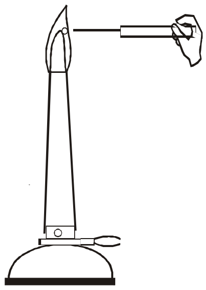
3. Flame test :

The chlorides of the metals are more volatile as compared to other salts and these are prepared in situ by mixing the compounds with a little concentrated hydrochloric acid. On heating in a non-luminous Bunsen flame they are volatilized and impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light as characteristic colour .

Colour of Flame	Inference
Crimson Red / Carmine Red	Lithium
Golden yellow	Sodium
Violet/Lilac	Potassium
Brick red	Calcium
Crimson	Strontium
Apple Green/Yellowish Green	Barium
Green with a Blue centre/Greenish Blue	Copper



(A) Dipping the platinum wire in the paste of salt and HCl.



(B) Introducing the wire in the flame

4. Borax Bead test :

On heating borax forms a colourless glassy bead of $NaBO_2$ and B_2O_3.

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

On heating with a coloured salt , the glassy bead forms a coloured metaborate in oxidising flame.

For example, in oxidising flame copper salts give blue bead.

$CuSO_4 \longrightarrow CuO + SO_3$; $CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$ (blue bead)

However, in reducing flame the colours may be different due to different reactions.

$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$

$2Cu(BO_2)_2 + 2C \longrightarrow 2Cu$ (brown red/red and opaque bead) $+ 2B_2O_3 + 2CO$.

Metal	**Colour in oxidising flame**		**Colour in reducing flame**	
	When Hot	**When Cold**	**When Hot**	**When Cold**
Copper	Green	Blue	Colourless	Brown red
Iron	Brown yellow	Pale yellow/Yellow	Bottle green	Bottle green
Chromium	Yellow	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet/Amethyst	Red/Amethyst	Grey/Colourless	Grey/Colourless
Nickel	Violet	Brown/Reddish brown	Grey	Grey

Analysis of ANIONS (Acidic Radicals) :

(a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP :

1. CARBONATE ION (CO_3^{2-}) :

- Dilute H_2SO_4 test : A colourless odourless gas is evolved with brisk effervescence.

  $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2\uparrow$

- Lime water/Baryta water ($Ba(OH)_2$) test : The liberated gas can be identified by its property of rendering lime water (or baryta water) turbid.

  $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow$ (milky) $+ H_2O$

  On prolonged passage of CO_2 the milkiness disappears.

  $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$ (soluble)

☞ Soluble bicarbonates give white precipitate with $MgSO_4$ (aq) / $MgCl_2$(aq) only on heating.

$Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\downarrow + H_2O + CO_2$

2. SULPHITE ION (SO_3^{2-}) :

- **Dilute H_2SO_4 test :** Decomposition of salt is more rapidly on warming, with the evolution of sulphur dioxide.

  $CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2\uparrow$

  SO_2 has suffocating odour of burning sulphur.

- **Acidified potassium dichromate test :** The filter paper dipped in acidified $K_2Cr_2O_7$ turns green.

  $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+}$ (green) $+ 3SO_4^{2-} + H_2O$.

- **Barium chloride/Strontium chloride solution :** White precipitate of barium (or strontium) sulphite is obtained.

  $SO_3^{2-} + Ba^{2+}/Sr^{2+} \longrightarrow BaSO_3/SrSO_3\downarrow$ (white).

☞ White precipitate is soluble in dilute HCl forming SO_2.

$BaSO_3 + 2HCl \longrightarrow BaCl_2 + SO_2 + H_2O$

- **Lime water test :** A white precipitate is formed. The precipitate dissolves on prolonged passage of the gas, due to the formation of hydrogen sulphite ions.

  $Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow$ (milky) $+ H_2O$

  $CaSO_3 \downarrow + SO_2 + H_2O \longrightarrow Ca(HSO_3)_2$ (soluble)

3. SULPHIDE ION (S^{2-}) :

- **Dilute H_2SO_4 test :** Pungent smelling gas like that of rotten egg is obtained.

  $S^{2-} + 2H^+ \longrightarrow H_2S \uparrow$

- **Lead acetate test :** Filter paper moistened with lead acetate solution turns black.

  $(CH_3COO)_2Pb + H_2S \longrightarrow PbS \downarrow$ (black) $+ 2CH_3COOH$.

- **Sodium nitroprusside test :** Purple coloration is obtained.

  $S^{2-} + [Fe(CN)_5(NO)]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$ (violet).

- **Cadmium carbonate suspension/ Cadmium acetate solution :** Yellow precipitate is formed.

  $Na_2S + CdCO_3 \longrightarrow CdS \downarrow + Na_2CO_3$

4. NITRITE ION (NO_2^-) :

- **Dilute H_2SO_4 test :** Solid nitrite in cold produces a transient pale blue liquid (due to the presence of free nitrous acid, HNO_2 or its anhydride, N_2O_3) first and then evolution of pungent smelling reddish brown vapours of NO_2 takes place.

  $NO_2^- + H^+ \longrightarrow HNO_2$; $(2HNO_2 \longrightarrow H_2O + N_2O_3)$;

  $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$; $2NO + O_2 \longrightarrow 2NO_2 \uparrow$

- **Starch iodide test :** The addition of a nitrite solution to a solution of potassium iodide, followed by acidification with acetic acid or with dilute sulphuric acid, results in the liberation of iodine, which may be identified by the blue colour produced with starch paste. A similar result is obtained by dipping potassium iodide–starch paper moistened with a little dilute acid into the solution.

  $2NO_2^- + 3I^- + 4CH_3COOH \longrightarrow I_3^- + 2NO \uparrow + 4CH_3COO^- + 2H_2O$

  Starch $+ I_3^- \longrightarrow$ Blue (starch iodine adsorption complex)

- **Ferrous sulphate test (Brown ring test) :** When the nitrite solution is added carefully to a concentrated solution of iron(II) sulphate acidified with dilute acetic acid or dilute sulphuric acid, a brown ring appears due to the formation of $[Fe(H_2O)_5NO]SO_4$ at the junction of the two liquids. If the addition has not been made slowly and caustiously, a brown colouration results.

  $NO_2^- + CH_3COOH \longrightarrow HNO_2 + CH_3COO^-$

  $3HNO_2 \longrightarrow H_2O + HNO_3 + 2NO \uparrow$

  $Fe^{2+} + SO_4^{2-} + NO \uparrow \longrightarrow [Fe, NO]SO_4$

- **Thiourea test :** When a dilute acetic acid solution of a nitrite is treated with a little solid thiourea, nitrogen is evolved and thiocyanic acid is produced. The latter may be identified by the red colour produced with dilute HCl and $FeCl_3$ solution.

  $NaNO_2 + CH_3COOH \longrightarrow HNO_2 + CH_3COONa$

  $HNO_2 + H_2NCSNH_2(s)$ (thiourea) $\longrightarrow N_2 + HSCN + 2H_2O$

  $FeCl_3 + 3HSCN \xrightarrow{\text{dil HCl}} Fe(SCN)_3$ (blood red colouration) $+ 3HCl$

5. ACETATE ION (CH_3COO^-)

- With dilute H_2SO_4 a vinegar like smell is obtained.

$$(CH_3COO)_2Ca + H_2SO_4 \longrightarrow 2CH_3COOH + CaSO_4$$

- ***Neutral ferric chloride test :*** A deep red/ blood red colouration (no precipitate) indicates the presence of acetate.

