ICAD

Creating & Nurturing Talent

NEET
CHEMISTRY
[C-29] : SALT ANALYSIS

Command Capsule

MODULE SIMPLIFIED

CONTENTS

C-29 : SALT ANALYSIS

Principles of qualitative analysis group I to V excluding interfering radicals.

The detection of cations (basic radicals) and anions(acidic radicals) in a salt or in a mixture is known as **Qualitative Analysis.**

Some Important Observations during Qualitative Analysis

1. List of different coloured salts

Salts	Colour
Copper salts	Bluish green
Nickel salts	Greenish blue
Chromium salts	Dark green
cobalt salts	Pinkish or purple
Manganese salts	Light pink
Ferrous salts	Light green
Ferric salts	Pale yellow

2. Action of Heat (Colour of Residue)

S. No.	Colour	Residue
i)	Yellow (hot) and white (cold)	ZnO
ii)	Reddish brown (hot) and yellow (cold)	PbO
iii)	Black (hot) and Red (cold)	HgO, Pb_3O_4
iv)	Black (hot) and Red brown (cold)	Fe_2O_3
v)	Decripitation	$Pb(NO_3)_2$,NaCl
vi)	White sublimate	Ammonium salts

3. Gases

S. No.	Nature	Gases
i)	Colourless and odourless gases	O_2, CO_2, N_2
ii)	Colourless gases with odour	NH_3, SO_2, HCl, H_2S
iii)	Coloured gases	NO_2 (brown), Br_2, (reddish brown), I_2 (violet), Cl_2 (greenish yellow)

4. Flame Test

Metals	Colour
Li	crimson red
Na	golden yellow
K	Violet
Ca	Brick red
Sr	crimson
Ba	apple green

Classification of Anions:

Methods available for the detection of anions are not as systematic as those used for the detection of cations. Furthermore anions are classified essentially on the basis of process employed.

Class A: Includes anions that are identified by volatile products obtained on treatment with acids. It is further dividd into two sub groups.

(i) Gases evolved with dil HCl/ dil. H_2SO_4 .

(ii) Gases or acid vapours evolved with conc. H_2SO_4

Class B: Includes anions that are identified by their reactions in solution. It is subdivided into two groups:

(i) Precipitation reactions

(ii) Oxidation and reduction in solution

Class A (i) : Anions which evolve gases on reaction with dil. HCl/dil. H_2SO_4 .

It includes - CO_3^{2-} ,SO_3^{2-}, S^{2-}, NO_2^{-}, CH_3COO^{-}, $S_2O_3^{2-}$

1. **Carbonate (CO_3^{2-}) :**

(i) Dilut HCl : gives effervescence, due to the evolution of carbon dioxide

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 \uparrow + H_2O$$

The gas gives white turbidity with lime water and baryta water

$$CO_2 + Ca^{2+} + 2OH^- \longrightarrow CaCO_3 \downarrow + H_2O$$

$$CO_2 + Ba^{2+} + 2OH^- \longrightarrow BaCO_3 \downarrow + H_2O$$

On prolonged passage of carbon dioxide in lime water, the turbidity slowly disappears due to the formation of soluble hydrogen carbonate.

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

The following tests performed with then aqueous salts solution.

(ii) Barium chloride or Calcium chloride solution: White ppt of barium or Calcium carbonate is obtained, which is soluble in mineral acid.

$$CO_3^{2-} + Ba^{2+} \longrightarrow BaCO_3 \downarrow$$

$$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3 \downarrow$$

(iii) Silver nitrate solution : White ppt of silver carbonate is obtained.

$$CO_3^{2-} + 2Ag^+ \longrightarrow Ag_2CO_3 \downarrow$$

The ppt so obtained is soluble in nitric acid and in ammonia, the ppt becomes yellow or brown on addition of excess reagent and same may also be happened if the mix is boiled, due to the formation of silver oxide

$$Ag_2CO_3 \downarrow \longrightarrow Ag_2O \downarrow + CO_2 \uparrow$$

2. **Sulphites (SO_3^{2-}):**

(i) Dilute HCl or Dilute H_2SO_4 : decomposes with the evolution of sulphur dioxide

$$SO_3^{2-} + 2H^+ \longrightarrow SO_2 + H_2O$$

The gas has a suffocating odour of burning sulphur.

(ii) Acidified potassium dichromate solution: The gas turns filter paper moistened with acidified potassium dichromate solution, green due to the formation of Cr^{3+} ions.

$$SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + H_2O$$

(iii) Lime water : On passing the gas through lime water, a milky ppt is formed.

$$SO_2 + Ca(OH)_2 \longrightarrow \underset{\text{milky}}{CaSO_3 \downarrow} + H_2O$$

Precipitate dissolves on prolonged passage of the gas, due to the formation of soluble hydrogen sulphite ions.

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

(iv) Barium chloride or Strontium chloride solution : Salt solutions gives white ppt of barium or strontium sulphite.

$$SO_3^{2-} + Ba^{2+} \rightarrow BaSO_3 \downarrow$$

$$SO_3^{2-} + Sr^{2+} \rightarrow SrSO_3 \downarrow$$

3. **Sulphide (S^{-2}):**

(i) Dil HCl or Dil H_2SO_4 : A colourless gas with a smell of rotten eggs (H_2S) is evolved

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

(ii) The gas turns lead acetate paper black

$$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{black}}{PbS \downarrow} + 2CH_3COOH$$

(iii) Salt solution gives yellow pt. with $CdCl_2$

$$Na_2S + CdCl_2 \longrightarrow \underset{\text{yellow}}{CdS \downarrow} + 2NaCl$$

(iv) Silver nitrate solution : black ppt. of silver sulphide insoluble in cold but soluble in hot dil nitric acid.

$S^{2-} + 2Ag^{+} \longrightarrow Ag_2S\downarrow$

(v) Sodium nitroprusside solution : Turns sodium nitroprusside solution purple

$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$

4. **Nitrites (NO_2^-):**

(i) Dil HCl and Dil. H_2SO_4 : Adding to solid nitrite in cold yield pale blue liquid (due to the presence of free nitrous acid HNO_2 or its anhydride N_2O_3) & the evolution of brown fumes of nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air

$NO_2^- + H^+ \longrightarrow HNO_2$

$2HNO_2 \longrightarrow H_2O + N_2O_3$

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

$2NO\uparrow + O_2\uparrow \longrightarrow 2NO_2\uparrow$

Following tests performed with an aqueous salt solution.

(ii) Silver nitrate solution : White crystalline ppt. is obtained

$NO_2^- + Ag^+ \rightarrow AgNO_2\downarrow$

(iii) Turns acidified KI – starch paper blue

$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2\uparrow$

Starch $+ I_2 \longrightarrow$ Blue Colour

(iv) Brown ring test : When the nitrite solution is added carefully to a conc. solution of Iron(II) sulphate acidified with dil acetic acid or with dilute sulphuric acid, a **brown ring**, due to the formation of $[Fe, NO]SO_4$ at the junction of the two liquids.

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

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

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

5. **Acetate (CH_3COO^-):**

(i) **Dilute Sulphuric Acid :** Smell of vinegar

$CH_3COO^- + H^+ \longrightarrow CH_3COOH\uparrow$

(ii) **Iron (III) Chloride Solution :** Gives deep - red colouration

$CH_3COONa + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$

Brown colour

6. **Thiosulphates ($S_2O_3^{2-}$) :**

(i) Dil Hydrochloric acid : Gives sulphur & sulphur di oxide

$S_2O_3^{2-} + 2H^+ \longrightarrow S\downarrow + SO_2\uparrow + H_2O$

(ii) Iodine Solution : Decolourise due to formation of tetrathionate ion

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

(iii) Barium chloride solution : White ppt. of barium thiosulphate is formed

$S_2O_3^{2-} + Ba^{2+} \longrightarrow BaS_2O_3\downarrow$

But no ppt. is obtained with $CaCl_2$ solution.

(iv) Silver nitrate solution : Gives white ppt. of silver thiosulphate.

$S_2O_3^{2-} + 2Ag^+ \longrightarrow Ag_2S_2O_3\downarrow$

The ppt. is unstable, turning dark on standing, due to the formation of silver sulphide.

$Ag_2S_2O_3\downarrow + H_2O \longrightarrow Ag_2S + H_2SO_4$

(v) Lead acetate or Lead nitrate solution : Gives white ppt.

$S_2O_3^{2-} + Pb^{2+} \longrightarrow PbS_2O_3\downarrow$

On boiling it turns black due to the formation of PbS.

$PbS_2O_3\downarrow + H_2O \longrightarrow PbS\downarrow + 2H^+ + SO_4^{2-}$

Class A(ii) : Gases or acid vapours evolved with conc. Sulphuric acid

It includes – Cl^-, Br^-, I^-, NO_3^-.

1. **Chloride (Cl^-) :**

(i) **Conc. H_2SO_4 :** decomposes with the evolution of HCl.

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

Gas so produced

1. Turns blue litmus paper red
2. Gives white fumes of NH_4Cl when a glass rod moistened with ammonia solution is brought to the mouth of test tube.

(ii) **Manganese dioxide and conc. sulphuric acid :** When a solid chloride is treated with MnO_2 and conc. H_2SO_4, yellowish green colour is obtained.

$$MnO_2 + 2H_2SO_4 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 \uparrow + 2SO_4^{2-} + 2H_2O$$

The following tests are performed with the salt solution.

(iii) **Silver nitrate solution :** White, curdy ppt. of AgCl insoluble in water & in dil nitric acid, but soluble in dilute ammonia solution.

$$Cl^- + Ag^+ \rightarrow AgCl \downarrow$$

$$AgCl \downarrow + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$$

$$Ag(NH_3)_2Cl + 2H^+ \rightarrow AgCl + 2NH_4^+.$$

(iv) **Lead acetate solution :** White ppt. of lead chloride is formed

$$2Cl^- + Pb^{+2} \rightarrow PbCl_2 \downarrow$$

(v) **Chromyl chloride test :** When a mix containing chloride ion is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 orange red fumes of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{orange–red fumes}}{2CrO_2Cl_2 \uparrow} + 3H_2O$$

Chlorides of mercury, owing to their slight ionization, do not respond to this test and only partial conversion to CrO_2Cl_2 occurs with the chlorids of lead, silver, antimony and tin.

When chromyl chloride vapours are passed into sodium hydroxide a yellow solution of sodium chromate is formed which when treated with lead acetate gives yellow ppt. of lead chromate.

$$CrO_2Cl_2 + 2NaOH \longrightarrow \underset{\text{Yellow solution}}{Na_2CrO_4} + 2HCl$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + \underset{\text{(yellow pt.)}}{PbCrO_4 \downarrow}$$

2. **Bromide (Br^-)**

(i) **Conc. H_2SO_4 :** Gives reddish brown vapours of bromine.

$$2KBr + H_2SO_4 \rightarrow K_2SO_4 + 2HBr$$

$$2KBr + H_2SO_4 \rightarrow 2H_2O + SO_2 \uparrow + \underset{\text{(reddish brown)}}{Br_2 \uparrow}$$

(ii) **Manganese dioxide and conc. sulphuric acid :** When a mix of solid bromide, MnO_2 and conc. H_2SO_4 is heated reddish brown vapours of bromine are evolved.

