

# Theory Notes

## QUALITATIVE ANALYSIS

### Introduction :

You know that the qualitative analysis involves the detection of the anions and the cations present in an inorganic mixture. Sometimes the knowledge of anions present in a mixture provides important clues about the cations which may be present in a mixture and the scheme of analysis to be followed. Therefore, it is desirable to first detect the presence of anions and after that the cations. In this unit, we will discuss the scheme of detection of anions which will be followed by the scheme of analysis of cations.

### Classification of the Anions :

For the systematic identification of the anions present in any mixture, the anions are divided into following three classes:

#### **Anions of Class I :**

The anions of Class I evolve gases or vapours on treatment with dil. HCl or dil.  $H_2SO_4$ . These anions are carbonate, sulphite, sulphide, thiosulphate, nitrite.

#### **Anions of Class II :**

The anions of Class II evolve gases or vapours on treatment with conc. HCl or conc.  $H_2SO_4$ . These anions are fluoride, chloride, bromide, iodide, nitrate and oxalate.

#### **Anions of Class III :**

The anions of this class do not evolve any gas on treatment with acids. These are identified by formation of precipitate on treatment with certain reagents. Sulphate, borate and phosphate ions are the anions of Class III.

Here we would like to emphasise the unlike scheme of classification of cations, the scheme of classification of anions is not a rigid one since some of the anions belong to more than one of the classes, e.g., acetate. Also, it is not always necessary to test for the presence of anions of Class I before testing for the presence of anions of Class II or Class III in any mixture.

### Preliminary Tests for the Anions

In this unit the tests for all these anions will be systematically discussed. We shall first discuss the preliminary tests for detecting the presence of anions of Class I and Class II, which will be followed by their confirmatory tests. As there are no preliminary tests for the anions of Class III only their confirmatory tests will be discussed.

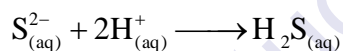
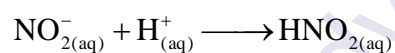
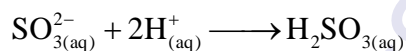
#### **Preliminary Tests for the Anions of Class I :**

Take about 0.2g of dry mixture in a test tube. Add 2 cm<sup>3</sup> of dilute hydrochloric or sulphuric acid. If a gas is evolved, note its colour and odour and draw inference with the help of Table 1. Heat the test tube if necessary. If no gas is evolved, anions of this class are absent in the

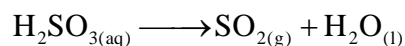
mixture.

Table 1: Preliminary Tests for the Anions of Class I			
S. No.	Observation	Inference	Explanation / Reaction
1.	Colourless, suffocating gas with smell of burning sulphur; the gas turns acidified $K_2Cr_2O_7$ paper green.	$SO_3^{2-}$ may be present	$SO_3^{2-} + 2H^+ \rightarrow H_2O_{(l)} + SO_{2(g)}$ $Cr_2O_7^{2-} + 2H^+ + 3SO_{2(g)} \rightarrow 2Cr^{3+}_{(aq)} + 3SO_4^{2-} + H_2O_{(l)}$ green
2.	Colourless gas which turns KI starch paper blue.	$S^{2-}$ may be present	$S^{2-}_{(aq)} + 2H^+_{(aq)} \rightarrow H_2S_{(g)}$ $Pb^{2+}_{(aq)} + H_2S_{(g)} \rightarrow PbS_{(s)} + 2H^+_{(aq)}$ Black
3.	Light brown gas which turns KI starch paper blue.	$NO_2^-$ may be present	$2NO_2^- + 2H^+ \rightarrow H_2O_{(l)} + NO_{(g)} + NO_{2(g)}$
4.	Colourless vapours with smell of vinegar on warming the test tube	$CH_3COO^-$ may be present	$CH_3COO^- + H^+ \rightarrow CH_3COOH_{(g)}$

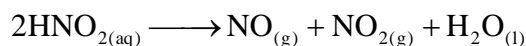
When salts of the anions of Class I are treated with strong, non-oxidising acids, corresponding acids are generated in the solution.



Out of these  $H_2CO_3$ ,  $H_2SO_3$  and  $HNO_2$  are thermally unstable and decompose into gaseous products, whereas  $H_2S$  and  $CH_3COOH$  are evolved as vapours on warming:



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**Preliminary Tests for the Anions of Class II :**

Take 0.2 to 0.3g of the mixture in a dry test tube and add 2-3 cm<sup>3</sup> of conc. sulphuric acid drop-wise. Observe the reaction at room temperature and then warm the test tube gently. If no gas or vapours are evolved, the anions of this class are absent. Draw interference inference with the help of Table 2.

<b>Table 2: Preliminary Tests for the Anions of Class I</b>			
S. No.	Observation	Inference	Explanation / Reaction
1	Colourless, pungent smelling gas is evolved, which gives white dense fumes of NH <sub>4</sub> Cl when a glass rod dipped in aqueous ammonia is placed in the evolved gas.	Cl <sup>-</sup> may be present	$\text{Cl}^{-}_{(aq)} + \text{H}^{+}_{(aq)} \rightarrow \text{HCl}_{(g)}$ $\text{HCl}_{(g)} + \text{NH}_{3(g)} \rightarrow \text{NH}_4\text{Cl}_{(g)}$
2	Reddish brown gas is evolved and the solution in the test tube acquires a yellow-red colour.	Br <sup>-</sup> may be present	$\text{Br}^{-}_{(aq)} + 6\text{H}^{+}_{(aq)} + 3\text{SO}_4^{2-}_{(aq)} \rightarrow 2\text{HSO}_4^{-}_{(aq)} + \text{Br}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
3	Violet vapours of I <sub>2</sub> are evolved, which turn the moist starch paper tube blue.	I may be present	$2\text{I}^{-}_{(aq)} + 6\text{H}^{+}_{(aq)} + 3\text{SO}_4^{2-}_{(aq)} \rightarrow 2\text{HSO}_4^{-}_{(aq)} + \text{SO}_{2(g)} + \text{I}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
4	Pungent smelling, brown fumes of NO <sub>2</sub> are evolved. The evolution of NO <sub>2</sub> increases on heating the reaction mixture with copper turnings.	NO <sub>3</sub> <sup>-</sup> may be present	$\text{NO}_3^{-}_{(aq)} + \text{H}^{+}_{(aq)} \rightarrow \text{HNO}_3_{(aq)}$ $4\text{HNO}_3_{(aq)} \rightarrow 4\text{NO}_{2(g)} + \text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$ $\text{Cu}_{(s)} + 4\text{HNO}_3_{(aq)} \rightarrow \text{Cu}(\text{NO}_3)_2_{(aq)} + 2\text{NO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$

**Preparation of Solution for Identification of the Anions**

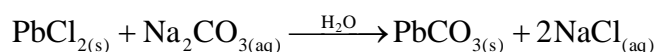
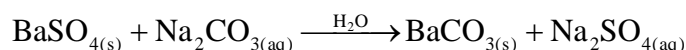
The preliminary tests described in the preceding section do not always offer very conclusive evidence for the presence of anions in a mixture. Therefore, further tests have to be performed for confirmation of those anions which are indicated by the preliminary tests and for the detection and confirmation of the anions of Class III which have no preliminary tests. These tests are called confirmatory tests and are performed on the solution of anions which is prepared as described below.