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

☞ When solution is diluted with water and boiled, brownish red precipitate of basic iron (III) acetate is obtained.

$$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \xrightarrow{\text{Boil}} 3Fe(OH)_2CH_3COO^- + 3CH_3COOH + H^+$$

Solved Examples

Ex.1 An aqueous solution of salt containing an anion X^{n-} gives the following reactions :

(i) It gives the purple or violet colouration with sodium nitroprusside solution.

(ii) It liberates a colourless unpleasant smelling gas with dilute H_2SO_4 which turns lead acetate paper black. Identify the anion (X^{n-}) and write the chemical reactions involved.

Sol. X^{n-} is S^{2-} because

(i) $[Fe(CN)_5NO]^{2-} + S^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$ (purple or violet colouration)

(ii) $S^{2-} + H_2SO_4 \longrightarrow H_2S \uparrow$ (colourless unpleasant smelling) + SO_4^{2-}

$H_2S + Pb(CH_3COO)_2 \longrightarrow PbS \downarrow$ (black) + $2CH_3COOH$

Ex.2 Sulphite on treatment with dil. H_2SO_4 liberates a gas which :

(1) turns lead acetate paper black (2) burns with blue flame

(3) smells like vinegar (4) turns acidified $K_2Cr_2O_7$ solution green

Sol. $SO_3^{2-} + H_2SO_4 \longrightarrow SO_2 + SO_4^{2-} + H_2O$

SO_2 turns acidified $K_2Cr_2O_7$ solution green.

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow Cr_2(SO_4)_3$ (Green) + $K_2SO_4 + H_2O$

Therefore, (4) option is correct.

(b) CONC . H_2SO_4 GROUP :

1. CHLORIDE ION (Cl^-) :

- **Concentrated H_2SO_4 test :** Colourless pungent smelling gas is evolved which gives fumes of NH_4Cl when a glass rod dipped in dil. HCl is brought in contact with evolving gas.

$$Cl^- + H_2SO_4 \longrightarrow HCl + HSO_4^-$$

- $NH_4OH + HCl \longrightarrow NH_4Cl \uparrow$ (white fumes) + H_2O.

☞ $2NaCl + MnO_2 + 2H_2SO_4$ (conc.) $\longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

- **Silver nitrate test :**

$$Cl^- + Ag^+ \longrightarrow AgCl \downarrow \text{ (white)}$$

☞ White precipitate is soluble in aqueous ammonia and precipitate reappears with HNO_3.

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl \text{ (Soluble)} + 2H_2O$$

$$[Ag(NH_3)_2]Cl + 2H^+ \longrightarrow AgCl \downarrow + 2NH_4^+.$$

- **Chromyl Chloride test :**

$$4Cl^- + Cr_2O_7^{2-} + 6H^+ \text{ (conc.)} \longrightarrow 2CrO_2Cl_2 \text{ (deep red vapours)} + 3H_2O$$

When deep red vapours are passed into sodium hydroxide solution, a yellow solution of sodium chromate is formed, which when treated with lead acetate gives yellow precipitate of lead chromate.

$$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$$

$$CrO_4^{2-} + Pb^{+2} \longrightarrow PbCrO_4 \downarrow \text{ (yellow)}$$

☞ **Heavy metal chlorides** such as Hg_2Cl_2, $HgCl_2$, $SnCl_2$, AgCl, $PbCl_2$ and $SbCl_3$ do not respond to this test as they are partially dissociated. This test is given generally by **ionic chlorides**.

☞ Test should be carried out in a dry test tube otherwise chromic acid will be formed.

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

2. BROMIDE ION (Br^-) :

- **Concentrated H_2SO_4 test :** First a reddish-brown solution is formed, then reddish-brown bromine vapour accompanies the hydrogen bromide (fuming in moist air) is evolved.

$$2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2\uparrow + 2H_2O + SO_2$$

☞ $2KBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2\uparrow + K_2SO_4 + MnSO_4 + 2H_2O$

- **Silver Nitrate test :** Pale yellow precipitate is formed

$$NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$$

☞ Yellow precipitate is partially soluble in dilute aqueous ammonia but readily dissolves in concentrated ammonia solution.

$$AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]\,Br + H_2O$$

- **Chlorine water test (organic layer test) :** When to a sodium carbonate extract of metal bromide containing CCl_4, $CHCl_3$ or CS_2, chlorine water is added and the content is shaken and then allow to settle down reddish brown colour is obtained in organic layer.

  $2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2\uparrow$.

  $Br_2 + CHCl_3 / CCl_4 \longrightarrow Br_2$ dissolve to give reddish brown colour in organic layer.

  With excess of chlorine water, the bromine is converted into yellow bromine monochloride and a pale yellow solution results.

$$Br_2\uparrow + Cl_2\uparrow \longrightarrow 2BrCl$$

3. IODIDE ION (I^-) :

- **Concentrated H_2SO_4 test :** Pungent smelling violet vapours are evolved.

$$2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow I_2\uparrow \text{ (dark violet)} + 2H_2O + SO_2$$

☞ Evolution of dark violet fumes intensifies on adding a pinch of MnO_2.

$$3I^- + MnO_2 + 2H_2SO_4 \longrightarrow I_3^-\uparrow + Mn^{2+} + 2SO_4^{2-} + 2H_2S$$

- **Starch paper test :** Iodides are readily oxidised in acid solution to free iodine; the free iodine may than be identified by deep blue colouration produced with starch solution.

$$3I^- + 2NO_2^- + 4H^+ \longrightarrow I_3^- + 2NO\uparrow + 2H_2O.$$

- **Silver nitrate test :** Bright yellow precipitate is formed.

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

☞ Bright yellow precipitate is insoluble in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.

- **Chlorine water test (organic layer test) :** When chlorine water is added to a solution of iodide, free iodine is liberated which colours the solution brown and on shaking with CS_2, $CHCl_3$ or CCl_4, it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

  $I_2 + CHCl_3 \longrightarrow I_2$ dissolves to give violet colour in organic layer.

  If excess of chlorine water is added, I_2 is oxidised to iodic acid (colourless).

$$I_3^- + 8Cl_2\uparrow + 9H_2O \longrightarrow 3IO_3^- + 16Cl^- + 18\,H^+$$

4. NITRATE ION (NO_3^-) :

- **Concentrated H_2SO_4 test :** Pungent smelling reddish brown vapours are evolved.

  $4NO_3^- + 2H_2SO_4 \longrightarrow 4NO_2\uparrow + O_2 + 2SO_4^{2-} + 2H_2O$

☞ Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.

$2NO_3^- + 4H_2SO_4 + 3Cu \longrightarrow 3Cu^{2+} + 2NO\uparrow + 4SO_4^{2-} + 4H_2O$; $2NO\uparrow + O_2 \longrightarrow 2NO_2\uparrow$

4 C (paper pellet) + $4HNO_3 \longrightarrow 2H_2O + 4NO_2 + 4CO_2$.

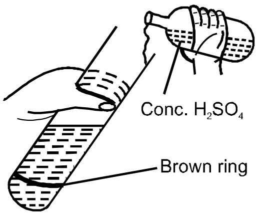
- **Brown ring test :** When a freshly prepared saturated solution of iron (II) sulphate is added to nitrate solution and then concentrated H_2SO_4 is added slowly from the side of the test tube, a brown ring is obtained at the junction of two layers.

