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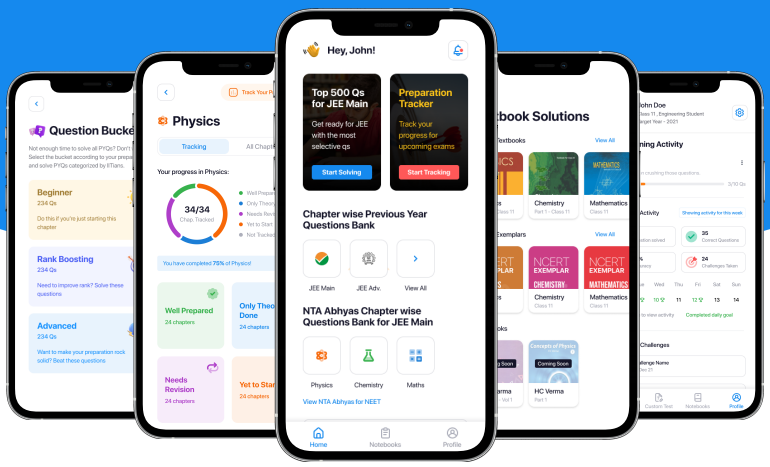

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QUALITATIVE ANALYSIS

QUALITATIVE ANALYSIS

Classification of Anions

Methods available for the 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 divided 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.

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

1. Carbonate CO_3^{2-}

(i) Dilute HCl : It 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 of calcium.

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

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 happened if the mixture is boiled, due to the formation of silver oxide.

$$Ag_2\ CO_3 \downarrow \longrightarrow Ag_2O \downarrow + CO_2 \uparrow$$

2. Sulphides (S^{2-})

(i) Dilute HCl or dilute H_2SO_4

Sulphide on treatment with dilute HCl or dilute H_2SO_4 gives a pungent smelling gas, H_2S (smell of rotten eggs).

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

The blackening of filter paper moistened with lead acetate solution may identify the gas.

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

Shining black

Alternatively, a filter paper moistened with cadmium acetate solution turns yellow.

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

Yellow ppt

(ii) Silver nitrate solution

With $AgNO_3$ solution, sulphides gives a black precipitate of silver sulphide insoluble in cold but soluble in hot dilute nitric acid.

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

Black ppt

(iii) Sodium nitroprusside solution

With sodium nitroprusside solution, ionic sulphide gives a purple colour in alkaline medium.

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

Purple colour

No reaction occurs with solutions of hydrogen sulphide or free gas. In however, filter paper moistened with a solution of the reagent is made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide also.

Class A (ii) : Gases or acid vapours evolved with conc. sulphuric acid. It includes Cl^-, Br^-, I^-, NO_3^-

3. Chloride (Cl^-)

Most chloride are soluble in water except Hg_2Cl_2, CuCl, AgCl, $PbCl_2$, BiOCl and SbOCl. $PbCl_2$ is soluble in hot water.

(i) Concentrated H_2SO_4

With concentrated H_2SO_4, chlorides gives vapours of HCl.

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

Vapour evolved

(a) turns blue litmus paper red.

(b) gives white fumes of NH_4Cl when a glass rod moistened with aqueous ammonia solution is brought close to the mouth of test tube.

(ii) Manganese dioxide and concentrated sulphuric acid

When a solid chloride is treated with MnO_2 and concentrated H_2SO_4, yellowish-green coloured gas (Cl_2) is evolved.

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

Yellowish green

(iii) Silver nitrate solution

Chlorides on treatment with $AgNO_3$ solution gives a white curdy precipitate of AgCl insoluble in water and in dilute nitric acid but soluble in dilute ammonia solution due to the formation of soluble complex.

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

White curdy ppt

$$AgCl\downarrow + 2NH_3 \longrightarrow [Ag(NH_3)_2Cl$$

Soluble

(iv) Lead acetate solution

With $(CH_3CO_2)_2Pb$ solution, chlorides gives a white precipitate of lead chloride.

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

White ppt

(v) Chromyl chloride test

When a mixture containing chloride ion is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, deep orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.

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

When chromyl chloride 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.

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

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + \underset{\text{Yellow ppt}}{PbCrO_4 \downarrow}$$

4. Bromide (Br^-)

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

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

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

(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.

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

(iii) The following tests are performed with the salt solution.

(a) **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.

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

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

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

(c) **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.

$$2KBr + Cl_2 \text{ (water)} \longrightarrow 2KCl + Br_2$$

$$Br_2 + \text{Chloroform} \longrightarrow \text{Orange red colour}$$

(d) **Potassium dichromate & conc. H_2SO_4 :** When a mixture 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.

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

5. Iodide (I^-)

Iodides are generally soluble in water except AgI, Hg_2I_2, HgI_2, CuI and PbI_2.

(i) Concentrated H_2SO_4

With concentrated H_2SO_4, iodides gives violet vapours of iodine on warming.

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

Violet vapours

(ii) Silver nitrate solution

With $AgNO_3$ solution, iodides form a yellow curdy precipitate of silver iodide, which is very slightly soluble in concentrated ammonia solution, but is completely insoluble in dilute HNO_3.

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

Yellow curdy ppt

(iii) Lead acetate solution

With $(CH_3CO_2)_2Pb$ solution, a yellow precipitate of lead iodide (PbI_2) is formed, which is soluble in hot water forming a colourless solution and yielding golden–yellow plates on cooling.

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

Yellow ppt

(iv) Potassium dichromate and concentrated sulphuric acid

When iodides are warmed with $K_2Cr_2O_7$ and concentrated H_2SO_4, iodine is liberated.

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

Violet vapours

(v) Chlorine water

When this reagent is added dropwise to a solution of an 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.

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

$$I_2 + \text{Chloroform} \longrightarrow \text{Violet solution}$$

(vi) Copper sulphate solution

With $CuSO_4$ solution, iodide produces a brown precipitate consisting of a mixture of copper (I) iodide and iodine. On addition of hypo ($Na_2S_2O_3$) to the solution, brown precipitate changes to white (colourless).

$$4I^- + 2Cu^{2+} \longrightarrow Cu_2I_2 \downarrow + I_2$$

Brown ppt

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

(vii) Mercury(II) chloride solution

With $HgCl_2$ solution, iodide gives a scarlet precipitate of HgI_2.

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

Scarlet ppt

The precipitate dissolves in excess of KI, forming tetraiodomercurate(II) complex.

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

Soluble

5. Nitrate $\left(NO_3^-\right)$

(i) Conc. H_2SO_4 : It 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.

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

(B) Group 'B' Radicals

7. Sulphate $\left(SO_4^{2-}\right)$

Sulphate of barium, strontium and lead are practically insoluble in water, those of calcium and mercury(II) are slightly soluble and most of the remaining metallic sulphates are soluble.

(i) Barium chloride solution

On adding $BaCl_2$ solution to a sulphate salt solution, a white precipitate of barium sulphate ($BaSO_4$) insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is formed.

$$SO_4^{2-} + Ba^{2+} \longrightarrow \underset{\text{White ppt}}{BaSO_4\downarrow}$$

(ii) Silver nitrate solution

With silver nitrate solution, SO_4^{2-} gives a white crystalline precipitate of silver sulphate.

$$SO_4^{2-} + 2Ag^{+} \longrightarrow \underset{\text{White ppt}}{Ag_2SO_4\downarrow}$$

(iii) Mercury(II) nitrate solution

With $Hg(NO_3)_2$ solution, sulphates form a yellow precipitate of basic mercury(II) sulphate.

$$SO_4^{2-} + 3Hg^{2+} + 2H_2O \longrightarrow \underset{\text{Yellow ppt}}{HgSO_4.2HgO\downarrow} + 4H^{+}$$

Physical appearance of inorganic salts

Sr No.	Salt	Colour
1	MnO, MnO_2, FeO, CuO, Co_3O_4, Ni_2O_3, sulfides of Ag^+, Cu^+, Cu^{2+}, Fe^{2+}, CO^{2+}, Pb^{2+}, Hg^{2+}	Black
2	Hydrated Cu^{2+} salts	Blue
3	HgO, HgI_2, Pb_3O_4	Red
4	Cr^{3+}, Cr^{6+}, Ni^{2+}, Hydrated Fe^{2+} salts	Green
5	Hydrated Mn^{2+} salts	Light Pink
6	KO_2, $K_2Cr_2O_7$, Sb_2S_3, ferricyanides	Orange
7	Hydrated Co^{2+} salts	Reddish Pink
8	Chromates AgBr, AgI, PbI_2, CdS	Yellow
9	CdO, Fe_2O_3, PbO_2, $CuCrO_4$	Dark brown

Effect of Heating

1. When a gas is evolved

(a) Coloured gas :

(i) NO_2, (Brown) turns starch Iodine paper blue.