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

The following tests are performed with the salt solution.

(iii) **Silver nitrate solution :** A pale yellow ppt. of silver bromide is obtained. This ppt. is sparingly soluble in dil but readily soluble in conc. ammonia solution and insoluble in dil. HNO_3.

$$Br^- + Ag^+ \longrightarrow AgBr$$

(iv) **Lead acetate solution :** White crystalline ppt. of lead bromide which is soluble in boiling water.

$$2Br^- + Pb^{+2} \longrightarrow PbBr_2 \downarrow$$

(v) **Chlorine water :** When this solution is added to a solution of bromide and chloroform free bromine is liberated, which colours the organic layer orange - red.

$$2KBr + Cl_2\,(water) \longrightarrow 2KCl + Br_2$$

$$Br_2 + Chloroform \longrightarrow Orange\ red\ colour$$

(vi) **Potassium dichromate & conc. H_2SO_4 :** When a mix of solid bromide, $K_2Cr_2O_7$, and conc. H_2SO_4 is heated and passing the evolved vapours into water, a yellowish brown solution is obtained.

$$2KBr + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Br_2 \uparrow + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O$$

3. **Iodide (I^-):**

(i) **Conc.** H_2SO_4 **:** Gives violet vapours of iodine

$$2I^- + 2H_2SO_4 \longrightarrow I_2 + SO_4^{2-} + 2H_2O + SO_2\uparrow$$

violet vapours

The following tests are performed with the salt solution.

(ii) **Silver nitrate solution :** Yellow, curdy ppt. of silver iodide AgI, very slightly soluble in conc. ammonia solution and insoluble in dil nitric acid.

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

(iii) **Lead acetate solution :** Yellow, curdy ppt. of lead iodide soluble in much hot water forming a colourless solution & yielding golden yellow plates (spangles) on cooling.

$$2I^- + Pb^{2+} \longrightarrow PbI_2\downarrow$$

(iv) **Potassium dichromate & conc. sulphuric acid :** Iodine is liberated

$$6I^- + Cr_2O_7^{2-} + 2H_2SO_4 \longrightarrow 3I_2\uparrow + 2Cr^{3+} + 7SO_4^{2-} + 7H_2O.$$

(v) **Chlorine water :** Iodine is liberated, by the dropwise addition of chlorine water to iodide, and on addition of $CHCl_3$ violet coloured organic layer is obtained.

$$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$$

$$I_2 + \text{chloroform} \longrightarrow \text{violet coloured layer}.$$

(vi) **Copper sulphate solution :** Gives brown ppt. consisting of a mixture of copper (I) iodide & iodine and on addition of hypo solution brown ppt changes to white ppt.

$$4I^- + 2Cu^{2+} \longrightarrow 2CuI + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

(vii) **Mercury (II) chloride solution :** Forms scarlet ppt. of HgI_2

$$2I^- + HgCl_2 \longrightarrow HgI_2\downarrow + 2Cl^-.$$

This ppt. dissolves in excess of KI, forming tetraiodo mercurate (II) complex.

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

4. **Nitrate (NO_3^-):**

(i) **Conc H_2SO_4 :** Gives reddish – brown vapours of nitrogen dioxide

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

The following tests are performed with the salt solution.

(ii) **Brown ring test :** When a freshly prepared solution of iron (II) sulphate is added to nitrate solution & conc. H_2SO_4 is poured slowly down the side of the test - tube, a brown ring is obtained.

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

$$Fe^{2+} + NO\uparrow \rightarrow [Fe(NO)]^{2+}$$

On shaking and warming the mix, the brown colour disappears, nitric oxide is evolved and a yellow solution of Iron (III) ions remains.

Action of heat : The result varies with the metal

1. Nitrates of sodium and potassium evolve oxygen (test with glowing splint) & leave solid nitrites (brown fumes with dilute acid)

   $$2NaNO_3 \longrightarrow 2NaNO_2 + O_2\uparrow.$$

2. Ammonium nitrate yields dinitrogen oxide & steam

   $$NH_4NO_3 \longrightarrow N_2O\uparrow + 2H_2O.$$

3. Nitrates of the noble metals leave a residue of the metal and a mix of nitrogen dioxide and oxygen is evolved.

   $$2AgNO_3 \longrightarrow 2Ag + 2NO_2\uparrow + O_2\uparrow$$

4. Nitrates of other metals, such as those of lead and copper, evolve oxygen and nitrogen dioxide and leave a residue of the oxide.

   $$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2\uparrow + O_2\uparrow.$$

Class B (i) Precipitation reaction : SO_4^{2-}

(ii) Oxidation and reduction in solution - CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-

1. Sulphate (SO_4^{2-}) :

All sulphates except those of Ba, Pb, Sr are soluble in water. Sulphates of calcium and mercury (II) are slightly soluble. The following tests are performed with the salt solution.

(i) Barium chloride solution : White ppt. of barium sulphate $BaSO_4$ insoluble in warm dil. hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, conc. hydrochloric acid.

$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4 \downarrow$$

(ii) Mercury (II) nitrate solution : Gives yellow ppt. of basic mercury (II) sulphate.

$$SO_4^{2-} + 3Hg^{2+} + 2H_2O \rightarrow HgSO_4.2HgO \downarrow + 4H^+$$

2. Chromate CrO_4^{2-} and Dichromate ($Cr_2O_7^{2-}$) :

Metallic chromates gives yellow solution when dissolved in water. In the presence of H^+ chromates are converted into dichromates (orange-red solution).

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

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

It may also be expressed as :

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

(i) Barium chloride solution : Pale - yellow ppt. of barium chromate soluble in dilute mineral acids but insoluble in water and acetic acid.

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

Dichromate ions also gives the same ppt. but due to the formation of strong acid precipitation is partial.

$$Cr_2O_7^{2-} + 2Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4 \downarrow + 2H^+$$

If sodium hydroxide or sodium acetate is added, precipitation becomes quantitative.

(ii) Silver nitrate solution : Brownish- red ppt. of silver chromate Ag_2CrO_4 which is soluble in dil. nitric acid & in ammonia solution but is in soluble in acetic acid.

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

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

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

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

A reddish brown ppt. of silver dichromate $Ag_2Cr_2O_7$ is formed with a conc. solution of a dichromate.

$$Cr_2O_7^{2-} + 2Ag^+ \longrightarrow Ag_2Cr_2O_7$$

(iii) Lead acetate solution : Yellow ppt. of lead chromate $PbCrO_4$ insoluble in acetic acid, but soluble in dil nitric acid

$$CrO_4^{2-} + Pb^{2+} \longrightarrow PbCrO_4 \downarrow .$$

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

(iv) H_2O_2 : If an acidic solution of a chromate is treated with H_2O_2 a deep blue solution of chromium penta oxide is obtained.

$$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow CrO_5 + 3H_2O$$

CrO_5 is unstable and it decomposes yielding oxygen and a green solution of a Cr^{+3} Salt.

3. Permanganate MnO_4^- :

(i) Hydrogen peroxide : It decolourises acidified potassium permanganate solution

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 5O_2 \uparrow + 2Mn^{2+} + 8H_2O$$

(ii) Iron (II) sulphate, in the presence of sulphuric acid, reduces permanganate to manganese (II). The solution becomes yellow because of the formation of iron (III) ions

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(iii) Action of heat : On heating, a residue of potassium manganate K_2MnO_4 and black manganese dioxide remains behind. Upon extracting with water and filtering, a green solution of potassium manganate is obtained.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2 \uparrow .$$

Exercise 1 : (i) How to distinguish between CO_3^{--} and SO_3^{--} ions?

(ii) A gas turns red litmus paper into blue and forms white fume with HCl, identify the gas

Classification of Cations:

For the purpose of systematic qualitative analysis, cations are classified into five groups on the basis of their behaviour with some reagents and classification is based on whether a cation reacts with these reagents by the formation of precipitate or not (solubility difference)

Group reagent : Hydrocholoric acid, hydrogen sulphide, ammonium sulphide and ammonium carbonate.

Group	Group Reagent	Ions	Colour & Ppt.
Group I	dil HCl	Pb^{2+}, Hg_2^{+2} , Ag^+	$PbCl_2$, Hg_2Cl_2, AgCl white
Group II Group II A	H_2S in dil HCl	Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}	Yellow – CdS, As_2S_3, As_2S_5, SnS_2
Group II B		As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+} Sn^{4+}	Black – HgS, CuS, PbS Orange - Sb_2S_3, Sb_2S_5 Brown - Bi_2S_3, SnS
Group III A	NH_4OH in presence of NH_4Cl	Fe^{3+}, Al^{3+}, Cr^{3+}	$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ Brown White Green
Group III B	H_2S in presence of NH_3 & NH_4Cl or NH_4S .	Ni^{2+}, Co^{+2}, Mn^{+2}, Zn^{+2s}	ZnS - white or grey, Black - CoS, NiS MnS-Buff (light pink)
Group IV	$(NH_4)_2CO_3$ in presence of NH_4Cl & NH_4OH	Ba^{+2}, Sr^{2+}, Ca^{+2}	$BaCO_3$, $SrCO_3$, $CaCO_3$ - white
Group V	No common group reagent.	Mg^{+2}, Na^+, K^+, NH_4^+	–

Points to Remember

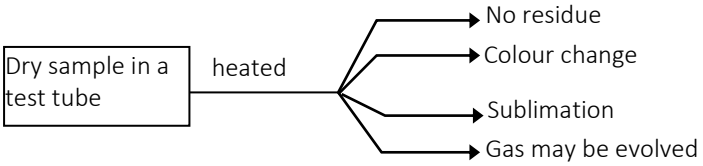
Dry Tests For Basic Radicals

All dry tests are preliminary tests because in most cases the proper oxidation state of the metal ion cannot be predicted in the original sample. The important dry tests carried out for identification of basic radicals is an unknown salt are described as follows.

Heating effects on the dry sample

The sample powder is taken in a dry test tube and heated slowly with Bunsen burner. The following observations are recorded with respect to

1. Residue 2. Colour change 3. Sublimation 4. Gas evolved



Residue

If no residue is obtained, then the cation present in the salt is not a metal ion. In general, salts of non-metallic cations such as NH_4^+ or PH_4^+ may be present.

Colour change

Most of the colour changes on heating are associated with the removal of water of crystallization or with the formation of f-centres under hot conditions. For example,

1. $\underset{\text{cold}}{ZnO(\text{white})} \underset{\text{cooled}}{\overset{\text{heated, }\Delta}{\rightleftharpoons}} \underset{\text{hot}}{ZnO\ (\text{yellow})}$

2. $\underset{\text{blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\Delta} \underset{\text{white}}{CuSO_4}$

3. $\underset{\text{pink}}{CoCl_2.6H_2O} \xrightarrow[-6H_2O]{\Delta} \underset{\text{blue}}{CoCl_2}$

Sublimation

1. White sublimates are given by $HgCl_2$, Hg_2Cl_2, As_2O_3, Sb_2O_3 and NH_4X (where X = Cl, Br, I). These white sublimates are distinguished by the following procedure. Dilute HCl is added to the white sublimate and H_2S gas is passed through the solution to obtain a precipitate. The different colours of the precipitates obtained correspond to different basic radicals which are described below.