**Preparation of Water Extract (W.E.):**

All common acetates, nitrites, nitrates and thiosulphates are soluble in water. Confirmatory tests for these anions can be performed with the water extract of the mixture. Water extract can be prepared by boiling 1-2g of the mixture with 10-15 cm<sup>3</sup> distilled water in a boiling tube for a minute or two. Residue, if any, is filtered. The filtrate is called water extract (W.E.).

**Preparation of Sodium Carbonate Extract (S.E.):**

If the mixture is found to be partially or wholly insoluble in water, it is boiled with saturated sodium carbonate solution. This treatment converts the anions present in mixture into soluble sodium salts as a result of double decomposition e.g.,



For preparing sodium carbonate extract, take 0.5-1.0g of powdered mixture, 1.0-2.0g of sodium carbonate and 5-10 cm<sup>3</sup> of distilled water in a boiling tube or a 50 ml beaker. Heat with stirring for 5-10 minutes. Cool the contents and filter. The filtrate is called sodium carbonate

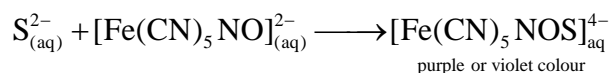
extract (S.E.). This extract is used for confirming the presence of most anions except for carbonate since sodium carbonate has been added during its preparation.

### Confirmatory Tests for the Anions

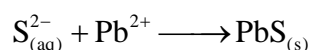
After preparation of the water extract or the sodium carbonate extract, the following tests are performed to confirm the presence of various anions in the mixture.

#### Tests for the Sulphide Ions

1. Take 1 ml of sodium carbonate extract in a test tube and add 1 – 2 ml of sodium nitroprusside solution. A purple or violet colour confirms sulphide ions:



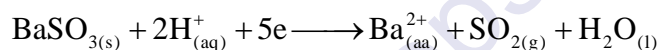
2. Take 1 – 2 ml of S.E. in a test tube, acidify it with acetic acid and boil to remove  $\text{CO}_2$ . Then add 1 – 2 ml of lead acetate solution. Formation of black precipitate confirms sulphide ions:



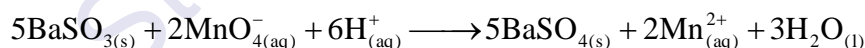
#### Tests for Sulphite Ions:

Take 2 – 3 ml of S.E. and add 2 – 3 cm<sup>3</sup> of  $\text{BaCl}_2$  solution to it. A white precipitate may appear due to the presence of  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  or excess of  $\text{CO}_3^{2-}$  ions present in the solution. Filter the precipitate and divide into three parts.

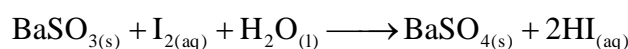
1. To the first part, add dil. HCl. Evolution of  $\text{SO}_2$  gas which turns acidified dichromate paper green confirms the presence of  $\text{SO}_3^{2-}$  ions



2. To the second part, and add a few drops of  $\text{KMnO}_4$  solution and acidify with dil.  $\text{H}_2\text{SO}_4$ . If the pink colour of  $\text{KMnO}_4$  is discharged, the presence of  $\text{SO}_3^{2-}$  ions is confirmed.

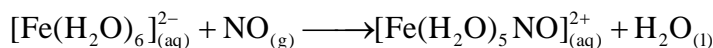
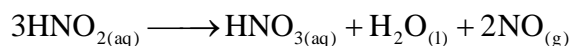
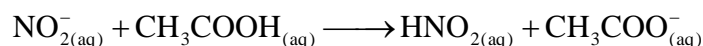


3. To the third part, add  $\text{I}_2$  solution. If colour of iodine is discharged,  $\text{SO}_3^{2-}$  is confirmed.



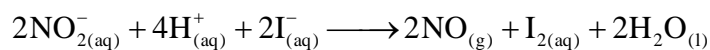
#### Tests for the Nitrite Ions

1. Take 5 drops of W.E. in a test tube. Dilute with 5 drops of distilled water. Add 5M acetic acid until the solution is just acidic. Cool the test tube in a cold water bath. Add 2-3 drops of freshly prepared 0.2M  $\text{FeSO}_4$  solution to the cooled solution. Appearance of a brown colour throughout the solution confirms the presence of nitrite ions.

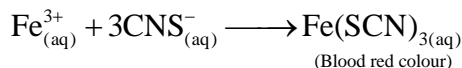
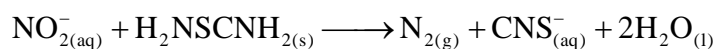


2. To 1 cm<sup>3</sup> of W.E. add 5 drops of KI solution, 1 cm<sup>3</sup> of starch solution and 1 cm<sup>3</sup> of dil.  $\text{H}_2\text{SO}_4$ . Appearance of a deep blue colour confirms the presence of nitrite ions.

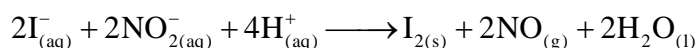
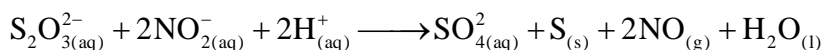
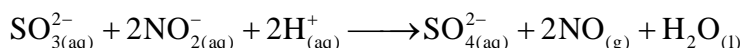
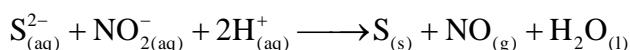
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3. Take 5 drops of W.E. in a test tube, acidify with 6 M acetic acid. Add a pinch of thiourea and stir well. Add 2 drops of  $\text{FeCl}_3$  solution. A blood red colour confirms nitrite ions.

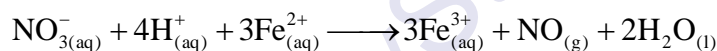


You should note that the nitrite ion is a moderately strong oxidizing agent in acidic medium. It oxidizes  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{I}^-$  ions to S,  $\text{SO}_4^{2-}$ , S and  $\text{I}_2$  respectively. Therefore, these anions cannot be present if  $\text{NO}_2^-$  ions are present in the mixture.



