

## QUALITATIVE ANALYSIS

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### Introduction :

Qualitative analysis involves the detection of cation(s) and anion(s) of a salt or a mixture of salts.

The systematic procedure for qualitative analysis of an inorganic salt involves the following steps :

#### (a) Preliminary tests

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

#### (b) Wet tests for acid radicals.

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

### 1. Physical Examination of the Mixture :

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

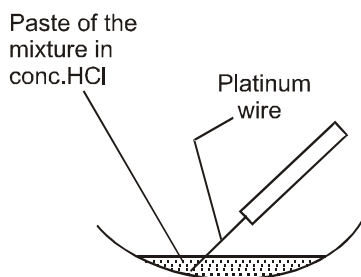
### 2. Dry Heating Test :

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

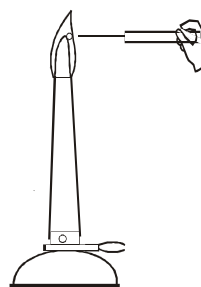
### 3. Flame test :

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

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



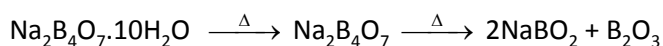
(A) Dipping the platinum wire in the paste of salt and HCl.



(B) Introducing the wire in the flame

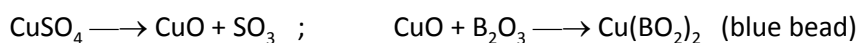
#### 4. Borax Bead test :

On heating borax forms a colourless glassy bead of  $\text{NaBO}_2$  and  $\text{B}_2\text{O}_3$ .

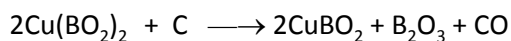


On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.

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



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



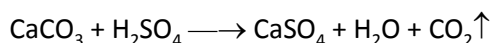
Metal	Colour in oxidising flame		Colour in reducing flame	
	When Hot	When Cold	When Hot	When Cold
Copper	Green	Blue	Colourless	Brown red
Iron	Brown yellow	Pale yellow/Yellow	Bottle green	Bottle green
Chromium	Yellow	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet/Amethyst	Red/Amethyst	Grey/Colourless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

## Analysis of ANIONS (Acidic Radicals) :

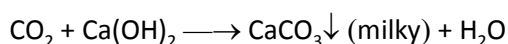
### (a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP :

#### 1. CARBONATE ION ( $\text{CO}_3^{2-}$ ) :

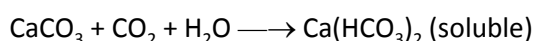
- Dilute  $\text{H}_2\text{SO}_4$  test : A colourless odourless gas is evolved with brisk effervescence.



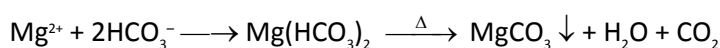
- Lime water/Baryta water ( $\text{Ba}(\text{OH})_2$ ) test : The liberated gas can be identified by its property of rendering lime water (or baryta water) turbid.



On prolonged passage of  $\text{CO}_2$  the milkiness disappears.

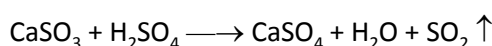


- ☞ Soluble bicarbonates give white precipitate with  $\text{MgSO}_4$  (aq) /  $\text{MgCl}_2$  (aq) only on heating.



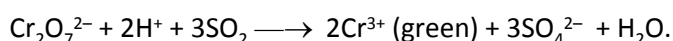
#### 2. SULPHITE ION ( $\text{SO}_3^{2-}$ ) :

- **Dilute  $\text{H}_2\text{SO}_4$  test** : Decomposition of salt is more rapidly on warming, with the evolution of sulphur dioxide.

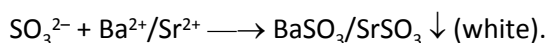


$\text{SO}_2$  has suffocating odour of burning sulphur.

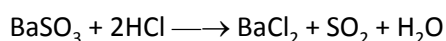
- **Acidified potassium dichromate test** : The filter paper dipped in acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green.



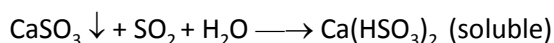
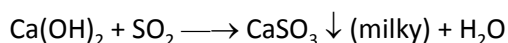
- **Barium chloride/Strontium chloride solution** : White precipitate of barium (or strontium) sulphite is obtained.



- ☞ White precipitate is soluble in dilute HCl forming  $\text{SO}_2$ .

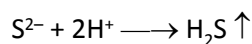


- **Lime water test** : A white precipitate is formed. The precipitate dissolves on prolonged passage of the gas, due to the formation of hydrogen sulphite ions.

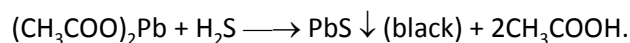


### 3. SULPHIDE ION ( $S^{2-}$ ) :

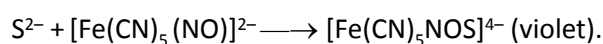
- **Dilute  $H_2SO_4$  test** : Pungent smelling gas like that of rotten egg is obtained.



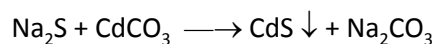
- **Lead acetate test** : Filter paper moistened with lead acetate solution turns black.



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

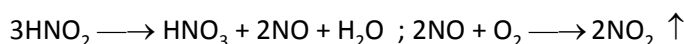
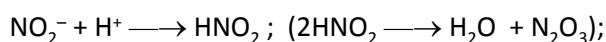


- **Cadmium carbonate suspension/ Cadmium acetate solution** : Yellow precipitate is formed.

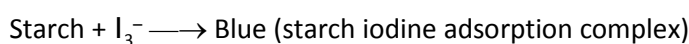
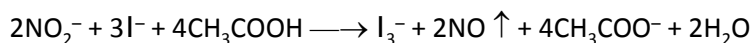


### 4. NITRITE ION ( $NO_2^-$ ) :

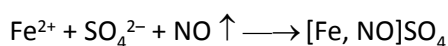
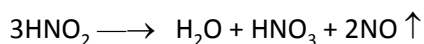
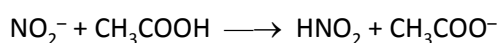
- **Dilute  $H_2SO_4$  test** : Solid nitrite in cold produces a transient pale blue liquid (due to the presence of free nitrous acid,  $HNO_2$  or its anhydride,  $N_2O_3$ ) first and then evolution of pungent smelling reddish brown vapours of  $NO_2$  takes place.



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

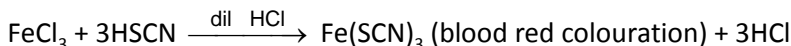
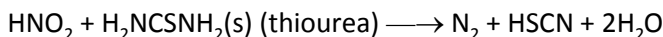
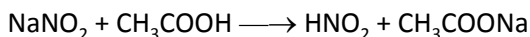


- **Ferrous sulphate test (Brown ring test)** : When the nitrite solution is added carefully to a concentrated solution of iron(II) sulphate acidified with dilute acetic acid or dilute sulphuric acid, a brown ring appears due to the formation of  $[Fe(H_2O)_5NO]SO_4$  at the junction of the two liquids.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



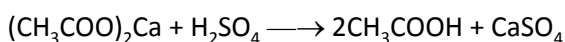


- **Thiourea test** : When a dilute acetic acid solution of a nitrite is treated with a little solid thiourea, nitrogen is evolved and thiocyanic acid is produced. The latter may be identified by the red colour produced with dilute HCl and FeCl<sub>3</sub> solution.

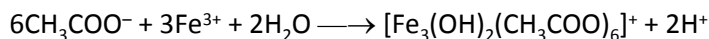


## 5. ACETATE ION (CH<sub>3</sub>COO<sup>-</sup>)

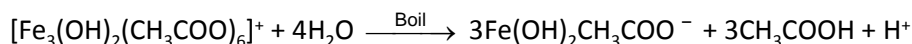
- With dilute H<sub>2</sub>SO<sub>4</sub> a vinegar like smell is obtained.



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



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

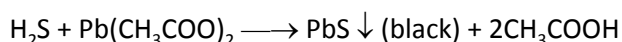
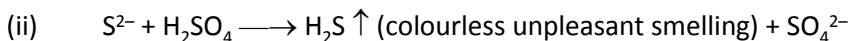


## Solved Examples

**Ex.1** An aqueous solution of salt containing an anion X<sup>n-</sup> gives the following reactions :

- It gives the purple or violet colouration with sodium nitroprusside solution.
- It liberates a colourless unpleasant smelling gas with dilute H<sub>2</sub>SO<sub>4</sub> which turns lead acetate paper black. Identify the anion (X<sup>n-</sup>) and write the chemical reactions involved.

**Sol.** X<sup>n-</sup> is S<sup>2-</sup> because



**Ex.2** Sulphite on treatment with dil.  $\text{H}_2\text{SO}_4$  liberates a gas which :

- (1) turns lead acetate paper black      (2) burns with blue flame  
 (3) smells like vinegar      (4) turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green

**Sol.**  $\text{SO}_3^{2-} + \text{H}_2\text{SO}_4 \longrightarrow \text{SO}_2 + \text{SO}_4^{2-} + \text{H}_2\text{O}$

$\text{SO}_2$  turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green.

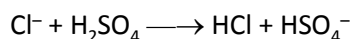
$\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \longrightarrow \text{Cr}_2(\text{SO}_4)_3$  (Green) +  $\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$

Therefore, (4) option is correct.

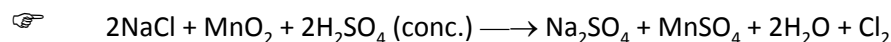
**(b) CONC.  $\text{H}_2\text{SO}_4$  GROUP :**

**1. CHLORIDE ION ( $\text{Cl}^-$ ) :**

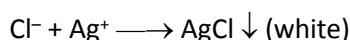
- **Concentrated  $\text{H}_2\text{SO}_4$  test :** Colourless pungent smelling gas is evolved which gives fumes of  $\text{NH}_4\text{Cl}$  when a glass rod dipped in dil. HCl is brought in contact with evolving gas.



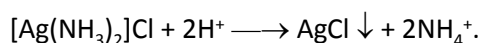
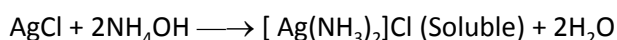
- $\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} \uparrow$  (white fumes) +  $\text{H}_2\text{O}$ .



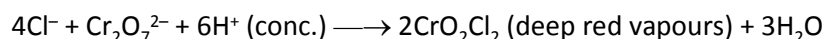
- **Silver nitrate test :**



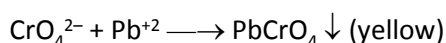
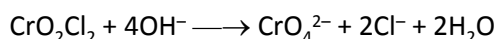
- ☞ White precipitate is soluble in aqueous ammonia and precipitate reappears with  $\text{HNO}_3$ .