Salt	Colour of the precipitate	Formula of the precipitate
$HgCl_2$	Black	HgS
Hg_2Cl_2	Black	Hg + HgS
As_2O_3	Yellow	As_2S_3
Sb_2O_3	Orange	Sb_2S_3
NH_4X	No reaction	

Reactions involved :

$$HgCl_2 + S^{2-} \rightarrow \underset{\text{black ppt.}}{HgS\downarrow} + 2Cl^-$$

$$Hg_2^{2+} \rightarrow Hg\downarrow + Hg^{2+} \xrightarrow{H_2S} \underbrace{Hg\downarrow + HgS\downarrow + 2H^+}_{\text{black ppt.}}$$

For M = As, Sb

$$M_2O_3 + 6HCl \rightarrow 2MCl_3 + 3H_2O$$

$$2M^{3+} + 3S^{2-} \rightarrow M_2S_3\downarrow$$

The above two black precipitates are also well distinguished when they are treated with Na_2S solution.

$$HgS + Na_2S \rightarrow \underset{\substack{\text{colourless}\\ \text{soluble complex}}}{[HgS_2]^{2-}} + 2Na^+$$

$$(Hg + HgS) + Na_2S \rightarrow \underset{\text{black ppt.}}{Hg\downarrow} + \underset{\substack{\text{colourless}\\ \text{soluble}\\ \text{complex}}}{[HgS_2]^{2-}} + 2Na^+$$

2. Coloured sublimates are indicative of the nature of basic radical described as follows.

a. If black : HgS (known as vermillion) or Hg_2S.

b. If yellow : HgI_2 and As_2S_3.

We can further distinguish between HgI_2 and As_2S_3 by the following procedure. On application of mechanical stress:

(i) If the yellow sublimate turns red, it indicates the presence of HgI_2.

(ii) No change in the sublimate shows the presence of As_2S_3.

This behaviour can be explained on the basis of changes shown in fig.

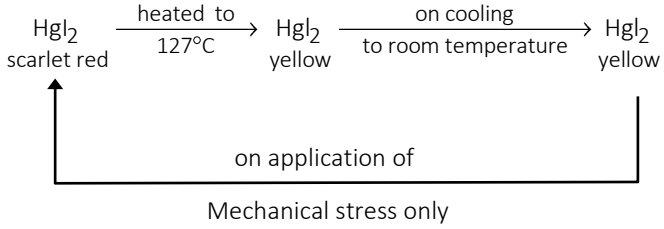


Fig. Changes during application of mechanical stress on the yellow sublimate.

Gas evolved

The evolved gas can be recognized based on its characteristic properties and is indicative of the nature of the acid radical present in the salt.

1. $CO_2 \Rightarrow$ Certain carbonates or organic materials are present.
2. $SO_2 \Rightarrow$ Sulphite, thiosulphates or sulphides may be present.
3. $Cl_2 \Rightarrow$ Certain chlorides may undergo thermal decomposition.
4. $Br_2 \Rightarrow$ Certain bromides may undergo thermal decomposition.
5. $I_2 \Rightarrow$ Certain iodides may undergo thermal decomposition.
6. $NO_2 \Rightarrow$ Decomposition of nitrates.
7. $CO \Rightarrow$ Decomposition of formats or oxalates.

Flame test

In the flame test, a platinum wire or glass rod is first dipped into concentrated HCl and then into a little of substance to be tested. It is then introduced into the lower oxidizing zone of the flame, and the imparted colour to the flame is observed. The different colours of the flame corresponding to different basic radicals are described below.

Metal	Colour observed
Na^+	Goden yellow flame
K^+	Violet (liac) flame
Li^+	Carmine red flame
Ca^{2+}	Brick red flame
Sr^{2+}	Crimson red flame
Ba^{2+}	Apple green flame
Cu^{2+} / borate	Green flame

When **Na^+ and K^+ are present together**, the yellow colouration of sodium flame masks that of potassium. To confirm the presence of potassium under this condition, repeat the test through double blue glass and observe the flame colour again. The colours observed are described below.

Metal	Colour of the flame with naked eye	Colour of the flame through double blue (cobalt) glass
Na^+	Golden yellow	Flame disappears
K^+	Violet (lilac)	Crimson red flame
$Na^+ + K^+$	Golden yellow	Crimson red flame

Note: Be^{2+} and Mg^{2+} do not impart any colour to the flame due to their high ionization energy.

Borax bead test

Borax powder is taken in a hot platinum wire loop and held in the hottest part of the flame; the borax powder swells up due to the loss of water of crystallization and shrinks upon the loop forming a transparent, colourless glassy bead which consists of sodium metaborate and boric anhydride

$$Na_2B_4O_7.10\,H_2O \xrightarrow[-10H_2O]{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy bead}}$$

Hot bead is touched on the salt sample, heated again and the colour of the bead is observed

$$MO + B_2O_3 \rightarrow M(BO_2)_2$$

The different colours observed with different metals are given in table.

Table : Colour of borax beads for different metals

Metal	Oxidizing flame		Reducing flame	
	Hot	**Cold**	**Hot**	**Cold**
Cr	Yellow	Green	Green	Green
Mn	Violet	Violet	Colourless	Colourless
Fe	Yellowish brown	Yellow	Green	Green
Co	Blue	Blue	Blue	Blue
Ni	Violet	Reddish brown	Grey	Grey
Cu	Green	Blue	Colourless	Opaque*

*This opacity is due to red colour metallic copper deposition.

Note: (i) Borax bead test is performed only for coloured salt samples.
(ii) The swelling characteristic is due to the loss of water of crystallization, but it is not mandatory that all compounds having water of crystallization will show swelling characteristic.
(iii) Alums also show swelling characteristic, but on strong heating they are converted into amorphous powder unlike the glassy bead in case of borax.

Sodium carbonate bead test

Small quantity of Na_2CO_3 powder is heated in platinum wire loop in the Bunsen flame, and a white, opaque bead is formed. Hot bead is dipped into a little KNO_3 powder and then into a sample powder and heated again.

Observation:

1. If green bead is formed, presence of manganese compound is confirmed.

$$MnO + Na_2CO_3 + O_2 \rightarrow \underset{\text{green bead}}{Na_2MnO_4} + CO_2 \uparrow$$

2. If yellow bead is formed, presence of chromium compound is confirmed.

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2 \uparrow$$

For all kinds of bead tests, the oxidation state of the metal ion in the original sample cannot be predicted.

1. Group I radicals (Ag^+, Pb^{+2}, Hg_2^{2+}) are precipitated as chlorides because the solubility product of these chlorides ($AgCl, PbCl_2, Hg_2Cl_2$) is less than the solubility products of all other chlorides which remain in solution.
2. Group II radicals are precipitated as sulphides because sulphides of other metals remain in solution because of their high solubility products, HCl acts as a source of H^+ and thus decreases the conc. of S^{2-} due to common ion effect. Hence decreased conc. of S^{2-} is only sufficient to precipitate the Group II radicals only.
3. Group III A radicals are precipitated as hydroxides and the NH_4Cl suppresses the ionisation of NH_4OH so that only the group III A radicals are precipitated because of their low solubility product.

Note :

(i) Excess of NH_4Cl should be added otherwise manganese will be ppt. as $MnO_2.H_2O$.

(ii) $(NH_4)_2SO_4$ can't be used in place of NH_4Cl because the SO_4^{2-} will ppt. barium as $BaSO_4$.

(iii) NH_4NO_3 can't be used in place of NH_4Cl because NO_3^- ions will oxidise Mn^{2+} to Mn^{2+} and thus $Mn(OH)_3$ will be precipitated in III A group.

(iv) Only $Al(OH)_3$ is soluble in excess of NaOH followed by boiling to form sodium metaluminate while $Fe(OH)_3$ and $Cr(OH)_3$ are insoluble.

4. Ammonium hydroxide increases the ionisation of H_2S by removing H^+ from H_2S as unionised water

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

Now excess of S^{2-} ions are available and hence the ionic product of hydroxides of Group III B exceed their solubility product and ppt. will be obtained. In case H_2S is passed through a neutral solution, incomplete precipitation will take place due to the formation of HCl which decreases the ionization of H_2S .

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

Identification of Basic Radicals (WET TEST For Basic Radicals)

All confirmatory tests for basic radicals are performed with the salt solution.

1. Group I (Pb^{2+}, Ag^+, Hg^+)

(a) $PbCl_2$ gives a yellow ppt. with K_2CrO_4 . The ppt. is insoluble in acetic acid but soluble in NaOH

$$Pb(NO_3)_2 + K_2CrO_4 \rightarrow \underset{\text{Yellow ppt.}}{PbCrO_4 \downarrow} + 2KNO_3$$

$$PbCrO_4 + 4NaOH \rightarrow Na_2[PbO_2] + Na_2CrO_4 + 2H_2O$$

(b) $$Pb(NO_3)_2 + 2KI \rightarrow \underset{\text{(Yellow)}}{PbI_2 \downarrow} + 2KNO_3$$

$$PbCl_2 + 2KI(\text{excess}) \rightarrow K_2[PbI_4]$$

2. AgCl is soluble in NH_4OH forming a complex while Hg_2Cl_2 forms a black ppt. with NH_4OH .

$$AgCl + 2NH_4OH \rightarrow Ag(NH_2)_2Cl + 2H_2O$$

$$Hg_2Cl_2 + 2NH_4OH \rightarrow \underset{\text{Amino mercuric Chloride}}{H_2N-Hg-Cl} + Hg\downarrow + NH_4Cl + 2H_2O$$

2. Group II A ($Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}$)

(i) Hg^{+2} ions in solution, on addition of $SnCl_2$, give white precipitate turning black.

$$2Hg^{+2} + SnCl \rightarrow Sn^{+4} + \underset{\text{White}}{Hg_2Cl_2 \downarrow}$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + \underset{\text{Black}}{2Hg \downarrow}$$

(ii) Cu^{+2} ions in solution gives a pale blue precipitate which gives a deep blue colour with excess of NH_4OH

$$Cu^{+2} + 4NH_4OH \rightarrow [Cu(NH_3)_4]^{+2} + 4H_2O$$

Deep blue in colour

Cu^{+2} ions give chocolate precipitate with $K_4Fe(CN)_6$.

