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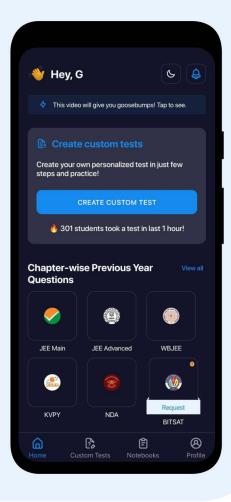
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QUALITATIVE ANALYSIS

QUALITATIVE ANALYSIS

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 divided into two sub groups.

- (i) Gases evolved with dil. $HCl/dil H_2SO_4$
- (ii) Gases or acid vapours evolved with conc. H₂SO₄

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.

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

$$CO_9 + Ba^{2+} + 2OH^- \longrightarrow BaCO_3 \downarrow + H_9O$$

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 H₂SO₄

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

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

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

$$(\mathrm{CH_3COO})_2\mathrm{Pb} \, + \, \mathrm{H_2S} \, \downarrow \, \longrightarrow \, \mathrm{PbS} \, (\downarrow) \, + \, 2\mathrm{CH_3COOH}$$
 Shining black

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

(ii) Silver nitrate solution

With AgNO₃ 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.

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 $\mathrm{Hg_2Cl_2}$, CuCl , AgCl , $\mathrm{PbCl_2}$, BiOCl and SbOCl . $\mathrm{PbCl_2}$ is soluble in hot water.

(i) Concentrated H_2SO_4

With concentrated H₂SO₄, 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 $\mathrm{H_2SO}_4$, yellowish-green coloured gas (Cl_9) is evolved.

$$\label{eq:mno2} \text{MnO}_2 + 2\text{H}_2\text{SO}_4 + 2\text{Cl}^- \longrightarrow \text{Mn}^{2+} + \text{Cl}_2 \uparrow + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O}$$
 Yellowish green

(iii) Silver nitrate solution

Chlorides on treatment with ${\rm AgNO_3}$ 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

(iv) Lead acetate solution

With $(CH_3CO_2)_2$ Pb solution, chlorides gives a white precipitate of lead chloride.

(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.

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.

$$\text{CrO}_2\text{Cl}_2$$
 \(\gamma + 2\text{NaOH} \) \(\bigcup_4\text{CrO}_4 + 2\text{HCl} \)

Yellow solution

$$\mathrm{Na_{2}CrO_{4} + (CH_{3}COO)_{2}Pb} \ \ \underline{\hspace{1cm}} \ \ 2CH_{3}COONa + PbCrO_{4} \ \downarrow}$$

Yellow ppt

4. Bromide (Br⁻)

(i) Conc. H₂SO₄: It gives reddish brown vapours of bromine.

$$\begin{split} 2\text{KBr} + \text{H}_2\text{SO}_4 &\rightarrow \text{K}_2\text{SO}_4 + 2\text{HBr} \\ 2\text{HBr} + \text{H}_2\text{SO}_4 &\rightarrow 2\text{H}_2\text{O} + \text{SO}_2 \; (\uparrow) + \text{Br}_2 \; \uparrow \\ &\text{(reddish brown)} \end{split}$$

(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 $_2$ SO $_4$ \rightarrow Br $_2$ ↑ + K $_2$ SO $_4$ + MnSO $_4$ + 2H $_2$ O

- (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. HNO₃.

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

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

$$2\mathrm{Br}^- + \mathrm{Pb}^{+2} \longrightarrow \mathrm{PbBr}_2 \downarrow$$

(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.

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

$$\operatorname{Br}_2 + \operatorname{Chloroform} \ \longrightarrow \ \operatorname{Orange} \ \operatorname{red} \ \operatorname{colour}$$

(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.

$$2 \text{KBr} + \text{K}_2 \text{Cr}_2 \text{O}_7 + 7 \text{H}_2 \text{SO}_4 \rightarrow 3 \text{Br}_2 \uparrow + \text{Cr}_2 (\text{SO}_4)_3 + 4 \text{K}_2 \text{SO}_4 + 7 \text{H}_2 \text{O}_4 + 7 \text{H}_2$$

5. Iodide (I⁻)

Iodides are generally soluble in water except AgI, Hg, I, HgI, CuI and PbI,

(i) Concentrated H₂SO₄

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

2I^ + 2H₂SO₄
$$\longrightarrow$$
 I₂ ↑+ SO₄ + 2H₂O + SO₂ ↑ Violet vapours

(ii) Silver nitrate solution

With ${\rm AgNO_3}$ 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 ${\rm HNO_3}$.

(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.

(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^ + Cr₂O₇²⁻ + 2H₂SO₄
$$\longrightarrow$$
 3I₂ ↑ + 2Cr³⁺ + 7SO₄²⁻ + 7H₂O 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 + Chloroform \longrightarrow Violet solution

(vi) Copper sulphate solution

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

(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.

5. Nitrate (NO_3^-)

(i) Conc. H_2SO_4 : It gives reddish-brown vapours of nitrogen dioxide

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

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. H₂SO₄ is poured slowly down the side of the test tube, a brown ring is obtained.

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

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

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).

$$2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2 \uparrow$$
.

(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.

$$2\text{Pb(NO}_3)_2 \ \longrightarrow \ 2\text{PbO} + 4\text{NO}_2 \uparrow + \text{O}_2 \uparrow$$

(B) Group 'B' Radicals

7. Sulphate (SO_4^{2-})

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.