- **Chromyl Chloride test :**

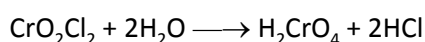


When deep red vapours are passed into sodium hydroxide solution, a yellow solution of sodium chromate is formed, which when treated with lead acetate gives yellow precipitate of lead chromate.



- ☞ **Heavy metal chlorides** such as  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$  and  $\text{SbCl}_3$  do not respond to this test as they are partially dissociated. This test is given generally by **ionic chlorides**.

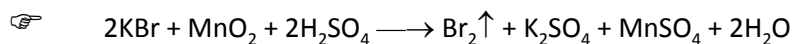
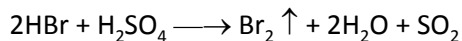
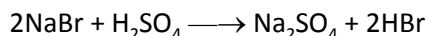
- ☞ Test should be carried out in a dry test tube otherwise chromic acid will be formed.



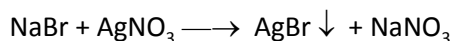


## 2. BROMIDE ION ( $\text{Br}^-$ ) :

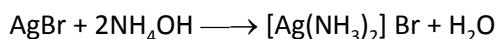
- **Concentrated  $\text{H}_2\text{SO}_4$  test** : First a reddish-brown solution is formed, then reddish-brown bromine vapour accompanies the hydrogen bromide (fuming in moist air) is evolved.



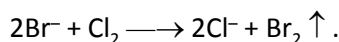
- **Silver Nitrate test** : Pale yellow precipitate is formed



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

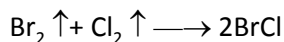


- **Chlorine water test (organic layer test)** : When to a sodium carbonate extract of metal bromide containing  $\text{CCl}_4$ ,  $\text{CHCl}_3$  or  $\text{CS}_2$ , chlorine water is added and the content is shaken and then allow to settle down reddish brown colour is obtained in organic layer.



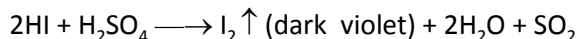
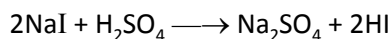
$\text{Br}_2 + \text{CHCl}_3 / \text{CCl}_4 \longrightarrow \text{Br}_2$  dissolve to give reddish brown colour in organic layer.

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

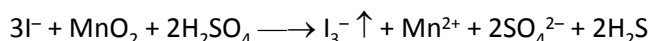


## 3. IODIDE ION ( $\text{I}^-$ ) :

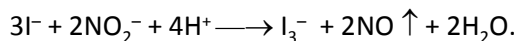
- **Concentrated  $\text{H}_2\text{SO}_4$  test** : Pungent smelling violet vapours are evolved.



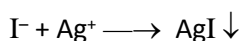
☞ Evolution of dark violet fumes intensifies on adding a pinch of  $\text{MnO}_2$ .



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

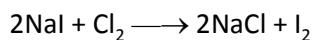


- **Silver nitrate test** : Bright yellow precipitate is formed.

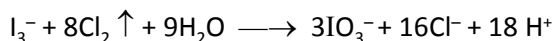


☞ Bright yellow precipitate is insoluble in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.

- **Chlorine water test (organic layer test)** : When chlorine water is added to a solution of iodide, free iodine is liberated which colours the solution brown and on shaking with  $\text{CS}_2$ ,  $\text{CHCl}_3$  or  $\text{CCl}_4$ , it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.

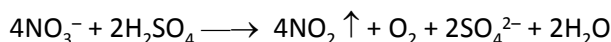


If excess of chlorine water is added,  $\text{I}_2$  is oxidised to iodic acid (colourless).

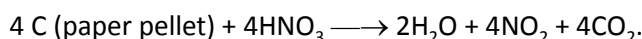
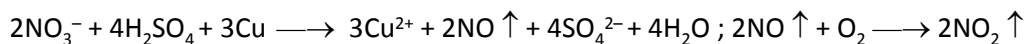


#### 4. NITRATE ION ( $\text{NO}_3^-$ ) :

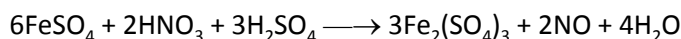
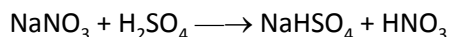
- **Concentrated  $\text{H}_2\text{SO}_4$  test** : Pungent smelling reddish brown vapours are evolved.



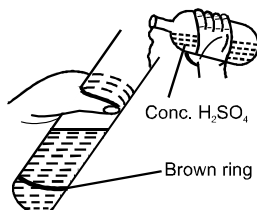
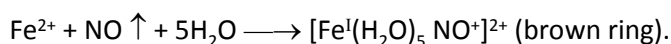
☞ Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.



- **Brown ring test** : When a freshly prepared saturated solution of iron (II) sulphate is added to nitrate solution and then concentrated  $\text{H}_2\text{SO}_4$  is added slowly from the side of the test tube, a brown ring is obtained at the junction of two layers.



or  $2\text{NO}_3^- + 4\text{H}_2\text{SO}_4 + 6\text{Fe}^{2+} \longrightarrow 6\text{Fe}^{3+} + 2\text{NO} \downarrow + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}.$



☞ On shaking and warming the mixture,  $\text{NO}$  escapes and a yellow solution of iron(III) ions is obtained.



**(B) GROUP 'B' RADICALS :**

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

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

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

- **Barium chloride test :**

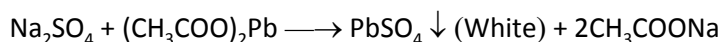
W.E. or S.E. + Barium chloride (aq)  $\longrightarrow$  White precipitate



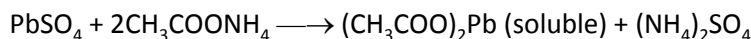
☞ White precipitate is insoluble in warm dil.  $HNO_3$  as well as HCl but moderately soluble in boiling concentrated hydrochloric acid.

- **Lead acetate test :**

W.E. or S.E. + Lead acetate  $\longrightarrow$  white precipitate

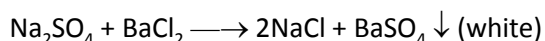


☞ White precipitate soluble in excess of hot ammonium acetate.

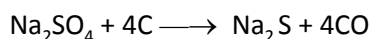
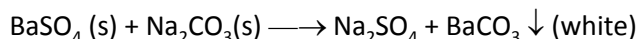


- **Match stick test :**

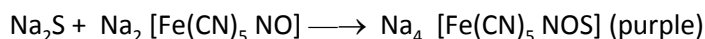
(a) W.E. or S.E. + Barium chloride  $\longrightarrow$  white precipitate



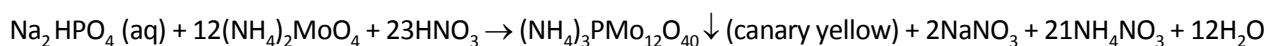
(b) White precipitate +  $Na_2CO_3(s)$  mix and apply the paste on the end of the carbonized match stick or a wooden splinter. Put it in the reducing flame.



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

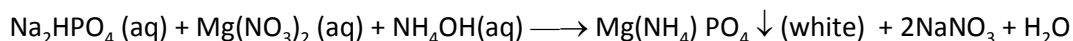
**2. PHOSPHATE ION ( $PO_4^{3-}$ ) :**

- **Ammonium molybdate test :**



☞ Some times ammonium phosphomolybdate is also represented by the formula  $(NH_4)_3 PO_4 \cdot 12MoO_3$

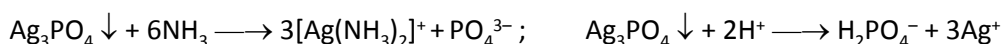
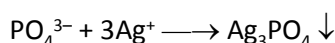
- **Magnesium nitrate or magnesia mixture test** : W.E. or S.E + Magnesium nitrate reagent (3-4 mL) and allows to stand for 4-5 minutes, white crystalline precipitate is formed.



Magnesia mixture is a solution containing  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Cl}$  and a little aqueous  $\text{NH}_3$ .

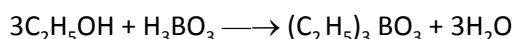
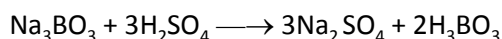
- ☞  $\text{PO}_4^{3-}$  also gives  $\text{BaCl}_2$  test due to the formation of white precipitate of  $\text{Ba}_3(\text{PO}_4)_2$ . So phosphate test should be carried out first and then conclude if  $\text{PO}_4^{3-}$  is present or absent before proceeding with the test for  $\text{SO}_4^{2-}$ .

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



### 3. BORATE ION ( $\text{BO}_3^{3-}$ ) :

Salt (0.2 g) + conc.  $\text{H}_2\text{SO}_4$  (1 mL) + Ethyl alcohol (4-5 mL) mix in a test tube and then heat. Ignite the evolved vapours with the help of Bunsen flame, green edged flame is obtained.



## Solved Examples

**Ex.1** A compound (A) of S, Cl and O has vapour density of 67.5 (approx.). It reacts with water to form two acids and reacts with KOH to form two salts (B) and (C) while (B) gives white precipitate with  $\text{AgNO}_3$  solution and (C) gives white precipitate with  $\text{BaCl}_2$  solution. Identify (A), (B) & (C).

**Sol.** As mixture give white precipitate with  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , it should contain  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions. As  $\text{SO}_2\text{Cl}_2$  when dissolved in water gives, a mixture of  $\text{H}_2\text{SO}_4$  &  $\text{HCl}$  which then react with KOH to form KCl and  $\text{K}_2\text{SO}_4$ . Therefore, (A) is  $\text{SO}_2\text{Cl}_2$  and (B) & (C) are  $\text{K}_2\text{SO}_4$  and KCl respectively.

Vapour density of  $\text{SO}_2\text{Cl}_2$  = molecular weight / 2.

Vapour density of  $\text{SO}_2\text{Cl}_2$  =  $135 / 2 = 67.5$ .

**Ex.2** Bromine vapours turn moist starch iodide paper :

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

**Sol.**  $2\text{I}^- + \text{Br}_2 \longrightarrow \text{I}_2 + 2\text{Br}^-$ ;  $\text{I}_2 + \text{starch} \longrightarrow \text{blue starch iodine adsorption complex}$ .

Therefore, (3) option is correct.

**Ex.3**  $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{NaI} + \dots\dots\dots [\text{X}]$ , [X] is :

- (1)  $\text{Na}_2\text{S}_4\text{O}_6$                       (2)  $\text{Na}_2\text{SO}_4$                       (3)  $\text{Na}_2\text{S}$                       (4)  $\text{Na}_3\text{ISO}_4$

**Sol.**  $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ .

Therefore, (1) option is correct.