Substance : Nitrites and Nitrates of heavy metals

e.g. $2Cu(NO_3)_2 \xrightarrow{\Delta} CuO + 4NO_2 \uparrow + O_2$

(ii) Br_2(Reddish Brown) turns starch paper yellow

Substance bromide : $2CdBr_2 + O_2 \rightarrow 2CdO + 2Br_2 \uparrow$

(iii) I_2 (Violet) turns starch paper blue

Iodides $2CdI_2 + O_2 \rightarrow 2CdO + 2I_2 \uparrow$

(iv) Cl_2 (Greenish yellow) bleaches moist litmus paper

Chlorides $CuCl_2 + H_2O \rightarrow CuO + 2HCl$

(moisture) $\downarrow\rightarrow Cu + H_2O + 1/2Cl_2$

(b) Colourless gas (odourless)

(i) O_2–supports glowing

Alkali nitrates : $2KNO_3 \rightarrow 2KNO_2 + O_2 \uparrow$

(ii) CO_2 – Turns lime water milky

Carbonates/Oxalates $CaCO_3 \rightarrow CaO + CO_2 \uparrow$

(c) Colourless gas (with odour)

(i) NH_3 – turns red litmus blue

Ammonium salts : $(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \uparrow$

(ii) SO_2 – Smell of burning sulphur, turns acidified $K_2Cr_2O_7$ paper green

Sulphites, thiosulphates

$CaSO_3 \rightarrow CaO + SO_2$

(iii) HCl – pungent smell, white fumes with ammonia

hydrates chlorides

$CaCl_2.6H_2O \rightarrow Ca(OH)_2 + 4H_2O + 2HCl \uparrow$

(iv) H_2S – Smell of rotten eggs, turns lead acetate paper black

sulphides.

$Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \uparrow$

2. A residue (oxide) is left and colour

(i) Yellow (on hot) & white (on cold) – ZnO

(ii) Reddish brown (hot) yellow (cold) – PbO

(iii) Black (hot) Red (cold) – HgO, Pb_3O_4

(iv) Black (hot) Red Brown (cold) – Fe_2O_3

3. Substance melts : Salts of alkali metals & salts having water of crystallisation.

4. Substance makes crackling noise : NaCl, KI, $Pb(NO_3)_2$, $Ba(NO_3)_2$

5. Substance Swells : Alums, borates & phosphates

6. Substance sublimes & colour of sublimate is :

(a) White : $HgCl_2$, Hg_2Cl_2, $AlCl_3$, As_2O_3, Sb_2O_3

(b) Yellow : As_2S_3, HgI_2 turns red on burning with glass rod

(c) Blue Black or Violet : Iodides

BASIC RADICALS

Separation of basic radicals into groups

For systematic analysis, the basic radicals have been classified into groups. Each group has a reagent, which shows the presence of the basic radical belonging to that particular group. It is necessary that the radical is completely removed in the respective group by using excess of group reagent, otherwise its presence creates difficulty in higher group.

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
1.	Dilute HCl	Ag^+	AgCl : white	Chloride insoluble in cold dilute HCl
		Pb^{2+}	$PbCl_2$: white	
		Hg_2^{2+}	Hg_2Cl_2 : white	
2.	H_2S in presence of dilute HCl	Hg^{2+}	HgS : black	Sulphides insoluble in dilute HCl
		Pb^{2+}	PbS : black	
		Bi^{3+}	Bi_2S_3 : black	
		Cu^{2+}	Cus : black	
		Cd^{2+}	CdS : yellow	

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
3.	NH_4OH in presence of NH_4Cl	Fe^{3+}	$Fe(OH)_3$: reddish brown	Hydroxides are insoluble in NH4OH
		Cr^{3+}	$Cr(OH)_3$: green	
		Al^{3+}	$Al(OH)_3$: white	
4.	H_2S in presence of NH_4OH	Zn^{2+}	ZnS greenish white	Sulphides are insoluble in NH_4OH
		Mn^{2+}	MnS : buff	
5.	$(NH_4)_2 CO_3$ in presence of NH_4OH	Ba^{2+}	$BaCO_3$: white	Carbonates are insoluble
		Ca^{2+}	$CaCO_3$: white	
6.	Na_2HPO_4	Mg^{2+}	$Mg(NH_4)PO_4$:	
7.	NaOH	NH_4^+	Ammonia gas is evolved.	

It should be noted that :

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 chlorides of all other metal ions, which remain in solution.

2. Group II radicals are precipitated as sulphides because of their low solubility, whereas sulphide 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 decreased concentration of S^{2-} is only sufficient to precipitate the Group II metals ions as sulphides.

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 cations are precipitated as hydroxide because of their low solubility product.

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

(ii) $(NH_4)_2SO_4$ cannot be used in placed of NH_4Cl because the SO_4^{2-} will give precipitate of $BaSO_4$

(iii) NH_4NO_3 cannot be used in place of NH_4Cl as NO_3^- ions will oxidise Mn^{2+} to Mn^{3+} and thus, $Mn(OH)_3$ will be precipitated in III A group.

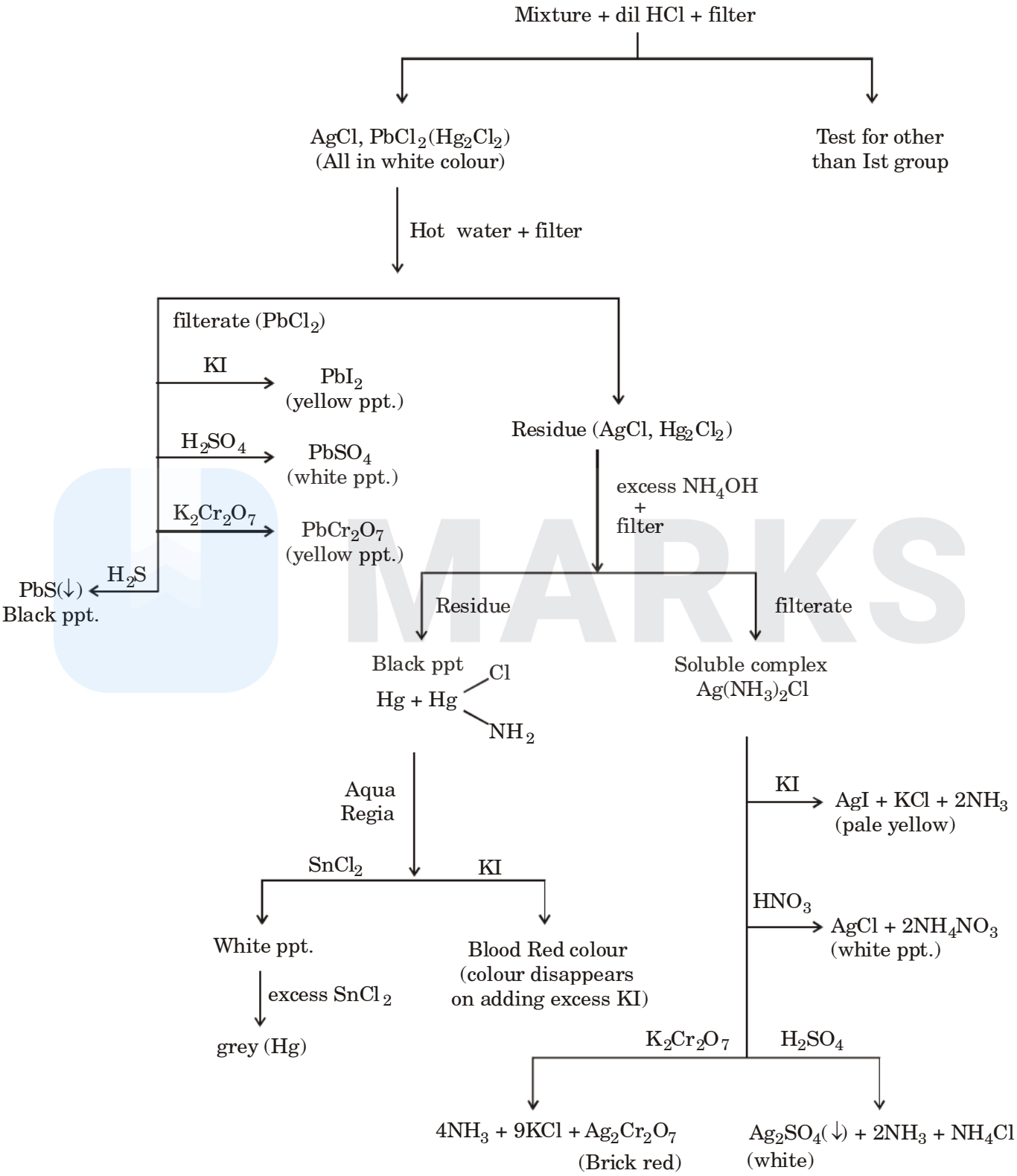
4. Ammonium hydroxide increases the ionisation of H_2S by removing H^+ from H_2S as unionised water.