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

(iii) Bi^{+3} ions in solution of HCl on addition of water give white cloudy precipitate.

$$BiCl_3 + H_2O \longrightarrow \underset{\text{White ppt.}}{BiOCl\downarrow} + 2HCl$$

When treated with sodium stannite a black ppt. is obtained.

$$2BiCl_3 + 3Na_2SnO_2 \longrightarrow \underset{\text{black}}{2Bi\downarrow} + 3Na_2SnO_3 + 6NaCl + 3H_2O$$

(iv) Cd^{+2} ions in solution, with ammonium hydroxide gives a white precipitate which dissolves.

$$Cd^{+2} + 2NH_4OH \longrightarrow \underset{\text{Yellow}}{Cd(OH)_2\downarrow} + 2NH_4^+$$

$$Cd(OH)_2 + 4NH_4OH \rightarrow [Cd(NH_3)_4](OH)_2$$

3. Group II B (As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+})

(v) As^{+3} ions in solution give yellow precipitate with ammonium molybadate and HNO_3.

$$As^{+3} \xrightarrow[\text{Oxidation}]{HNO_3} As^{+5} (\text{as } H_3AsO_4)$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow ppt.}}{(NH_4)_3AsMo_{12}O_{40}\downarrow} + 21NH_4NO_3 + 12H_2O$$

(vi) Sn^{2+} ions in solution as $SnCl_2$ give white ppt. with $HgCl_2$, which turns black on standing.

$$SnCl_2 + 2HgCl_2 \longrightarrow \underset{\text{White}}{SnCl_4 + Hg_2Cl_2\downarrow}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{Black}}{2Hg\downarrow}$$

(vii) Sb^{+3} ions in solution as $SbCl_3$, on addition of water give white precipitate.

$$SbCl_3 + H_2O \rightarrow \underset{\text{White}}{SbOCl\downarrow} + 2HCl$$

4. Group III A (Al^{3+}, Fe^{3+}, Cr^{3+})

(i) White precipitate of $Al(OH)_3$ is soluble in NaOH

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

(ii) Precipitate of $Cr(OH)_3$ is soluble in NaOH + Br_2 water and addition of $BaCl_2$ to this solution gives yellow precipitate.

$$Br_2 + H_2O \rightarrow 2HBr + (O)$$

$$2Cr(OH)_3 + 4NaOH + 3(O) \rightarrow 2Na_2CrO_4 + 5H_2O$$

$$Na_2CrO_4 + BaCl_2 \rightarrow \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow} + 2NaCl$$

$Fe(OH)_3$ is insoluble in NaOH

(iii) Brown precipitate of $Fe(OH)_3$ is dissolved in HCl and addition of KCNS to this solution gives blood red colour.

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$$

$$Fe(OH)_3 + 3HCl \rightarrow \underset{\text{blood red}}{Fe(CNS)_3} + 3KCl$$

Also on addition of $K_4Fe(CN)_6$ to this solution, a Prussian blue colour is obtained.

$$FeCl_3 + 3K_4Fe(CN)_6 \rightarrow \underset{\text{prussian blue colour}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

5. Group III B (Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+})

(i) Ni^{2+} and Co^{2+} ions in solution, on addition of $KHCO_3$ and Br_2 water give apple green colour if Co^{+2} is present and black precipitate if Ni^{+2} is present.

$$CoCl_2 + 6KHCO_3 \rightarrow K_4[Co(CO_3)_3] + 2KCl + 3CO_2 \uparrow + 3H_2O$$

$$2K_4[Co(CO_3)_3] + 2KHCO_3 + [O] \rightarrow \underset{\text{Apple green colour}}{2K_3[Co(CO_3)_3]} + 2K_2CO_3 + H_2O$$

$$NiCl_2 + 2KHCO_3 \rightarrow NiCO_3 + 2KCl + H_2O + CO_2 \uparrow$$

$$2NiCO_2 + 4NaOH + [O] \rightarrow \underset{\text{Black ppt.}}{Ni_2O_3 \downarrow} + 2Na_2CO_3 + 2H_2O$$

(ii) Zn^{+2} ions in solution give a white precipitate with NaOH, which dissolves in excess of NaOH.

$$Zn^{+2} + 2NaOH \rightarrow \underset{\text{White}}{Zn(OH)_2 \downarrow} + 2Na^+$$

$$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$$

(iii) Mn^{+2} ions in solution give pink precipitate with NaOH turning black or brown on heating.

$$Mn^{+2} + 2NaOH \longrightarrow \underset{\text{Pink}}{Mn(OH)_2} + 2Na^+$$

$$Mn(OH)_2 + [O] \xrightarrow{\Delta} \underset{\text{Brown or black}}{MnO_2} + H_2O$$

6. Group IV (Ba^{2+}, Sr^{2+}, Ca^{2+})

(i) Ba^{2+} ions in solution give

(a) Yellow precipitate with K_2CrO_4

$$Ba^{+2} + K_2CrO_4 \rightarrow \underset{\text{Yellow}}{BaCrO_4 \downarrow} + 2K^+$$

(b) White precipitate with $(NH_4)_2SO_4$

$$Ba^{+2} + (NH_4)_2SO_4 \rightarrow \underset{\text{White}}{BaSO_4 \downarrow} + 2NH_4^+$$

(c) White precipitate with $(NH_4)_2C_2O_4$

$$Ba^{+2} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{White}}{BaC_2O_4 \downarrow} + 2NH_4^+$$

(ii) Sr^{+2} ions give white precipitate with $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$

$$Sr^{+2} + (NH_4)_2SO_4 \rightarrow \underset{\text{White ppt.}}{SrSO_4 \downarrow} + 2NH_4^+$$

$$Sr^{+2} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{White}}{SrC_2O_4 \downarrow} + 2NH_4^+$$

(iii) Ca^{+2} ions give white precipitate with $(NH_4)_2C_2O_4$ only.

$$Ca^{+2} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{White}}{CaC_2O_4 \downarrow} + 2NH_4^+$$

7. Group V (NH_4^+, Na^+, K^+, Mg^{+2})

(i) All ammonium salts on heating with alkali say NaOH give a colourless, pungent smelling gas (NH_3).

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

(a) Gas evolved gives white fumes with a rod dipped in conc. HCl

$$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl \uparrow}$$

(b) Paper soaked in $CuSO_4$ solution, becomes deep blue due to complex formation with NH_3.

$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]SO_4}$$

(c) With $Hg_2(NO_3)_2$, a black colour is obtained

$$Hg_2(NO_3)_2 + 2NH_3 \longrightarrow \underset{\text{black}}{Hg \downarrow} + Hg(NH_2)NO_3 \downarrow + NH_4NO_3$$

(d) An aqueous solution of an ammonium gives a brown ppt. with Nessler's reagent (alkaline solution of potassium tetraiodomercurate(II).

$$NH_4Cl + 2K_2HgI_4 + 3KOH \rightarrow O\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}Hg \\ \\ Hg\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix}NH_2I + 4KI + 2H_2O + 3\,NaI$$

(Brown)
(Iodide of Millon's base)

(ii) Potassium salts give a yellow ppt. with sodium cobaltinitrite

$$Na_3[Co(NO_2)_6] + 3KCl \longrightarrow \underset{\text{Yellow}}{K_3[Co(NO_2)_6]} + 3NaCl$$

(iii) Sodium salts give a heavy white ppt. with potassium dihydrogen antimonate

$$KH_2SbO_4 + NaCl \longrightarrow \underset{\text{White ppt.}}{NaH_2SbO_4\downarrow} + KCl$$

(iv) Mg^{2+} gives white ppt. of magnesium hydroxide with sodium hydroxide

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

The ppt. obtained is sparingly soluble in water but readily soluble in ammonium salt.

Problem 1: An aqueous solution of gas (X) shows the following reactions :-
(i) It turns red litmus blue.
(ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
(iii) On addition of $FeCl_3$ solution a brown ppt. soluble in dilute nitric acid is obtained.
Identify (X) and give equations for the reactions at step (ii) & (iii)

Solution: $X - NH_3$

Reactions :

(i) $CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{deep blue}}{Cu(NH_3)_4\,SO_4} + H_2O$

(ii) $FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3\downarrow} + 3NH_4Cl$

$$Fe(OH)_3 + 3HNO_3 \longrightarrow \underset{\text{Soluble}}{Fe(NO_3)_3} + 3H_2O$$

Problem 2 : An aqueous solution of a gas (X) gives the following reactions:
(i) It decolourizes an acidified $K_2Cr_2O_7$ solution.
(ii) On boiling with H_2O_2 , cooling it and then adding an aqueous solution of $BaCl_2$, a white ppt. insoluble in dilute HCl is obtained.
(iii) On passing H_2S into the solution, turnbidity is obtained.
Identify (X) and give equations for the steps (i), (ii), (iii).

Solution: $X - SO_2$

Reactions :

(i) $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_3)_3 + H_2O$

(ii) $SO_2 + H_2O \longrightarrow H_2SO_4$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{white ppt.}}{BaSO_4\downarrow} + 2HCl$$

(iii) $SO_2 + 2H_2S \longrightarrow \underset{\substack{\text{white}\\ \text{turbidity}}}{3S\downarrow} + 2H_2O$

Problem 3 : A white amorphous powder (A) on strongly heating gives a colourless non-combustible gas (B) and solid (C). The gas (B) turns lime water milky and turbidity disappears with the passage of excess of gas. The solution of (C) in dilute HCl gives a white ppt. with an aqueous solution of $K_4[Fe(CN)_6]$. The solution of (A) in dilute HCl gives a white ppt. (D) on passing H_2S in presence of excess of NH_4OH . Identify (A) to (D) by giving chemical equations.

Solution : (A) - $ZnCO_3$ (B) - CO_2 (C) - ZnO (D) – ZnS

Reactions :

(i) $\underset{(A)}{ZnCO_3} \rightarrow \underset{(C)}{ZnO} + \underset{(B)}{CO_2}$

(ii) $\underset{(B)}{CO_2} + Ca(OH)_2 \rightarrow \underset{\text{White}}{CaCO_3} + H_2O$

$$CaCO_3 + H_2O + CO_2 \rightarrow \underset{\text{Excess}\quad\text{Soluble}}{Ca(HCO_3)_2}$$

(iii) $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$$2ZnCl_2 + K_4Fe(CN)_6 \rightarrow \underset{\text{White ppt.}}{Zn_2[Fe(CN)_6]} + 4KCl$$

(iv) $ZnCl_2 + H_2S \rightarrow \underset{(D)}{ZnS} + 2HCl$

Problem 4: A certain compound (X) is used in laboratory for analysis. Its aq. Solution gave the following reactions.
(i) On addition to copper sulphate solution, a brown ppt. is obtained which turns white on addition of excess of $Na_2S_2O_3$ solution.

(ii) On addition to Ag^+ ion solution, a yellow ppt. is obtained which is insoluble in NH_4OH. Identify (X), giving reactions

Solution: X- KI

Reactions: (i) $2CuSO_4 + 2KI \longrightarrow 2CuI_2 + K_2SO_4$

$2CuI_2 \longrightarrow \underset{\text{White}}{Cu_2I_2} + I_2$

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

(ii) $Ag^+ + KI \longrightarrow \underset{\text{Yellow ppt.}}{AgI} + K^+$

The white ppt. of Cu_2I_2 is coloured brown due to the presence of I_2. On adding sodium thiosulphate, I_2 is consumed. Therefore the ppt. appears white.

Problem 5: An aqueous solution of inorganic compound (X) gives the following reactions:
(i) With an aq. Solution of barium chloride a ppt. insoluble in dil. HCl is obtained.
(ii) Addition of excess of KI gives a brown ppt. which turns on addition of excess of hypo.
(iii) With an aqueous solution of $K_4[Fe(CN)_6]$ a chocolate coloured ppt. is obtained.
Identify (X) and give equations for the reactions for (i), (ii) and (iii) observations.