  $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

  $6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

or $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO\downarrow + 4SO_4^{2-} + 4H_2O$.

$Fe^{2+} + NO\uparrow + 5H_2O \longrightarrow [Fe^{I}(H_2O)_5\,NO^+]^{2+}$ (brown ring).



☞ On shaking and warming the mixture, NO escapes and a yellow solution of iron(iii) ions is obtained.

(B) GROUP 'B' RADICALS :

Group of anions which do not give any gas with dilute as well as concentrated H_2SO_4 in cold but give precipitate with certain reagents :

These acid radicals are identified in inorganic salts by their individual tests as given below

1. SULPHATE ION (SO_4^{2-}) :

- **Barium chloride test :**

  W.E. or S.E. + Barium chloride (aq) ⟶ White precipitate

  $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow$ (white) + 2NaCl.

☞ White precipitate is insoluble in warm dil. HNO_3 as well as HCl but moderately soluble in boiling concentrated hydrochloric acid.

- **Lead acetate test :**

  W.E. or S.E. + Lead acetate ⟶ white precipitate

  $Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow PbSO_4\downarrow$ (White) + $2CH_3COONa$

☞ White precipitate soluble in excess of hot ammonium acetate.

$PbSO_4 + 2CH_3COONH_4 \longrightarrow (CH_3COO)_2Pb$ (soluble) + $(NH_4)_2SO_4$

- **Match stick test :**

  (a) W.E. or S.E. + Barium chloride ⟶ white precipitate

  $Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4\downarrow$ (white)

  (b) White precipitate + $Na_2\,CO_3$(s) mix and apply the paste on the end of the carbonized match stick or a wooden splinter. Put it in the reducing flame.

  $BaSO_4$ (s) + Na_2CO_3(s) $\longrightarrow Na_2SO_4 + BaCO_3\downarrow$ (white)

  $Na_2SO_4 + 4C \longrightarrow Na_2\,S + 4CO$

  (c) Now dip the match stick in sodium nitroprusside solution, purple colour near the fused mass is developed.

  $Na_2S + Na_2\,[Fe(CN)_5\,NO] \longrightarrow Na_4\,[Fe(CN)_5\,NOS]$ (purple)

2. PHOSPHATE ION (PO_4^{3-}) :

- **Ammonium molybdate test :**

Na_2HPO_4 (aq) + $12(NH_4)_2MoO_4$ + $23HNO_3 \rightarrow (NH_4)_3PMo_{12}O_{40}\downarrow$ (canary yellow) + $2NaNO_3$ + $21NH_4NO_3$ + $12H_2O$

☞ Some times ammonium phosphomolybdate is also represented by the formula $(NH_4)_3PO_4 \cdot 12MoO_3$

- **Magnesium nitrate or magnesia mixture test :** W.E. or S.E + Magnesium nitrate reagent (3-4 mL) and allows to stand for 4-5 minutes, white crystalline precipitate is formed.

  Na_2HPO_4 (aq) + $Mg(NO_3)_2$ (aq) + NH_4OH(aq) $\longrightarrow Mg(NH_4)PO_4\downarrow$ (white) + $2NaNO_3$ + H_2O

  Magnesia mixture is a solution containing $MgCl_2$, NH_4Cl and a little aqueous NH_3.

☞ PO_4^{3-} also gives $BaCl_2$ test due to the formation of white precipitate of $Ba_3(PO_4)_2$. So phosphate test should be carried out first and then conclude if PO_4^{3-} is present or absent before proceeding with the test for SO_4^{2-}.

- **Silver nitrate solution :** Yellow precipitate is formed which is soluble in dilute ammonia and in dilute nitric acid.

  $PO_4^{3-} + 3Ag^+ \longrightarrow Ag_3PO_4\downarrow$

  $Ag_3PO_4\downarrow + 6NH_3 \longrightarrow 3[Ag(NH_3)_2]^+ + PO_4^{3-}$; $Ag_3PO_4\downarrow + 2H^+ \longrightarrow H_2PO_4^- + 3Ag^+$

3. BORATE ION (BO_3^{3-}) :

Salt (0.2 g) + conc. H_2SO_4 (1 mL) + Ethyl alcohol (4-5 mL) mix in a test tube and then heat. Ignite the evolved vapours with the help of Bunsen flame, green edged flame is obtained.

$Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$

$3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$

Solved Examples

Ex.1 A compound (A) of S, Cl and O has vapour density of 67.5 (approx.). It reacts with water to form two acids and reacts with KOH to form two salts (B) and (C) while (B) gives white precipitate with $AgNO_3$ solution and (C) gives white precipitate with $BaCl_2$ solution. Identify (A), (B) & (C).

Sol. As mixture give white precipitate with $BaCl_2$ and $AgNO_3$, it should contain SO_4^{2-} and Cl^- ions. As SO_2Cl_2 when dissolved in water gives, a mixture of H_2SO_4 & HCl which then react with KOH to form KCl and K_2SO_4 . Therefore, (A) is SO_2Cl_2 and (B) & (C) are K_2SO_4 and KCl respectively.

Vapour density of SO_2Cl_2 = molecular weight / 2.

Vapour density of SO_2Cl_2 = 135 / 2 = 67.5.

Ex.2 Bromine vapours turn moist starch iodide paper :

(1) brown (2) red (3) blue (4) colourless

Sol. $2I^- + Br_2 \longrightarrow I_2 + 2Br^-$; I_2 + starch $\longrightarrow$ blue starch iodine adsorption complex.

Therefore, (3) option is correct.

Ex.3 $Na_2S_2O_3 + I_2 \longrightarrow NaI$ + ... [X], [X] is :

(1) $Na_2S_4O_6$ (2) Na_2SO_4 (3) Na_2S (4) Na_3ISO_4

Sol. $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$.

Therefore, (1) option is correct.

Analysis of CATIONS (Basic Radicals) :

Group	Group reagent	Basic radical	Composition and colour of precipitate
Zero	NaOH or $Ca(OH)_2$, heat if required	NH_4^+	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 1^{st} 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 2^{nd} 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 II^{nd} 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.