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

Now the excess of S^{2-} ions is available and hence the ionic product of group III B exceeds their solubility product 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,

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

Group I


Mixture + dil HCl + filter
AgCl, PbCl2(Hg2Cl2) (All in white colour)
Test for other than Ist group
Hot water + filter
filterate (PbCl2)
KI
PbI2 (yellow ppt.)
H2SO4
PbSO4 (white ppt.)
K2Cr2O7
PbCr2O7 (yellow ppt.)
H2S
PbS(↓) Black ppt.
Residue (AgCl, Hg2Cl2)
excess NH4OH + filter
Residue
filterate
Black ppt
Hg + Hg
Cl
NH2
Soluble complex Ag(NH3)2Cl
Aqua Regia
SnCl2
KI
White ppt.
excess SnCl2
grey (Hg)
Blood Red colour (colour disappears on adding excess KI)
KI
AgI + KCl + 2NH3 (pale yellow)
HNO3
AgCl + 2NH4NO3 (white ppt.)
K2Cr2O7
H2SO4
4NH3 + 9KCl + Ag2Cr2O7 (Brick red)
Ag2SO4(↓) + 2NH3 + NH4Cl (white)

Some Salient Reactions :

(1) $Hg_2Cl_2 \xrightarrow{NH_4OH} \underbrace{Hg(\downarrow) + Hg\begin{matrix}Cl\\NH_2\end{matrix}}_{\text{Black (shing black)}}$

(2) Aqua Regia is a very strong oxidizing agent and it converts the black precipitate into soluble $HgCl_2$.

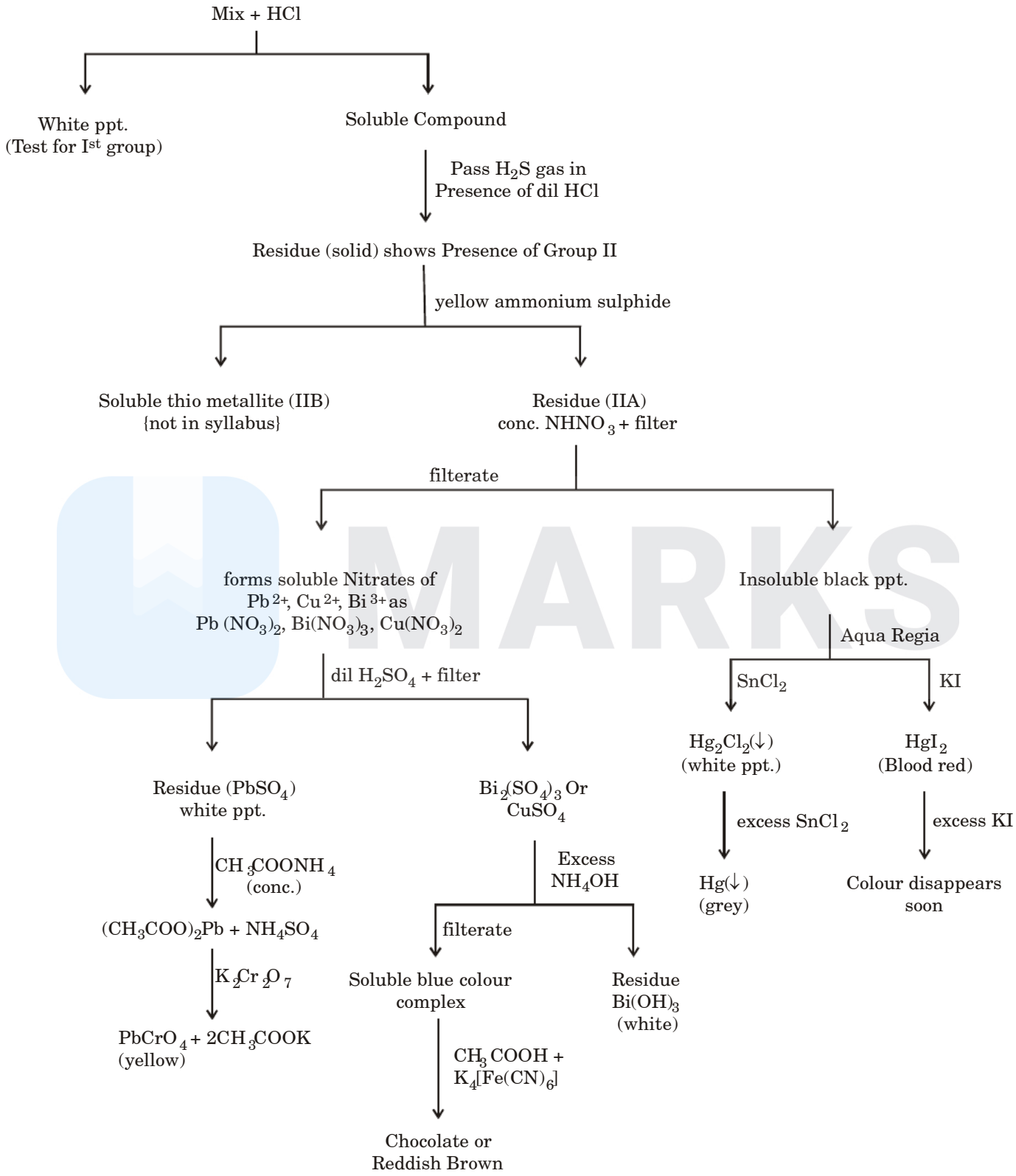
Aqua Regia is a mixture of ($3HCl + HNO_3 \rightarrow NOCl + 2H_2O + Cl_2$)

$$HgCl_2 + SnCl_2 \longrightarrow \underset{\text{(white)}}{Hg_2Cl_2\ \text{(white)}} \xrightarrow{SnCl_2} \underset{\text{(grey)}}{2Hg(\downarrow) + SnCl_4}$$

$$HgCl_2 + KI \longrightarrow \underset{\text{(Blood red)}}{HgI_2} + 2KCl$$

$$HgI_2 + 2KI \longrightarrow \underset{\text{(nessler's Reagent)}}{K_2[HgI_4]}$$

Group II


Mix + HCl
White ppt.
(Test for I st group)
Soluble Compound
Pass H_2S gas in
Presence of dil HCl
Residue (solid) shows Presence of Group II
yellow ammonium sulphide
Soluble thio metallite (IIB)
{not in syllabus}
Residue (IIA)
conc. $NHNO_3$ + filter
filterate
forms soluble Nitrates of
Pb^{2+}, Cu^{2+}, Bi^{3+} as
$Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$
Insoluble black ppt.
Aqua Regia
$SnCl_2$
KI
$Hg_2Cl_2(\downarrow)$
(white ppt.)
HgI_2
(Blood red)
excess $SnCl_2$
excess KI
$Hg(\downarrow)$
(grey)
Colour disappears
soon
dil H_2SO_4 + filter
Residue ($PbSO_4$)
white ppt.
$Bi_2(SO_4)_3$ Or
$CuSO_4$
CH_3COONH_4
(conc.)
$(CH_3COO)_2Pb + NH_4SO_4$
$K_2Cr_2O_7$
$PbCrO_4 + 2CH_3COOK$
(yellow)
Excess
NH_4OH
filterate
Soluble blue colour
complex
Residue
$Bi(OH)_3$
(white)
CH_3COOH +
$K_4[Fe(CN)_6]$
Chocolate or
Reddish Brown

Some Salient Reactions

(1) $3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + S + H_2O$

(soluble)

(2) $Bi(OH)_3 \xrightarrow{\text{dil. HCl}} BiCl_3$

(3) $BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow 3Na_2SnO_3 + 2Bi(\downarrow) + 6NaCl + 3H_2O$

(Black)