Solution: $X - CuSO_4$

Reactions: (i) $CuSO_4 + BaCl_2 \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(insoluble in HC(I)}}}{BaSO_4} + CuCl_2$

(ii) $2CuSO_4 + 4KI \longrightarrow 2CuI_2 \downarrow + 2K_2SO_4$

$Cu_2I_2 + I_2$

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

(iii) $CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Chocolate}\\ \text{Coloured ppt.}}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$

Problem 6: An aq. Solution of an inorganic compound (X) shows the following reactions.
(i) It decolorizes an acidified $KMnO_4$ solution accompanied with evolution of O_2.
(ii) It liberates I_2 from acidified KI solution.
(iii) It gives brown ppt. with alkaline $KMnO_4$ solution with evolution of O_2.
(iv) It is used to restore old oil paintings. Identify (X) and give chemical reactions for the steps (i) to (iv).

Solution: $X - H_2O_2$

Reactions: (i) $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(ii) $H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 \uparrow K_2SO_4 + 2H_2O$

(iii) $3H_2O_2 + 2KMnO_4 \longrightarrow 2MnO_2 \downarrow + 2KOH + 3O_2 + 2H_2O$

(iv) $4H_2O_2 + PbS \longrightarrow \underset{\text{white}}{PbSO_4} + 4H_2O$

Problem 7: A certain compound (X) shows the following reactions:
(i) When KI is added to an aq. Suspension of (X) containing acetic acid, iodine is liberated
(ii) When CO_2 is passed through an aq. Suspension of (X) the turbidity transforms to a ppt.
(iii) When a paste of (X) in water is heated with ethyl alcohol a product of anaesthetic use is obtained.
Identify (X) and write down chemical equation for reactions involved in steps (i), (ii) and (iii).

Solution: $X - CaOCl_2$

Reactions: (i) $CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + Cl_2 + H_2O$

$2KI + Cl_2 \longrightarrow 2KCl + I_2$

(ii) $CaOCl_2(aq) + CO_2 \longrightarrow \underset{\text{white ppt.}}{CaCO_3} + Cl_2$

(iii) $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

$C_2H_5OH + Cl_2 \longrightarrow CH_2CHO + 2HCl$

$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO \xrightarrow{Ca(OH)_2} \underset{\text{Anaesthetic}}{CHCl_3}$

Problem 8: An inorganic Lewis acid (X) shows the following reactions :

(i) It fumes in moist air,

(ii) The intensity of fumes increases when a rod dipped in NH_4OH is brought near it.

(iii) An acidic solution of (X) on addition of NH_4Cl and NH_4OH gives a precipitate which dissolves in NaOH solution.

(iv) An acidic solution of (X) does not give a precipitate with H_2S . Identify (X) and give chemical equation for steps (i) to (iii).

Solution: $X - AlCl_3$

Reactions:

(i) $AlCl_3 + 3H_2O \rightarrow \underset{\text{fumes}}{Al(OH)_3} + 3HCl\uparrow$

(ii) $HCl + NH_4OH \rightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow} + H_2O$

(iii) $AlCl_3 + 3NH_4OH \rightarrow \underset{\text{White ppt.}}{Al(OH)_3} + 3NH_4Cl$

$Al(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$

Problem 9: (i) A black mineral (A) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (B) and (C).

(ii) The solution of (B) on reaction with zinc gives a precipitate of metal (D).

(iii) (D) is dissolved in dil. HNO_3 and the resulting solution gives a white precipitate (E) with dil. HCl.

(iv) (E) on fusion with sodium carbonate gives (D).

(v) (E) dissolves in aqueous solution of ammonia giving a colourless solution of (F). Identify (A) to (F) and give chemical equations for reactions involved in steps (i) to (v).

Solution: (A) - Ag_2S (B) - $NaAg(CN)_2$

(C) - Na_2SO_4 (D) Ag

(E) AgCl (F) - $Ag(NH_3)_2Cl$

Reactions:

(i) $\underset{(A)}{Ag_2S} + 4NaCN + 2O_2 \rightarrow \underset{(B)}{2NaAg(CN)_2} + \underset{(C)}{Na_2SO_4}$

(ii) $2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + \underset{(D)}{2Ag}$

(iii) $3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + \underset{HCl}{2H_2O}$

(iv) $AgNO_3 \longrightarrow AgCl + HNO_3$

(v) $\underset{(E)}{AgCl} + 2NH_3 \rightarrow \underset{(F)}{Ag(NH_3)_2Cl}$

(vi) $4AgCl + 2Na_2CO_3 \rightarrow 4Ag + 4NaCl + 2CO_2 + O_2$

Problem 10: A solid laboratory reagent (A) gives the following reactions.

(i) It imparts green colour to flame.

(ii) Its solution does not give ppt. on passing H_2S .

(iii) When it is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 a red gas is evolved. The gas when passed in aq. NaOH solution turns it yellow. Identify (A) giving chemical reactions.

Solution: $A - BaCl_2$

Reactions:

(i) $2BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{red gas}}{2CrO_2Cl_2} + 2BaSO_4 + 3H_2O$

(ii) $CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\substack{\text{yellow}\\\text{solution}}}{Na_2CrO_4} + 2NaCl + 2H_2O$

Problem 11: NH_4SCN can be used to test one or more out of Fe^{3+}, Co^{2+}, Cu^{2+}

(A) Fe^{3+} only (B) Co^{2+}, Cu^{2+} (C) Fe^{3+}, Cu^{2+} (D) All

Solution: (D)

Problem 12: Ag_2S is soluble in NaCN due to formation of

(A) $Na[Ag(CN)_2]$ (B) $Ag(CN)_2$ (C) $Na_2Ag(CN)_3$ (D) $Na_2[Ag(CN)_2]$

Solution: (A)

Problem 13: There is foul smell in presence of moisture with

(A) $AlCl_3$ (B) $Al_2(SO_4)_3$ (C) FeS (D) $FeSO_4$

Solution: (C)

Problem 14: $AgNO_3$ on treatment with hypo gives white ppt. changing to black after some time. Black ppt. is

(A) $Ag_2S_2O_3$ (B) Ag_2SO_4 (C) $Ag_2S_4O_6$ (D) Ag_2S

Solution:(D)

Problem 15: Yellow coloured solution of $FeCl_3$ changes to light green when

(A) $SnCl_2$ is added (B) Zn is added

(C) H_2S gas is passed (D) Any one of the above is added.

Solution:(D)

Problem 16: $Fe(OH)_3$ and $Cr(OH)_3$ precipitate are separated by

(A) $[Ag(NH_3)_2]^+$ (B) HCl (C) $NaOH/H_2O_2$ (D) H_2SO_4

Solution:(C)

Problem 17: Evolution of deep red vapours when an inorganic salt is mixed with powdered $K_2Cr_2O_7$ and heated with conc. H_2SO_4 confirms the presence of a

(A) chloride (B) fluoride (C) borate (D) phosphate

Solution:(A)

Problem 18: Which of the following would enable you to remove SO_4^{2-} ions from a mixture of SO_4^{2-}, $C_2O_4^{2-}$ and Cl^- ions ?

(A) NaOH (B) KOH (C) $Ba(OH)_2$ (D) $BaSO_4$

Solution:(C)

Problem 19: Which of the following sulphates is insoluble in water?

(A) $CuSO_4$ (B) $CdSO_4$ (C) $PbSO_4$ (D) $Bi(SO_4)_3$

Solution:(C)

Problem 20: A fire work gave bright crimson light. It probably contained a salt of

(A) Ca (B) Sr (C) Ba (D) Mg

Solution:(B)

GROUP I

Group Reagent : dil. HCl

Cations : Pb^{2+}, Hg_2^{2+}, Ag^+

Observation : White insoluble chloride precipitated out

Confirmatory Tests

REAGENT	Pb^{2+}	Hg_2^{2+}	Ag^+
Dilute HCl	White ppt. of $PbCl_2$ which is soluble in excess forming $[PbCl_4]^{2-}$	White ppt. of Hg_2Cl_2 which gives grey ppt. of $Hg(NH_2)Cl + Hg$ with ammonia; Hg_2Cl_2 is soluble in aqua regia	White ppt. of AgCl soluble in excess HCl, ammonia, KCN and hypo and also decomposes in the presence of UV light
H_2S	Black ppt. of PbS; In excess Cl^-, red ppt. of Pb_2SCl_2 which on dilution gives black PbS which turns white in H_2O_2, dissolves in HNO_3 and $AcONH_4$	Black ppt. of $HgS + Hg$ that dissolves in aqua regia and Na_2S forming $[HgS_2]^{2-}$ which gives HgS again with H^+.	Black ppt. of Ag_2S that is soluble in hot conc. HNO_3 but not in YAS, KCN and hypo.
NH_4OH	White ppt. of $Pb(OH)_2$ that is insoluble in excess	Grey ppt. of $Hg + HgO.Hg(NH_3)NO_3$	Brown ppt. of Ag_2O that is soluble in excess giving $Ag(NH_3)^{2+}$
NaOH	White ppt. of $Pb(OH)_2$ that dissolves in excess giving $Pb(OH_4)^{2-}$ which forms black PbO_2 with OA	Black ppt. of Hg_2O that turns to grey $HgO + Hg$ on boiling.	Brown ppt. of Ag_2O that is insoluble in excess.
KI	Canary yellow PBI_2 that dissolves to given $[PbI_4]^{2-}$	Green ppt. of Hg_2I_2 that dissolves in KI and turns to read HgI_2 and grey Hg on	Yellow ppt. of AgI that is insoluble in ammonia but dissolves in KCN and hypo

		boiling	
K_2CrO_4	Yellow ppt. of $PbCrO_4$ soluble in HNO_3 and NaOH	Red ppt. of Hg_2CrO_4 that turns to black Hg_2O with NaOH	Red ppt. of Ag_2CrO_4 that dissolves in HNO_3 and ammonia
KCN	White ppt. of $Pb(CN)_2$ insoluble in excess KCN	White ppt. of $Hg(CN)_2$ soluble in excess KCN	White ppt. of AgCN soluble in excess KCN
Na_2HPO_4	Ppt. of white phosphate	White ppt. of hydrogen phosphate	Ppt. of white phosphate
Na_2CO_3	White ppt. of BASIC lead carbonate	Yellow ppt. of Hg_2CO_3 that turns to black HgO and grey Hg	Yellow ppt. of Ag_2CO_3 that turns to brown Ag_2O then grey Ag
H_2SO_4	White ppt. of $PbSO_4$ that is insoluble in excess but dissolves in $AcONH_4$	White ppt. of $HgSO_4$ and SO_2 gas evolved	White ppt. of Ag_2SO_4 and SO_2 gas evolved
$SnCl_2$	-	Grey ppt of Hg	-
Na_2SO_3	White ppt of $PbSO_3$ which is less soluble than $PbSO_4$	-	
KCN	White of $Pb(CN)_2$ which is insoluble in excess	Grey ppt of Hg and $Hg(CN)_2$	White ppt which is soluble in excess of KCN
$Na_2S_2O_3$	White ppt of PbS_2O_3 soluble in excess of reagent. On boiling black ppt of PbS	-	White ppt of thiosulphate which is soluble in excess of reagent. On heating Ag_2S is formed.