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. $NH_3 + HCl \longrightarrow NH_4Cl \uparrow$ (white fumes)

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

$$2HgNO_3 + 2NH_3 \longrightarrow \underbrace{Hg\ (NH_2)\ NO_3 + \ Hg}_{\text{black}} + NH_4NO_3$$

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

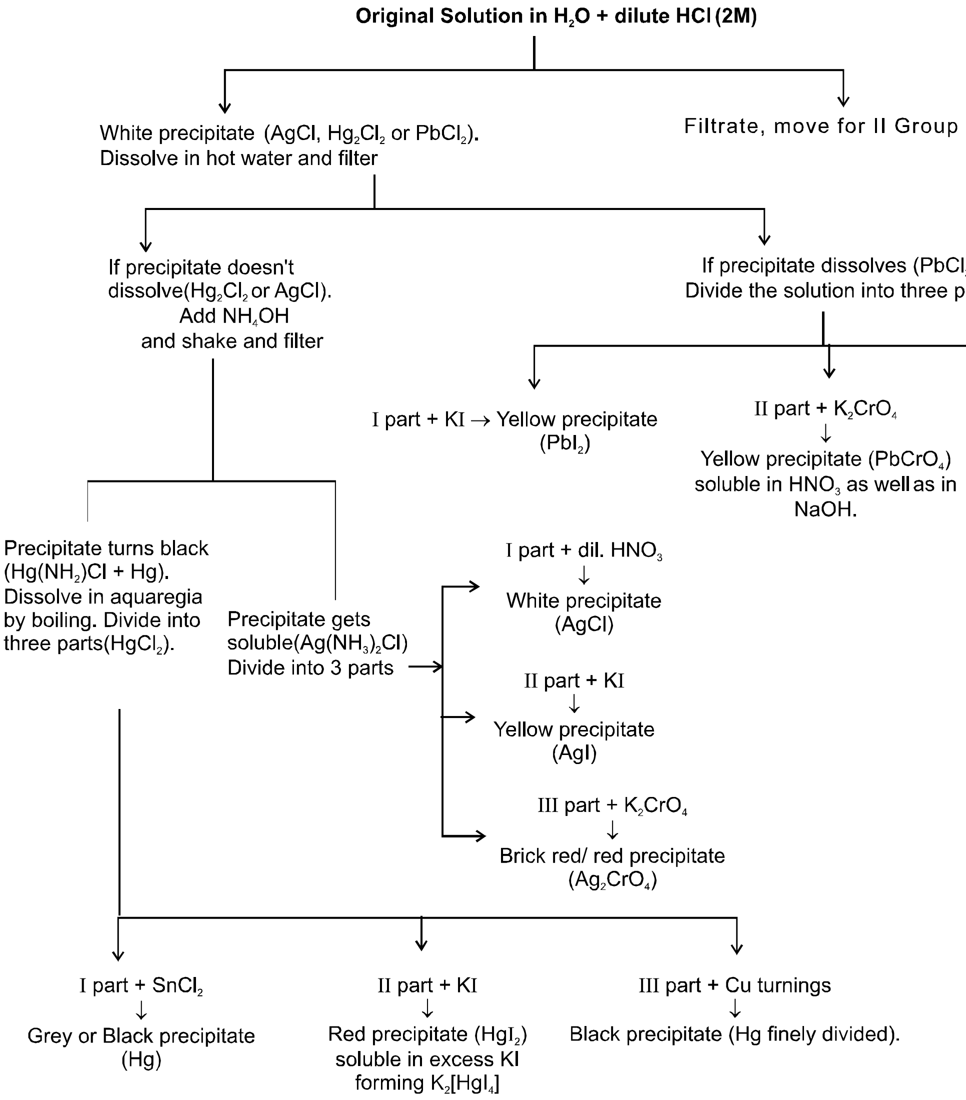
$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

- **Nessler's reagent (Alkaline solution of potassium tetraidomercurate(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.

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

Ist 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.

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

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

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

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

$$PbCl_2 + 2KI \longrightarrow PbI_2 \downarrow + 2KCl ; \qquad PbI_2 + KI\ (6M) \rightleftharpoons K_2[PbI_4] \downarrow$$

Yellow precipitate reappears on dilution with water.

- **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).

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

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

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 :**

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

(a) Stannous chloride test : White precipitate is formed which finally turns to black.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4\ ; \qquad Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow \text{(black)} + 2SnCl_4$$

(b) Potassium iodide test : Scarlet/red precipitate is formed which is soluble in excess of the reagent.

$$HgCl_2 + KI \longrightarrow HgI_2\downarrow + 2KCl\ ; \qquad HgI_2 + KI\ \text{(excess)} \longrightarrow K_2[HgI_4]\ \text{(soluble)}$$

(c) Copper chips test : Shining grey deposition of mercury on copper chips is formed.

$$HgCl_2 + Cu \longrightarrow Hg\downarrow \text{(grey)} + CuCl_2$$

- **Reaction with H_2S gas :**

$$Hg_2^{2+} + H_2S \longrightarrow HgS\downarrow \text{(black)} + Hg\downarrow \text{(grey)} + 2H^+$$

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.

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

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.

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

- **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 $Na_2S_2O_3$.

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

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

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

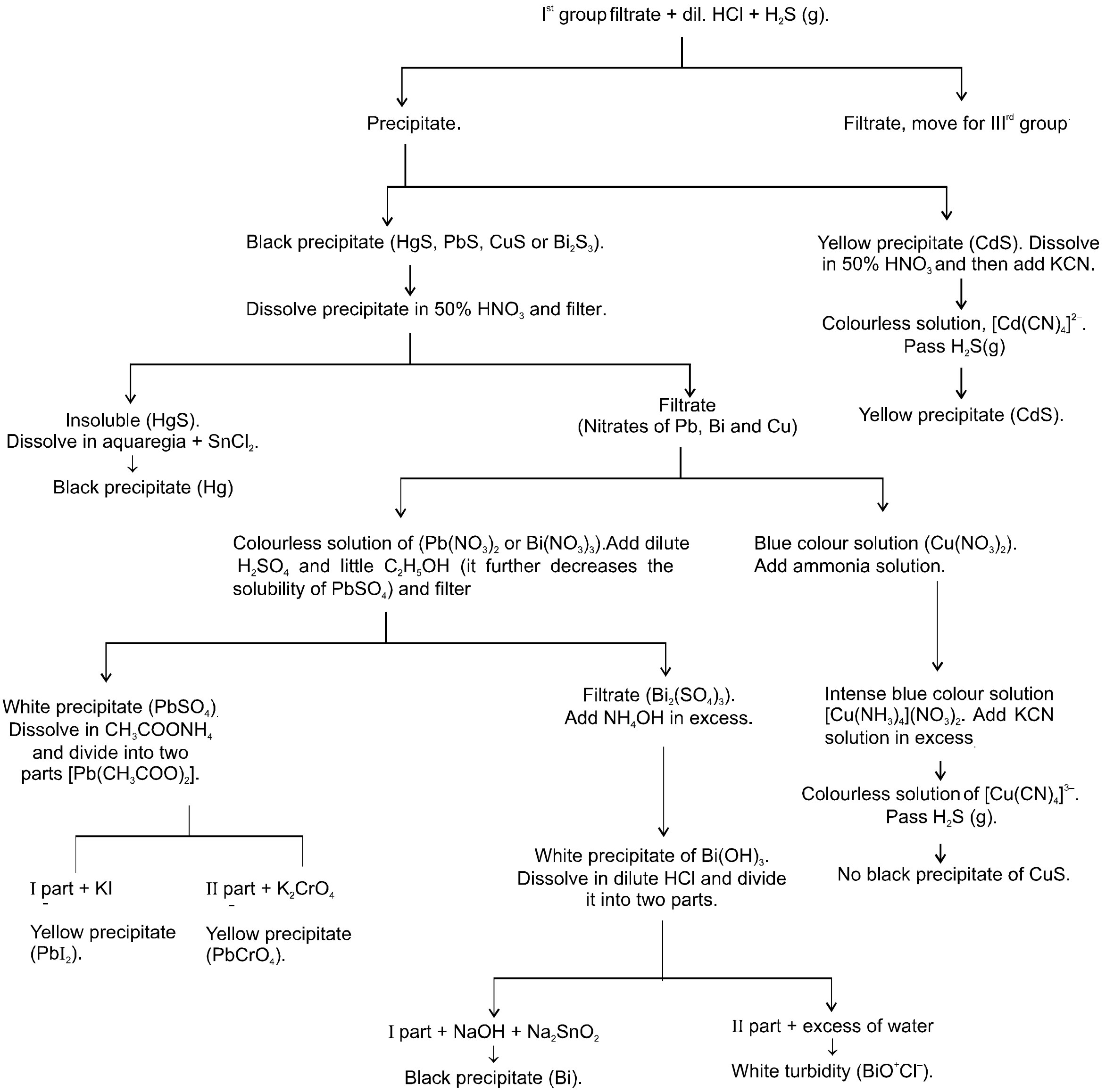
IInd Group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+})

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.