(4) $CuSO_4 + NH_4OH \longrightarrow [Cu(NH_3)_4]\ SO_4 + H_2O$

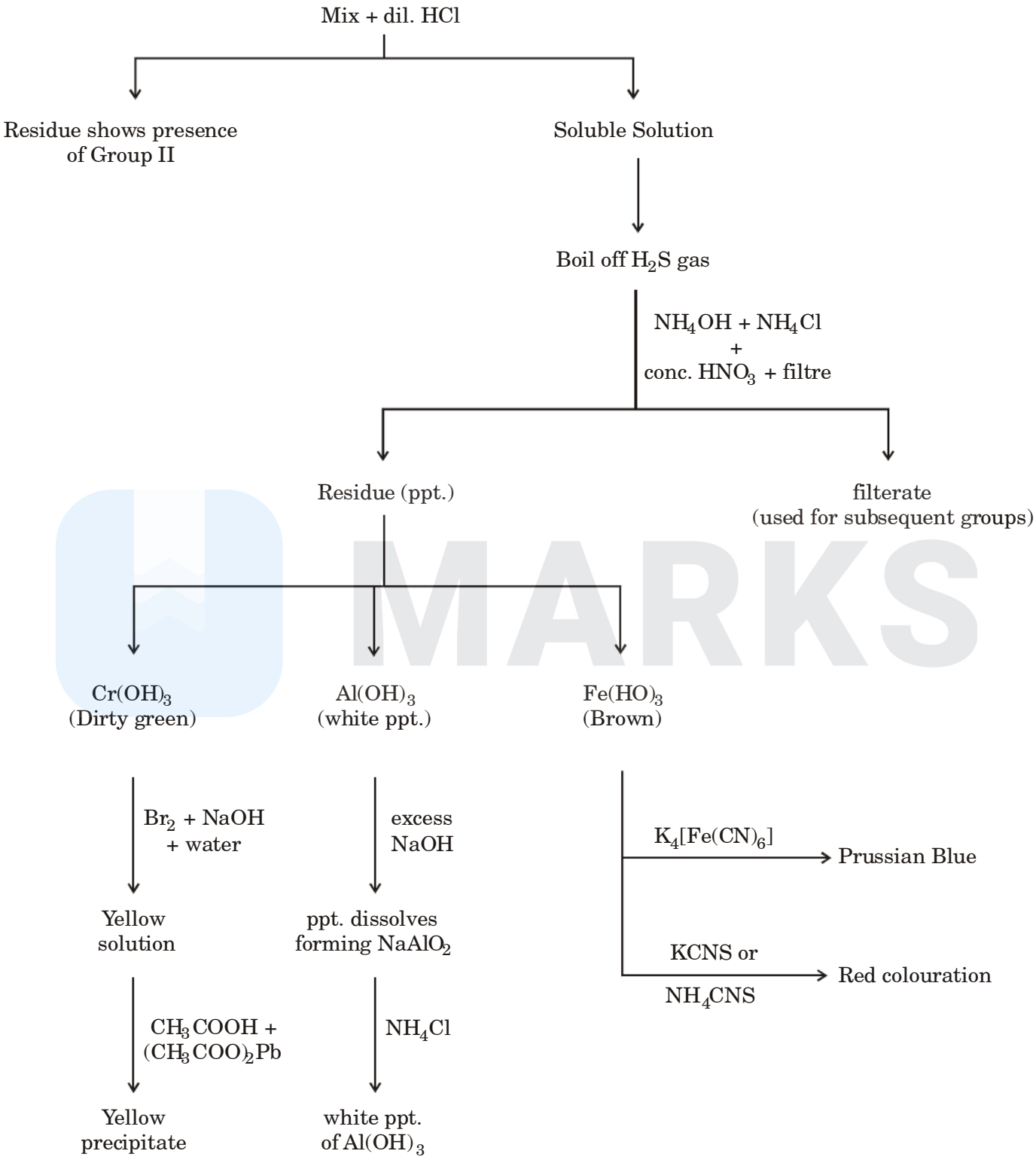
(Blue colour)

(5) $[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$

$2CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$

Chocolate or
reddish brown

Group III


Mix + dil. HCl
Residue shows presence of Group II
Soluble Solution
Boil off H_2S gas
$NH_4OH + NH_4Cl$ + conc. HNO_3 + filtre
Residue (ppt.)
filterate (used for subsequent groups)
$Cr(OH)_3$ (Dirty green)
$Al(OH)_3$ (white ppt.)
$Fe(HO)_3$ (Brown)
Br_2 + NaOH + water
excess NaOH
$K_4[Fe(CN)_6]$
Prussian Blue
KCNS or NH_4CNS
Red colouration
Yellow solution
ppt. dissolves forming $NaAlO_2$
CH_3COOH + $(CH_3COO)_2Pb$
NH_4Cl
Yellow precipitate
white ppt. of $Al(OH)_3$

Note :

Initially HNO_3 was added to convert Fe^{2+} (light green) into Fe^{3+} (deep yellow)

Some salient reactions :

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

$NaAlO_2 + NH_4Cl + H_2O \xrightarrow{\Delta} NaCl + Al(OH)_3(\downarrow) + NH_3$

white ppt

(2) $Cr(OH)_3 + 3Br_2 + 10NaOH \longrightarrow 2Na_2CrO_4 + 6NaBr + 8H_2O$

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4\ (\downarrow) + 2CH_3COONa$

(yellow ppt)

(3) $Fe(OH)_3 \xrightarrow[(HNO_3 + HCl)]{\text{aqua Regia}} FeCl_3 + 3H_2O$

(4) $FeCl_3 + KCNS \longrightarrow Fe(CNS)_3 + NH_4Cl/KCl$

or

NH_4CNS

(5) $4\ Fe(OH)_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6] + 12KOH$

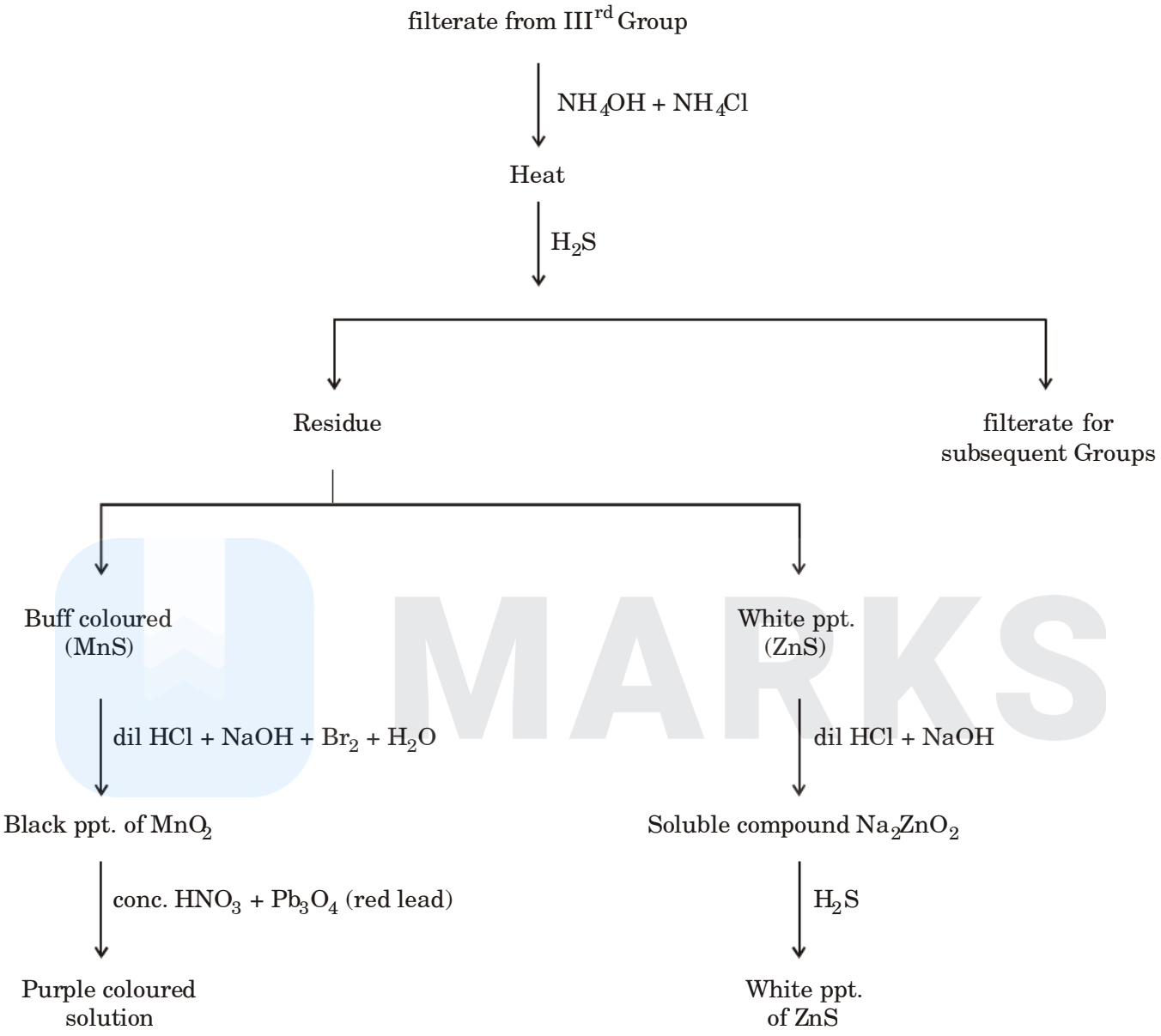
(Prussian blue)

$4Fe(OH)_2 + 4K_4[Fe(CN)_6] \longrightarrow 4KFe[Fe(CN)_6] + KOH$

(soluble)

* These reactions can be used to distinguish between Fe^{2+} and Fe^{3+}

Group IV


filterate from III rd Group
NH4OH + NH4Cl
Heat
H2S
Residue
filterate for subsequent Groups
Buff coloured (MnS)
White ppt. (ZnS)
dil HCl + NaOH + Br2 + H2O
dil HCl + NaOH
Black ppt. of MnO2
Soluble compound Na2ZnO2
conc. HNO3 + Pb3O4 (red lead)
H2S
Purple coloured solution
White ppt. of ZnS

Some salient reactions

(1) $ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 + 2NaCl$

$\downarrow$ NaOH

$Na_2ZnO_2 + 2H_2O$

Sodium zincate

$Na_2ZnO_2 + H_2S \longrightarrow 2NaOH + ZnS\ (\downarrow)$

(White ppt)

(2) $MnCl_2 + NaOH \longrightarrow Mn(OH)_2 + 2NaCl$

air | [O]

$\downarrow$

$MnO_2 + H_2O$

(Black ppt)