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

(ii) Silver nitrate solution

With silver nitrate solution, SO₄²⁻ gives a white crystalline precipitate of silver sulphate.

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

(iii) Mercury(II) nitrate solution

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

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

Yellow ppt

Physical appearance of inorganic salts

Sr No.	Salt	Colour
1	${\rm MnO,MnO_2,FeO,CuO,Co_3O_4,Ni_2O_3,}$	
	sulfides of Ag^+ , Cu^+ , Cu^{2+} , Fe^{2+} , CO^{2+} , Pb^{2+} , Hg^{2+}	Black
2	Hydrated Cu ²⁺ salts	Blue
3	$\mathrm{HgO,\ HgI}_{2},\ \mathrm{Pb_{3}O_{4}}$	Red
4	Cr ³⁺ , Cr ⁶⁺ , Ni ²⁺ , Hydrated Fe ²⁺ salts	Green
5	Hydrated Mn ²⁺ salts	Light Pink
6	$\mathrm{KO_2},\ \mathrm{K_2Cr_2O_7},\ \mathrm{Sb_2S_3},\ \mathrm{ferricyanides}$	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) NO₂, (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) $\begin{array}{ll} {\rm Br_2(Reddish\ Brown)\ turns\ starch\ paper\ yellow} \\ {\rm Substance\ bromide:\ 2CdBr_2+O_2\to 2CdO+2Br_2} \uparrow \end{array}$

 - (iv) Cl₂ (Greenish yellow) bleaches moist litmus paper $\begin{array}{c} {\rm Chlorides} \ {\rm CuCl}_2 + {\rm H_2O} \rightarrow {\rm CuO} + 2{\rm HCl} \\ \\ {\rm (moisture)} \end{array} \qquad \downarrow \rightarrow {\rm Cu} + {\rm H_2O} + 1/2{\rm Cl}_2$
- (b) Colourless gas (odourless)
 - (i) $\rm O_2\!\!-\!\!supports$ glowing $\rm Alkali\ nitrates: 2KNO_3 \rightarrow 2KNO_2 + O_2 \uparrow$
 - (ii) ${
 m CO}_2$ Turns lime water milky Carbonates/Oxalates ${
 m CaCO}_3 \to {
 m CaO} + {
 m CO}_2 \uparrow$
- (c) Colourless gas (with odour)
 - (i) NH $_3$ turns red litmus blue ${\rm Ammonium~salts:~(NH}_4)_2 {\rm SO}_4 \to {\rm NH}_4 {\rm HSO}_4 + {\rm NH}_3 \uparrow$
 - (ii) SO $_2$ Smell of burning sulphur, turns acidified K $_2$ Cr $_2$ O $_7$ paper green Sulphites, thiosulphates ${\rm CaSO}_3 \to {\rm CaO} + {\rm SO}_2$
 - (iii) HCl pungent smell, white fumes with ammonia hydrates chlorides ${\rm CaCl_2.6H_2O} \rightarrow {\rm Ca(OH)_2} + 4{\rm H_2O} + 2{\rm HCl} \uparrow$

 (iv) H₂S - 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, Pb₃O₄
 - $(iv) \quad Black \ (hot) \ Red \ Brown \ (cold) Fe_2O_3$
- 3. Substance melts: Salts of alkali metals & salts having water of crystallisation.
- 4. Substance makes crackling noise: NaCl, KI, Pb(NO₃)₂, Ba(NO₃)₂
- 5. Substance Swells: Alums, borates & phosphates
- 6. Substance sublimes & colour of sublimate is:
 - (a) White: HgCl₂, Hg₂Cl₂, AlCl₃, As₂O₃, Sb₂O₃
 - (b) Yellow: As₂S₃, HgI₂ 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	oup Group Basic reagent radical		Composition and colour of the precipitate	
1.	Dilute HCl	Ag ⁺ Pb ²⁺	AgCl : white PbCl ₂ : white	Chloride insoluble in
		Hg_2^{2+}	$\mathrm{Hg_2Cl_2}$: white	cold dilute HCl
2.	$\mathrm{H_2S}$ in	Hg^{2+}	HgS: black	
	presence of	Pb ²⁺	PbS: black	Sulphides
	dilute HCl	Bi ³⁺	$\mathrm{Bi}_2\mathrm{S}_3$: black	insoluble in
		Cu^{2+}	Cus : black	dilute HCl
		Cd^{2+}	CdS : yellow	J

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
3.	NH ₄ OH in	Fe ³⁺	Fe(OH) ₃ :	
	presence of		reddish brown Hydroxides	
	NH₄Cl	Cr^{3+}	$\operatorname{Cr(OH)}_3$: green are insoluble	
	+	Al^{3+}	$Al(OH)_3$: white in NH4OH	
4.	$ m H_2S$ in	Zn^{2+}	ZnS Sulphides are	
	presence of		greenish white insoluble in	
	$\mathrm{NH_4OH}$	Mn^{2+}	MnS: buff NH ₄ OH	
5.	${\rm (NH_4)}_2{\rm CO}_3$ in presence of	Ba ²⁺	$BaCO_3$: white $race{}{}{}$ Carbonates	
	NH ₄ OH	Ca^{2+}	CaCO_3 : white \int are insoluble	
6.	$\mathrm{Na_2HPO}_4$	Mg^{2+}	$Mg(NH_4)PO_4$:	
7.	NaOH	$\mathrm{NH_4^+}$	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 S²⁻ due to common ion effect. Hence, the decreased concentration of S²⁻ is only sufficient to precipitate the Group II metals ions as sulphides.
- 3. Group III A radicals are precipitated as hydroxides and the $\mathrm{NH_4Cl}$ suppresses the ionisation of $\mathrm{NH_4OH}$ so that only the group III A cations are precipitated as hydroxide because of their low solubility product.