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.

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

☞ Aqua regia dissolves the precipitate.

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

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

- **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.

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

- **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.

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

☞ 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

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

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

● **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.

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

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

● **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).

$$2\,Cu^{2+} + 5\,I^- \longrightarrow Cu_2I_2\downarrow + I_3^-$$

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.

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

(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.

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

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).

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

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

$$2Bi^{3+} + 3H_2S \xrightarrow{\text{Heat}} Bi_2S_3\downarrow\ (\text{black}) + 6H^+$$

$$Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi\,(NO_3)_3 + 2NO + 3S + 4H_2O$$

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

- **Alkaline sodium stannite (Sodium tetrahydroxidostannate (II)) :** A black precipitate of metallic bismuth is obtained.

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

$2Bi(OH)_3\downarrow + [Sn(OH)_4]^{2-} \longrightarrow 2Bi\downarrow + 3\,[Sn(OH)_6]^{2-}$

(OA) (RA)

☞ The reagent must be freshly prepared and test must be carried out in cold solution.

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

$Bi^{3+} + NO_3^- + H_2O \longrightarrow BiO(NO_3)\downarrow + 2H^+$

$Bi^{3+} + Cl^- + H_2O \longrightarrow BiOCl\downarrow$ (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.

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

4. CADMIUM ION (Cd^{2+}) :

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

$Cd^{2+} + H_2S \xrightarrow{H^+} CdS\downarrow + 2H^+$

$CdS + 8HNO_3 \longrightarrow 3Cd\,(NO_3)_2 + 4H_2O + 2NO + 3S$

- **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 .

$Pb^{2+} + H_2S \longrightarrow PbS\downarrow$ (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.

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

$PbSO_4 + 2CH_3\,COONH_4 \longrightarrow (CH_3COO)_2\,Pb + (NH_4)_2\,SO_4$

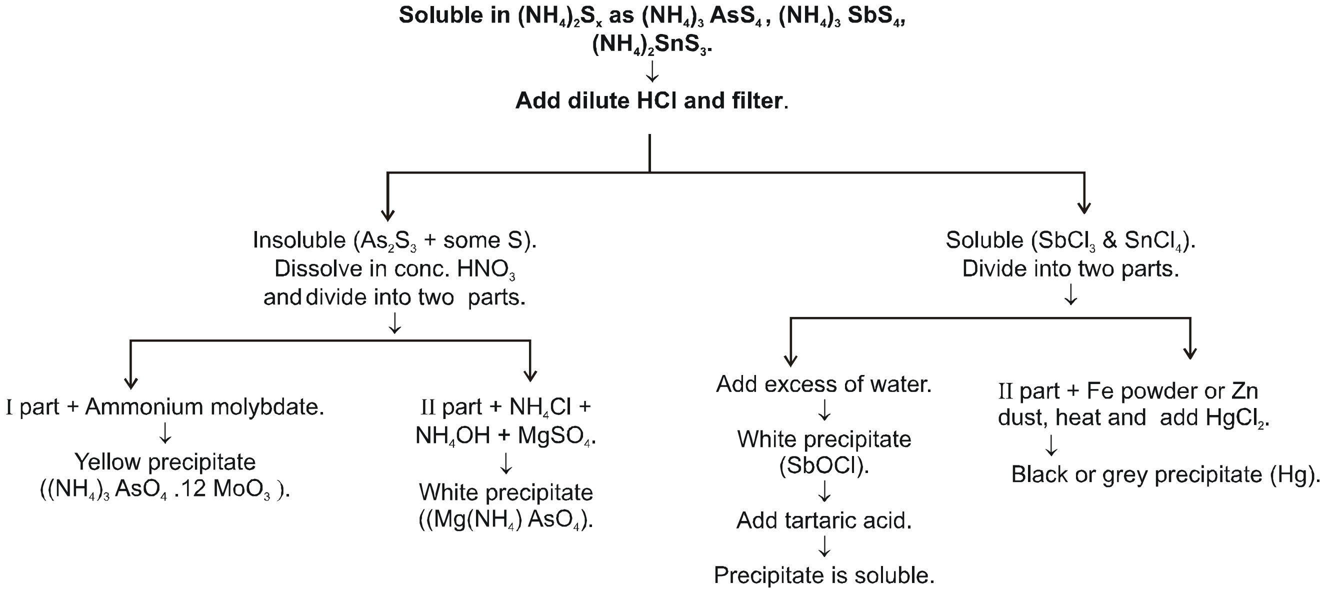
- **Potassium iodide :** Yellow precipitate is formed which is soluble in excess more concentrated (6M) solution of the reagent. Yellow precipitate of PbI_2 is moderately soluble in boiling water to give a colourless solution.

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

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

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

IIB Group (As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+})



1. ARSENIC ION (As^{3+}) :

- **Precipitation with H_2S in acidic medium :** Yellow precipitate is formed which is soluble in warm concentrated nitric acid, sodiumhydroxide solution and yellow ammonium sulphide.

$$2As^{3+} + 3H_2S \xrightarrow{H^+} As_2S_3 \downarrow + 6H^+$$

$$3\, As_2S_3 \downarrow + 28\, HNO_3 + 4\, H_2O \longrightarrow 6\, AsO_4^{3-} + 9\, SO_4^{2-} + 36\, H^+ + 28\, NO \uparrow$$

$$As_2S_3 \downarrow + 6OH^- \longrightarrow AsO_3^{3-} + AsS_3^{3-} + 3\, H_2O$$

$$As_2S_3 \downarrow + 4\, S_2^{2-} \longrightarrow 2\, AsS_4^{3-} + S_3^{2-}$$

- **Magnesia mixture :** White crystalline precipitate of magnesium ammonium arsenate $Mg(NH_4)AsO_4.6\, H_2O$ is formed from neutral or ammonical solution. Upon treating the white precipitate with silver nitrate solution containing a few drops of acetic acid, red silver arsenate is formed (distinction from phosphate).

$$H_3AsO_4 + MgSO_4 + 3NH_4OH \longrightarrow Mg(NH_4)AsO_4 \downarrow + (NH_4)_2SO_4 + 3H_2O$$

$$MgNH_4AsO_4 \downarrow + 3\, Ag^+ \longrightarrow Ag_3AsO_4 \downarrow + Mg^{2+} + NH_4^+$$

2. ANTIMONY ION (Sb^{3+}) :

- **Precipitation with H_2S in acidic medium :** A orange red precipitate is formed from mildly acidic solutions.

$$Sb^{3+} + 3H_2S \xrightarrow{H^+} Sb_2S_3 \downarrow \text{(orange)} + 6H^+$$

Precipitate is soluble in warm concentrated HCl, in ammonium polysulphide and in alkali hydroxides.

$$Sb_2S_3 \downarrow + 6\, HCl \longrightarrow 2\, Sb^{3+} + 6\, Cl^- + 3\, H_2S \uparrow$$

$$Sb_2S_3 \downarrow + 4\, S_2^{2-} \longrightarrow 2\, SbS_4^{3-} + S_3^{2-}$$

$$Sb_2S_3 \downarrow + 4\, OH^- \longrightarrow SbO_2^- + 3\, SbS_2^- + 2\, H_2O$$

- **Dilution with water :** When water is poured in a solution of soluble $SbCl_3$, a white precipitate of antimonyl chloride (SbOCl) is formed, soluble in HCl. With a large excess of water, the hydrated oxide $Sb_2O_3.xH_2O$ is produced.