### Analysis of CATIONS (Basic Radicals) :

Group	Group reagent	Basic radical	Composition and colour of precipitate
Zero	$\text{NaOH}$ or $\text{Ca}(\text{OH})_2$ , heat if required	$\text{NH}_4^+$	Ammonia gas is evolved.
1.	Dil HCl	$\text{Ag}^+$ $\text{Hg}_2^{2+}$ $\text{Pb}^{2+}$	$\text{AgCl}$ ; White $\text{Hg}_2\text{Cl}_2$ ; White $\text{PbCl}_2$ ; White
2.(A)	$\text{H}_2\text{S}$ in presence of dil HCl (Insoluble in YAS)	$\text{Hg}^{2+}$ $\text{Pb}^{2+}$ $\text{Bi}^{3+}$ $\text{Cu}^{2+}$ $\text{Cd}^{2+}$	$\text{HgS}$ ; Black $\text{PbS}$ ; Black $\text{Bi}_2\text{S}_3$ ; Black $\text{CuS}$ ; Black $\text{CdS}$ ; Yellow
2.(B)	$\text{H}_2\text{S}$ in presence of dil HCl (Soluble in YAS)	$\text{As}^{3+}$ $\text{Sb}^{3+}$ $\text{Sn}^{2+}$ $\text{Sn}^{4+}$	$\text{As}_2\text{S}_3$ ; Yellow $\text{Sb}_2\text{S}_3$ ; Orange $\text{SnS}$ ; Brown $\text{SnS}_2$ ; Yellow
3.	$\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$	$\text{Fe}^{3+}$ $\text{Cr}^{3+}$ $\text{Al}^{3+}$	$\text{Fe}(\text{OH})_3$ ; Reddish brown $\text{Cr}(\text{OH})_3$ ; Green $\text{Al}(\text{OH})_3$ ; Gelatinous white

4.	H <sub>2</sub> S in presence of NH <sub>4</sub> OH and NH <sub>4</sub> Cl	Zn <sup>2+</sup>	ZnS ; White
		Mn <sup>2+</sup>	MnS ; Buff (or Pink)
		Co <sup>2+</sup>	CoS ; Black
		Ni <sup>2+</sup>	NiS ; Black
5.	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> in presence of NH <sub>4</sub> OH	Ba <sup>2+</sup>	BaCO <sub>3</sub> ; White
		Sr <sup>2+</sup>	SrCO <sub>3</sub> ; White
		Ca <sup>2+</sup>	CaCO <sub>3</sub> ; White
6.	Na <sub>2</sub> HPO <sub>4</sub> in presence of NH <sub>4</sub> OH	Mg <sup>2+</sup>	Mg(NH <sub>4</sub> )PO <sub>4</sub> ; White

☞ [YAS = Yellow ammonium sulphide. (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>].

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

1. **Group 1<sup>st</sup> radicals** (Ag<sup>+</sup>, Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>) are precipitated as chloride because the solubility product of these chlorides (AgCl, PbCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>) is less than the solubility products of chlorides of all other metal ions, which remain in solution. Lead chloride is slightly soluble in water and therefore, lead is never completely precipitated by adding dilute hydrochloric acid to a sample ; the rest of the lead ions are precipitated with H<sub>2</sub>S in acidic medium together with the cations of the second group.

2. **Group 2<sup>nd</sup> radicals** are precipitated as sulphides because of their low solubility products whereas sulphides of other metals remain in solution because of their high solubility products. HCl acts as a source of H<sup>+</sup> which decreases the concentration of S<sup>2-</sup> due to common ion effect. Hence, the concentration of S<sup>2-</sup> ion is too low that it exceeds only the solubility products of the metal sulphides of II<sup>nd</sup> group.

We can not use H<sub>2</sub>SO<sub>4</sub> in place of HCl because some cations of higher groups i.e. v<sup>th</sup> group will also precipitate as their sulphates like BaSO<sub>4</sub>, SrSO<sub>4</sub>, CaSO<sub>4</sub> etc.

HNO<sub>3</sub> can't be used in place of HCl. HNO<sub>3</sub> is a powerful oxidising agent. HNO<sub>3</sub> will oxidize H<sub>2</sub>S forming sulphur (yellow precipitate) or colloidal solution causing confusion with CdS, As<sub>2</sub>S<sub>3</sub> even though Cd<sup>2+</sup>, As<sup>3+</sup> will be absent. The colloidal solution is white-yellow and that cannot be filtered causing unnecessary trouble.

3. **Group 3<sup>rd</sup> radicals** are precipitated as hydroxides and the addition of NH<sub>4</sub>Cl suppresses the ionisation of NH<sub>4</sub>OH so that only the group 3 cations are precipitated as hydroxides because of their low solubility products.

(i) Excess of NH<sub>4</sub>Cl should not be added, as manganese will precipitate as MnO<sub>2</sub>.H<sub>2</sub>O

(ii) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> cannot be used in place of NH<sub>4</sub>Cl because the SO<sub>4</sub><sup>2-</sup> will also give the precipitate of BaSO<sub>4</sub>, SrSO<sub>4</sub> etc.

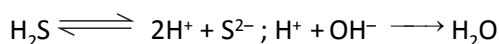


(iii) While proceeding for 3<sup>rd</sup> group from 2<sup>nd</sup> group, the filtrate of 2<sup>nd</sup> group is boiled off to remove the dissolved H<sub>2</sub>S and then one drop of concentrated HNO<sub>3</sub> is added and again boil so that if Fe<sup>2+</sup> is present is oxidised to Fe<sup>3+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

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

(v) In place of NH<sub>4</sub>OH, NaOH solution can't be used for the precipitation as their hydroxides because in excess of it we get soluble complexes of Al<sup>3+</sup> and Cr<sup>3+</sup>.

4. In 4<sup>th</sup> group, ammonium hydroxide increases the ionisation of H<sub>2</sub>S by removing H<sup>+</sup> from H<sub>2</sub>S as unionised water.



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

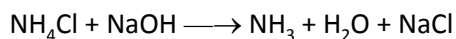


5. In 5<sup>th</sup> group the reagent ammonium carbonate should be added in alkaline or neutral medium. In the absence of ammonia or ammonium ions, magnesium will also be precipitated.

## ZERO GROUP :

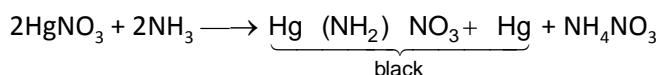
### 1. AMMONIUM ION (NH<sub>4</sub><sup>+</sup>) :

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

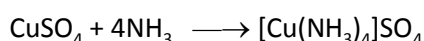


☞ The gas can be identified by the following characteristics / reactions.

- Its characteristic smell.
- The evolution of the white fumes of ammonium chloride when a glass rod dipped in dilute HCl is held in the vapour.  $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} \uparrow$  (white fumes)
- Its ability to turn filter paper moistened with Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution black.

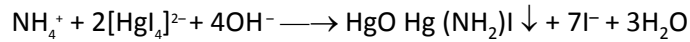


- Its ability to turn filter paper moistened with CuSO<sub>4</sub> solution deep blue.

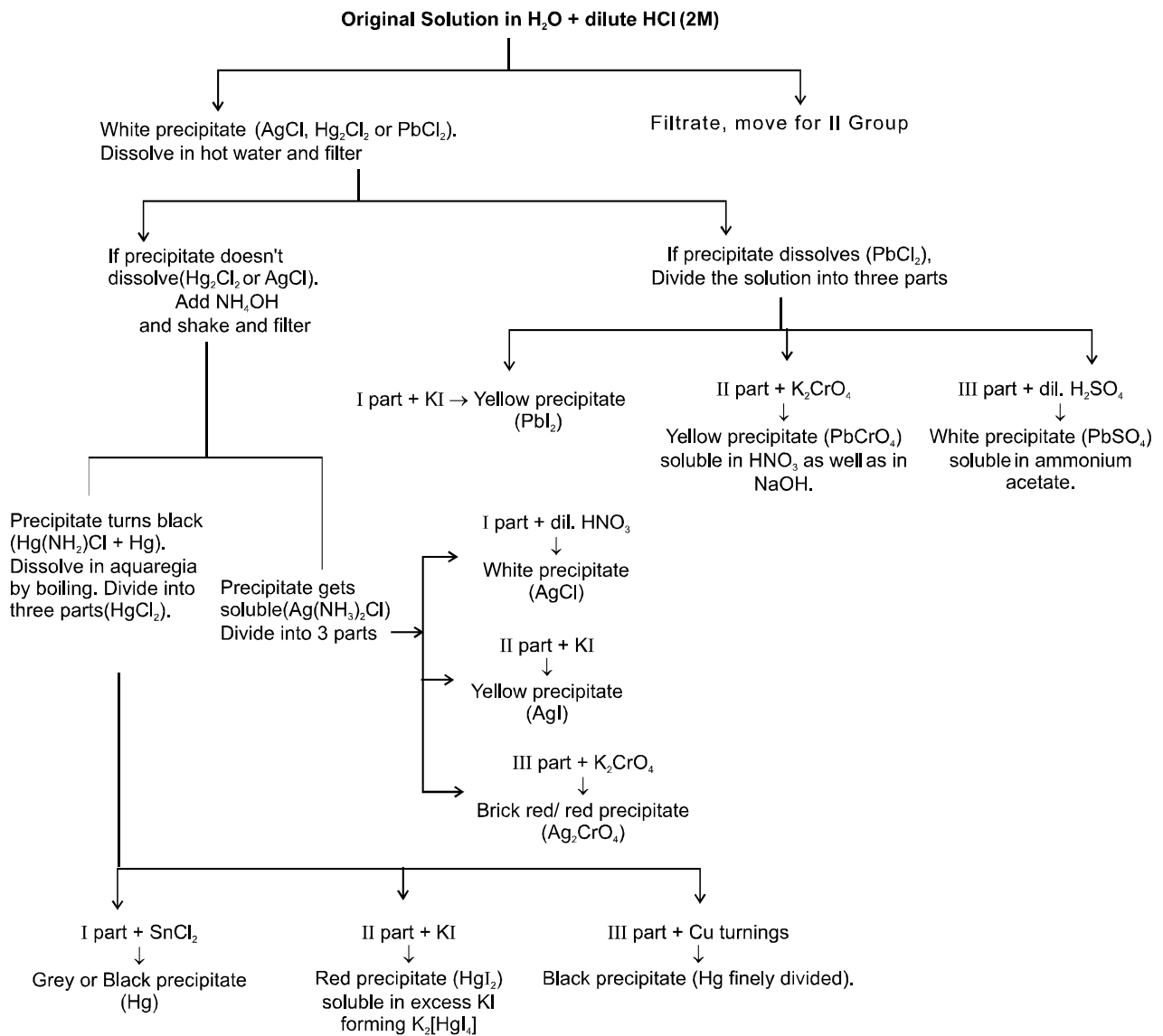


● **Nessler's reagent (Alkaline solution of potassium tetraiodomercurate(II)) :**

Brown precipitate or brown or yellow colouration is obtained according to the amount of ammonia or ammonium ions present. The precipitate is a basic mercury (II) amido-iodide.