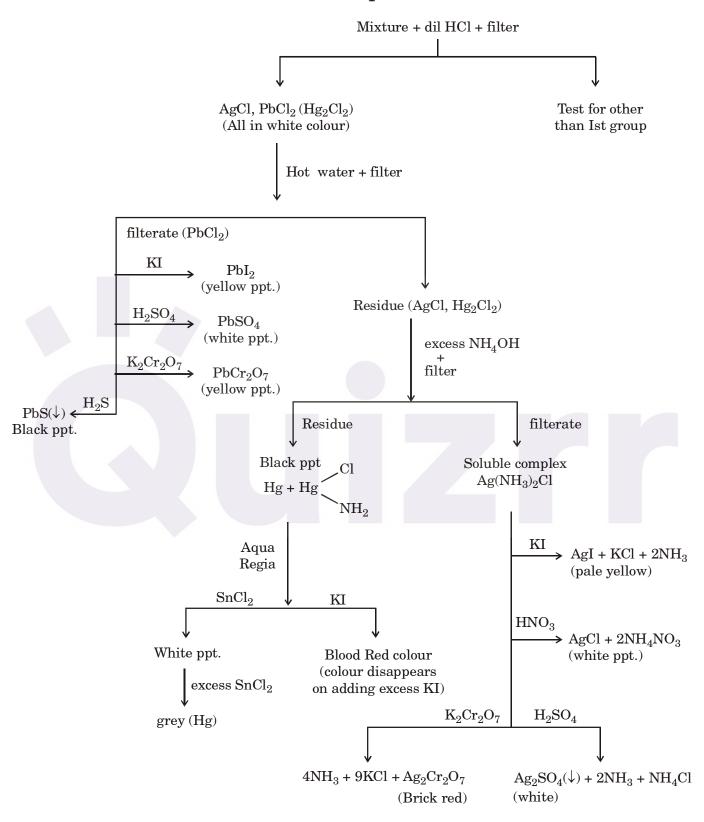
- (i) Excess of $\mathrm{NH_4Cl}$ should not be added, else manganese will precipitate as $\mathrm{MnO_2.H_2O}$
- (ii) $(NH_4)_2SO_4$ cannot be used in placed of NH_4Cl because the SO_4^{2-} will give precipitate of $BaSO_4$.
- (iii) $\mathrm{NH_4NO_3}$ cannot be used in place of $\mathrm{NH_4Cl}$ as $\mathrm{NO_3^-}$ ions will oxidise $\mathrm{Mn^{2+}}$ to $\mathrm{Mn^{3+}}$ and thus, $\mathrm{Mn(OH)_3}$ will be precipitated in III A group.
- 4. Ammonium hydroxide increases the ionisation of $\rm H_2S$ by removing $\rm H^+$ from $\rm H_2S$ as unionised water.

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,

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

15

Group I

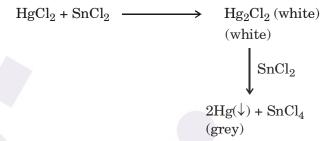


Some Salient Reactions:

(1)
$$\text{Hg}_2\text{Cl}_2$$
 $\xrightarrow{\text{NH}_4\text{OH}}$ $\text{Hg}(\downarrow) + \text{Hg} \xrightarrow{\text{Cl}}$ $\xrightarrow{\text{NH}_2}$ $\text{Black (shing black)}$

(2) Aqua Regia is a very strong oxidizing agent and it converts the black precipitate into soluble ${\rm HgCl}_{2}$.

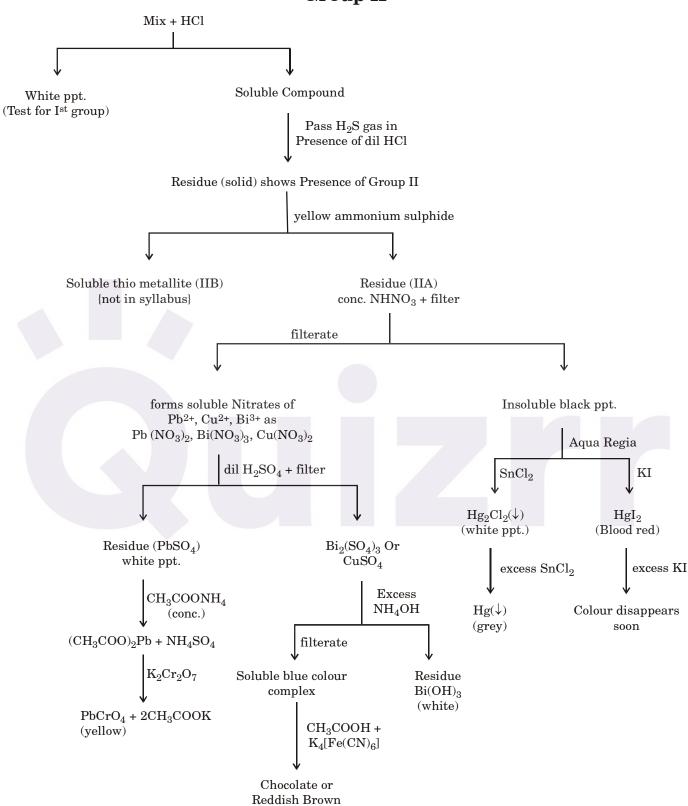
Aqua Regia is a mixture of (3HCl + HNO $_3$ \rightarrow NOCl + 2H $_2$ O + Cl $_2$)



$$HgI_2 + 2KI \longrightarrow K_2[HgI_4]$$

(nessler's Reagent)