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2\ HCl$$

- **Reduction with zinc or tin :** Sb^{3+} ions give black precipitate of metal.

$$2\ Sb^{3+} + 3\ Zn \longrightarrow 2\ Sb \downarrow + 3\ Zn^{2+}\ ;\ \ 2\ Sb^{3+} + 3\ Sn \longrightarrow 2\ Sb \downarrow + 3\ Sn^{2+}$$

3. TIN (II) ION (Sn^{2+}) AND TIN (IV) ION (Sn^{4+}) :

- **Precipitation with H_2S in acidic medium :**

Brown precipitate is obtained with Sn^{2+} which is soluble in concentrated HCl and yellow ammonium sulphide forming thiostannate but not in colourless ammonium sulphide.

$$Sn^{2+} + H_2S \longrightarrow SnS \downarrow \text{ (brown) ; } SnS \downarrow + S_2^{2-} \longrightarrow SnS_3^{2-} \text{ (thiostannate)}$$

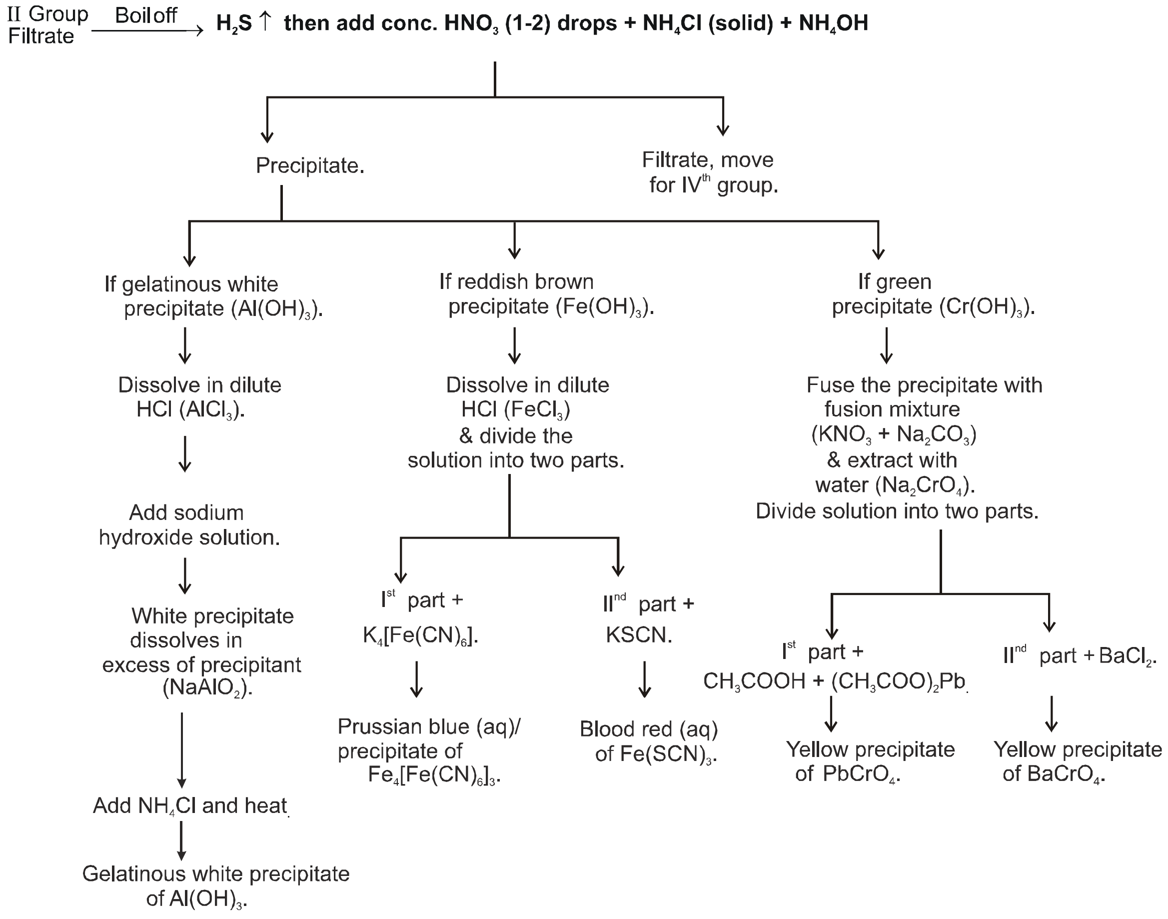
$$Sn^{4+} + 2H_2S \longrightarrow SnS_2 \downarrow \text{ (yellow) } + 4\ H^+$$

Precipitate is soluble in concentrated HCl (difference from As^{3+} and Hg^{2+}) and in alkali hydroxide, and also in ammonium sulphide and yellow ammonium sulphide.

- **Reduction of stannic chloride to stannous chloride by iron filling or granulated zinc :**

$$SnCl_4 + Zn \longrightarrow SnCl_2 + ZnCl_2$$

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



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

- **Precipitation with NH_4OH in presence of NH_4Cl :** White gelatinous precipitate is formed.

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

- **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 aluminimum 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.

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

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

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

- **Lake Test :**

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow \text{(white)} + 3\,NH_4Cl$$

The precipitation of aluminium hydroxide is done in presence of blue litmus. Originally the solution will appear red when the group precipitate is dissolved in HCl as blue litmus turns red in acid medium. On adding large excess of NH_4OH, $Al(OH)_3$ will be reprecipitated and will adsorb the litmus as it is flocculent by nature. After a while a blue mass will be seen floating in a colourless solution as all the colour from the solution will adsorbed.

- **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.

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

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

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

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

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

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

Turnbull's blue

- **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.

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

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

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

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

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

☞ The green precipitate of $Cr(OH)_3$ can be dissolved by using any of the following methods.

(A) Fusion with fusion mixture ($Na_2CO_3 + KNO_3$)

$$2\,Cr(OH)_3 + 2Na_2CO_3 + 3\,KNO_3 \longrightarrow 2\,Na_2CrO_4 + 3\,KNO_2 + 2\,CO_2 + 3\,H_2O$$

Fused mass on extraction with water gives yellow solution of Na_2CrO_4.

(B) $2\,Cr(OH)_3 + 3\,Na_2O_2 \longrightarrow 2Na_2\,CrO_4 + 2NaOH + H_2O$

(C) Precipitate is heated with NaOH and bromine water.