### Test for the Nitrate Ions :

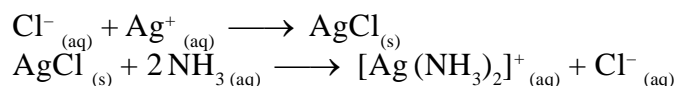
Take 2 cm<sup>3</sup> W.E. in a test tube. Add 4 cm<sup>3</sup> concentrated sulphuric acid, mix two liquids thoroughly and cool the mixture under a stream of cold water from the tap. Pour few cc of saturated solution of  $\text{FeSO}_4$  slowly down the side of the test tube so that it forms a separate layer on top of the solution in the test tube. A brown ring will be formed at the zone of contact of the two liquids.



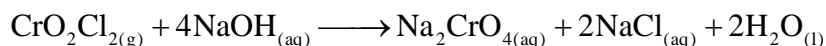
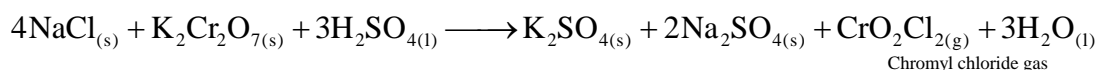
This test for nitrate ion is based on its ability to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in acidic solution with the product of NO gas. Since NO is more soluble in water at low temperature, in well cooled solution it reacts with excess  $\text{Fe}^{2+}$  present in solution to form brown nitrosyliron (II) complex ion,  $[\text{Fe}(\text{H}_2\text{O})\text{NO}]^{2+}$ . Nitrite, bromide and iodide ions interfere in this test.

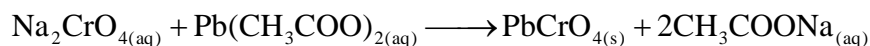
### Test for the Chloride Ions

1. Acidify 2 – 3 cm<sup>3</sup> of S.E. with dil.  $\text{HNO}_3$ . Boil off  $\text{CO}_2$ . Then add  $\text{AgNO}_3$  solution. Formation of a curdy white precipitate, which is soluble in aqueous ammonia, confirms the presence of chloride ions in the mixture.



2. Heat 0.5g of dry mixture with 0.5g of  $\text{K}_2\text{Cr}_2\text{O}_7$  and 2 ml of conc.  $\text{H}_2\text{SO}_4$  in a dry test tube, red vapours of chromyl chloride will be evolved. Pass the vapours in dil. NaOH solution, a yellow solution will be obtained. Acidify the solution with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate, which is soluble in NaOH, confirms the presence of chloride ions.

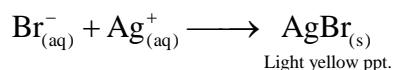




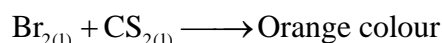
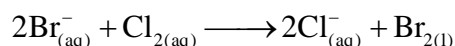
Due to the formation of chromyl chloride gas, this test is called chromyl chloride test. The test fails if the mixture contains chlorides of  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Ag}^+$ .

### **Test for the Bromide Ions**

1. Acidify 2-3 ml of S.E. with dil.  $\text{HNO}_3$  and boil off  $\text{CO}_2$ . Add  $\text{AgNO}_3$  solution. Formation of a light yellow precipitate which is partially soluble in aqueous ammonia solution, confirms the presence of bromide ions.

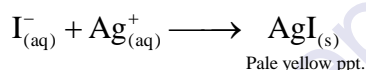


2. Take 2 cm<sup>3</sup> of S.E., acidify it with dil.  $\text{HCl}$  and boil off  $\text{CO}_2$ . Add 2 cm<sup>3</sup> of carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water drop-wise and shake. Bromide ions are oxidized to bromine, which imparts an orange colour to the organic layer. This confirms the presence of bromide ions in the mixture.

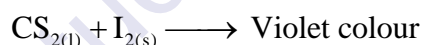


### **Tests for the Iodide Ions**

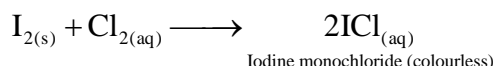
1. Acidify 2 – 3 cm<sup>3</sup> of S.E., with dil.  $\text{HNO}_3$  and boil off  $\text{CO}_2$ . Add  $\text{AgNO}_3$  solution. Formation of a pale yellow precipitate insoluble in aqueous ammonia confirms the presence of iodide ions in the mixture.



2. Take 2 cm<sup>3</sup> of S.E. in a test tube. Acidify it with dil.  $\text{HCl}$  and boil off  $\text{CO}_2$ . Add 2 cm<sup>3</sup> carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water drop-wise and shake. Iodide ions are oxidized to iodine, which imparts a violet colour to the organic layer.

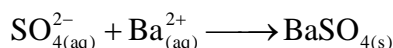


The violet colour disappears on addition of excess of chlorine water. This confirms the presence of iodide ions in the mixture.



### **Test for the Sulphate Ions:**

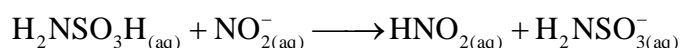
Take 1 – 2 cm<sup>3</sup> of S.E., in a test tube. Acidify it with dil.  $\text{HCl}$  and boil off  $\text{CO}_2$ . Add  $\text{BaCl}_2$  solution. Appearance of a white precipitate, which is insoluble in conc.  $\text{HCl}$  and conc.  $\text{HNO}_3$ , confirms the presence of sulphate ions.



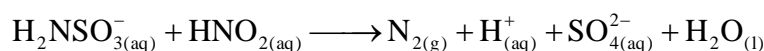
### **Test for Nitrate Ions in Presence of Nitrite Ions:**

In presence of nitrite, nitrate cannot be tested either by heating with conc.  $\text{H}_2\text{SO}_4$  or by the ring test because both liberate  $\text{NO}_2$ . Therefore, nitrite must be destroyed completely before testing for the nitrate. Nitrite ions can be destroyed by any one of the following methods:

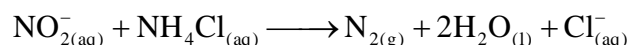
1. Add sulphamic acid,  $\text{H}_2\text{NSO}_3\text{H}$ , to the water extract containing  $\text{NO}_2^-$  and  $\text{NO}_3^-$  ions. Acidify the solution with dilute  $\text{H}_2\text{SO}_4$ . Nitrite will be decomposed and nitrogen gas will be evolved.



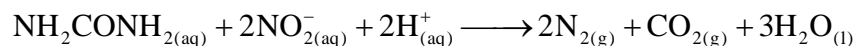
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2. Take 2 – 3 ml of water extract, add 1 g solid  $\text{NH}_4\text{Cl}$  and boil till effervescence ceases.



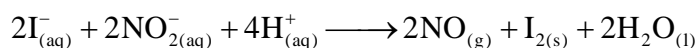
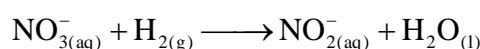
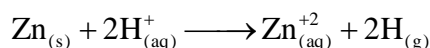
3. Take 2 – 3 ml of water extract, add urea and acidify with dil.  $\text{H}_2\text{SO}_4$ . Boil the solution till evolution of gases ceases.