**1<sup>st</sup> GROUP ( $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ) :**



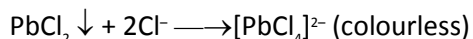


### 1. LEAD ION (Pb<sup>2+</sup>) :

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



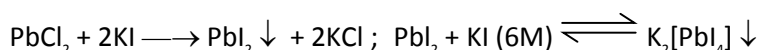
White precipitate is soluble in hot water. White precipitate is also soluble in concentrated HCl or concentrated KCl.



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

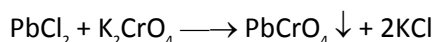


- **Potassium iodide solution** : A yellow precipitate is formed.



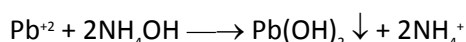
Yellow precipitate reappears on dilution with water.

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



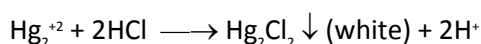
Yellow precipitate is soluble in sodium hydroxide and HNO<sub>3</sub> (nitric acid).

- **Ammonia solution** : With ammonia solution, Pb<sup>2+</sup> gives a white precipitate of lead hydroxide.

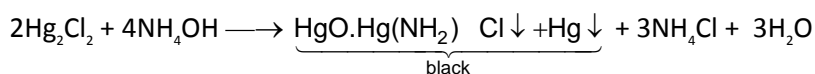


### 2. MERCURY(I) ION (Hg<sub>2</sub><sup>2+</sup>) :

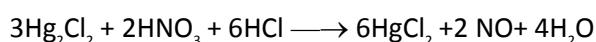
- **Dilute HCl solution** : White precipitate is formed in cold solution.



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



- **Dissolution of white precipitate (Hg<sub>2</sub>Cl<sub>2</sub>) in aquaregia** :



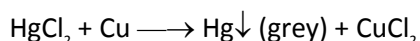
(a) **Stannous chloride test** : White precipitate is formed which finally turns to black.



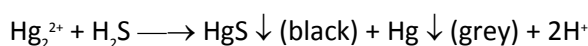
(b) **Potassium iodide test** : Scarlet/red precipitate is formed which is soluble in excess of the reagent.



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

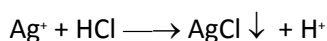


● **Reaction with H<sub>2</sub>S gas** :

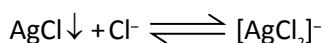


### 3. SILVER ION (Ag<sup>+</sup>) :

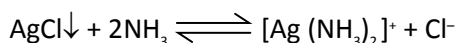
● **Dilute hydrochloric acid/soluble chlorides** : White precipitate is formed.



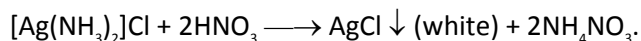
The precipitate obtained after filtration is soluble in concentrated HCl.



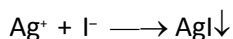
Dilute ammonia solution dissolves the precipitate forming a soluble complex.



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



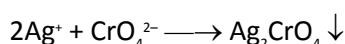
● **Potassium iodide solution** : A bright yellow precipitate is formed which is insoluble in dilute ammonia but partially soluble in concentrated ammonia.



The yellow precipitate is soluble in KCN and in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.



● **Potassium chromate solution** : Red precipitate is formed which is soluble in dilute HNO<sub>3</sub> and in ammonia solution.





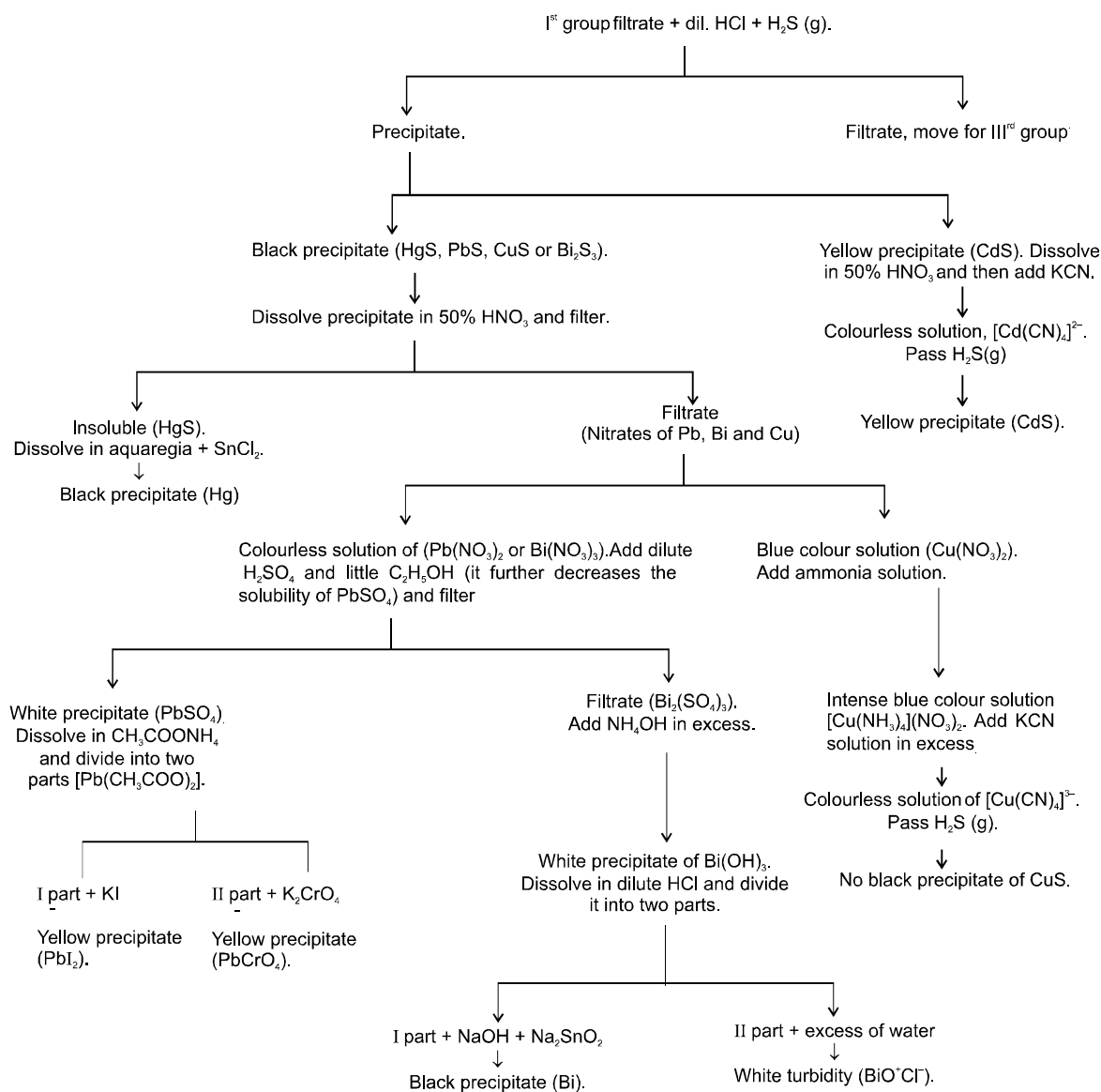
## II<sup>nd</sup> Group ( $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{As}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Sn}^{2+}$ )

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

**IIA** :  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{Bi}_2\text{S}_3$ , all black but  $\text{CdS}$  is yellow. All insoluble in yellow ammonium sulphide.

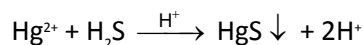
**IIB** :  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$  are yellow,  $\text{Sb}_2\text{S}_3$  is orange &  $\text{SnS}$  is dark brown All soluble in yellow ammonium sulphide.

### IIA Group ( $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ )

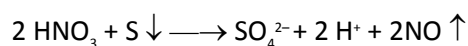
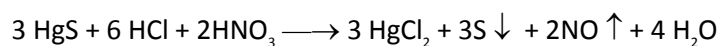


### 1. MERCURY (II) ION (Hg<sup>2+</sup>) :

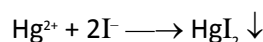
● **Precipitation with H<sub>2</sub>S in acidic medium** : Black precipitate is formed. Precipitate insoluble in water, hot dilute HNO<sub>3</sub>, alkali hydroxides, or colourless ammonium sulphide.



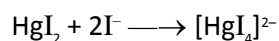
☞ Aqua regia dissolves the precipitate.



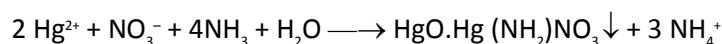
● **Potassium iodide solution** : On slow addition red precipitate is formed.



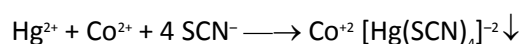
Precipitate dissolves in excess of KI forming colourless soluble complex.



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



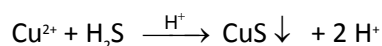
● **Cobalt (II) thiocyanate test** : When reagent is added to an aqueous solution of Hg<sup>2+</sup> ions and the walls of the test tube is stirred with a glass rod, deep-blue crystalline precipitate is formed.



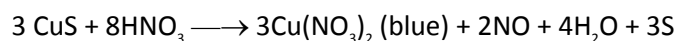
☞ In place of Cobalt (II) thiocyanate, Co(CH<sub>3</sub>COO)<sub>2</sub> and NH<sub>4</sub>SCN can be added to the aqueous solution of Hg<sup>2+</sup> ions.

### 2. COPPER ION (Cu<sup>2+</sup>) :

● **Precipitation with H<sub>2</sub>S in acidic medium** : Black precipitate is formed.



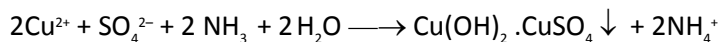
Precipitate is insoluble in boiling dilute (M) H<sub>2</sub>SO<sub>4</sub> (distinction from cadmium), in NaOH, Na<sub>2</sub>S and (NH<sub>4</sub>)<sub>2</sub>S. Precipitate dissolves in hot concentrated HNO<sub>3</sub>



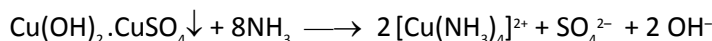
When boiled for longer S is oxidised to H<sub>2</sub>SO<sub>4</sub> and a clear solution of Cu(NO<sub>3</sub>)<sub>2</sub> is obtained.



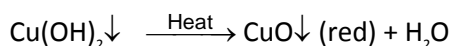
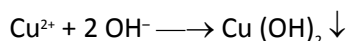
- **Ammonia solution** : When added sparingly a blue precipitate of basic salt (basic copper sulphate) is formed with  $\text{CuSO}_4$ .