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

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

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

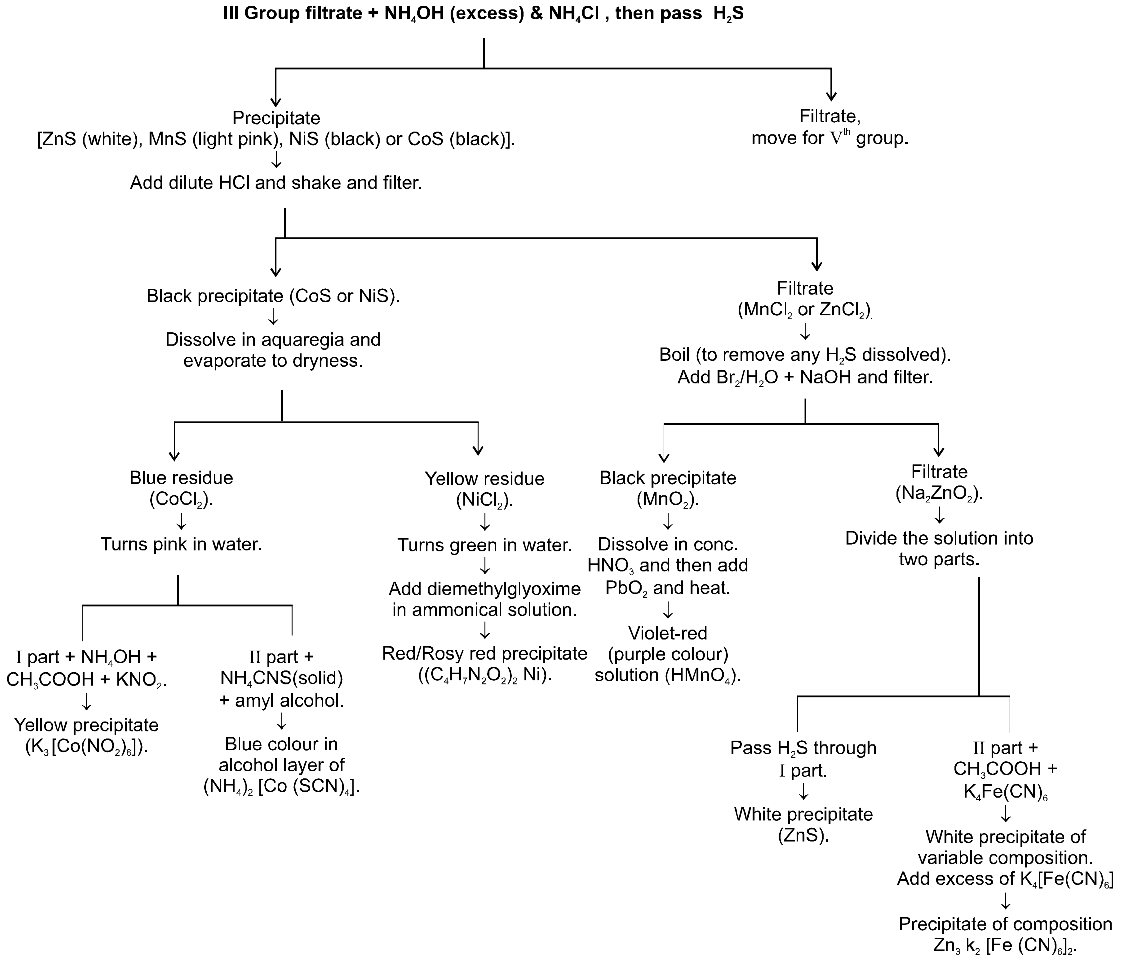
(a) Lead acetate solution : Yellow precipitate is formed.

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

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

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

IV^th 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).

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

- **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.

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

$Mn(OH)_2 \downarrow + O_2 \longrightarrow 2\,MnO(OH)_2 \downarrow$ (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) $+ 2NaBr + 2H_2O$

- **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.

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

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 .

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

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.

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

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

- **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.

3. COBALT ION (Co^{2+}) :

- **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.

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

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

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

☞ 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)

- **Potassium cyanide solution :**

$$Co^{2+} + 2\,CN^- \longrightarrow Co(CN)_2\downarrow \text{ (reddish brown / buff coloured)}$$

In excess of reagent, a brown solution of a soluble complex is formed.

$$Co(CN)_2\downarrow + 4\,CN^- \longrightarrow [Co(CN)_6]^{4-}$$

On acidification precipitate reappears.

$$[Co(CN)_6]^{4-} + 4\,H^+ \text{ (cold and dilute)} \longrightarrow Co(CN)_2\downarrow + 4HCN\uparrow$$

☞ If brown solution is boiled for a longer time in air or some H_2O_2 is added and solution is heated it turns yellow.

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

$$2\,[Co(CN)_6]^{4-} + H_2O_2 \longrightarrow 2\,[Co(CN)_6]^{3-} \text{ (yellow solution)} + 2\,OH^-$$

4. NICKEL ION (Ni^{2+}) :

- **Precipitation with H_2S in presence of $NH_4OH + NH_4Cl$:**

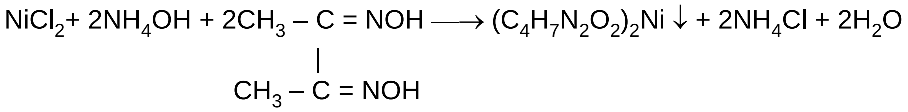
A black precipitate is formed which is insoluble in cold dilute HCl and CH_3COOH but dissolves in hot concentrated HNO_3 and in aquaregia.

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

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

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

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



$$NiCl_2 + 2NH_4OH + 2\begin{array}{l}CH_3-C=NOH\\ \quad\;\;\,|\\ CH_3-C=NOH\end{array} \longrightarrow (C_4H_7N_2O_2)_2Ni\downarrow + 2NH_4Cl + 2H_2O$$

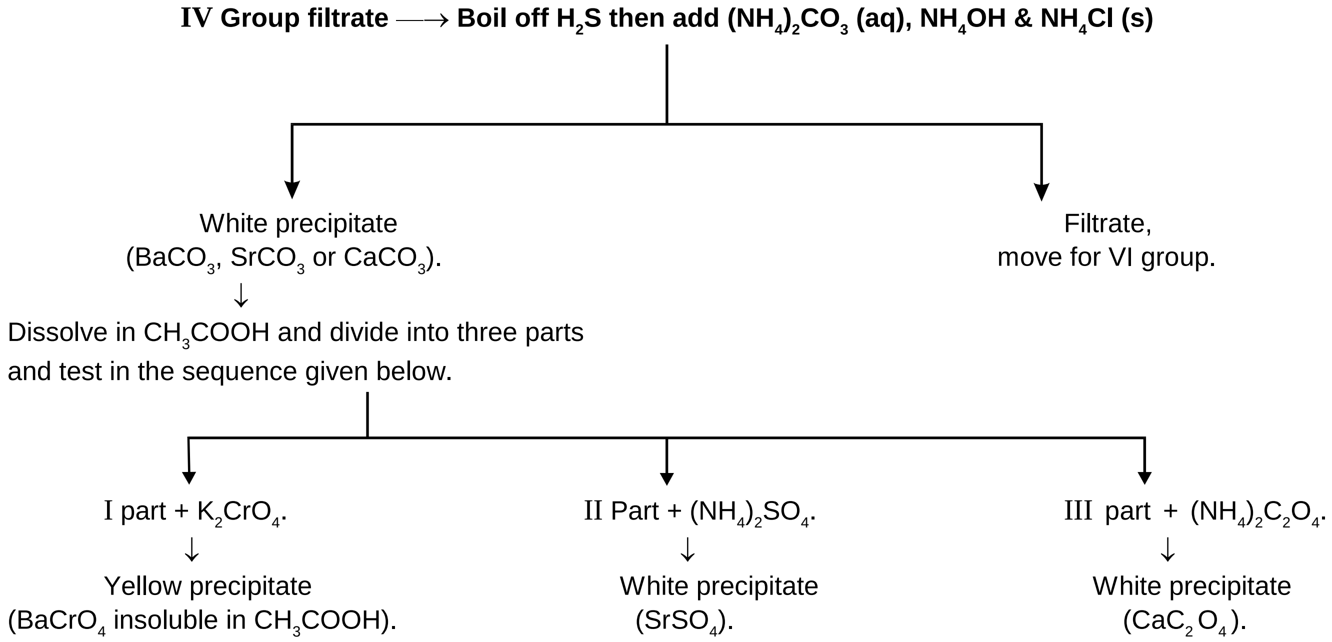
- **Bromine water test (alkaline medium) :** A black precipitate of Ni_2O_3 is formed.