Group II



18

Some Salient Reactions

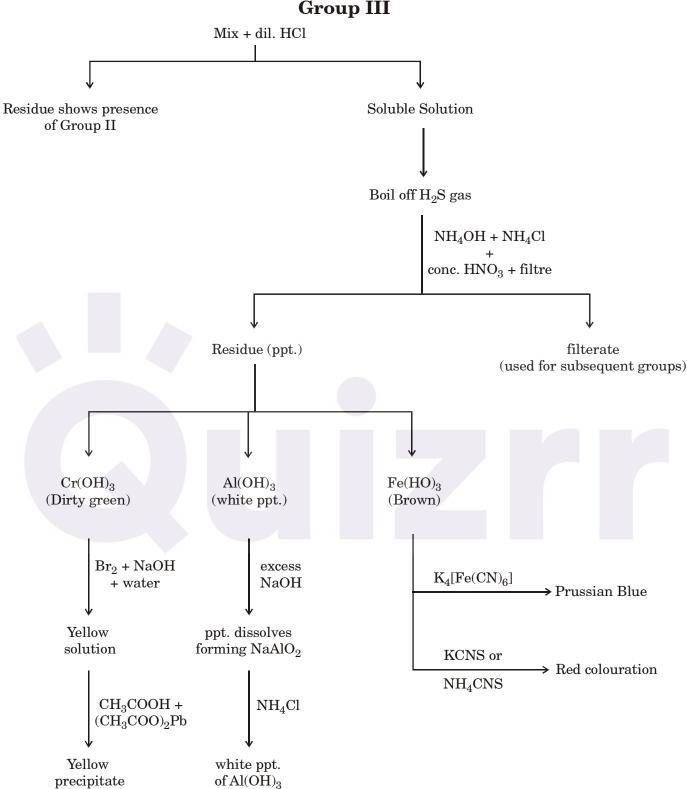
(1) 3PbS + 8HNO
$$_3$$
 \longrightarrow 3Pb(NO $_3$) $_2$ + 2NO + S + H $_2$ O (soluble)

- $(2) \quad \text{ Bi (OH)}_{3} \xrightarrow{\quad \text{dil. HCl} \quad} \text{BiCl}_{3}$
- (3) $\operatorname{BiCl}_3 + 3\operatorname{Na}_2\operatorname{SnO}_2 + 6\operatorname{NaOH} \longrightarrow 3\operatorname{Na}_2\operatorname{SnO}_3 + 2\operatorname{Bi}(\downarrow) + 6\operatorname{NaCl} + 3\operatorname{H}_2\operatorname{O}$ (Black)
- $(5) \quad [\mathrm{Cu(NH_3)_4}]\mathrm{SO_4} \, + \, 4\mathrm{CH_3COOH} \, \longrightarrow \, \mathrm{CuSO_4} \, + \, \, 4\mathrm{CH_3COONH_4}$

$$2 \text{CuSO}_4 \ + \ \text{K}_4 \text{Fe} \ (\text{CN})_6 \ \longrightarrow \ \text{Cu}_2 \ [\text{Fe}(\text{CN})_6] \ + \ 2 \text{K}_2 \text{SO}_4$$

Chocolate or reddish brown

Group III



Note:

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

Some salient reactions:

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

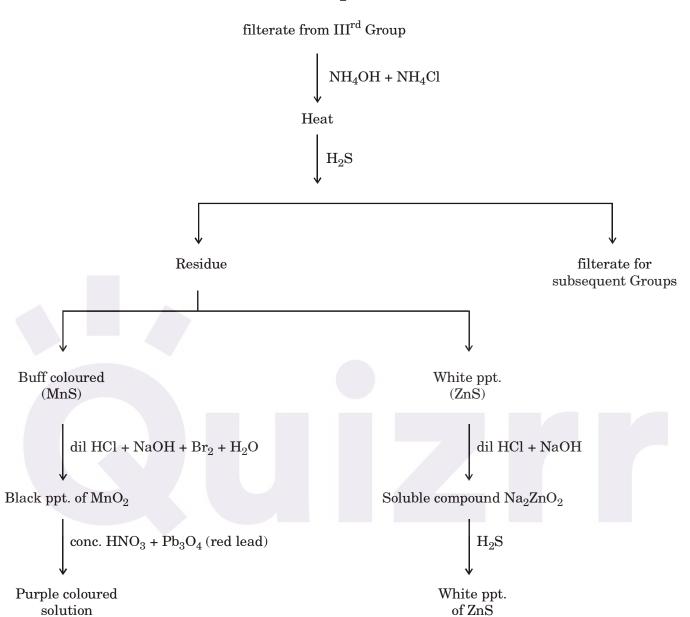
(2)
$$Cr(OH)_3 + 3Br_2 + 10NaOH \longrightarrow 2Na_2CrO_4 + 6NaBr + 8H_2O$$

$$(3) \quad \text{Fe(OH)}_{3} \xrightarrow{\quad \text{aqua Regia} \\ \quad \text{(HNO}_{3} + \text{HCl)} \rightarrow \quad \text{FeCl}_{3} + 3\text{H}_{2}\text{O}$$

$$\begin{array}{ccc} \text{(4)} & \text{FeCl}_3 + \text{KCNS} & \longrightarrow & \text{Fe(CNS)}_3 + \text{NH}_4\text{Cl/KCl} \\ & \text{or} \\ & \text{NH}_4\text{CNS} \\ \end{array}$$