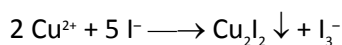
It is soluble in excess of reagent forming a deep blue colouration.



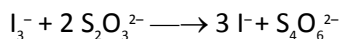
- **Sodium hydroxide in cold solution** : A blue precipitate is formed.



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

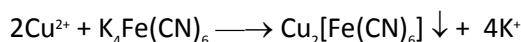


The solution becomes colourless and a white precipitate is visible when excess of sodium thiosulphate solution is added.

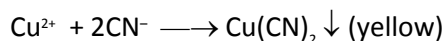


These reactions are used in quantitative analysis for the iodometric determination of copper.

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



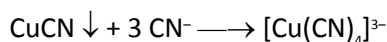
- (vi) **Potassium cyanide** : When added sparingly forms first a yellow precipitate.



Precipitate quickly decomposes into CuCN and cyanogen.



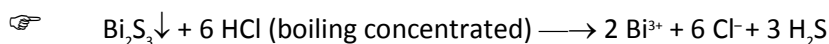
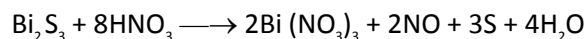
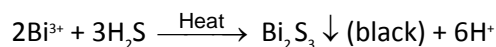
Excess reagent dissolves the precipitate forming a colourless soluble complex.



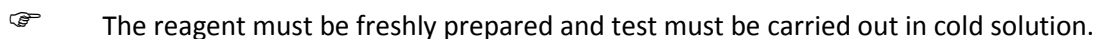
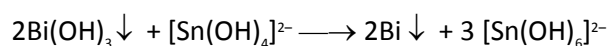
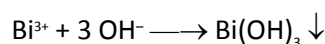
Complex is so stable that  $\text{H}_2\text{S}$  cannot precipitate Cu (I) sulphide (distinction from cadmium).

### 3. BISMUTH ION ( $\text{Bi}^{3+}$ ) :

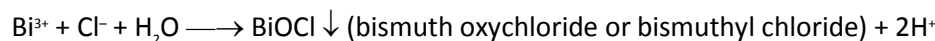
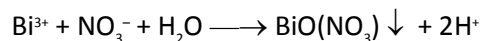
- **Precipitation with  $\text{H}_2\text{S}$  in acidic medium** : Black precipitate is formed which is soluble in cold dilute  $\text{HNO}_3$  and ammonium sulphide.



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

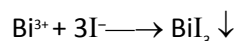


- **Dilution with water** : Solution of bismuth salts gives white precipitate when water is added in larger quantity.

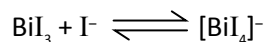


Soluble in mineral acids (dilute) but insoluble in tartaric acid (distinction from antimony) and in alkali hydroxide (distinction from tin).

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

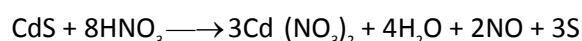
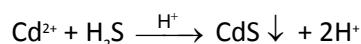


The precipitate dissolves in excess KI forming orange coloured soluble complex.



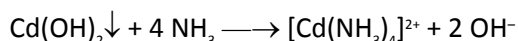
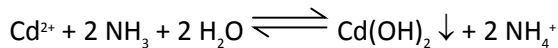
### 4. CADMIUM ION ( $\text{Cd}^{2+}$ ) :

- **Precipitation with  $\text{H}_2\text{S}$  in acidic medium** : Yellow precipitate is formed which dissolves in hot dilute  $\text{HNO}_3$ .

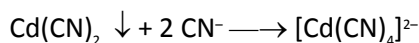
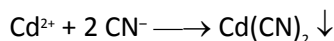




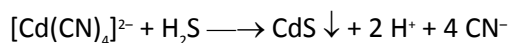
- **Ammonia solution (Dropwise addition)** : Ammonium hydroxide first gives white precipitate of  $\text{Cd}(\text{OH})_2$  which gets dissolve in excess of reagent forming a soluble complex.



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



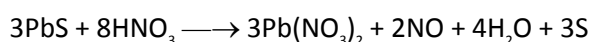
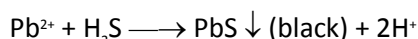
The colourless soluble complex is not too stable, therefore, reacts with  $\text{H}_2\text{S}$  gas forming a yellow precipitate of  $\text{CdS}$ .



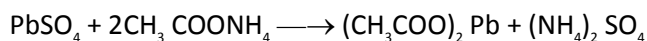
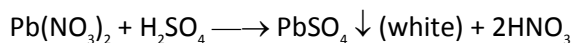
KI forms no precipitate (distinction from Copper)

## 5. LEAD ION ( $\text{Pb}^{2+}$ ) :

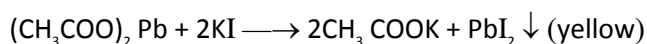
- **Precipitation with  $\text{H}_2\text{S}$  in acidic medium** : Black precipitate is formed which is soluble in hot dilute  $\text{HNO}_3$ .



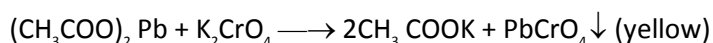
- **Dilute  $\text{H}_2\text{SO}_4$**  : White precipitate is formed which is soluble in ammonium acetate.



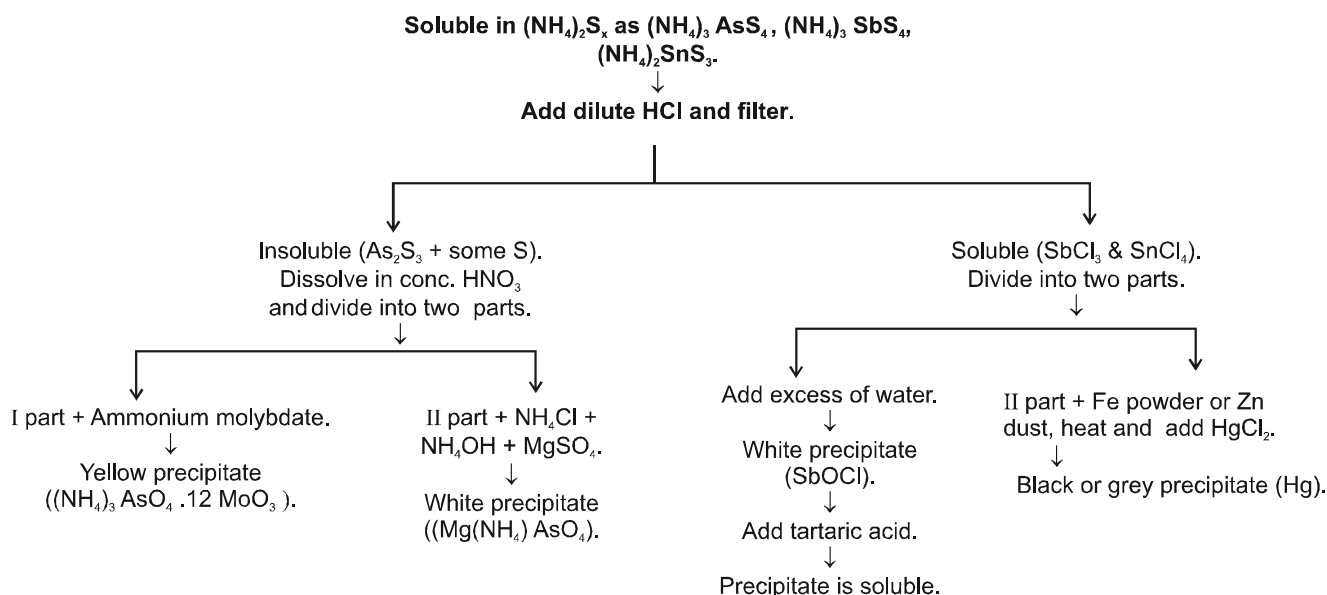
- **Potassium iodide** : Yellow precipitate is formed which is soluble in excess more concentrated (6M) solution of the reagent. Yellow precipitate of  $\text{PbI}_2$  is moderately soluble in boiling water to give a colourless solution.



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

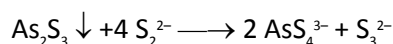
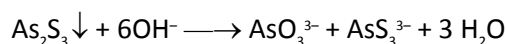
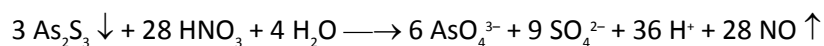
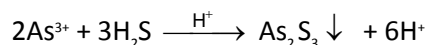


**IIB Group (As<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>)**

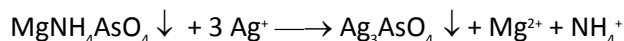


**1. ARSENIC ION (As<sup>3+</sup>) :**

● **Precipitation with H<sub>2</sub>S in acidic medium** : Yellow precipitate is formed which is soluble in warm concentrated nitric acid, sodiumhydroxide solution and yellow ammonium sulphide.

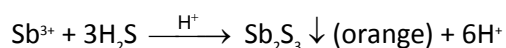


● **Magnesia mixture** : White crystalline precipitate of magnesium ammonium arsenate Mg(NH<sub>4</sub>)AsO<sub>4</sub> · 6H<sub>2</sub>O is formed from neutral or ammonical solution. Upon treating the white precipitate with silver nitrate solution containing a few drops of acetic acid, red silver arsenate is formed (distinction from phosphate).

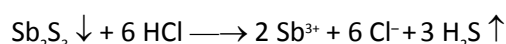


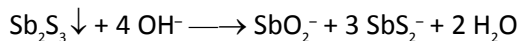
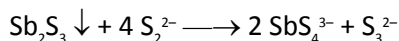
**2. ANTIMONY ION (Sb<sup>3+</sup>) :**

● **Precipitation with H<sub>2</sub>S in acidic medium** : A orange red precipitate is formed from mildly acidic solutions.

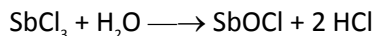


Precipitate is soluble in warm concentrated HCl, in ammonium polysulphide and in alkali hydroxides.

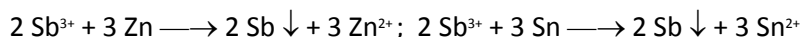




- **Dilution with water** : When water is poured in a solution of soluble  $\text{SbCl}_3$ , a white precipitate of antimonyl chloride ( $\text{SbOCl}$ ) is formed, soluble in HCl. With a large excess of water, the hydrated oxide  $\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  is produced.



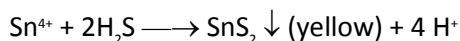
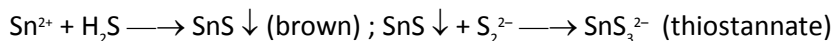
- **Reduction with zinc or tin** :  $\text{Sb}^{3+}$  ions give black precipitate of metal.