Now divide the nitrite free solution thus obtained in two parts.

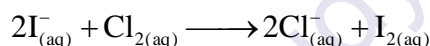
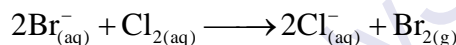
(a) Perform ring test with one part to confirm the presence of nitrate ions.

(b) Acidify the other part with dil.  $\text{H}_2\text{SO}_4$ . Add a little KI and 1  $\text{cm}^3$  starch solution. Absence of any blue colour indicates the complete removal of nitrite ions. Now add a piece of granulated zinc to the solution. Appearance of a blue colour confirms the presence of nitrate ions.



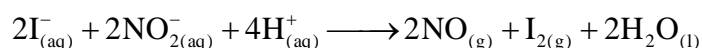
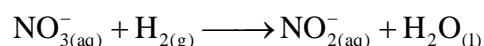
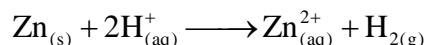
### Tests for Nitrate Ions in Presence of Bromide and/or Iodide Ions

1. Bromide and iodide interfere in the ring test of nitrate because of the colour of liberated bromine and iodine. In order to identify nitrate in presence of iodide and/or bromide, the interfering halide should be expelled before performing the ring test. This can be done by boiling 2 – 3  $\text{cm}^3$  of water extract or sodium carbonate extract with excess of chlorine water in a china dish, till no more vapours of  $\text{Br}_2$  or  $\text{I}_2$  evolve.



Now perform the ring test on the halide free solution to identify the nitrate ion in the mixture.

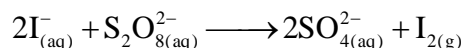
2. Alternatively, take 2 – 3  $\text{cm}^3$  of water extract in a test tube. Acidify with dil.  $\text{H}_2\text{SO}_4$ . Now add 1  $\text{cm}^3$  of KI solution, 1  $\text{cm}^3$  of starch solution and a few granules of zinc. Appearance of a blue colour confirms the presence of nitrate ions in the mixture.



### Test for Chloride, Bromide and Iodide Ions in Presence of Each Other:

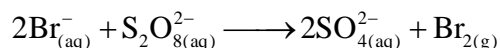
As you know that chloride, and iodide ions react with  $\text{AgNO}_3$  solution to form a precipitate, special tests are required to identify if more than one of them are present in the mixture. These anions can be detected in presence of one another by any one of the following methods.

1. Acidify 2 – 3  $\text{cm}^3$  of S.E., with excess dil.  $\text{H}_2\text{SO}_4$  in a china dish. Add 0.5g of potassium persulphate and heat gently. Add distilled water if necessary of to prevent dryness. Evolution of violet vapours of  $\text{I}_2$  will confirm the presence of  $\text{I}^-$  ions.

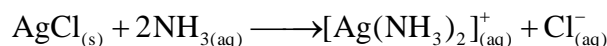
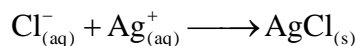




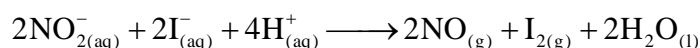
Boil till evolution of  $I_2$  ceases. If the solution after elimination of  $I_2$  is brown, it indicates the presence of  $Br^-$  ions. Continue boiling, brown vapours of  $Br_2$  will be evolved.



Add more  $K_2S_2O_8$  if required. Continue boiling till the residual solution becomes colourless. Cool the solution, add dil.  $HNO_3$  and  $AgNO_3$  solution. A curdy white precipitate soluble in ammonia confirms the presence of  $Cl^-$  ions in the mixture.

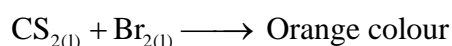
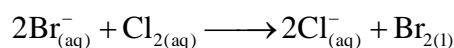


2. Acidify 2 – 3 cm<sup>3</sup> of S.E. with dil.  $H_2SO_4$  in a china dish. Boil off  $CO_2$ . Add solid sodium nitrite and boil. Evolution of violet vapours of  $I_2$  confirms the presence of iodide ions.

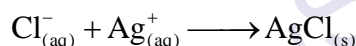


Add distilled water if necessary to prevent dryness. Continue boiling till all iodine is expelled. Cool the solution and divide into 2 parts.

To 1<sup>st</sup> part add 1 cm<sup>3</sup>  $CS_2$  (or  $CH_2Cl_2$  or  $CCl_4$ ), 2 cm<sup>3</sup> chlorine water and shake. Appearance of an orange colour in organic layer confirms the presence of bromide ions.



If  $Br^-$  is present, boil the 2<sup>nd</sup> part with 1 cm<sup>3</sup> of conc.  $HNO_3$  to expel  $Br_2$  gas. This treatment can be avoided if  $Br^-$  ion is absent. Then add  $AgNO_3$  solution. Formation of a curdy white precipitate confirms the presence of  $Cl^-$  ions.



## TEST OF CATIONS

### Flame Test on Dry Samples

#### Bunsen Flame :

A Luminous Bunsen flame (air holes completely closed), about 5 cm long, is employed for conducting *blowpipe test*. A reducing flame is produced by placing the nozzle of a mouth pipe just outside the flame, and blowing gently, so as to cause the inner cone to play on the substance under examination. An oxidizing flame is obtained by hold holding the nozzle of the blowpipe about one third within the flame and blowing somewhat more vigorously in a direction parallel with the burner top, the extreme, tip of the flame is allowed to play upon the substance.

#### Charcoal Cavity Test :

The test are carried out upon a clean charcoal block in which a small cavity has been made. aA little of the substance is placed in the cavity and heated in the oxidizing flame, crystalline salts break into smaller pieces: burning indicates the presence of an oxidizing agent (nitrate, chlorate etc.). More frequently the powdered substance is mixed with twice its bulk of anhydrous  $Na_2CO_3$  or preferably with fusion mixture (an equimolar mixture of together  $Na_2CO_3$  and  $K_2CO_3$ ; this has a lower mp than  $Na_2CO_3$ ) in a reducing flame. The initial reaction consists of the formation of the carbonates of the cations present and the alkali salts of anions. The alkali salts are largely adsorbed by the porous charcoal, and the carbonates are, for the most part, decomposed into oxides and  $CO_2$ . The oxides of the metal may further decompose, or be reduced to the metals, or they may remain unchanged. The final products of the reaction are, therefore, either the metals alone, metals and their oxides, or oxides. The oxides of the noble



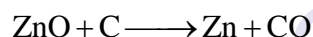
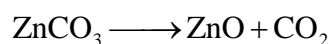
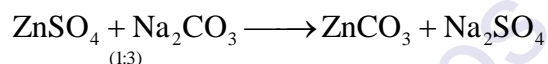
## QUALITATIVE ANALYSIS

metals (Ag and Au) are decomposed without the aid of the charcoal, to the metal, which is often obtained as a globule and oxygen. The oxides of Pb, Cu, Bi, Sb, Sn, Fe, Ni and Co are reduced either to a fused metallic globule (lead, bismuth, tin and antimony) or to a sintered mass (copper) or to a glistening metallic fragments (iron, nickel and cobalt). The oxides of cadmium, arsenic and zinc are readily reduced to the metal but these are so volatile that they vapourise and are carried from the reducing to the oxidizing flame zone, where they are converted into sparingly volatile oxides. The oxides thus formed are deposited as an incrustation round the cavity of the charcoal block, zinc yields an incrustation which is yellow while not hot and white when cold.