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

Group IV



Some salient reactions

(1)
$$\operatorname{ZnCl}_2 + \operatorname{NaOH} \longrightarrow \operatorname{Zn(OH)}_2 + \operatorname{2NaCl}$$

$$\downarrow \operatorname{NaOH}$$

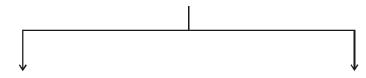
$$\operatorname{Na}_2\operatorname{ZnO}_2 + \operatorname{2H}_2\operatorname{O}$$
 Sodium zincate

(3)
$$\operatorname{ZnCl}_2 + \operatorname{K}_4[\operatorname{Fe(CN)}_6] \to \operatorname{Zn}_2[\operatorname{Fe(CN)}_6] \ (\downarrow) + 2\operatorname{KCl}$$
 Bluish white ppt

Group V

Filterate from IVth group

Boil off H_2S gas and add solid NH_4Cl and NH_4OH followed by $(NH_4)_2CO_3$ solution



White ppt. shows presence of Group V

Filterate use for subsequent groups



Some Salient Reactions

$$(1) \quad \text{BaCO}_3 + 2\text{CHCOOH} \longrightarrow (\text{CH}_3\text{COO})_2\text{Ba} + \text{CO}_2 + \text{H}_2\text{O}$$

$$\text{CaCO}_3 + 2\text{CH}_3\text{COOH} \longrightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{CO}_2 + \text{H}_2\text{O}$$

$${\rm (2)} \quad {\rm Ba(CH_3COO)}_2 + {\rm K_2CrO}_4 \longrightarrow {\rm BaCrO}_4 + 2{\rm CH_3COOK}$$

Group VI (Mg²⁺)

Filterate of group V + NH $_4$ OH + Na $_2$ HPO $_4 \rightarrow$ a fine crystalline ppt on scratching the side of the test tube.

$$\label{eq:mgCl2} \begin{array}{c} \mathrm{MgCl_2} + \mathrm{NH_4OH} + \mathrm{Na_2HPO_4} \rightarrow \mathrm{Mg(NH_4)PO_4} \ (\downarrow) + 2\mathrm{NaCl} + 2\mathrm{H_2O} \\ \\ \mathrm{(white ppt)} \\ \\ \Delta \\ \\ \mathrm{Mg_2P_2O_7} + 2\mathrm{NH_3} + \mathrm{H_2O} \\ \\ \mathrm{(white)} \end{array}$$

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

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

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

$$\mathrm{NH_3(g)} + \mathrm{HCl} \longrightarrow \mathrm{NH_4Cl}$$

white fumes

• Salt + NaOH $\xrightarrow{\Delta}$ gas $\xrightarrow{\text{add Nesler's}}$ Reagent

Brown ppt or brown or yellow colouration (oxydimercuri ammonium iodide) called iodide of Millon's base.

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

Solubility Trends

		dil. HNO_3	$\mathrm{NH_4OH}$	Hypo soln	CN^- soln.
1.	AgCl		3	3	3
	AgBr		3	3	3
	AgI			3	3
	$\mathrm{Ag}_2\mathrm{S}$	3		3	3

- 2. All water insoluble black metal sulphide are soluble in hot and dil. ${\rm HNO_3}$ 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. HNO₃ & 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.

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

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.

$$Na_{2}B_{4}O_{7}.10H_{2}O \xrightarrow{\quad Heat \quad} Na_{2}B_{4}O_{7} \xrightarrow{\quad Heat \quad} \underbrace{2NaBO_{2} + B_{2}O_{3}}_{\quad Glassy\ bead}$$

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

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.

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.

	Colour of the bead in			
Metal	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.

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.

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

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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]
$$\longrightarrow$$
 CaCO₃ + H₂O

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

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

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

(vii) [G]
$$\xrightarrow{\Delta}$$
 Na₂CO₃ + H₂O + [B]

Solution:

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

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

$${\rm (iii)} \quad {\rm Ca(OH)}_2 + {\rm CO}_2 \longrightarrow \\ {\rm CaCO}_3 + {\rm H}_2 {\rm O}$$

(vii) 2NaHCO
$$_3$$
 $\xrightarrow{\Delta}$ Na $_2$ CO $_3$ + H $_2$ O + CO $_2$ (B)

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 NH4Cl.