$$NiCl_2 + 2NaOH \text{ (excess)} \longrightarrow Ni(OH)_2\downarrow \text{ (green)} + 2\,NaCl$$

Green precipitate is formed which gradually turns black on adding bromine water.

$$Br_2 + H_2O \longrightarrow 2HBr + [O]\;; \qquad 2Ni(OH)_2 + H_2O + [O] \longrightarrow 2\,Ni(OH)_3\downarrow$$

Vth 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.

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.

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

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.

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

☞ 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.

VI^th^ 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.

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

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

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

- **Titan Yelllow (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 qty.) 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.

Solved Examples

Ex.1 Which of the following salt will give white precipitate with the solution containing Pb^{2+} ions ?

(1) Na_2CO_3 (2) NaCl (3) Na_2SO_3 (4) All of these

Sol. $Pb^{2+} + CO_3^{2-} \longrightarrow PbCO_3\downarrow$ (white)

$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2\downarrow$ (white)

$Pb^{2+} + SO_3^{2-} \longrightarrow PbSO_3\downarrow$ (white) ; Therefore, (D) option is correct.

Ex.2 Why Na_2S cannot be used in place of H_2S (in presence of HCl) as a reagent for II^nd^ group cations ?

Sol. With Na_2S, along with 2nd group cations, some cations of higher groups i.e., III^rd^ and IV^th^ groups may be precipitated because the higher concentration of S^{2-} ions is obtained according to following reaction.

$$Na_2S \rightleftharpoons 2\,Na^+ + S^{2-}$$

To precipitate II^nd^ group cation lower concentration of S^{2-} ions is required (because of low K_{sp} of II^nd^ group sulphides) and this can be obtained easily by H_2S in presence of dilute HCl.

$$H_2S \rightleftharpoons 2\,H^+ + S^{2-}\ ;\ HCl \rightleftharpoons H^+ + Cl^-$$

Due to common ion effect the ionisation of H_2S is suppressed and the concentration of S^{2-} ions obtained is just sufficient to precipitate the cations of II^nd^ group.

Ex.3 Why Zn(II) salt is not precipitated as $Zn(OH)_2$ by ammonia solution in the presence of excess of ammonium chloride ?

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

It is due to the lowering of OH^- ion concentration because of common ion effect of NH_4^+ to such a value that the K_{sp} of $Zn(OH)_2$ is not attained.

Ex.4 Column I and column II contains four entries each. Entries of column I are to be matched with some entries of column II. Each entry of column I may have the matching with one or more than one entries of column II.

	Column I		**Column II**
(A)	Forms coloured precipitate on addition of CrO_4^{2-} ions but precipitate dissolves in ammonia solution.	(p)	Ag^+
(B)	Forms coloured precipitate with ammonia solution but dissolves forming coloured solution in excess of precipitant.	(q)	Cu^{2+}
(C)	Forms coloured precipitate on addition of I^- ions but in excess of precipitant precipitate dissolves forming coloured solution.	(r)	Ni^{2+}
(D)	Forms white precipitate, when salt (chloride or nitrate) is poured into a large volume of water.	(s)	Bi^{3+}

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

(A) $2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4\downarrow$ (red)

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

(B) $2Cu^{2+} + SO_4^{2-} + 2NH_3 + H_2O \longrightarrow Cu(OH_2)_2.\ CuSO_4\downarrow$ (blue) $+ 2NH_4^+$

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

$Ni^{2+} + 2NH_3 + 2H_2O \longrightarrow Ni(OH)_2\downarrow$ (green) $+ 2NH_4^+$

$Ni(OH)_2\downarrow + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$ (deep blue) $+ 2OH^-$

(C) $Bi^{3+} + 3I^- \longrightarrow BiI_3\downarrow$ (black)

$BiI_3 + I^- \longrightarrow [BiI_4]^-$ (orange colouration)

(D) $Bi^{3+} + NO_3^- + H_2O \longrightarrow \underset{\text{basic salt}}{BiO(NO_3)}\downarrow$ (white) $+ 2H^+$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Chocolate brown precipitate is formed with :

(1) Cu^{2+} ions and $[Fe\,(CN)_6]^{3-}$
(2) Cu^{2+} ions and $[Fe(CN)_6]^{4-}$
(3) Fe^{2+} ions and $[Fe\,(CN)_6]^{4-}$
(4) Fe^{2+} ions and dimethylglyoxime

Ans. (2)

Sol (1) $Cu_3\,[Fe(CN)_6]_2\downarrow$ (green) ; (2) $Cu_2\,[Fe(CN)_6]\downarrow$ (chocolate brown)

(3) $Fe_4[Fe(CN)_6]_3\downarrow$ (Prussian blue) ; (4) red solution of iron(II) dimethylglyoxime.

2. Pink colour of acidified $KMnO_4$ is decolourised but there is no evolution of any gas. This may happen with the compound containing the following acid radical.

(1) SO_3^{2-} (2) NO_2^- (3) S^{2-} (4) All of these

Ans. (4)

Sol. (1) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

(2) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(3) $2MnO_4^- + H_2S + 6H^+ \longrightarrow 2Mn^{2+} + 5S\downarrow + 8H_2O$

3. When H_2S gas is passed through an ammonical salt solution X, a slightly white precipitate is formed. The X can be :

(1) a cobalt salt (2) a lead salt (3) a zinc salt (4) a silver salt

Ans. (3)

Sol. $Zn^{2+} + H_2S \longrightarrow ZnS \downarrow$ (white) $+ 2H^+$

4. **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.

(1) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(2) Both Statement-1 and Statement-2 are true but Statement-2 is not correct explanation of Statement-1.
(3) Statement-1 is true but Statement-2 is false.
(4) Statement-1 is false but Statement-2 is true

Ans. (4)

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

5. **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

(1) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(2) Both Statement-1 and Statement-2 are true but Statement-2 is not correct explanation of Statement-1.
(3) Statement-1 is true but Statement-2 is false.
(4) Statement-1 is false but Statement-2 is true

Ans. (1)

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

Subjective :

6. 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.