Incrustation of cadmium is brown and is moderately volatile, that of arsenic is white and is accompanied by a garlic odour due to the volatilization of the arsenic. A characteristic incrustation accompanies the globules of lead, bismuth and antimony.

The oxides of Al, Ca, Sr, Ba and Mg are not reduced by charcoal; they are infusible and glow brightly when strongly heated. If the white residue or white incrustation left on a charcoal block is treated with cobalt nitrate solution and again heated, a bright blue colour, which probably consists of either a compound or a solid solution of cobalt (II) and aluminium oxide (Thenard's blue) indicates the presence of aluminium; a pale green colour, probably of similar composition (Rinmann's green), is indicative of zinc oxide; and pale zinc mass is formed when magnesium oxide is present.

### Principle of Charcoal Cavity Test



Colour of bead, residue or incrustation will be used to diagnose the metal.

Colour of Bead	Colour of Residue or Incrustation	Inference
White bright bead which does not impart mark on paper on rubbing	Incrustation does not form	Ag <sup>+</sup>
White brittle bead	White Incrustation	Sb <sup>3+</sup>
Red bead	Reddish brown incrustation	Cu <sup>2+</sup>
Brittle bead	Violet Red when hot and yellow incrustation when cold	Bi <sup>3+</sup>
White soft ball which mark on paper	Brown incrustation when hot and yellow when cold	Pb <sup>2+</sup>
Bead does not form	Yellow incrustation when hot while white when cold	Zn <sup>2+</sup>
—	Garlic smell like fumes	As <sup>3+</sup>
—	Yellow incrustation on hot while on cold dirty white incrustation	Sn
—	Reddish brown incrustation	Cd <sup>2+</sup>

— Incrustation does not form but black residue is left in the cavity

Fe, CO, Ni, Mn

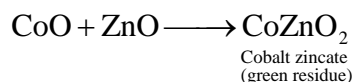
### Cobalt Nitrate Bead Test:

This is also like charcoal cavity test. This test is performed in oxidizing flame rather than in reducing flame.

The oxides of Al, Ca, Sr, Ba and Mg are not reduced by charcoal; they are infusible and glow brightly when strongly heated. If the white residue or white incrustation left on a charcoal block is treated with a drop of cobalt nitrate solution and again heated, a bright blue colour, which probably consists of either a compound or a solid solution of cobalt II and aluminium oxide indicates the presence of aluminium. Other colours are listed in Table.

### Principle

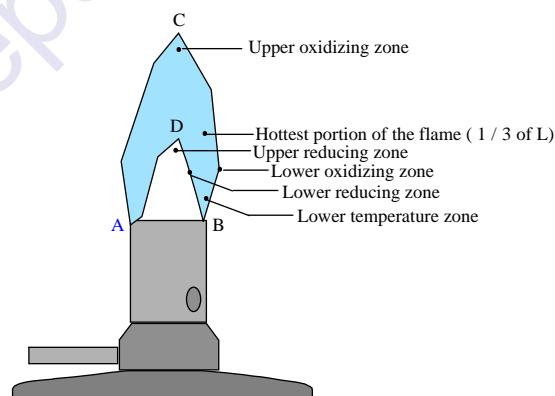
$\text{ZnSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{ZnCO}_3 + \text{Na}_2\text{SO}_4$	<b>Colour of Residue</b>	<b>Inference</b>
$\text{ZnCO}_3 \longrightarrow \text{ZnO} + \text{CO}_2$	Green	$\text{Zn}^{2+}$
$2\text{Co}(\text{NO}_3)_2 \longrightarrow 2\text{CoO} + 4\text{NO}_2 + \text{O}_2$	Blue	$\text{Al}^{3+}$
	Light Pink	$\text{Mg}^{2+}$
	Bluish Pink	$\text{PO}_4^{3-}, \text{AsO}_4^{3-}$ , silicates borates



1. Inner blue cone ADB continuing consisting largely of unburnt gas.
2. A luminous tip at D (this is only visible when the air holes are slightly closed).
3. An outer mantle ACBD in which complete combustion of gas occurs.

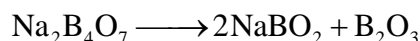
**(Luminous flame is obtained when air holes are completely closed)**

**(Non luminous flame is obtained when air holes are completely opened)**



### Borax Bead Test :

A point wire is used for borax bead test. The free end of the point wire is coiled into small loop through which ordinary match will barely pass. The loop is heated in Bunsen flame until it is red hot and then quickly dipped into powdered borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . The adhering solid is held in the hottest part of the flame, the salt swells up as it loses its water of crystallization and shrinks upon the loop forming a colourless, transparent, glass like bead consisting of a mixture of sodium metaborate and boric anhydride.



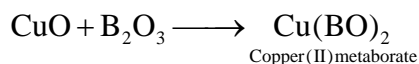
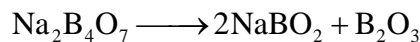
the head is moistened and dipped into the finely powdered substance so that a minute amount of it adheres to the bead. It is important to employ a minute amount of substance as otherwise the bead will become dark and opaque in the subsequent heating. The head and adhering substance are first heated in the lower reducing flame, allowed to cool and the colour is observed

## QUALITATIVE ANALYSIS

again.

Characteristic coloured beads are produced with salts of Cu, Fe, Cr, Mn, Co and Ni. Carry out borax bead test with salts of these metals and compare results with those given below:

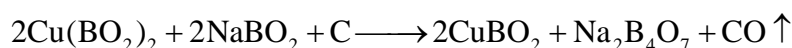
The coloured borax beads are due to the formation of colour borates; in those cases when different coloured beads are obtained in the oxidizing and the reducing flames, borates corresponding to varying stages of oxidation of the metal are produced. Thus, with the copper salts in the oxidizing flame, one has.



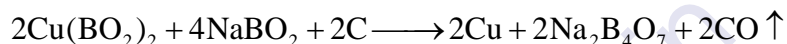
The reaction,  $\text{CuO} + \text{NaBO}_2 \longrightarrow \text{NaCuBO}_3$   
Orthoborate

probably also occurs. In the reducing flame (i.e. in the presence of carbon), two reactions may take place.