$$\begin{array}{c} \mathrm{K_2Cr_2O_7} + 2\mathrm{H_2SO_4} & \longrightarrow 2\mathrm{KHSO_4} + 2\mathrm{CrO_3} + \mathrm{H_2O} \\ \mathrm{NH_4Cl} + \mathrm{H_2SO_4} & \longrightarrow \mathrm{NH_4HSO_4} + \mathrm{HCl} \\ \mathrm{CrO_3} + 2\mathrm{HCl} & \longrightarrow \mathrm{CrO_2Cl_2} \uparrow + \mathrm{H_2O} \\ \mathrm{(A)} \\ \mathrm{Reddish\text{-}brown\ gas} \\ \mathrm{CrO_2Cl_2} + 4\mathrm{NaOH} & \longrightarrow \mathrm{Na_2CrO_4} + 2\mathrm{NaCl} + 2\mathrm{H_2O} \\ \mathrm{(B)} \\ \mathrm{Yellow\ coloured\ solution} \\ \mathrm{Na_2CrO_4} + (\mathrm{CH_3COO)_2Pb} & \longrightarrow \mathrm{CH_3COOH} & \mathrm{PbCrO_4} \downarrow + 2\mathrm{CH_3COONa} \\ \mathrm{(C)} \\ \mathrm{Yellow\ ppt} \\ \mathrm{NH_4Cl} + \mathrm{NaOH} & \longrightarrow \mathrm{NaCl} + \mathrm{NH_3} + \mathrm{H_2O} \\ \end{array}$$

Colourless gas

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-NH₃

Reactions : (i)
$$CuSO_4 + 4NH_4OH \longrightarrow Cu(NH_3)_4 SO_4 + H_2O$$
 deep blue

(ii)
$$\operatorname{FeCl}_3 + 3\operatorname{NH}_4\operatorname{OH} \longrightarrow \operatorname{Fe(OH)}_3 \downarrow + 3\operatorname{NH}_4\operatorname{Cl}$$
 brown ppt
$$\operatorname{Fe(OH)}_3 + 3\operatorname{HNO}_3 \longrightarrow \operatorname{Fe(NO}_3)_3 + 3\operatorname{H}_2\operatorname{O}$$

Example 5

An aqueous solution of a gas (X) gives the following reactions:

- (i) It decolourizes an acidified $K_9Cr_9O_7$ 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 $\rm H_2S$ into the solution, turbidity is obtained. Identify (X) and given equations for the steps (i), (ii), (iii).

Solution:

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

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:

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

$$\begin{array}{cccc} \text{(ii)} & \mathrm{CO_2} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{CaCO_3} + \mathrm{H_2O} \\ & \text{(B)} & \text{White} \\ & \mathrm{CaCO_3} + \mathrm{H_2O} + \mathrm{CO_2} & \rightarrow & \mathrm{Ca(HCO_3)_2} \\ & & \mathrm{Excess} & \mathrm{Soluble} \end{array}$$

(iii) ZnO + 2HCl
$$\rightarrow$$
 ZnCl₂ + H₂O
$$2ZnCl_2 + K_4Fe(CN)_6 \rightarrow Zn_2[Fe(CN)_6] + 4KCl$$
 White ppt.

$$\begin{array}{ccc} \text{(iv)} & \text{ZnCl}_2 \, + \, \text{H}_2\text{S} \, \rightarrow \, \text{ZnS} \, + \, 2\text{HCl} \\ & \text{(D)} \end{array}$$

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 $Na_9S_9O_3$ solution.
- (ii) On addition to Ag^+ ion solution, a yellow ppt. is obtained which is insoluble in NH_4OH .

Identify (X), giving reactions.

Solution:

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:

(iii)
$$\text{CuSO}_4 + \text{K}_4[\text{Fe(CN)}_6] \longrightarrow \text{Cu}_2[\text{Fe(CN)}_6] + 2\text{K}_2\text{SO}_4$$
 (Chocolate, coloured ppt.)

Example 9

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

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

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

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

Solution:

$$\begin{array}{c} \text{CuCO}_3.\text{Cu(OH)}_2 \xrightarrow{\quad \text{calcination} \quad} 2\text{CuO} \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} \\ \text{Malachite (A}_1) & \text{Black (C)} \end{array}$$

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

$$-Cu_{2}S+2Cu_{2}O \longrightarrow \\ +Cc_{(M)}Cc_{($$

Example 10

$$Na_2CO_3 \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow{elements} (C) \xrightarrow{I_2} (D)$$

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

Solution:

 $(A): NaHSO_3$

(B): Na₂SO₃

 $(C): Na_2S_2O_3$

(D) : Na₂S₄O₆

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 H₉S gas in acidic medium.
- (b) C is soluble in aqua-regia and on adding SnCl₂, it gives white precipitate, which finally turns to greyish black precipitate D.

The white precipitate on treatment with NH₄OH gives a brown precipitate.

- (i) The sodium carbonate extract of the salt A with CCl₄/FeCl₃ 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:

$$(A): Kl_{q}$$
 $(B): HgCl_{q}$ $(C): HgS$ $(D): Hg$

(a)
$$\operatorname{HgCl}_2 + \operatorname{H}_2 S \longrightarrow \operatorname{HgS} + 2\operatorname{HCl}$$
(B) $\operatorname{Black\ ppt}$
(C)

(b)
$$3 \text{HgS} + 6 \text{HCl} + 2 \text{HNO}_3 \longrightarrow 3 \text{HgCl}_2 + 2 \text{NO} + 3 \text{S} + 4 \text{H}_2 \text{O}$$

$$2 \overline{\text{HgCl}}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2 \text{Cl}_2 \downarrow + \text{SnCl}_4$$
White ppt

$$\mathrm{Hg_2Cl_2} + 2\mathrm{NH_4OH} \longrightarrow \mathrm{Hg} + \mathrm{Hg(NH_2)Cl} + \mathrm{NH_4Cl}$$

Brown

[B]

Example 12

[A]