Note:

	AgCl	AgBr	AgI	Soluble Ag^+
In NH_3	Soluble	Partially Soluble	Insoluble	Soluble
In KCN	Soluble	Soluble	Soluble	Soluble
In Hypo	Soluble	Soluble	Soluble	Soluble

GROUP II [A]

Group Reagent : dil. $HCl + H_2S$ gas

Cations : Hg^{2+}, Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Fe^{2+},

Observation: Sulphides precipitated out that are insoluble in YAS. [HgS, PbS, CuS, Bi_2S_3, FeS are black while Cds is yellow]

REAGENT	Hg^{2+}	Cu^{2+}	Bi^{3+}	Cd^{2+}	Fe^{2+}
Ammonia	Black ppt of $HgO.NH_2.NO_3$	Blue ppt. of $Cu(OH)_2$ that dissolves in excess giving $[Cu(NH_3)_4]^{2+}$	White ppt. of $[Bi(OH)_2]^+$ that in insoluble in excess ammonia	White ppt. of $Cd(OH)_2$ that disappears on adding excess ammonia	Green ppt. of $Fe(OH)_2$ is seen but disappears on adding excess ammonia
NaOH	Yellow ppt. of HgO that is insoluble in excess but dissolves in acids	Blue ppt. of $Cu(OH)_2$ that in insoluble in excess and turns to black CuO on heating	White ppt. of $Bi(OH)_3$ that turns to yellow BiO.OH of BiO_3^{3-}.BiO.OH convert to yellowish brown BiO_3^-	White ppt. of $Cd(OH)_2$ that is insoluble in excess	Green ppt. of $Fe(OH)_2$ which on exposure to air gets oxidized to $Fe(OH)_3$

KCN	No ppt. observed	Yellow ppt. of $Cu(CN)_2$ which turns to white CuCN and dissolves in excess giving $K_3Cu(CN)_4$	-	White ppt. of $Cd(CN)_2$ which dissolves in excess giving unstable $K_2Cd(CN)_4$	Yellow ppt. of $Fe(CN)_2$ which dissolves in excess giving $K_4Fe(CN)_6$
KI	Red ppt. of HgI_2 that dissolves in excess forming K_2HgI_4	White ppt. of Cu_2I_2 that dissolves in excess giving $K_3[CuI_4]$; solution becomes dark brown due to KI_3	Black ppt. of BiI_3 that dissolves in excess giving orange $[BiI_4]$ and hydrolyses to BiOI	No ppt. observed	
$Co(SCN)_2$ or NH_4SCN	Deep blue ppt of $Co[Hg(SCN)_4]$	Black ppt. of $Cu(SCN)_2$. It decomposes slowly to white ppt of CuSCN	-	-	No colouration

<u>Special Tests for Group II [A] Cations</u>

1. Ferrous $[Fe^{2+}]$ ion

(a) With $K_4Fe(CN)_6$, bluish-white ppt. of $K_2Fe[Fe(CN)_6]$.

(b) With $K_3Fe(CN)_6$, Turnbull's Blue $Fe_3[Fe(CN)_6]_2$

(c) With Hypo: No color with pure Fe^{2+}

2. Cadmium $[Cd^{2+}]$ ion

(a) With $K_4Fe(CN)_6$, bluish-white ppt. of $Cd_2[Fe(CN)_6]$.

3. Bismuth $[Bi^{3+}]$ ion

(a) With alkaline Na_2SnO_2 , black Bi metal is obtained.

(b) Excessive dilution is a Bi salt of a strong acid leads to ppt. of white oxy-salt of Bi .

(c) Bright orange solution of $(CrO_4)-Bi-O-Bi-(CrO_4)$

4. Cupric $[Cu^{2+}]$ ion

(a) Black ppt. of $Cu(SCN)_2$ with KSCN

(b) With $K_4Fe(CN)_6$ in acidic medium, chocolate brown ppt. of $Cu_2[Fe(CN)_6]$

5. Mercuric $[Hg^{2+}]$ ion

(a) Black ppt. of HgS is soluble in aqua regia but not in conc. HNO_3

(b) With $SnCl_2$, white ppt. of Hg_2Cl_2 that turns to grey Hg in excess.

(c) With $Co(SCN)_2$, deep blue ppt. of $Co[Hg(SCN)_4]$

DMG Test:

(a) **With Fe^{2+}** : Soluble red iron (II) dimethylglyoxime in ammoniacal solution.

(b) **With Fe^{3+}** : No colouration

(c) **With Bi^{3+}** : Yellow ppt in ammoniacal solution.

(d) **With Co^{2+}** : Brown colouration in ammoniacal solution.

(e) **With Ni^{2+}** : Red ppt in ammoniacal solution.

(f) **With Cu^{2+}** : Black or Blue in ammoniacal solution.

GROUP II [B]

Group Reagent : dil. $HCl + H_2S$ gas

Cations : As^{3+}, SN^{2+}, Sb^{3+}, Sn^{4+}

Observation: Sulphides precipitated out that are soluble in YAS. [As_2S_3 is yellow and forms As_2S_5, Sb_2S_3 is organge and forms Sb_2S_5, SnS in brown while SnS_2 is yellow]

REAGENT	As^{3+} As AsO_3^{3-}	As^{5+} As AsO_4^{3-}
Dil $HCl + H_2S$	As_2S_3 is yellow is insoluble in conc HCl but soluble in conc HNO_3, Alkali, Ammonia, $(NH_4)_2S$ and YAS $3As_2S_3 + 28HNO_3 + 4H_2O \rightarrow 6AsO_4^{3-} + 9SO_4^{2-} + 36H^+ + 28NO\uparrow$ $As_2S_3 + 6OH^- \rightarrow AsO_3^{3-} + AsS_3^{3-} + 3H_2O$ $As_2S_3 + 3S^{2-} \rightarrow 2AsS_3^{3-}$ $2AsS_3^{3-} + 6H^+ \rightarrow As_2S_3\downarrow + 3H_2S\uparrow$ $As_2S_3\downarrow + 4S_2^{2-} \rightarrow 2As_2S_4^{3-} + S_3^{2-}$ $2AsS_4^{3-} + 6H^+ \rightarrow As_2S_5\downarrow + 3H_2S\uparrow$	As_2S_5 is yellow soluble in Alkali, NH_3, $(NH_4)_2S$ and YAS and in sod or amm Carbonate. $As_2S_5\downarrow + 6OH^- \rightarrow AsS_4^{3-} + AsO_3S^{3-} + 3H_2O$ $As_2S_5\downarrow + 3S^{2-} \rightarrow 2AsS_4^{3-}$ $As_2S_5\downarrow + 6S_2^{2-} \rightarrow 2AsS_4^{3-} + 3S_3^{2-}$ $As_2S_5\downarrow + 3CO_3^{2-} \rightarrow AsS_4^{3-} + AsO_3S^{3-} + 3CO_2$ $2AsS_4^{3-}\downarrow + 6H^+ \rightarrow As_2S_5\downarrow + 3H_3S\uparrow$
$AgNO_3$	Yellow ppt. of arsenite which is soluble in HNO_3 and ammonia	Brownish-red ppt of arsenate which is soluble in nitric acid and ammonia
Magnesia mixture	No ppt.	White ppt of $MgNH_4AsO_4$
Iodine in KI	Violet colour disappeared	
$SnCl_2$	Black As	
$(NH_4)_2MoO_4$		Yellow ppt of $(NH_4)3(Mo_3O_{10})_4$
KI in H^+ med		Brown I_2 in excess KI_3

REAGENTS	Sb^{3+}	Sb^{5+}
Dil $HCl + H_2S$	Sb_2S_3 is orange red soluble in Conc HCl,conc HNO_3, Alkali and YAS $2Sb^{3+} + 3H_2S \rightarrow Sb_2S_3\downarrow + 6H^+$ $Sb_2S_3\downarrow + 6HCl \rightarrow 2Sb^{3+} + 6Cl^- + 3H_2S\uparrow$ $Sb_2S_3\downarrow + 4s_2^{2-} \rightarrow 2SbS_4^{3-} + S_3^{2-}$ $2SbS_4^{3-} + 6H^+ \rightarrow Sb_2S_5\downarrow + 3H_2S\uparrow$ $Sb_2S_5\downarrow \rightarrow Sb_2S_3\downarrow + 2S\downarrow$ $2Sb_2S_3\downarrow + 4OH^- \rightarrow Sb_2O_2^- + 3SbS_2^- + 2H_2O$ $SbO_2^- + 3SbS_2^- + 4H^- \rightarrow 2Sb_2S_3\downarrow + 2H_2O$	Sb_2S_5 is orange red soluble in conc. HCl, Alkali, $(NH_4)_2S$ and YAS $2Sb^{5+} + 5H_2S \rightarrow Sb_2S_5\downarrow + 10H^+$ $Sb_2S_5\downarrow + 3S^{2-} \rightarrow 2SbS_4^{3-}$ $Sb_2S_5\downarrow + 6OH^- \rightarrow SbO_3S_4^{3-} + SbS_4^{3-} + 3H_2O$ $Sb_2S_5\downarrow + 6H^+ \rightarrow 2Sb^{3+} + 2S\downarrow + 3H_2S\uparrow$ $2SbS_4^{3-} + 6H^+ \rightarrow Sb_2S_5\downarrow + 3H_2S\uparrow$ $SbO_3S^{3-} + SbS_4^{3-} + 6H^+ \rightarrow Sb_2S_5\downarrow + 3H_2O$
H_2O	White ppt of SbO. Cl soluble in HCl and Tartareic acid (difference from bismuth)	White ppt of basic salt, ultimately antimonic acid is formed
Zn / Sn / Fe	Black ppt of Sb. Some stibine SbH_3 may be evolved.	Black ppt of Sb. Some stibine SbH_3 may be evolved.
KI	Yellow complex $[SbI_6]^{3-}$ is formed.	Brown I_2 and Sb^{3+} which dissolves in excess of KI forming, Yellow compelx $[SbI_6]^{3-}$
Rhodamine - B	No colour	Violet colour

REAGENTS	Sn^{2+}	Sn^{4+}
Dil HCl + H_2S	SnS is brown soluble in conc. HCl and YAS $Sn^{2+} + H_2S \rightarrow SnS\downarrow + 2H^+$ $SnS\downarrow + S_2^{2-} \rightarrow SnS_3^{2-}$ $SnS_3^{2-} + 2H^+ \rightarrow SnS_2\downarrow + H_2S\uparrow$	SnS_2 is yellow soluble in conc. HCl, Alkali, Ammonium sulphide and YAS $Sn^{4+} + 2H_2S \rightarrow SnS_2\downarrow + 4H^+$ $SnS_2\downarrow + S^{2-} \rightarrow SnS_3^{2-}$ $SnS_2\downarrow + 2S_2^{2-} \rightarrow SnS_3^{2-} + S_3^{2-}$ $SnS_3^{2-} + 2H^+ \rightarrow SnS_2\downarrow + H_2S\uparrow$
NaOH	White ppt, soluble in excess of NaOH, but not in NH_3	White ppt, soluble in excess of NaOH, but not in NH_3
$HgCl_2$	Grey colour Hg ppted	-
Zn	Spongy Sn is deposited	-
Fe	-	Mixture of Fe^{2+} and Sn^{2+}