$2MnO_2 + 3Pb_3O_4 + 10HNO_3 \longrightarrow 2\ HMnO_4 + 4Pb(NO_3)_2 + 8H_2O$

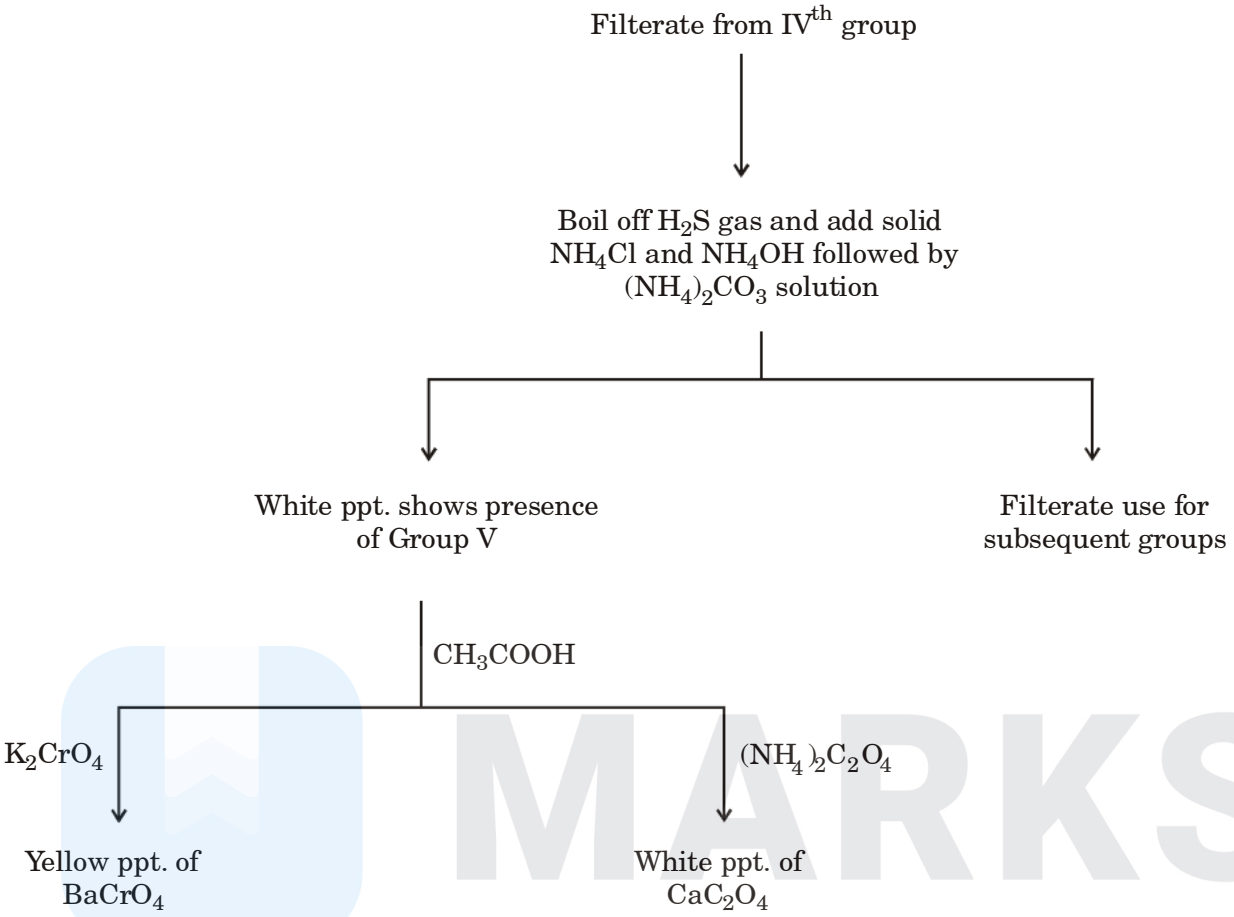
(PbO_2 can also be used)

(Purple colour)

(3) $ZnCl_2 + K_4[Fe(CN)_6] \rightarrow Zn_2[Fe(CN)_6]\ (\downarrow) + 2KCl$

Bluish white ppt

Group V



Some Salient Reactions

(1) $BaCO_3 + 2CHCOOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$

$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$

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

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

(White ppt)

Group VI (Mg^{2+})

Filterate of group V + NH_4OH + Na_2HPO_4 $\rightarrow$ a fine crystalline ppt on scratching the side of the test tube.

$$MgCl_2 + NH_4OH + Na_2HPO_4 \rightarrow \underset{\text{(white ppt)}}{Mg(NH_4)PO_4\ (\downarrow)} + 2NaCl + 2H_2O$$

$$\xrightarrow{\Delta}$$

$$Mg_2P_2O_7 + 2NH_3 + H_2O$$
(white)

Group zero : $\left(NH_4^+\right)$

- Salt + NaOH $\xrightarrow{\Delta}$ gas giving white fumes with HCl

  $NH_4Cl + NaOH \xrightarrow{\Delta} NH_3\ (g) + NaCl + H_2O$

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

- Salt + NaOH $\xrightarrow{\Delta}$ gas $\xrightarrow[\text{Reagent}]{\text{add Nesler's}}$ Brown ppt or brown or yellow colouration (oxydimercuri ammonium iodide) called iodide of Millon's base.

$NH_4Cl + NaOH \xrightarrow{\Delta} NH_3$

$$NH_3 + 3NaOH + \underset{\substack{\text{Nessler's}\\ \text{Reagent}}}{2K_2HgI_4} \longrightarrow \left[\begin{array}{c} Hg \\ O \quad\quad NH_2 \\ Hg \end{array}\right]^+ I^- + 4KI + 3NaI + 2H_2O$$

Solubility Trends

		dil. HNO_3	NH_4OH	Hypo soln	CN^- soln.
1.	AgCl		3	3	3
	AgBr		3	3	3
	AgI			3	3
	Ag_2S	3		3	3

2. All water insoluble black metal sulphide are soluble in hot and dil. HNO_3 except HgS. (Soluble in aqua regia)

3. FeS is the only black metal sulphide soluble in non- oxidising acid.

4. In general Pb salts are soluble in dil. HNO_3 & Ex. NaOH Soln.

5. All water insoluble $C_2O_4^{2-}$ salts are insoluble in acetic acid except BaC_2O_4 (white).

Dry Tests

Dry tests are of great importance as these tests give clear indications of the presence of certain radicals. The following tests are performed in dry state :

(i) Flame test

(ii) Borax bead test

(iii) Microcosmic salt bead test

(i) Flame test

Some volatile salts impart characteristic colour to the non-luminous flame. The chlorides of the metals are more volatile in comparison to other salts. The metal chloride volatilises and its thermal ionisation takes place.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$$

The cations impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light of characteristic colour.

Procedure : The platinum wire fused in a glass rod is heated in the flame till it imparts colourless flame. This is achieved by dipping the wire in conc. HCl and heating it. The process is repeated till it gives a colourless flame. The tip of the wire is now dipped in conc. HCl and then into the substance. The tip of the wire is strongly heated in the non-luminous flame and the colour of the flame is observed by the naked eye.

	Colour of flame	**Inference**
1.	Golden yellow	Sodium
2.	Violet	Potassium
3.	Brick red	Calcium
4.	Crimson red	Strontium
5.	Apple green	Barium
6.	Green with a blue centre	Copper

Note : Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.

(ii) Borax bead test

On heating borax the colourless glassy bead formed consists of sodium metaborate and boric anhydride.

$$Na_2B_4O_7.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

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

$$CusO_4 \longrightarrow CuO + SO_3$$

$$CuO + B_2O_3 \longrightarrow \underset{\substack{\text{Copper metaborate}\\ \text{(Blue)}}}{Cu(BO_2)_2}$$

The metaborates posses different characteristic colours. The shade of the colour gives a clue regarding the presence of the radical.

However, in reducing flame the colours may be different due to different reactions. For example, copper metaborate may be reduced to colourless cuprous metaborate or to metallic copper, which appears red and opaque.

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

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

Procedure : The free end of a platinum wire is coiled into a small loop and heated in the Bunsen flame until red hot. It is dipped in borax and again heated, when borax swells up and then fused into a glassy bead.

The bead is moistened with water and dipped in the coloured salt. It is now heated first in the oxidising flame and then in the reducing flame and colours are noted in both the flames in hot and cold conditions.

Metal	Colour of the bead in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Brown-red
Iron	Brown-yellow	Pale-yellow	Bottle green	Bottle-green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst red	Grey	Grey
Nickel	Violet	Brown	Grey	Grey

(iii) Microcosmic salt bead test

This test is similar to borax bead test. When microcosmic salt is heated, a colourless transparent bead of sodium metaphosphate is formed.

$$Na(NH_4)HPO_4 \longrightarrow \underset{\text{Sodium metaphosphate}}{NaPO_3} + NH_3 + H_2O$$

Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured. The shade of the colour gives a clue regarding the presence of metal. Like borax bead test, colours are noted both in oxidising and reducing flames in hot and cold conditions.