An aqueous solution containing one mole of ${\rm HgI}_2$ 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.

flame

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 $\mathrm{Na}_2\mathrm{HgI}_4$ is formed.

$$2\text{NaI} + \text{HgI}_2 \longrightarrow \text{Na}_2\text{HgI}_4$$

The Na₂HgI₄ on addition of NaOCl, oxidises as :

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

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 NH₄OH is brought near it.
- (iii) An acidic solution of (X) on addition of $\mathrm{NH_4Cl}$ and $\mathrm{NH_4OH}$ 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) $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl ↑$ fumes

(ii) HCl + NH₄OH
$$\rightarrow$$
 NH₄Cl \uparrow + H₂O White fumes

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

White ppt

$$\label{eq:aloose} \begin{split} \text{Al(OH)}_3 + \text{NaOH} &\rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O} \\ \text{Soluble} \end{split}$$

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. ${\rm HNO_3}$ and the resulting solution gives a white precipitate (E) with dil. ${\rm HCl.}$

QUIZRR

- (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:

$$(A) - Ag_2S$$
 $(B) - NaAg(CN)_2$ $(C) - Na_2SO_4$ $(D) Ag$

$${\rm (E)-AgCl} \qquad {\rm (F)-Ag(NH_3)_2Cl}$$

$${\rm (ii)} ~~ 2{\rm NaAg(CN)}_2 + {\rm Zn} \rightarrow {\rm Na}_2{\rm Zn(CN)}_4 + 2{\rm Ag} \label{eq:constraint}$$
 (D)

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

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

$$\begin{array}{ccc} \text{(v)} & \text{AgCl + 2NH}_3 \rightarrow \text{Ag(NH}_3)_2\text{Cl} \\ \\ \text{(E)} & \text{(F)} \end{array}$$

(vi)
$$4\text{AgCl} + 2\text{Na}_2\text{CO}_3 \rightarrow 4\text{Ag} + 4\text{NaCl} + 2\text{CO}_2 + \text{O}_2$$

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_oS
- (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:

$${\rm A-BaCl}_2$$

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

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)

Example 17

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

- (i) $(A) \xrightarrow{\Delta}$ glassy transparent bead (B) on platinum wire (B) + CuSO₄ \longrightarrow coloured bead (C)
- (ii) (A) + conc. H_2SO_4 + $CH_3CH_2OH \xrightarrow{ignite}$ 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 (Na₂B₄O₇.10H₂O)

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

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

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

 $Na[B(OH)_A]$ 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:

Ag⁺ and Ba²⁺

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

I and Cl **(c)**

I and Br **(d)**

(v) SO_3^{2-} and SO_4^{2-}

Fe³⁺ and Cu²⁺ **(f)**

Solution:

 K_2CrO_4 : (a)

$$2Ag^{+} + CrO_{4}^{2-} \longrightarrow Ag_{2}CrO_{4} \downarrow$$

$$Ba^{2+} + CrO_{4}^{2-} \longrightarrow BaCrO_{4} \downarrow$$
vollage

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

 $\mathbf{K}_{2}\mathbf{CrO}_{4}:$ **(b)**

$$Cu^{2+} + CrO_4^{2-} \longrightarrow CuCrO_4$$

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

 $AgNO_3$: **(c)**

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

(d) Cl₂ water + CHCl₃:

(e) BaCl₂:

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

$$\mathrm{BaCl}_2 + \mathrm{SO}_4^{2-} \longrightarrow \mathrm{BaSO}_4 \downarrow$$
 white ppt insoluble in conc. HCl

(f) $NH_{4}SCN$:

$$\mathrm{Cu^{2^+}}$$
 + 2SCN⁻ \longrightarrow $\mathrm{Cu(SCN)_2}$ \downarrow black

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 $\rm K_2HgI_4$. 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 $K_3 Fe(CN)_6$ indicates the presence of Fe^{2+} ion.

$$(iv) \quad \text{Mixture + K_2Cr}_2O_7 \xrightarrow{\quad H_2SO_4 \quad \\ \triangle \quad \quad } \text{Red vapours } \left(\text{CrO}_2\text{Cl}_2\right)$$

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

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

$$K_2HgI_4 + NaOH + NH_3 \rightarrow O \underbrace{\begin{array}{c} Hg \\ Hg \\ (Brown \; ppt) \end{array}}_{(Brown \; ppt)} NH_2I + KI + H_2O + NaI$$

(iii)
$$3\text{FeSO}_4 + 2\text{K}_3\text{Fe}(\text{CN})_6 \longrightarrow 3\text{K}_2\text{SO}_4 + \text{Fe}_3[\text{Fe}(\text{CN})_6]_2$$
Ferrous ferricyanide (Blue)

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.

$$S + O_2 \longrightarrow SO_2$$
 (E)

$$\begin{array}{ccc} \text{CuSO}_4 & + & 5\text{H}_2\text{O} & \longrightarrow & \text{CuSO}_45\text{H}_2\text{O} \\ & & \text{Blue} \\ \text{(Anhydrous)} \end{array}$$

$${\rm ZnSO_4} \ + \ {\rm 2NH_4OH} \ \longrightarrow \ {\rm Zn} \left({\rm OH} \right)_2 \ + \ \left({\rm NH_4} \right)_2 {\rm SO_4}$$