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

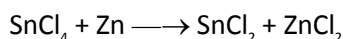
- **Precipitation with  $\text{H}_2\text{S}$  in acidic medium** :

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



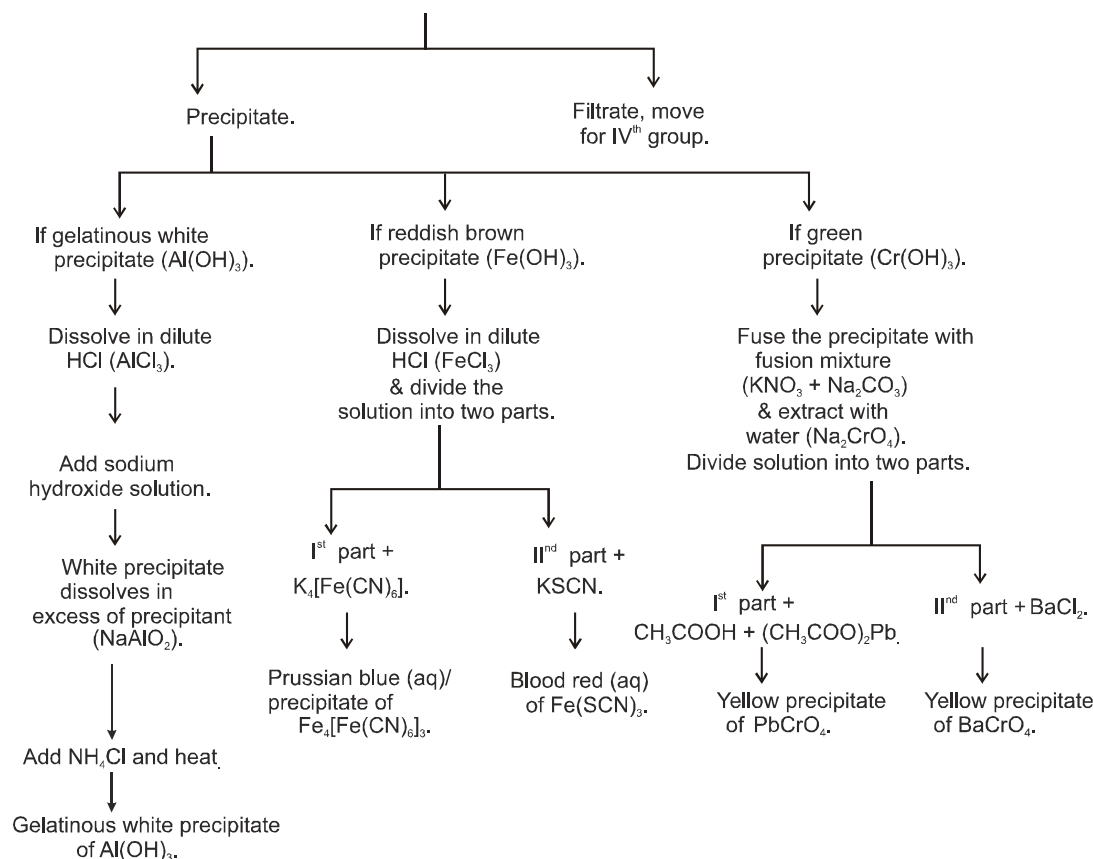
Precipitate is soluble in concentrated HCl (difference from  $\text{As}^{3+}$  and  $\text{Hg}^{2+}$ ) and in alkali hydroxide, and also in ammonium sulphide and yellow ammonium sulphide.

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



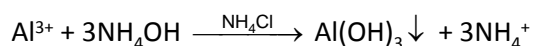
### III<sup>rd</sup> Group (Al<sup>+3</sup>, Cr<sup>+3</sup>, Fe<sup>+3</sup>)

II. Group Filtrate  $\xrightarrow{\text{Boiloff}}$  H<sub>2</sub>S ↑ then add conc. HNO<sub>3</sub> (1-2 drops) + NH<sub>4</sub>Cl (solid) + NH<sub>4</sub>OH

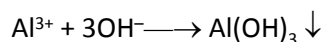


#### 1. ALUMINIMUM ION (Al<sup>3+</sup>) :

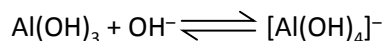
- **Precipitation with NH<sub>4</sub>OH in presence of NH<sub>4</sub>Cl** : White gelatinous precipitate is formed.



- **Sodium hydroxide** : A solution containing Al<sup>3+</sup> ions give a white precipitate with the reagent.

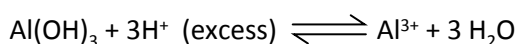
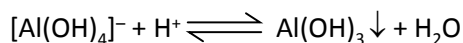
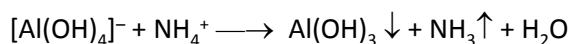


White precipitate dissolves in excess sodium hydroxide according to following reaction.

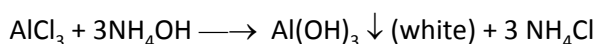


The reaction is reversible and any reagent, which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration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



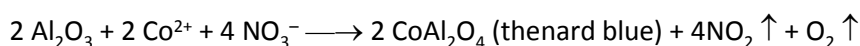


● **Lake Test :**



The precipitation of aluminium hydroxide is done in presence of blue litmus. Originally the solution will appear red when the group precipitate is dissolved in HCl as blue litmus turns red in acid medium. On adding large excess of  $\text{NH}_4\text{OH}$ ,  $\text{Al}(\text{OH})_3$  will be reprecipitated and will adsorb the litmus as it is flocculent by nature. After a while a blue mass will be seen floating in a colourless solution as all the colour from the solution will adsorbed.

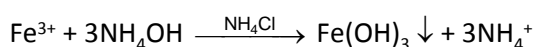
● **Dry test :** Aluminium compounds when heated with sodium carbonate upon charcoal gives a white infusible solid, which glows when hot. If the residue is moistened with a little cobalt nitrate solution and again heated, a blue infusible mass is obtained.



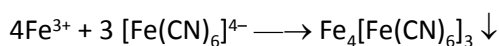
Use of excess cobalt nitrate solution should be avoided since this will produce black cobalt oxide ( $\text{Co}_3\text{O}_4$ ) upon ignition, which will mask the blue colour.

**2. IRON ION ( $\text{Fe}^{3+}$ ) :**

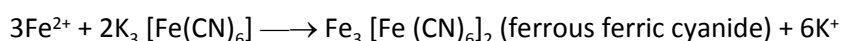
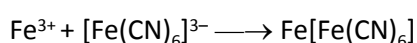
● **Precipitation with  $\text{NH}_4\text{OH}$  in presence of  $\text{NH}_4\text{Cl}$  :** Gelatinous reddish brown precipitate is formed which is insoluble in excess reagent but soluble in acids.



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

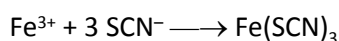


● **Potassium ferricyanide (Potassium hexacyanidoferrate(III)) :** A brown colouration is formed.



Turnbull's blue

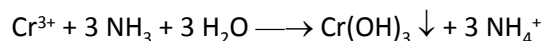
● **Potassium thiocyanate (Potassium sulphocyanide) :** In slightly acidic medium, a deep red colouration is produced due to the formation of a non-dissociated iron(III) thiocyanate complex.



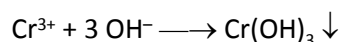
This neutral molecule can be extracted by ether or amyl alcohol.

### 3. CHROMIUM ION ( $\text{Cr}^{3+}$ ) :

- **Precipitation with  $\text{NH}_4\text{OH}$  in presence of  $\text{NH}_4\text{Cl}$**  : A grey-green to green gelatinous precipitate is formed.

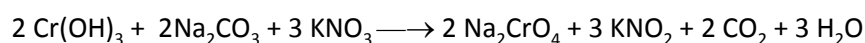


- **Sodium hydroxide solution** : A green precipitate is formed.



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

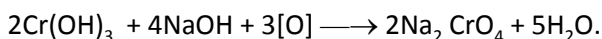
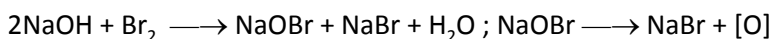
- (A) Fusion with fusion mixture ( $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ )



Fused mass on extraction with water gives yellow solution of  $\text{Na}_2\text{CrO}_4$ .

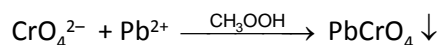
- (B)  $2 \text{Cr}(\text{OH})_3 + 3 \text{Na}_2\text{O}_2 \longrightarrow 2 \text{Na}_2\text{CrO}_4 + 2 \text{NaOH} + \text{H}_2\text{O}$

- (C) Precipitate is heated with  $\text{NaOH}$  and bromine water.

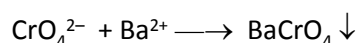


The yellow solution of  $\text{Na}_2\text{CrO}_4$  gave the following reactions with lead acetate, barium chloride and silver nitrate solutions.

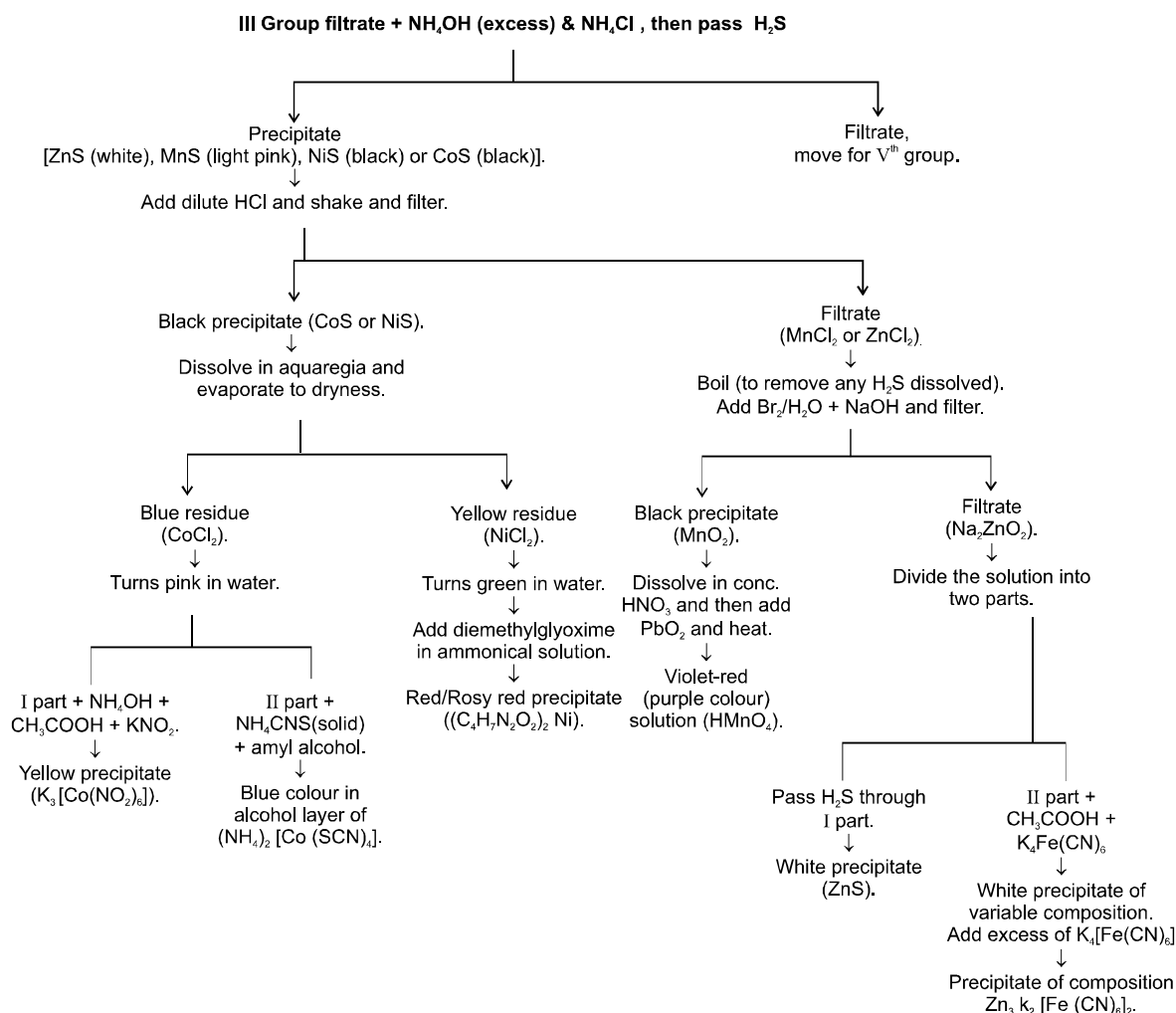
- (a) **Lead acetate solution** : Yellow precipitate is formed.