Metal	Colour of the bead in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Red
Iron	Yellow or reddish-brown	Yellow	Yellow	Colourless
Chromium	Green	Green	Green	Green
Manganese	Violet	Violet	Colourless	Colourless
Nickel	Brown	Brown	—	Grey

SOLVED EXAMPLES

Example 1

Complete the following reactions :

(i) $CaCO_3 \xrightarrow{\Delta}$ **[A] + [B]** (gas)

(ii) **[A]** $+ H_2O \longrightarrow$ **[C]**

(iii) **[C] + [B]** $\longrightarrow CaCO_3 + H_2O$

(iv) **[D] + [C]** $\xrightarrow{\Delta}$ **E** (gas)

(v) **[E]** $+ H_2O +$ **[B]** $\longrightarrow$ **[F]**

(vi) **NaCl + [F]** $\longrightarrow$ **[G] + [D]**

(vii) **[G]** $\xrightarrow{\Delta} Na_2CO_3 + H_2O +$ **[B]**

Solution :

(i) $CaCO \xrightarrow{\Delta} \underset{(A)}{CaO} + \underset{(B)}{CO_2}$

(ii) $\underset{(A)}{CaO} + H_2O \longrightarrow \underset{(C)}{Ca(OH)_2}$

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

(iv) $\underset{(D)}{2NH_4Cl} + \underset{(C)}{Ca(OH)_2} \xrightarrow{\Delta} \underset{(E)}{2NH_3}\uparrow + CaCl_2 + 2H_2O$

(v) $\underset{(E)}{NH_3} + \underset{(B)}{H_2O} + CO_2 \longrightarrow \underset{(F)}{NH_4HCO_3}$

(vi) $NaCl + \underset{(F)}{NH_4HCO_3} \longrightarrow \underset{(G)}{NaHCO_3} + \underset{(D)}{NH_4Cl}$

(vii) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + \underset{(B)}{CO_2}$

Example 2

True or False :

(a) The carbonates of barium and calcium are soluble in acid.

(b) Copper sulphate forms a violet colour with potassium ferrocyanide solution.

(c) Ammonium sulphate can be used in place of ammonium chloride in third group.

Solution :

(a) True

(b) False. Chocolate precipitate.

(c) False. Sulphates of V group radicals will be precipitated.

Example 3

When a crystalline compound (X) is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish-brown gas (A) is evolved. On passing (A) into caustic soda, a yellow coloured solution of (B) is obtained. Neutralizing the solution of (B) with acetic acid and on subsequent addition of lead acetate, a yellow precipitate of (C) is obtained. When (X) is heated with NaOH, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish-brown precipitate (D) is formed. Identify (A), (B), (C), (D) and (X). Write the equation of reactions involved.

Solution :

The given information in the question infers that compound (X) should be NH_4Cl.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$NH_4Cl + H_2SO_4 \longrightarrow NH_4HSO_4 + HCl$$

$$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 \uparrow + H_2O$$

(A)

Reddish-brown gas

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

(B)

Yellow coloured solution

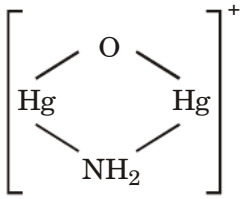
$$Na_2CrO_4 + (CH_3COO)_2Pb \xrightarrow[CH_3COOH]{} PbCrO_4 \downarrow + 2CH_3COONa$$

(C)

Yellow ppt

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

Colourless gas

$$NH_3 + 2K_2[HgI_4) + H_2O \longrightarrow$$  $$I + 4KI + 3HI$$

Example 4

An aqueous solution of gas (X) shows the following reaction

(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) $CuSO_4 + 4NH_4OH \longrightarrow Cu(NH_3)_4\ SO_4 + H_2O$

deep blue

(ii) $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 \downarrow + 3NH_4Cl$

brown ppt

$Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$

Soluble

Example 5

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, turbidity is obtained.

Identify (X) and given 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) $SO_2 + H_2O_2 \longrightarrow H_2SO_4$

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

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

Example 6

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

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

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

Example 7

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) $2CuSO_4 + 2KI \longrightarrow 2CuI_2 + K_2SO_4$

$2CuI_2 \longrightarrow Cu_2I_2 + I_2$

white

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

(ii) $Ag^+ + KI \longrightarrow AgI + K^+$

Yellow ppt.

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.

Example 8

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 Kl gives a brown ppt. which turns white 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) $CuSO_4 + BaCl_2 \longrightarrow BaSO_4 + CuCl_2$

White ppt

(insoluble in HCl)

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

$\downarrow$

$Cu_2I_2 + I_2$

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

(iii) $CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$

(Chocolate, coloured ppt.)

Example 9

Two ores of the same metal (M) are (A_1) and (A_2).

$$(A_1) \xrightarrow{\text{calcination}} \text{Black ppt } (C) + CO_2 + H_2O; \qquad (A_1) \xrightarrow[HCl]{KI} I_2 + \text{ppt } (D)$$

$$(A_2) \xrightarrow{\text{Roasting}} \text{gas } (G) + \text{metal } (M); \qquad (G) + K_2Cr_2O_7 \xrightarrow{\text{acidified}} \text{Green solution}$$

Identify (M), (A_1), (A_2), (C), (D) and (G).

Solution :

$$\underset{\text{Malachite } (A_1)}{CuCO_3.Cu(OH)_2} \xrightarrow{\text{calcination}} \underset{\text{Black (C)}}{2CuO\downarrow} + CO_2\uparrow + H_2O$$

$$CuCO_3.Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + CO_2\uparrow + 3H_2O$$

$$2CuCl_2 + 4KI \longrightarrow \underset{(D)}{Cu_2I_2\downarrow} + 4KCl + I_2$$

$$\underset{\text{copper glance } (A_2)}{2Cu_2S} + 3O_2 \xrightarrow{\text{Roasting}} 2Cu_2O + \underset{(G)}{2SO_2}$$

$$Cu_2S + 2Cu_2O \longrightarrow \underset{(M)}{6Cu} + SO_2;\ 3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 4H_2O$$

Example 10

$$Na_2CO_3 \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow[\text{sulphur}]{\text{elements}} (C) \xrightarrow{I_2} (D)$$

Find (A), (B), (C) and (D). Give oxidation state of sulphur in each compound.

Solution :

(A) : $NaHSO_3$ (B) : Na_2SO_3

(C) : $Na_2S_2O_3$ (D) : $Na_2S_4O_6$

Oxidation state of sulphur in (A) is + 4, in (B) is also + 4, in (C) is + 2 and in (D) is + 5/2.

Example 11

A mixture consisting of A (yellow solid) and B (colourless solid) gives lilac colour in flame.

(a) Mixture gives black precipitate C on passing H_2S gas in acidic medium.

(b) C is soluble in aqua-regia and on adding $SnCl_2$, it gives white precipitate, which finally turns to greyish black precipitate D.

The white precipitate on treatment with NH_4OH gives a brown precipitate.

(i) The sodium carbonate extract of the salt A with $CCl_4/FeCl_3$ gives a violet layer.

(ii) The sodium carbonate extract of the salt A gives yellow precipitate in $AgNO_3$ solution, which is insoluble in NH_3. Identify A and B and the precipitate C and D.

Solution :

(A) : KI_3 (B) : $HgCl_2$ (C) : HgS (D) : Hg

(a) $\underset{(B)}{HgCl_2} + H_2S \longrightarrow \underset{\substack{\text{Black ppt}\\(C)}}{HgS} + 2HCl$

(b) $3HgS + 6HCl + 2HNO_3 \longrightarrow 3HgCl_2 + 2NO + 3S + 4H_2O$

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

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

$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Brown}}{Hg + Hg(NH_2)Cl} + NH_4Cl$

(i) $\underset{\left(\begin{smallmatrix}\text{From soda}\\\text{extract}\end{smallmatrix}\right)}{I^-} + FeCl_3 \longrightarrow I_2 \xrightarrow{CCl_4} \underset{\text{Violet layer}}{CCl_4 - I_2}$

(ii) $\underset{\text{(From soda extract)}}{I^-} + AgNO_3 \longrightarrow \underset{\substack{\text{Yellow ppt}\\\text{(Insoluble in } NH_3\text{)}}}{AgI \downarrow}$

KI_3	+	$HgCl_2$	→	Lilac
yellow		white		colour in
[A]		[B]		flame

Example 12

An aqueous solution containing one mole of HgI_2 and two mole of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations.

Solution :

A solution containing one mole of HgI_2 and two mole of NaI is orange in colour due to the partial solubility of HgI_2. On addition of excess of NaI, the colourless complex Na_2HgI_4 is formed.

$$2NaI + HgI_2 \xrightarrow[\text{Excess}]{} Na_2HgI_4$$

The Na_2HgI_4 on addition of NaOCl, oxidises as :

$$3Na_2HgI_4 + 2NaOCl + 2H_2O \longrightarrow 3HgI_2 + 2NaCl + 4NaOH + NaI_3$$

Thus, colour of partially soluble HgI_2 is restored.

Example 13

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) $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \uparrow$
fumes

(ii) $HCl + NH_4OH \rightarrow NH_4Cl \uparrow + H_2O$
White fumes

(iii) $AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$
White ppt

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

Example 14

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

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

(iii) $3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$

(iv) $AgNO_3 \xrightarrow{HCl} AgCl + HNO_3$

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

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

Example 15

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) $2BaCl_2 + K_2Cr_2O_7 + 3HSO_4 \rightarrow K_2SO_4 + \underset{\text{red gas}}{2CrO_2Cl_2} + 2BaSO_4 + 3H_2O$

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

Example 16

(A) is yellow coloured solid partially soluble in aqueous NH_3. (A) is soluble in $Na_2S_2O_3$ (hypo) solution forming a complex (B) which on heating is converted into (C) (black). (C) is converted into white ppt (D) on reaction with HCl and HNO_3 . (D) is soluble in aqueous NH_3 forming (E). Identify (A), (B), (C), (D) and (E) and explain reactions.