- The coloured copper (II) is reducing to colourless copper (I) metaborate.



- The copper (II) borate is reduced to metallic copper, that the bead appears red and opaque.



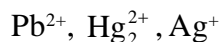
With iron salts  $\text{Fe(BO)}_2$  and  $\text{Fe(BO)}_3$  are formed in reducing and oxidizing flames respectively.

### Colours of Borax Beads

Oxidizing Flame		Reducing Flame		Metal
Hot	Cold	Hot	Cold	
Green	Blue	Colourless	Opaque Red brown	Copper
Yellowish green	Yellow	Green	Green	Iron
Yellow	Green	Green	Green	Chromium
Violet	Amethyst	Colourless	Colourless	Manganese
Blue	Blue	Blue	Blue	Cobalt
Violet	Reddish	Green	Grey	Nickel
	Brown			
Yellow	Colourless	Brown	Brown	Molybdenum
Rose Violet	Rose Violet	Red	Violet	Gold
Yellow	Colourless	Yellow	Yellowish brown	Tungston
Yellow	Pale Yellow	Green	Bottle green	Uranium
Yellow	Greenish	Brownish	Green	Vanadium
	Yellow			

Yellow	Colourless	Grey	Pale violet	Titanium
Orange Red	Colourless	Colourless	Colourless	Cerium

## Group I : Radicals



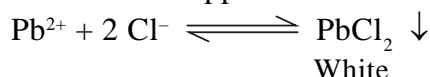
Group Reagent – dil. HCl

Precipitates as – Chlorides

Since  $\text{PbCl}_2$  is not completely precipitated in group I as chloride because of its solubility in hot water is 33.4g/litre of solvent. So  $\text{Pb}^{2+}$  has been placed in both the groups.

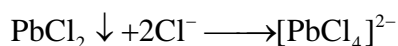
## Reactions of $\text{Pb}^{2+}$ ion

- Dilute HCl:** A white ppt. in cold solution of the acid is not too dilute.



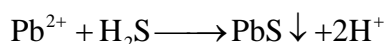
Soluble in hot water (33.4g/L at 100°C, 9.9 g/L at 20°C)

It is also soluble in conc. HCl or conc. KCl when the tetrachloroplumbate (II) ion is formed.

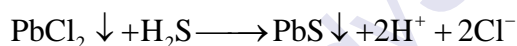


If the ppt is washed and dil.  $\text{NH}_3$  is added, no visible change occurs (difference from  $\text{Hg}_2^{2+}$  or  $\text{Ag}^+$  ions), through a ppt. exchange reaction takes place and lead hydroxide is formed.

- $\text{H}_2\text{S}$  (gas or saturated aqueous solution) in neutral or dilute acid medium, black ppt. of lead sulphide is obtained



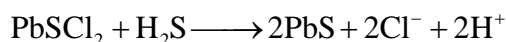
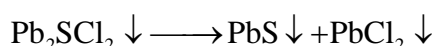
When  $\text{H}_2\text{S}$  gas is introduced into a mixture which contains a ppt. of white lead chloride, the latter is converted into lead sulphide (black) in a precipitate exchange reaction.



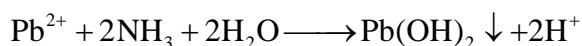
If the test is carried out in the presence of larger amounts of  $\text{Cl}^-$  (KCl saturated), initially a red ppt. of lead sulphochloride is formed when introducing  $\text{H}_2\text{S} \uparrow$ .



This, however, decomposes on dilution or on further addition of  $\text{H}_2\text{S}$  and a black ppt. of PbS is formed.

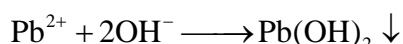


- $\text{NH}_3$  solution: White ppt of  $\text{Pb}(\text{OH})_2$  is obtained

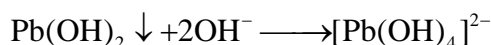


$\text{Pb}(\text{OH})_2$  is insoluble in  $\text{NH}_3$  solution excess.

- NaOH: White ppt. of  $\text{Pb}(\text{OH})_2$



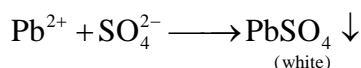
The ppt. is dissolved in excess of NaOH, when tetrahydroxoplumbate (II) ions are formed.



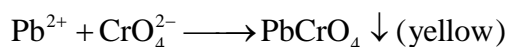
thus, lead hydroxide has an amphoteric character.

### QUALITATIVE ANALYSIS

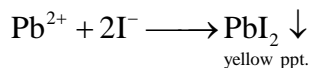
5.  $\text{H}_2\text{SO}_4$  (or soluble sulphate) white ppt. of  $\text{PbSO}_4$  is obtained



6.  $\text{K}_2\text{CrO}_4$ : Potassium chromate in neutral, acetic acid or ammonium solution yellow ppt of lead chromate is obtained.

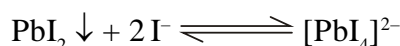


7. KI: yellow ppt of lead iodide is formed.



The ppt. is moderately soluble in boiling water to yield a colourless solution, from which it separates as golden yellow plates on cooling.

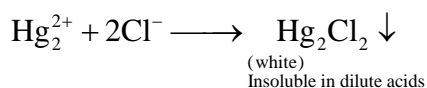
An excess of a more conc. (6M) solution of the reagent dissolves the ppt. and tetraiodoplumbate (II) ions are formed



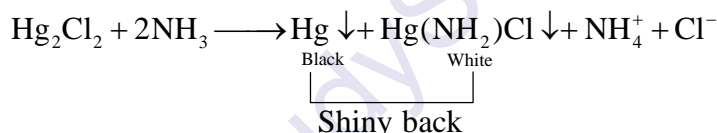
The reaction is reversible, on cooling ppt. reappears.

### Reactions of $\text{Hg}_2^{2+}$ ions

1. **Dilute Hydrochloric acid or Soluble Chlorides:** White precipitate of  $\text{Hg}_2\text{Cl}_2$  (calomel) is obtained.

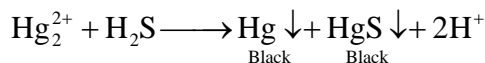


Ammonia solution converts the ppt. into a mixture of mercury (II) amidochloride and mercury metal, which are both insoluble.

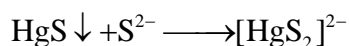


Mercury (II) chloride dissolves in aqua-regia, forming undissociated but soluble mercury (II) chloride.

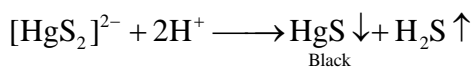
2. **Hydrogen Sulphide (Gas or Saturated Aqueous Solution):** In neutral or dilute acid medium black precipitate, is obtained which is a mixture of  $\text{Hg}(\text{II})$  sulphide and mercury metal.