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

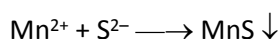


### IV<sup>th</sup> GROUP ( $Zn^{2+}$ , $Mn^{2+}$ , $Ni^{2+}$ , $Co^{2+}$ ) :

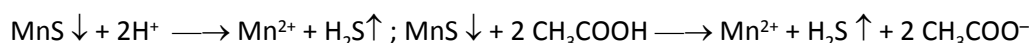


### 1. MANGANESE ION ( $Mn^{2+}$ ) :

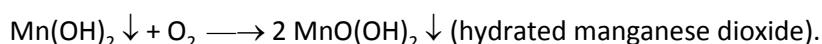
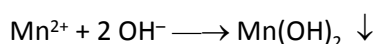
- **Precipitation with  $H_2S$  in presence of  $NH_4OH + NH_4Cl$  :** A buff coloured (light pink) precipitate is formed.



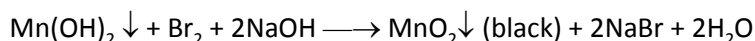
It is readily soluble in mineral acids (distinction with Ni and Co) and even in acetic acid (distinction with Ni, Co and Zn).



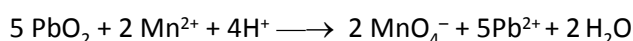
- **Sodium hydroxide solution :** Initially white precipitate of  $Mn(OH)_2$  is formed which is insoluble in excess reagent and rapidly oxidised on exposure to air, becoming brown.



☞ With sodium hydroxide and bromine water initially a white precipitate is formed which immediately turns to black owing to the formation of  $\text{MnO}_2$ .

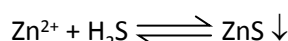


● **Lead dioxide ( $\text{PbO}_2$ ) and concentrated nitric acid** : On boiling a dilute solution of manganese(II) ions with lead dioxide and a little concentrated nitric acid and allowing the suspended solid containing unattacked lead dioxide to settle, the supernatant liquid acquired a violet-red (or purple) colour due to permanganic acid.

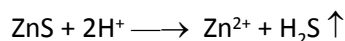


## 2. ZINC ION ( $\text{Zn}^{2+}$ ) :

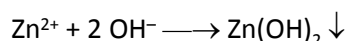
● **Precipitation with  $\text{H}_2\text{S}$  in presence of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$**  : A white precipitate is formed. In neutral solutions, precipitation is partial as  $\text{H}^+$  ions concentration produced depressed the ionisation of  $\text{H}_2\text{S}$ .



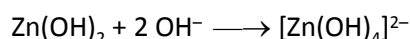
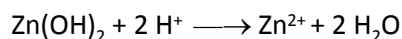
The precipitate is soluble in dilute HCl.



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

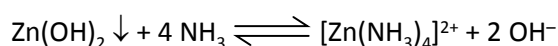
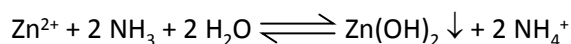


The precipitate is soluble in acids as well as in excess of the reagent.

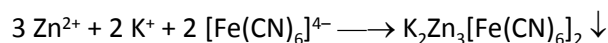


● **Ammonia solution** : A white gelatinous precipitate is formed which is readily soluble in excess of the reagent and in solutions of ammonium salts forming the tetraamminezinc(II).

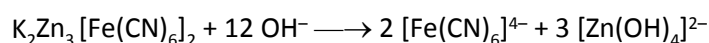
Non-precipitation of  $\text{Zn(OH)}_2$  by ammonia solution in the presence of  $\text{NH}_4\text{Cl}$  is due to the lowering of  $\text{OH}^-$  ion concentration to such a value that the  $K_{sp}$  of  $\text{Zn(OH)}_2$  is not attained.



● **Potassium ferrocyanide (Potassium hexacyanidoferrate(II)) solution** : A white precipitate of variable composition is formed. If excess reagent is added, the composition of precipitate is  $\text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2$ .



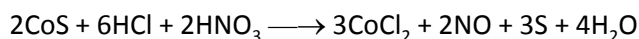
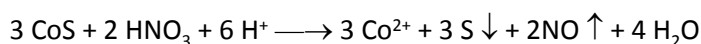
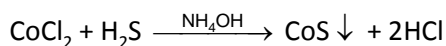
The precipitate is insoluble in dilute acids, but dissolves in sodium hydroxide readily.



This reaction can be used to distinguish zinc from aluminium.

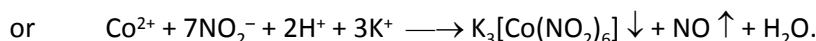
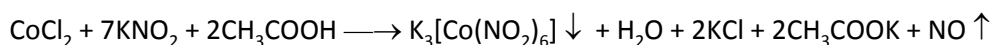
### 3. COBALT ION (Co<sup>2+</sup>) :

● **Precipitation with H<sub>2</sub>S in presence of NH<sub>4</sub>OH + NH<sub>4</sub>Cl** : A black precipitate is formed. The black precipitate of CoS is insoluble in dilute HCl or acetic acid but hot concentrated HNO<sub>3</sub> or aquaregia dissolves it and white sulphur remains. On longer heating the mixture becomes clear as because sulphur is oxidised to sulphate.

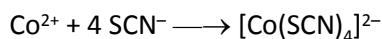


☞ Solution on evaporation to dryness gives blue residue (CoCl<sub>2</sub>) which turns pink on adding water.

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

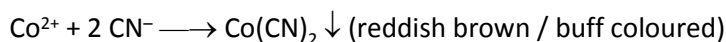


● **Ammonium thiocyanate solution** : A neutral or acid solution of cobalt(II) gives a blue colouration in amyl alcohol or ether layer when a few crystals of ammonium thiocyanate are added.

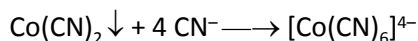


☞ In amyl alcohol or ether, the free acid H<sub>2</sub>[Co(SCN)<sub>4</sub>] is formed and dissolved by the organic solvent (distinction from nickel)

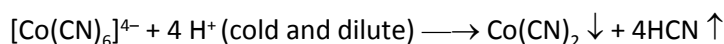
● **Potassium cyanide solution** :



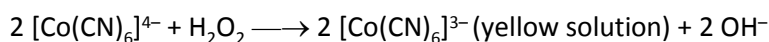
In excess of reagent, a brown solution of a soluble complex is formed.



On acidification precipitate reappears.



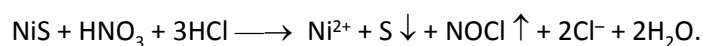
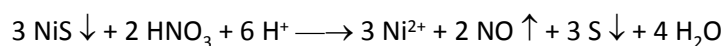
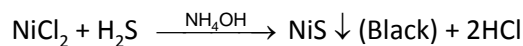
☞ If brown solution is boiled for a longer time in air or some H<sub>2</sub>O<sub>2</sub> is added and solution is heated it turns yellow.



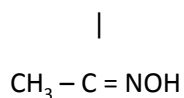
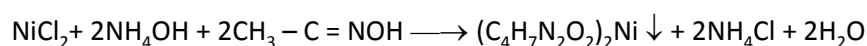
#### 4. NICKEL ION (Ni<sup>2+</sup>) :

- **Precipitation with H<sub>2</sub>S in presence of NH<sub>4</sub>OH + NH<sub>4</sub>Cl :**

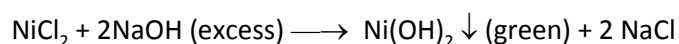
A black precipitate is formed which is insoluble in cold dilute HCl and CH<sub>3</sub>COOH but dissolves in hot concentrated HNO<sub>3</sub> and in aquaregia.



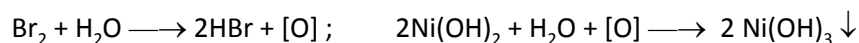
- **Dimethylglyoxime reagent :** A red precipitate is obtained from the solution just made alkaline or acid solutions buffered with sodium acetate.



- **Bromine water test (alkaline medium) :** A black precipitate of Ni<sub>2</sub>O<sub>3</sub> is formed.

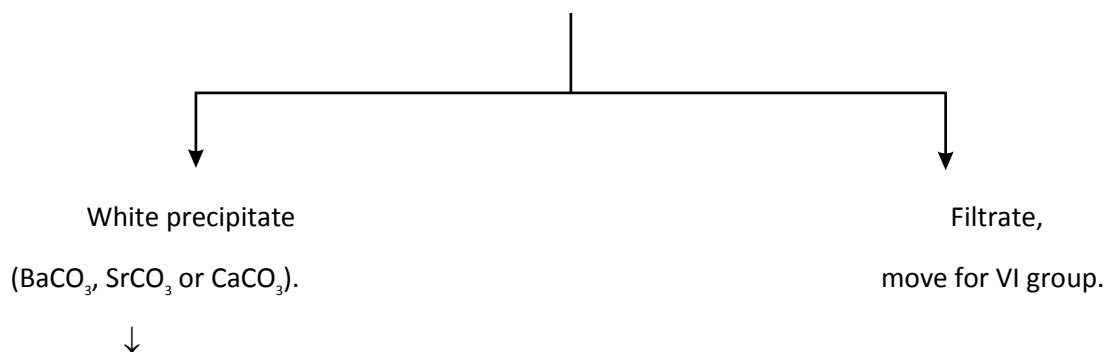


Green precipitate is formed which gradually turns black on adding bromine water.