Solution :

(A) is AgBr (present in photographic plate)

$$AgBr + \underset{\text{hypo}}{2Na_2S_2O_3} \longrightarrow \underset{\substack{\text{soluble}\\(B)}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

$$\underset{(E)}{[Ag(NH_3)_2Cl]} \xleftarrow{NH_3} \underset{(D)}{AgCl\downarrow} \xleftarrow{HCl + HNO_3} \underset{(C)}{Ag_2S}$$

Example 17

Identify (A), (B), (C) and (D) based on following observations :

(i) $(A) \xrightarrow{\Delta}$ glassy transparent bead (B) on platinum wire (B) + $CuSO_4 \longrightarrow$ coloured bead (C)

(ii) (A) + conc. H_2SO_4 + $CH_3CH_2OH \xrightarrow{\text{ignite}}$ green flame (D)

(iii) Aqueous solution of (A) is alkaline.

Solution :

(i) (A) forms glassy transparent bead which is characteristic property of borax.

$\Rightarrow$ (A) is borax ($Na_2B_4O_7.10H_2O$)

(ii) $$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} \underbrace{NaBO_2 + B_2O_3}_{\text{(B) glassy bead}} + 10H_2O$$

$$B_2O_3 + CuSO_4 \xrightarrow{\Delta} \underset{\text{coloured bead(C)}}{Cu(BO_2)_2} + SO_3\uparrow$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\substack{\text{green flame (on ignition)}\\(D)}}{(C_2H_5)_3BO_3} + Na_2SO_4 + 4H_3BO_3$$

(iii) $Na_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{weak acid}}{2H_3BO_3} + 2Na[B(OH)_4]$

$Na[B(OH)_4]$ reacts with acid (HCI) hence aqueous solution (A) is alkaline.

Example 18

Name one common reagent that can precipitate or react and differentiate following pairs :

(a) Ag^+ **and** Ba^{2+} **(b)** Cu^{2+} **and** Pb^{2+}

(c) I^- **and** Cl^- **(d)** I^- **and** Br^-

(v) SO_3^{2-} **and** SO_4^{2-} **(f)** Fe^{3+} **and** Cu^{2+}

Solution :

(a) K_2CrO_4 **:**

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

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

(b) K_2CrO_4 **:**

$$Cu^{2+} + CrO_4^{2-} \longrightarrow \underset{\text{chocolate}}{CuCrO_4}\downarrow$$

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

(c) $AgNO_3$ **:**

$$Ag^+ + I^- \longrightarrow \underset{\text{yellow}}{AgI}\downarrow$$

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

(d) Cl_2 **water +** $CHCl_3$ **:**

$$2I^- + Cl_2 \longrightarrow \underset{\substack{\text{(violet in}\\ CHCl_3 \text{ layer)}}}{I_2} + 2Cl^-$$

$$2Br^- + Cl_2 \longrightarrow \underset{\substack{\text{(orange in}\\ CHCl_3 \text{ layer)}}}{Br_2} + 2Cl^-$$

(e) $BaCl_2$:

$$BaCl_2 + SO_3^{2-} \longrightarrow \underset{\text{white ppt soluble in conc. HCl}}{BaSO_3 \downarrow}$$

$$BaCl_2 + SO_4^{2-} \longrightarrow \underset{\text{white ppt insoluble in conc. HCl}}{BaSO_4 \downarrow}$$

(f) NH_4SCN :

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{red colour}}{[Fe(SCN)]^{2+}}$$

$$Cu^{2+} + 2SCN^- \longrightarrow \underset{\text{black}}{Cu(SCN)_2 \downarrow}$$

Example 19

The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours (A) are produced. The aqueous solution of mixture gives a deep blue colouration (B) with potassium ferricyanide. Identify the radicals in given mixture and write the balanced equation for formation of (A) and (B).

Solution :

(i) Gas given by heating mixture with NaOH gives brown ppt with Nessler's reagent K_2HgI_4. It shows that the salt is a ammonium salt.

(ii) $BaCl_2$ solution gives white precipitate sparingly soluble in HCl. It shows the presence of SO_4^{2-} ion in the mixture

(iii) Blue colour with $K_3Fe(CN)_6$ indicates the presence of Fe^{2+} ion.

(iv) $\text{Mixture} + K_2Cr_2O_7 \xrightarrow[\Delta]{H_2SO_4} \underset{(A)}{\text{Red vapours } (CrO_2Cl_2)}$

It shows that the mixture contains Cl^- ion. Reactions involved may be given as :

(i) $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 \uparrow + H_2O$

$$K_2HgI_4 + NaOH + NH_3 \rightarrow \underset{\text{(Brown ppt)}}{O\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}Hg \\ Hg\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix}} NH_2I + KI + H_2O + NaI$$

(ii) $FeSO_4 + BaCl_2 \longrightarrow \underset{\text{(White ppt)}}{BaSO_4} + FeCl_2$

(iii) $3FeSO_4 + 2K_3Fe(CN)_6 \longrightarrow 3K_2SO_4 + \underset{\substack{\text{Ferrous ferricyanide}\\\text{(Blue)}}}{Fe_3[Fe(CN)_6]_2}$

(iv) $4NH_4Cl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} + K_2SO_4 + 3H_2O + 2(NH_4)_2SO_4$

Example 20

A white substance (A) reacts with dilute H_2SO_4 to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified K_2CrO_7 solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to (C) produces first a precipitate, which dissolves in the excess of respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E) write the equations of the reactions involved.

Solution :

The white substance (A) is ZnS.

$$\underset{\text{(A)}}{ZnS} + H_2SO_4 \longrightarrow \underset{\substack{\text{Colourless}\\\text{(C)}}}{ZnSO_4} + \underset{\substack{\text{Gas (colourless)}\\\text{(B)}}}{H_2S}$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow \underset{\text{Green solution}}{Cr_2(SO_4)_3} + K_2SO_4 + 7H_2O + \underset{\substack{\text{White grey}\\\text{(D)}}}{3S}$$

$$\underset{\text{(D)}}{S} + \underset{\text{(air)}}{O_2} \longrightarrow \underset{\text{(E)}}{SO_2}$$

$$\underset{\text{(E)}}{SO_2} + 2\underset{\text{(B)}}{H_2S} \longrightarrow \underset{\text{(D)}}{3S} + \underset{\text{Colourless liquid}}{2H_2O}$$

$$\underset{\substack{\text{White}\\\text{(Anhydrous)}}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4 5H_2O}$$

$$\underset{(C)}{ZnSO_4} + 2NaOH \longrightarrow \underset{\text{White ppt}}{Zn(OH)_2} + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Soluble in water}\\(\text{Clear solution})}}{Na_2ZnO_2} + 2H_2O$$

$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

Example 21

Identify (A) to (G) in the following scheme and name the process.

$$\mathbf{CaCO_3 \xrightarrow{\Delta} (A) + (B)\,gas}$$

$$\mathbf{(A) + H_2O \longrightarrow (C)}$$

$$\mathbf{(C) + (B) \longrightarrow CaCO_3 + H_2O}$$

$$\mathbf{(D) + (C) \xrightarrow{\Delta} (E)\,gas}$$

$$\mathbf{(E) + H_2O + (B) \longrightarrow (F)}$$

$$\mathbf{NaCl + (F) \longrightarrow (G) + (D)}$$

$$\mathbf{(G) \xrightarrow{\Delta} Na_2CO_3 + H_2O + (B)}$$

Solution :

Scheme represents the Solvay process of manufacture of Na_2CO_3.

$$\underset{}{CaCO_3} \xrightarrow{\Delta} \underset{(A)}{CaO} + \underset{(B)}{CO_2}(g)$$

$$\underset{(A)}{CaO} + H_2O \longrightarrow \underset{(C)}{Ca(OH)_2}$$

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

$$\underset{(D)}{2NH_4Cl} + \underset{(C)}{Ca(OH)_2} \xrightarrow{\Delta} \underset{(E)}{2NH_3}\uparrow + CaCl_2 + 2H_2O$$

$$\underset{(E)}{NH_3} + H_2O + \underset{(B)}{CO_2} \longrightarrow \underset{(F)}{NH_4HCO_3}$$

$$NaCl + \underset{(F)}{NH_4HCO_3} \longrightarrow \underset{(G)}{NaHCO_3} + \underset{(D)}{NH_4Cl}$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + \underset{(B)}{CO_2}$$