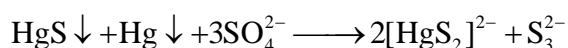
Sodium sulphide (colourless) dissolves the mercury (II) sulphide (but leaves mercury metal) and a disulphomercurate (II) complex is formed.



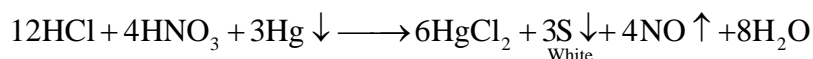
After removing the mercury metal by filtration black  $\text{HgS}$  can again be precipitated by acidification with dilute mineral acid.



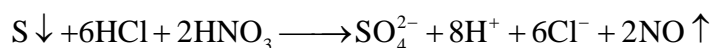
Sodium disulphate (yellow) dissolves both mercury and mercury (II) sulphide.



Aqua-regia dissolves the precipitate, yielding undissociated mercury (II) chloride and sulphur.

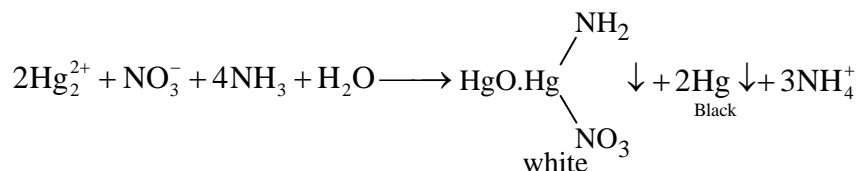


When heated with aqua-regia, sulphur is oxidized to  $\text{H}_2\text{SO}_4$  and the solution becomes clear.



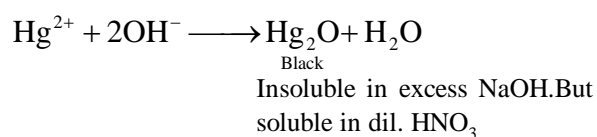
**3. Ammonia Solution:**

Black ppt. which is a mixture of Hg metal and basic mercury (I) amidonitrate (white ppt.)

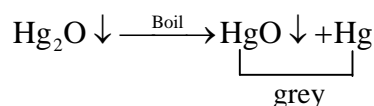


This reaction can be used to differentiate between  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  ions.

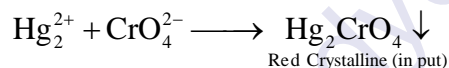
**4. Sodium Hydroxide:** Black ppt. of mercury (I) oxide.



When boiling, the colour of the ppt. turns to grey, owing to disproportionation, when HgO and Hg are formed.

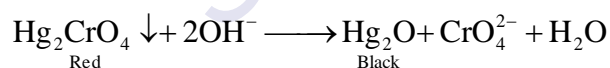


**5. Potassium Chromate:** In hot solution a red crystalline ppt. of  $\text{Hg}_2\text{CrO}_4$  is obtained..

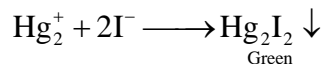


If the test is carried out in cold, a brown amorphous ppt. with an undefined composition is obtained, when heated the ppt. turns to red crystalline  $\text{HgCrO}_4$ .

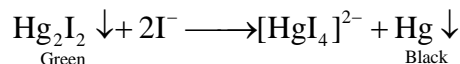
Sodium hydroxide turns into black mercury (I) oxide.



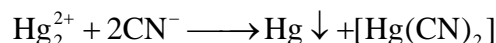
**6. KI Solution:** Added slowly in cold solution, green ppt. of mercury (I) iodide.



If excess of reagent is added disproportionation takes place, soluble tetraiodomercurate (II) ions and a black ppt. of finely divided mercury being formed.

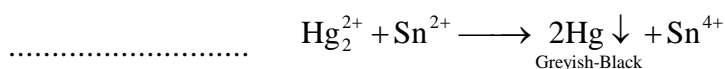


Produces a mercury (II) cyanide solution and black ppt. of Hg metal. Is obtained.



Hg(I) ions to mercury metal (grayish black ppt)

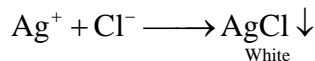
## QUALITATIVE ANALYSIS



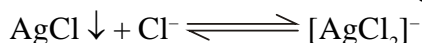
Hg (II) ions react in a similar way.

### Reactions of Silver (I) Ions

1. **Dilute Hydrochloric Acid (or Soluble Chlorides):** White ppt. of AgCl is obtained.

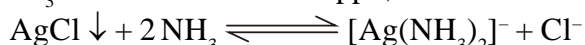


With conc. HCl precipitation does not occur. After decanting from over the ppt., it can be dissolved in conc. HCl, when dichloroargentate complex is formed.



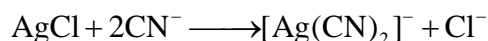
On dilution with H<sub>2</sub>O, the equilibrium shifts back to the left and the ppt. reappears.

Dilute NH<sub>3</sub> solution dissolves the ppt., to form the diammine silver ion.

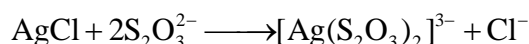


Dilute HNO<sub>3</sub> or HCl neutralizes the excess of NH<sub>3</sub>, and the ppt. reappears because the equilibrium is shifted back towards the left.

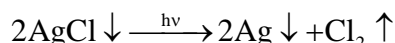
KCN dissolves the ppt. with formation of the dicyanoargentate complex.



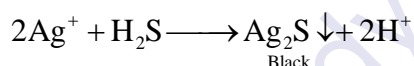
Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> dissolves the ppt. with the formation of a dithiosulphatoargentate complex.



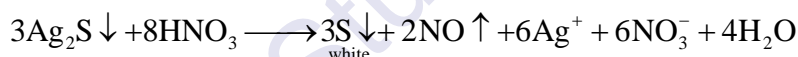
Sunlight or ultraviolet light decomposes the AgCl precipitates, which turns to grayish or black owing to the formation of the metal.



2. **H<sub>2</sub>S (Gas or Saturated aqueous Solution):** Black ppt. of Ag<sub>2</sub>S is formed.

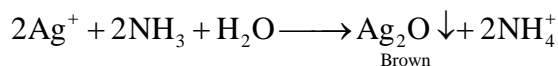


Hot conc. HNO<sub>3</sub> decomposes the Ag<sub>2</sub>S, and sulphur remains in the form of a white ppt.

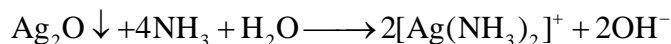


If the mixture is heated with conc. HNO<sub>3</sub> for a considerable time, sulphur is oxidized to SO<sub>4</sub><sup>2-</sup> and the precipitate disappears.