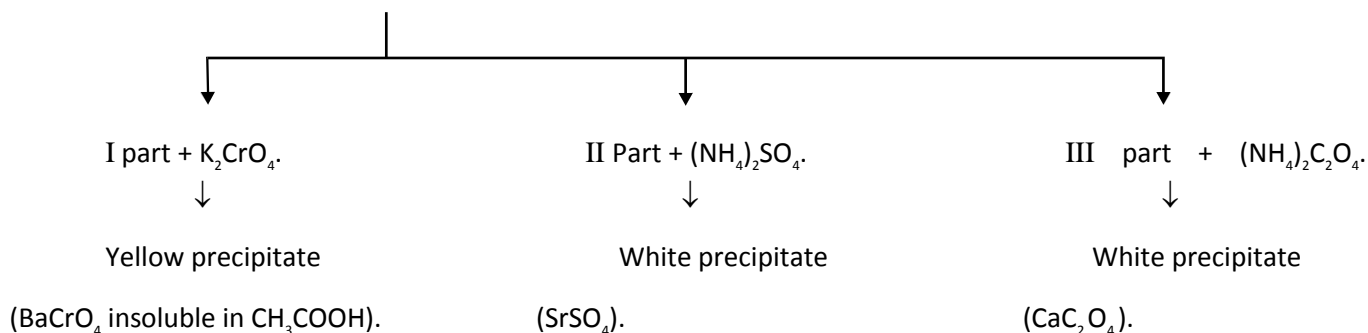


### V<sup>th</sup> Group ( $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ca}^{2+}$ ) :

IV Group filtrate  $\longrightarrow$  Boil off  $\text{H}_2\text{S}$  then add  $(\text{NH}_4)_2\text{CO}_3$  (aq),  $\text{NH}_4\text{OH}$  &  $\text{NH}_4\text{Cl}$  (s)

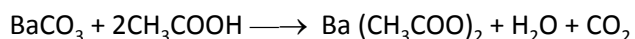
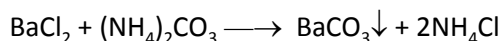


Dissolve in  $\text{CH}_3\text{COOH}$  and divide into three parts  
and test in the sequence given below.

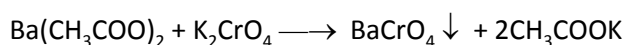


#### 1. BARIUM ION ( $\text{Ba}^{2+}$ ) :

- **Precipitation with  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$**  : A white precipitate is formed which is soluble in acetic acid and dilute mineral acids



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

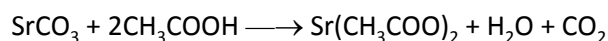
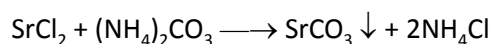


- ☞ Precipitate is insoluble in dilute acetic acid (distinction from strontium and calcium) but readily soluble in mineral acids.

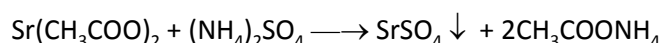
## 2. STRONTIUM ION ( $\text{Sr}^{2+}$ ) :

- **Precipitation with  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  :**

A white precipitate is formed which is soluble in acetic acid.

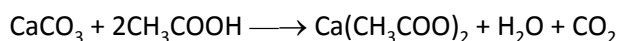
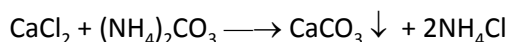


- **Ammonium sulphate solution :** A white precipitate is formed which is slightly soluble in boiling hydrochloric acid.

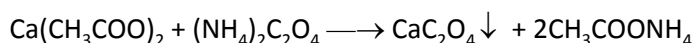


## 3. CALCIUM ION ( $\text{Ca}^{2+}$ ) :

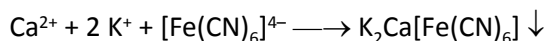
- **Precipitation with  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  :** A white precipitate is formed. The precipitate is soluble in water which contains excess carbonic acid (e.g freshly prepared soda water) because of the formation of soluble hydrogen carbonate. On boiling precipitate reappears again, as  $\text{CO}_2$  is removed. The precipitate is also soluble in acetic acid.



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



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

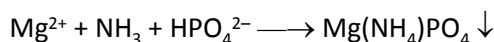


The confirmatory test for the basic radicals of (V) group have to be done in the order of  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  then  $\text{Ca}^{2+}$  (i.e BSC) because  $\text{Ba}^{2+}$  give positive test with all the reagents used in the confirmatory test of these group radicals,  $\text{K}_2\text{CrO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  &  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . So performs the test for  $\text{Sr}^{2+}$  with  $(\text{NH}_4)_2\text{SO}_4$  only when  $\text{Ba}^{2+}$  is absent. Similarly  $\text{Sr}^{2+}$  gives the test with both  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . So proceeds with  $\text{Ca}^{2+}$  only when  $\text{Sr}^{2+}$  is absent otherwise it will respond to ammonium oxalate test.

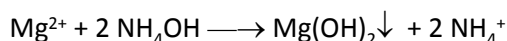


VI<sup>th</sup> GROUP :1. MAGNESIUM ION (Mg<sup>2+</sup>) :

● **Disodium hydrogen phosphate solution** : To the filtrate of V group or Mg<sup>2+</sup> ions solution add 1 ml (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution and heat if white precipitate is formed then filter it. Now to filtrate add a solution of disodium hydrogen phosphate. A white crystalline precipitate is formed in the presence of NH<sub>4</sub>Cl (prevent precipitation of Mg(OH)<sub>2</sub>) and ammonia solution.



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



● **Titan Yellow (a water soluble yellow dyestuff)** : It is adsorbed by Mg(OH)<sub>2</sub> producing a deep red colour or precipitate.

Dissolved the precipitate in dilute HCl (minimum qty.) and to 1 drop of this add 1 drop of NaOH solution (2 M) followed by 1 drop of titan yellow solution a deep red colour solution or precipitate is obtained.

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### *Solved Examples*

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**Ex.1** Which of the following salt will give white precipitate with the solution containing Pb<sup>2+</sup> ions ?

- (1) Na<sub>2</sub>CO<sub>3</sub>                      (2) NaCl                              (3) Na<sub>2</sub>SO<sub>3</sub>                      (4) All of these

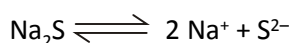
**Sol.** Pb<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup> → PbCO<sub>3</sub> ↓ (white)

Pb<sup>2+</sup> + 2Cl<sup>-</sup> → PbCl<sub>2</sub> ↓ (white)

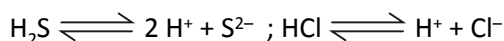
Pb<sup>2+</sup> + SO<sub>3</sub><sup>2-</sup> → PbSO<sub>3</sub> ↓ (white) ;                      Therefore, (D) option is correct.

**Ex.2** Why Na<sub>2</sub>S cannot be used in place of H<sub>2</sub>S (in presence of HCl) as a reagent for II<sup>nd</sup> group cations ?

**Sol.** With Na<sub>2</sub>S, along with 2<sup>nd</sup> group cations, some cations of higher groups i.e., III<sup>rd</sup> and IV<sup>th</sup> groups may be precipitated because the higher concentration of S<sup>2-</sup> ions is obtained according to following reaction.

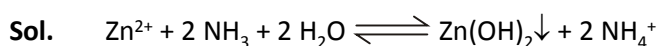


To precipitate II<sup>nd</sup> group cation lower concentration of S<sup>2-</sup> ions is required (because of low K<sub>sp</sub> of II<sup>nd</sup> group sulphides) and this can be obtained easily by H<sub>2</sub>S in presence of dilute HCl.



Due to common ion effect the ionisation of H<sub>2</sub>S is suppressed and the concentration of S<sup>2-</sup> ions obtained is just sufficient to precipitate the cations of II<sup>nd</sup> group.

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

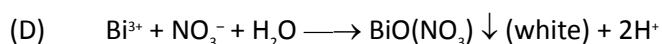
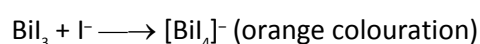
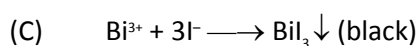
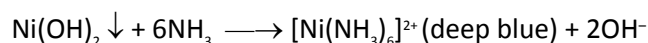
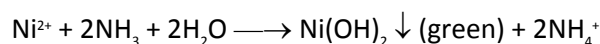
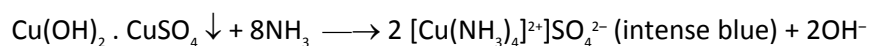
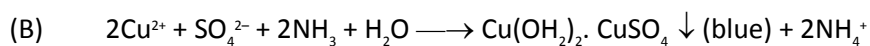
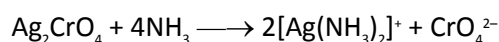
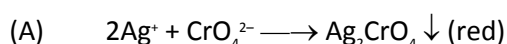


It is due to the lowering of  $OH^-$  ion concentration because of common ion effect of  $NH_4^+$  to such a value that the  $K_{sp}$  of  $Zn(OH)_2$  is not attained.

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

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

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



basic salt



5. **Statement - 1 :** Sodium meta aluminate on boiling with ammonium chloride produces white gelatinous precipitate.

**Statement - 2 :** Aluminium hydroxide is formed which is not soluble in water

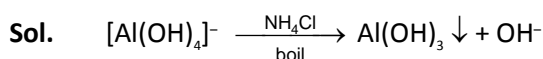
(1) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.

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

(3) Statement-1 is true but Statement-2 is false.

(4) Statement-1 is false but Statement-2 is true

**Ans.** (1)

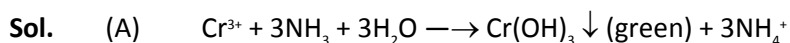


**Subjective :**

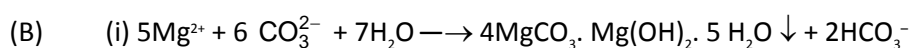
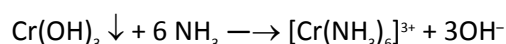
6. What happens when ?

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

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

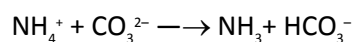


$Cr(OH)_3$  precipitate formed becomes slightly soluble in excess of precipitant in cold forming a violet or pink solution containing  $[Cr(NH_3)_6]^{3+}$  complex ions.



White precipitate of basic magnesium carbonate is formed.

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



is shifted towards the formation of  $HCO_3^-$  ions.