Example 22

Identify (A), (B), (C)..... (H) in the following and explain reactions :

$$\mathbf{(A)\ black + dil\ H_2SO_4 \longrightarrow B(aq) + C(aq) + D(g)}$$

$$\mathbf{(B) + KI \longrightarrow brown\ coloured\ solution}$$

$$\Big\downarrow \mathbf{hypo}$$

$$\mathbf{white\ ppt\ (E)}$$

$$\mathbf{(C) + MnO_4^- + H^+ \longrightarrow colourless\ solution}$$

$$\mathbf{(C) + K_3[Fe(CN)_6] \longrightarrow blue\ (F)}$$

$$\mathbf{(D) + (CH_3COO)_2Pb \longrightarrow black(G)}$$

$$\mathbf{(B)\ or\ (C) + BaCl_2 \longrightarrow white\ ppt\ (H)}$$

$$\mathbf{(B) + (D) \longrightarrow black\ ppt\ (I)}$$

Solution :

(D) + $(CH_3COO)_2Pb$ ⟶ black (G)

⇒ (D) is H_2S gas and (G) is PbS

⇒ (A) also has S^{2-}

(A) + dil. H_2SO_4 ⟶ (B), (C)

(B) and (C) both are sulphates as confirmed by white ppt (H) with $BaCl_2$

(B) + KI ⟶ brown coloured solution changing to white ppt (E)

Thus, (B) is $CuSO_4$

$$2CuSO_4 + 4KI \longrightarrow \underset{(E)}{Cu_2I_2} + 2K_2SO_4 + I_2$$

$$I_2 + KI \rightleftharpoons KI_3$$

Due to KI_3, solution appears reddish brown. On adding hypo, I_2 disappears and white ppt of Cu_2I_2 appears.

$$\left(I_3^-\right) I_2 + \underset{\text{hypo}}{2Na_2S_2O_3} \longrightarrow 2NaI + Na_2S_4O_6$$

(C) decolorises MnO_4^- / H^+. (C) also gives blue colour with $K_3[Fe(CN)_6$ thus (C) is $FeSO_4$.

$$FeSO_4 + K_3[Fe(CN)_6] \longrightarrow \underset{\text{Turnbull's blue (F)}}{KFe^{II}[Fe^{III}(CN)_6]} + K_2SO_4$$

(A) : CuS + FeS ($CuFeS_2$)
(B) : $CuSO_4$
(C) : $FeSO_4$
(D) : H_2S
(E) : Cu_2I_2
(F) : $KFe^{II}[Fe^{III}(CN)_6]$
(G) : PbS
(H) : $BaSO_4$
(I) : CuS

Example 23

Black coloured (insoluble in H_2O) solid (A) does not dissolve in dil. HNO_3. Aqua regia can dissolve (A) forming (B). (B) gives yellow ppt. (C) with NaOH. (B) also gives orange ppt (D) with KI; (D) dissolves in excess of KI forming (E). (E) gives brown ppt with NH_4^+ salt in presence of NaOH. (A) is precipitated if H_2S gas is passed into solution of (B) in dil. HCl. Identify (A) to (E) and explain reactions.

Solution :

(A) is insoluble in dil. HNO_3.

$\Rightarrow$ (A) is of group II (copper sub-group) and is HgS [only HgS (black) is insoluble in dil. HNO_3]

$$(A) + \underbrace{3HCl + HNO_3}_{\text{aqua regia}} \longrightarrow \underset{(B)}{HgCl_2}$$

$$HgCl_2 + 2NaOH \longrightarrow \underset{\text{yellow ppt (C)}}{HgO\downarrow} + 2NaCl + H_2O$$

$$HgCl_2 + 2KI \longrightarrow \underset{\text{(D) (orange)}}{HgI_2\downarrow} + 2KCl + H_2O$$

$$HgI_2 + 2KI \longrightarrow \underset{\text{(E) (soluble)}}{K_2HgI_4}$$

$$NH_4^+ + NaOH \xrightarrow{\Delta} NH_3 + H_2O + Na^+$$

$$3NaOH + NH_3 + 2K_2HgI_4 \rightarrow O\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}Hg \\ Hg\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix} NH_2I\downarrow + 4KI + 3NaI + 2H_2O$$

brown ppt
(iodide of MIllion's base)

$$\underset{\text{(B)}}{HgCl_2} + H_2S \longrightarrow \underset{\text{black}}{HgS\downarrow} + 2HCl$$

Example 24

Colourless salt, (A) (insoluble in water) + dil. H_2SO_4 ⟶ (B) + C(g)

(B) $\xrightarrow{+NaOH}$ (D) (white ppt) $\xrightarrow[\text{(excess)}]{NaOH}$ (E) (soluble)

(B) $\xrightarrow{NH_4Cl + NH_4OH}$ no ppt $\xrightarrow{(C)}$ (A)

(D) (white ppt) $\xleftarrow{(C)}$ (A)

(C) + (F) (yellow coloured solution) ⟶ light green (G)

light green (G) $\xrightarrow{K_4[Fe(CN)_6]}$ blue (H)

light green (G) $\xrightarrow{AgNO_3}$ white ppt (I) (soluble in NH_3)

light green (G) $\xrightarrow[\Delta]{+O_2}$ H_2O + (J) $\xrightarrow{+C}$ colloidal white turbidity

H_2O + (J) $\xrightarrow{Cr_2O_7^{2-}/H^+}$ green

H_2O + (J) $\xrightarrow{Ca(OH)_2}$ milky

Identify (A) to (J) and explain reactions.

Solution :

Gas (C) is vital compound in this scheme.

$$\text{Gas}(C) \xrightarrow[\Delta]{O_2} H_2O + (J)$$

$$\text{milky} \xleftarrow{Ca(OH)_2} \text{Gas}(J) \xrightarrow{Cr_2O_7^{2-}/H^+} \text{green}$$

$\Rightarrow$ (J) is SO_2

$\Rightarrow$ (C) is H_2S (giving H_2O and SO_2 by combustion in O_2).

(B) gives white ppt only if (C) is passed into its ammoniacal solution containing NH_4Cl ($NH_4OH + NH_4Cl$)

$\Rightarrow$ (B) has Zn^{2+} and (B) is $ZnSO_4$

$\Rightarrow$ (A) is ZnS

(F) gives blue colour with $K_4[Fe(CN)_6]$

$\Rightarrow$ (F) has Fe^{3+} ion

(F) gives white ppt with $AgNO_3$

$\Rightarrow$ (F) has Cl^- ion. Thus, F is $FeCl_3$.

Explanation :

$$\underset{(A)}{ZnS} + H_2SO_4 \longrightarrow \underset{(B)}{ZnSO_4} + \underset{(C)}{H_2S}$$

$$\underset{(B)}{ZnSO_4} + 2NaOH \longrightarrow \underset{(D)}{Zn(OH)_2} + Na_2SO_4$$

$$\underset{(D)}{Zn(OH)_2} + 2NaOH \longrightarrow \underset{\text{soluble (E)}}{Na_2ZnO_2} + 2H_2O$$

$$\underset{(E)}{Na_2ZnO_2} + \underset{(C)}{H_2S} \longrightarrow \underset{(A)}{ZnS} + 2NaOH$$

$$\underset{(C)}{H_2S} + 2\,\underset{\substack{(F)\\ \text{yellow}}}{FeCl_3} \longrightarrow \underset{\text{(G) green}}{2FeCl_2} + 2HCl + S$$

$$\underset{(F)}{FeCl_3} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(H), Prussian blue}}{K\overset{III}{Fe}[\overset{II}{Fe}(CN)_6]} + 3KCl$$

$$FeCl_3 + 3AgNO_3 \longrightarrow Fe(NO_3)_3 + \underset{\text{white ppt (I)}}{3AgCl\downarrow}$$

$$\underset{\text{(I)}}{AgCl} + 2NH_3 \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$$

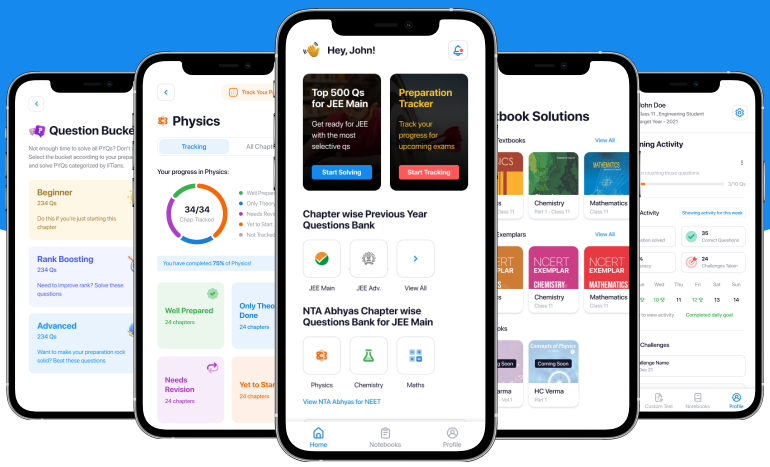
$$2H_2S + 3O_2 \xrightarrow{\Delta} 2H_2O + \underset{\text{(J)}}{2SO_2}$$

$$\underset{\text{(J)}}{SO_2} + \underset{\text{(C)}}{2H_2S} \longrightarrow 2H_2O + \underset{\text{colloidal white turbidity}}{3S\downarrow}$$

$$3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow \underset{\text{green}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O$$

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

MARKS



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