Example 21

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

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

$$(A) + H_2O \longrightarrow (C)$$

$$(C) + (B) \longrightarrow CaCO_3 + H_2O$$

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

$$(E) + H_2O + (B) \longrightarrow (F)$$

$$NaCl + (F) \longrightarrow (G) + (D)$$

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

Solution:

Scheme represents the Solvay process of manufacture of Na₂CO₃.

$$\begin{array}{cccc} \operatorname{CaO} & + & \operatorname{H_2O} & \longrightarrow & \operatorname{Ca(OH)}_2 \\ {}_{(\operatorname{C})} & & {}_{(\operatorname{C})} \end{array}$$

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

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QUIZRR

$$2 \text{NaHCO}_3 \ \stackrel{\Delta}{-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-} \ \text{Na}_2 \text{CO}_3 \ + \ \text{H}_2 \text{O} \ + \ \text{CO}_2 \ \ \text{(B)}$$

Example 22

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

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

 $(B) + KI \longrightarrow brown coloured solution$



white ppt (E)

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

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

$$(D) + (CH_3COO)_2 Pb \longrightarrow black(G)$$

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

(B) + (D)
$$\longrightarrow$$
 black ppt (I)

Solution:

(D) +
$$(CH_3COO)_2Pb \longrightarrow black (G)$$

 \Rightarrow (D) is H₂S gas and (G) is PbS

 \Rightarrow (A) also has S^{2-}

(A) + dil.
$$H_2SO_4 \longrightarrow (B)$$
, (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 $CuSO_4$

$$I_2 + KI \rightleftharpoons KI_3$$

Due to KI_3 , solution appears reddish brown. On adding hypo, I_2 disappears and white ppt of $\mathrm{Cu}_2\mathrm{I}_2$ appears.

$$\left(I_3^- \right) I_2 \ + \ 2 N a_2 S_2 O_3 \ \longrightarrow \ 2 N a I \ + \ N a_2 S_4 O_6$$

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

(A) : CuS + FeS (CuFeS₂)

 $(B) : CuSO_4$

(C): $FeSO_A$

 $(D): H_2S$

 $(E): Cu_2I_2$

(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. HNO₃.

 \Rightarrow (A) is of group II (copper sub-group) and is HgS [only HgS (black) is insoluble in dil. HNO $_3$]

$$\text{(A)} \ + \ \underbrace{\text{3HCl} \ + \ \text{HNO}_3}_{\text{aqua regia}} \ \longrightarrow \ \underset{\text{(B)}}{\text{HgCl}_2}$$

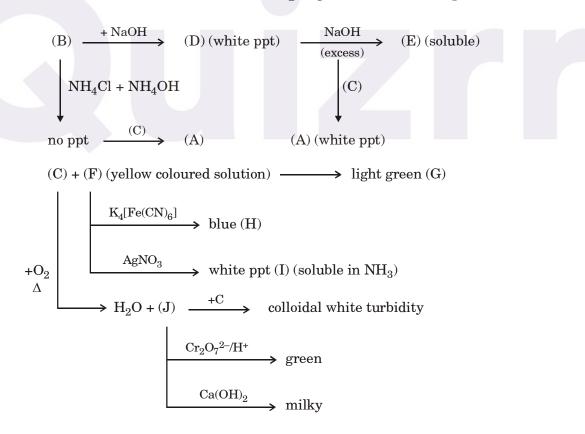
$$\label{eq:hgCl2} \operatorname{HgCl}_2 \ + \ 2\operatorname{NaOH} \ \longrightarrow \ \underset{\operatorname{yellow} \ \operatorname{ppt} \ (\operatorname{C})}{\operatorname{HgO}} \ + \ 2\operatorname{NaCl} \ + \ \operatorname{H}_2\operatorname{O}$$

3NaOH + NH₃ +
$$2K_2HgI_4 \rightarrow O$$

$$Hg \longrightarrow NH_2I \downarrow + 4KI + 3NaI + 2H_2O$$
brown ppt
(iodide of MIllion's base)

Example 24

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



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

Solution:

Gas (C) is vital compound in this scheme.

$$Gas(C) \xrightarrow{O_2} H_2O + (J)$$

$$\text{milky} \; \xleftarrow{\; \operatorname{Ca(OH)}_2 \;} \; \text{Gas} \; (J) \; \xrightarrow{\; \operatorname{Cr}_2 \operatorname{O}_7^{2-} \; / \; \operatorname{H}^+ \;} \; \text{green}$$

- \Rightarrow (J) is SO₂
- $\Rightarrow~$ (C) is $\rm H_2S$ (giving $\rm H_2O$ and $\rm SO_2$ by combustion in $\rm O_2).$
 - (B) gives white ppt only if (C) is passed into its ammoniacal solution containing $\rm NH_4Cl$ (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 Fe³⁺ ion
 - (F) gives white ppt with AgNO₃
- \Rightarrow (F) has Cl⁻ ion. Thus, F is FeCl₃.

Explanation:

$$\underset{(A)}{\operatorname{ZnS}} \ + \ \operatorname{H}_2{\operatorname{SO}}_4 \ \longrightarrow \ \underset{(B)}{\operatorname{ZnSO}}_4 \ + \ \operatorname{H}_2{\operatorname{S}}$$

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

$$\text{FeCl}_{3} \ + \ 3\text{AgNO}_{3} \ \longrightarrow \ \text{Fe}\big(\text{NO}_{3}\big)_{\!\!3} \ + \ 3\text{AgCl} \downarrow \\ \text{white ppt}(I)$$

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

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