GROUP III

Group Reagent : $NH_4OH + NH_4Cl$

Cations : Fe^{3+}, Al^{3+}, Cr^{3+}

Observation: Hydroxides precipitated out

REAGENT	Fe^{3+}	Al^{3+}	Cr^{3+}
Ammonia	Reddish-brown ppt. of $Fe(OH)_3$ that is insoluble in excess but soluble in acids	White gelations ppt. of $Al(OH)_3$ that is insoluble in excess but soluble in acids	Green ppt. of $Cr(OH)_3$ that in soluble in excess ammonia giving violet $[Cr(NH_3)_6]^{3+}$
NaOH	Reddish-brown ppt. of $Fe(OH)_3$ that is insoluble in excess but soluble in acids	White gelationous ppt. of $Al(OH)_3$ that is soluble in excess giving $[Al(OH)_4]^-$	Green ppt. of $Cr(OH)_3$ that is soluble in excess ammonia giving green $[Cr(OH)_4]^-$
AcONa	Reddish-brown solution of $[Fe_3(OH)_2(OAc)_6]^+$	Boiling with excess solution gives white ppt. of $Al(OH)_2(AcO)$	Red ppt. of $Cr_2(OAc)_4(H_2O)_2$

Special Tests for Group III Cations

1. Ferric $[Fe^{3+}]$ ion

(a) With KCN, reddish-brown ppt. of $Fe(CN)_3$ that dissolves in excess to give $K_3[Fe(CN)_6]$.

(b) With $K_3[Fe(CN)_6]$, brown ppt. of $Fe[Fe(CN)_6]$ that is reduced to Prussian Blue $Fe_4[Fe(CN)_6]$.

(c) With $K_4[Fe(CN)_6]$, Prussian blue $Fe_4[Fe(CN)_6]$ that decomposes in conc. NaOH to given red $Fe(OH)_3$

(d) With KSCN, blood red ppt. of $Fe(SCN)_3$

(e) With Hypo, Fe^{3+} first gives violet complex $[Fe(S_2O_3)_2]$, on standing the color disappeared rapidly and green color Fe^{2+} ions are formed.

2. Aluminium $[Al^{3+}]$ ion

(a) With Alizarin, Red Lake obtained.

3. Chromium $[Cr^{3+}]$ ion and Chromate $[CrO_4^{2-}]$

(a) Green ppt. of $Cr(OH)_3$ obtained by treating slat with Na_2CO_3 can be converted into yellow CrO_4^{2-} using alkaline Br_2 water, aqueous Na_2O_2 soln., alkaline H_2O_2 soln, or $K_2S_2O_8$

(b) Yellow residue to CrO_4^{2-} obtained on fusion test as well as treating $Pb(OAc)_2$ or $BaCl_2$ acidified with AcOH with CrO_4^{2-}

(c) Reacting CrO_4^{2-} with H_2O_2 in ethereal solution gives clear blue solution of CrO_5 that decomposes to Cr^{3+} in aqueous solution.

GROUP IV

Group Reagent : $NH_4OH + H_2S$

Cations : Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+}

Observation: Sulphides precipitated out [ZnS is white and dissolves in HCl, MnS is dirty pink and dissolves in HCl and AcOH, Nis and CoS are black and dissolve in conc. HNO_3 and aqua regia]

REAGENT	Mn^{2+}	Zn^{2+}
Ammonia	White ppt. of $Mn(OH)_2$ that is soluble in excess due to reverse reaction	White ppt. of $Zn(OH)_2$ that is soluble in excess forming $[Zn(NH_3)_4]^{2+}$
NaOH	White ppt. of $Mn(OH)_2$ that is insoluble in excess and is oxidized to $MnO_2.H_2O$	White ppt. of $Zn(OH)_2$ that is soluble in excess forming $[Zn(OH)_4]^{2-}$

REAGENT	Co^{2+}	Ni^{2+}
NaOH	Pink color ppt of $Co(OH)_2$ insoluble in excess of NaOH but soluble in NH_3 or amm. slats.	Green ppt of $Ni(OH)_2$ insoluble in excess of NaOH but soluble in NH_3 or amm. salts.
NH_3	Basic salt of $Co(OH)NO_3$ dissolves in excess forming $[Co(NH_3)_6]^{2+}$	Green ppt of $Ni(OH)_2$ soluble in excess of NH_3 forming deep blue $[Ni(NH_3)_6]^{2+}$
KCN	Brown ppt of $Co(CN)_2$ soluble in excess forming brown solution of $[Co(CN)_6]^{2-}$ on boiling with air or H_2O_2 it oxidises to yellow solution of $[Co(CN)_6]^{3-}$	Green ppt of $Ni(CN)_2$ soluble in excess of reagent forming yellow solution of $[Ni(CN)_4]^{2-}$ when it is heated with NaOBr solution black color $Ni(OH)_3$ is formed
KNO_2	Yellow ppt of $K_3[Co(NO_2)_6]$	No ppt
NH_4SCN	Blue color solution of $[Co(SCN)_4]^{2-}$	-
1-Nitroso-2-naphthol	Reddish brown ppt	Brown ppt

Special Tests for Group IV Cations

1. Manganese [Mn^{2+}]

(a) Mn^{2+} can be oxidized to MnO_4^- by using PbO_2 , Pb_3O_4 or $KClO_3$ with conc. HNO_3 giving a purple coloration of $HMnO_4$; $S_2O_8^{2-}$ in dil. acid or $NaBiO_3$ in dil. acid.

(b) Green residue of Na_2MnO_4 obtained after fusion test.

2. Zinc [Zn^{2+}]

(a) With $K_4[Fe(CN)_6]$,bluish-white ppt. of $Zn_2[Fe(CN)_6]$ and $K_2Zn_3[Fe(CN)_6]_2$

(b) Cobalt nitrate test gives Rinmann Green $CoZnO_2$.

3. Nickel [Ni^{2+}]

(a) Rosy red ppt. of $Ni(dmgH)_2$ with dimethyl glyoxime (dmg)

(b) Violet ppt of $[Ni(en)_3]S_2O_3$ is formed when $[Ni(en)_3](NO_3)_2$ is treated with Hypo.

GROUP V

Group Reagent : $NH_4OH + (NH_4)_2CO_3$

Cations : Ca^{2+}, Sr^{2+}, Ba^{2+}

Observation: White carbonates are precipitated out.

REAGENT	Ca^{2+}	Sr^{2+}	Ba^{2+}
Dilute H_2SO_4	White ppt. of $CaSO_4$ that dissolves in hot conc. H_2SO_4 giving $[Ca(SO_4)_2]^{2-}$	White ppt. of $SrSO_4$ that dissolves in boiling HCl	White ppt. Of $BaSO_4$ that is insoluble in dil. and conc. acids.
$(NH_4)_2C_2O_4$	White ppt. of CaC_2O_4 that is insoluble in water and AcOH but soluble in mineral acids.	White ppt. of SrC_2O_4 that is insoluble in water and AcOH but soluble in mineral acids.	White ppt. of BaC_2O_4 that is insoluble in water but soluble in AcOH and mineral acids.
$K_2Cr_2O_4$	No ppt. observed	Yellow ppt. of $SrCrO_4$ that dissolves in dilute soln., AcOH and mineral acids	Yellow ppt. of $BaCrO_4$ that dissolves in mineral acids but not in AcOH

STEP-3

1. Which reagent is used to remove SO_4^{2-} or $Cl^{\ominus}$ from water?
(a) NaOH (b) $Pb(NO_3)_2$ (c) $BaSO_4$ (d) KOH

2. Which compound will not give positive chromyl chloride test?
(a) Copper chloride, $CuCl_2$
(b) Mercuric chloride, $HgCl_2$
(c) Zinc chloride, $ZnCl_2$
(d) Anilinium chloride, $C_6H_5NH_3^{\oplus}Cl^{\ominus}$

3. A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of:
(a) CO_3^{2-} (b) S^{2-} (c) SO_3^{2-} (d) $NO_2^{\ominus}$

4. Conc. H_2SO_4 on addition to dry KNO_3 gives brown fumes of:
(a) SO_2 (b) SO_3 (c) NO (d) NO_2

5. A white metal sulphide soluble in water is
(a) CuS (b) Na_2S (c) PbS (d) ZnS

6. A salt having BO_3^{3-} on burning with conc. H_2SO_4 gives ……. Edge flame.
(a) Green (b) Yellow (c) Red (d) White

7. KBr, on reaction with conc. H_2SO_4, gives reddish-brown gas:
(a) Bromine
(b) Mixture of bromine and HBr
(c) HBr
(d) NO_2

8. An inorganic salt when heated evolves coloured gas which bleaches moist litmus paper. The evolved gas is
(a) NO_2 (b) SO_2 (c) N_2O (d) I_2

9. The colour developed when sodium sulphide is added to sodium nitroprusside is
(a) Violet (b) Yellow (c) Red (d) Black

10. Using dil. HCl, which of the following radical cannot be confirmed
(a) S^{2-} (b) $S_2O_3^{2-}$ (c) CO_3^{2-} (d) $NO_2^{\ominus}$

11. The solution of a chemical compound X reacts with $AgNO_3$ solution to form a white precipitate of Y which dissolves in NH_4OH to give a complex Z. When Z is treated with dil. HNO_3, Y reappears. The chemical compound X can be
(a) NaCl (b) CH_3Cl (c) NaBr (d) NaT

12. Preparation of Na_2CO_3 extract is made for acid radical analysis because:
(a) All anions react with Na to give water soluble compound
(b) Na is more reactive
(c) Na_2CO_3 is water soluble
(d) None of these

13. H_2S and SO_2 can be distinguished by
(a) Litmus paper (b) $MnO_4^{\ominus}$
(c) $Pb(CH_3COO)_2$ (d) HCl

14. Two test tubes containing a nitrate and a bromide are treated separately with H_2SO_4 brown fumes evolved are passed in water. The water will be coloured by vapours evolved from the test tube containing:
(a) Nitrate (b) Bromide
(c) Both a and b (d) None of these

15. A solution of white crystals gives a yellow precipitate with $AgNO_3$ but no precipitate with a solution of Na_2CO_3. The action of conc. H_2SO_4 on the crystals yields a brown gas. The crystals are of:
(a) $NaNO_3$ (b) KCl (c) $Ca(ON_3)_2$ (d) NaBr

16. A white precipitate insoluble in conc. HNO_3 is formed when aqueous solution of X in NaOH is treated with barium chloride and bromine water. The X is
(a) SO_3 (b) SO_2
(c) CO_2 (d) none of these

17. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 water gives
(a) $Na_2S_4O_4$ (b) Na_2SO_4
(c) $Na_2S_4O_6$ (d) NaOH

18. When CS_2 layer containing both Br_2 and I_2 is shaken with excess of Cl_2 water, the violet colour due to I_2 disappears and a pale yellow colour appears in the solution. The disappearance of violet colour and appearance of pale yellow colour is due to the formation of:
(a) $I_3^{\ominus}$ and Br_2, respectively
(b) HIO_3 and BrCl, respectively
(c) ICl and BrCl, respectively
(d) $I^{\ominus}$ and $Br^{\ominus}$, respectively

19. Which of the following pair of acid radicals can be distinguished by using dil. H_2SO_4 ?
(a) $C_2O_4^{2-}$ and $NO_3^{\ominus}$ (b) $NO_3^{\ominus}$ and $NO_2^{\ominus}$
(c) $Cl^{\ominus}$ and $Br^{\ominus}$ (d) $HCO_3^{\ominus}$ and CO_3^{2-}

20. The aqueous solution of salt gives white ppt. with lead acetate solution which is insoluble in hot water and nitric acid. The salt contains
(a) $Cl^{\ominus}$ (b) Ba^{2+} (c) CO_3^{2-} (d) SO_4^{2-}

21. Some pale-green crystals are strongly heated. The gases given off are passed into a container surrounded by ice and then through a solution of acidified $KMnO_4$. The $KMnO_4$ is decolorized, a waxy white solid is formed in the ice container; this is dissolved in water. The solution will
(a) Give a precipitate with silver nitrate solution
(b) Give a precipitate with barium chloride solution
(c) Turn red litmus blue
(d) Give blue colour with starch solution

22. For testing sodium carbonate solution for the presence of sulphate ions as impurities one should add:
(a) Excess hydrochloric acid and silver nitrate solution
(b) Excess sulphuric acid and silver nitrate solution
(c) Excess nitric acid and silver nitrate solution
(d) Excess hydrochloric acid and barium chloride solution

23. Salt A $\xrightarrow{\text{Layer test}}$ If reddish-brown layers come first, then
(a) $Br^{\ominus}$ present (b) $Br^{\ominus}$ absent
(c) $Cl^{\ominus}$ present (d) $I^{\ominus}$ present

24. $CaCO_3(s) + CH_3COOH \xrightarrow[Na_2C_2O_4 \text{ solution}]{} ?$
Comment on the product of this reaction.
(a) No reaction
(b) White ppt. of $(CH_3COO)_2Ca$ is obtained
(c) White ppt. of CaC_2O_4 is formed
(d) No ppt. is obtained

25. The compound formed in the borax bead test of Cu^{2+} ion in oxidizing flame is
(a) Cu (b) $CuBO_2$
(c) $Cu(BO_2)_2$ (d) None of these

26. Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitates thus obtained are insoluble in acetic acid. These are subjected to flame test; the colour of the flame is
(a) Lilac (b) Apple green
(c) Crimson red (d) Golden yellow

27. White cation is detected by the flame test?
(a) $NH_4^{\oplus}$ (b) $K^{\oplus}$ (c) Mg^{2+} (d) Al^{3+}

28. Which gives violet colour with borax?
(a) Fe (b) Pb (c) Co (d) Mn

29. A green mass is formed in the charcoal cavity test when a colourless salt (X) is fused with cobalt nitrate. (X) may contain
(a) Aluminium (b) Copper
(c) Barium (d) Zinc

30. Carbonates of Ba, Sr and Ca are
(a) White (b) Blue (c) Green (d) Yellow

31. The metal that does not give the borax bead test is
(a) Cr (b) Ni (c) Pb (d) Mn

32. Which metal gives blue ash when is salt heated with Na_2CO_3 solid and $Co(NO_3)_2$ on a charcoal piece?
(a) Cu (b) Mg (c) Al (d) Zn

33. A minute quantity of cupric salt is heated on borax bead in reducing flame of Bunsen burner; the colour of bead after cooling will be
(a) Blue (b) Red
(c) Colourless (d) Green

34. Aqueous solution of a salt (Y) is alkaline to litmus. On strong heating, it swells-up to give a glassy material. When conc. H_2SO_4 is added to a hot concentrated solution of (Y), white crystals of a weak acid separate out. Hence, the compound (Y) is
(a) $Na_2SO_4 \cdot 10H_2O$ (b) $Ca_2P_6O_{11} \cdot 10H_2O$
(c) $Na_2B_6O_{11}$ (d) $Na_2B_4O_7 \cdot 10H_2O$

35. Strongly acidified solution of barium nitrate gives a white precipitate with ..... which did not dissolve even after large addition of water.
(a) Sodium phosphate (b) Sodium carbonate
(c) Sodium sulphate (d) Sodium chloride

36. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to:

(a) Decrease concentration of $OH^{\ominus}$ ions

(b) Prevent interference by phosphate ions

(c) Increase concentration of $Cl^{\ominus}$ ions

(d) Increase concentration of $NH_4^{\oplus}$ ions

37. H_2S gas, on passing through an alkaline solution, forms a white precipitate. The solution contains ions of

(a) Pb (b) Zn (c) Cu (d) Ni

38. Yellow ammonium sulphide solution is a suitable reagent used for the separation of

(a) HgS and PbS (b) PbS and Bi_2S_3

(c) Bi_2S_3 and CuS (d) CdS and As_2S_3

39. An orange red precipitate obtained by passing H_2S through an acidified solution of an inorganic salt indicates the presence of

(a) Cadmium (b) Tin

(c) Antimony (d) Bismuth

40. Excess of concentrated sodium hydroxide can separate mixture of

(a) Al^{3+} and Cr^{3+} (b) Cr^{3+} and Fe^{3+}

(c) Al^{3+} and Zn^{2+} (d) Zn^{2+} and Pb^{2+}

41. Which of the following sulphides has the maximum solubility product?

(a) HgS (b) PbS (c) CuS (d) MnS

42. Lead has been placed in qualitative group analysis 1^{st} and 2^{nd} because:

(a) It shows the valency one and two

(b) It forms insoluble $PbCl_2$

(c) It forms lead sulphide

(d) $PbCl_2$ is partially soluble in water

43. As_2S_3 is

(a) Black (b) Yellow

(c) Orange (d) White

44. A black sulphide is formed by the action of H_2S on

(a) $CuCl_2$ (b) $CdCl_2$

(c) $ZnCl_2$ (d) NaCl

45. The group II precipitates soluble in yellow ammonium sulphide may be

(a) As, Sb, Sn (b) Cu, Hg, Bi, Cd

(c) Both a and b (d) None of these

46. Nitric acid is generally not used for preparation of original solution in analysis of basic radicals, because it

(a) is oxidising agent (b) is reducing agent

(c) forms insoluble nitrates (d) forms soluble nitrates

47. The sulphide not soluble in hot dilute nitric acid is

(a) CuS (b) ZnS (c) CdS (d) HgS

48. H_2S will precipitate the sulphides of all the metals from the solution of chlorides of Cu, Zn and Cd if

(a) The solution is aqueous

(b) The solution is acidic

(c) The solution is dilute acidic

(d) Any of the above solutions is present

49. To a solution of a substance, gradual addition of ammonium hydroxide results in a black precipitate which does not dissolve in excess of NH_4OH. However, when HCl is added to the original solution, a white precipitate is formed. The solution contained

(a) Lead salt (b) Silver salt

(c) Mercurous salt (d) Copper salt

50. A compound is soluble in water. If ammonia is added to aqueous solution of the compound, a brown precipitate appears which is soluble in dil. HCl. The compound has

(a) Aluminium (b) Zinc

(c) Iron (d) Cadmium

51. A light green coloured salt soluble in water gives black precipitate on passing H_2S which dissolves readily in HCl. The metal ion present is

(a) Co^{2+} (b) Fe^{2+} (c) Ni^{2+} (d) $Ag^{\oplus}$

52. All ammonium salt liberate ammonia when:

(a) Heated with HCl (b) Heated with caustic soda

(c) Heated with H_2SO_4 (d) Heated with $NaNO_2$

53. Manganese salt + PbO_2 + conc.$HNO_3 \rightarrow$ The solution has purple colour. The colour is due to

(a) $HMnO_4$ (b) A lead salt

(c) $Mn(NO_3)_2$ (d) H_2MnO_4

54. A orange precipitate of group II is dissolved in conc. HCl; the solution when treated with excess of water turns milky due to formation of

(a) Sn(OH)Cl (b) $Sb(OH)Cl_2$

(c) SbOCl (d) $Sb(OH)_2Cl$

55. Which of the following solutions gives precipitate with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$?

(a) Sodium chloride

(b) Sodium sulphate

(c) Sodium nitrate

(d) Sodium hydrogen phosphate

56. A white powder when strongly heated gives off brown fumes. A solution of this powder gives a yellow precipitate with a solution of KI. When a solution of barium chloride is added to a solution of powder, a white precipitate results. This white powder may be

(a) soluble sulphate (b) KBr or NaBr

(c) $Ba(NO_3)_2$ (d) $AgNO_3$

57. The ion that cannot be precipitated by both by HCl and H_2S is

(a) Pb^{2+} (b) $Cu^{\oplus}$ (c) $Ag^{\oplus}$ (d) Sn^{2+}

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

(a) $Mg(HCO_3)_2$ (b) $MgNH_4PO_4$

(c) $MgNH_4(HCO_3)_3$ (d) $MgCO_3$

59. In qualitative inorganic analysis, phosphate, if present, is to be eliminated in the appropriate group in order to detect the radical:

(a) Pb^{2+} (b) As^{3+} (c) Ca^{2+} (d) Cd^{2+}

60. Na_2CO_3 cannot be used in place of $(NH_4)_2CO_3$ for the precipitation of group V because

(a) $Na^{\oplus}$ interferes in the detection of group V

(b) Concentration of CO_3^{2-} is very low

(c) Na will react with acid radicals

(d) Mg will be precipitated

61. Disodium hydrogen phosphate is used to test:

(a) Mg^{2+} (b) $Na^{\oplus}$ (c) Ca^{2+} (d) All of these

62. Reddish-brown (chocolate) ppt. is formed with:

(a) Cu^{2+} and $Fe(CN)_6^{4-}$ (b) Ba^{2+} and SO_4^{2-}

(c) Pb^{2+} and $I^{\ominus}$ (d) None of these

63. Addition of $SnCl_2$ to $HgCl_2$ gives ppt.:

(a) White turning to grey (b) Black turning to white

(c) White turning to red (d) None of these

Topic: Salt Analysis (C-29)

STEP-3

1. b	**2.** a	**3.** a	**4.** c	**5.** a	**6.** a	**7.** d
8. d	**9.** a	**10.** a	**11.** b	**12.** b	**13.** b	**14.** b
15. b	**16.** c	**17.** c	**18.** b	**19.** b	**20.** b	**21.** b
22. d	**23.** a	**24.** b	**25.** c	**26.** b	**27.** d	**28.** c
29. b	**30.** d	**31.** a	**32.** c	**33.** b	**34.** c	**35.** b
36. c	**37.** b	**38.** c	**39.** a	**40.** b	**41.** d	**42.** b
43. c	**44.** b	**45.** a	**46.** c	**47.** a	**48.** a	**49.** a
50. a	**51.** c	**52.** b	**53.** b	**54.** a	**55.** c	**56.** b
57. d	**58.** b	**59.** a	**60.** d	**61.** b	**62.** b	**63.** b

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