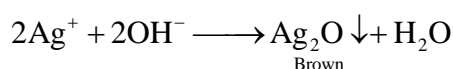
3. **Ammonia Solution:** Brown ppt. of Ag<sub>2</sub>O is obtained..



The reaction reaches an equilibrium and therefore precipitation is incomplete at any stage (if the NH<sub>4</sub>NO<sub>3</sub> is present in the original solution or the solution is strongly acidic, no precipitation occurs). The ppt dissolves in excess of NH<sub>3</sub> solution, and diammine silver (I) complex is formed.



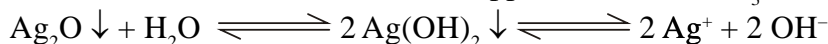
4. **Sodium Hydroxide:** Brown ppt. of Ag<sub>2</sub>O is obtained.



A well washed suspension of the ppt. shows a slight alkaline reaction owing to the hydrolysis reaction.

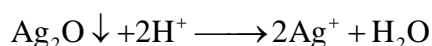
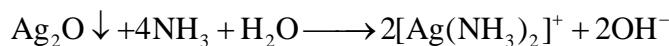


The ppt. is insoluble in excess of NaOH. The ppt. dissolves in NH<sub>3</sub> solution and in HNO<sub>3</sub>.

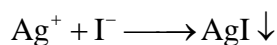




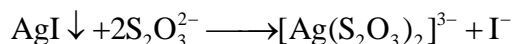
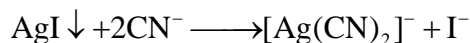
The ppt. is insoluble in excess of NaOH. The ppt. dissolves in  $\text{NH}_3$  solution and in  $\text{HNO}_3$ .



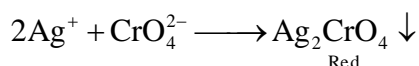
5. **Potassium Iodide:** Yellow ppt. of AgI is obtained.



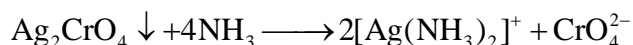
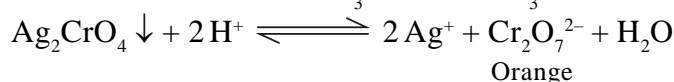
The ppt. is insoluble in dil. or conc.  $\text{NH}_3$  solution, but dissolves readily in KCN and in  $\text{Na}_2\text{S}_2\text{O}_3$ .



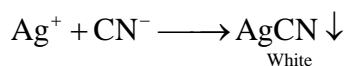
6. **Potassium Chromate:** Red ppt. of  $\text{Ag}_2\text{CrO}_4$  is obtained..



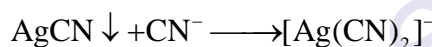
The ppt. is soluble in diluted  $\text{HNO}_3$  acid and  $\text{NH}_3$  solution.



7. **Potassium Cyanide:** When added drop wise to a neutral solution of  $\text{AgNO}_3$ ; white ppt. of AgCN is obtained.



When KCN is added in excess, ppt. dissolves owing to formation of dicyanoargentate (I) ion.



## Second Group of Cations

Group Reagent	$\text{H}_2\text{S}$ in presence of dil. HCl
IIA	$\text{Cu}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Cd}^{2+}, \text{Hg}^{2+}$
IIB	$\text{As}^{3+}, \text{As}^{5+}, \text{Sb}^{3+}, \text{Sb}^{5+}, \text{Sn}^{2+}, \text{Sn}^{4+}$
Precipitates as	Sulphides
Black	$\text{PbS}, \text{CuS}, \text{HgS}$
Yellow	$\text{CdS}, \text{As}_2\text{S}_3, \text{As}_2\text{S}_5, \text{SnS}_2$
Orange	$\text{Sb}_2\text{S}_3, \text{Sb}_2\text{S}_5$
Brown	$\text{Bi}_2\text{S}_3, \text{SnS}$

Cations of II<sup>nd</sup> group are traditionally divided into two sub-groups the copper sub group and are arsenic group. The basis of this division is the solubility of the precipitates in ammonium polysulphide. White sulphides of the copper sub-groups are insoluble in this reagent, those of the arsenic sub-group are soluble in this reagent with the formation of thiosalts.

### II A Group :

The copper sub-group consists of Hg(II), Pb(II), Bi(III), Cu(II) and Cd(II). Although the bulk of the lead ions are precipitated with dil. HCl together with other ions of the group –I, this precipitation is rather incomplete owing to relatively high solubility of  $\text{PbCl}_2$ . In the course of systematic analysis therefore, leads ions will still be present when the precipitation of the second

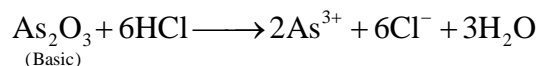
## QUALITATIVE ANALYSIS

group of the cations is the task.

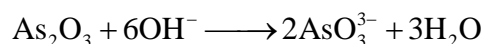
The chlorides, nitrates and sulphates of the cations of the copper sub-group are quite soluble in water. The sulphides, Hydroxides and carbonates are insoluble. Some of the ions of copper sub-group ( $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) tend to form complexes ( $\text{NH}_3$ ,  $\text{RCOO}^-$ , etc.)

### II B Group:

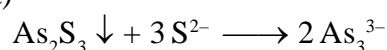
The arsenic sub-group consists of  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sb}^{5+}$  and  $\text{Sn}^{4+}$  ions. These ions both acids and bases. Thus  $\text{As(III)}$  oxide can be dissolved in  $\text{HCl}$  (6M) and  $\text{As(III)}$  cations are formed.



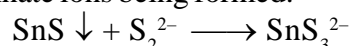
The same time  $\text{As}_2\text{O}_3$  dissolves in  $\text{NaOH}$  (2M) forming arsenite anions.



The dissolution of sulphides in ammonium polysulphide can be regarded as the formation of thiosalts from anhydrous thioacids. Thus the dissolution of  $\text{As}_2\text{S}_3$  (anhydrous thioacid) in ammonium sulphide (anhydrous thiobase) yield the formation of ammonium and thioarsenite ions (a thiosalt)



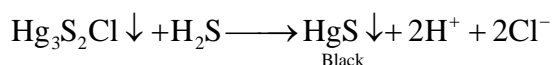
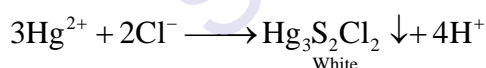
All the sulphides of the arsenic sub-group dissolve in ammonia sulphide except tin (II) sulphide ( $\text{SnS}$ ); to dissolve latter, ammonium polysulphide is needed, which acts partly as an oxidizing agent, thiostannate ions being formed:



Note that while tin is bivalent in the tin (II) sulphide ppt., it is tetravalent in the thiostannate ion.  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$  and  $\text{Sn}^{2+}$  ions can be oxidized to  $\text{As}^{5+}$ ,  $\text{Sb}^{5+}$  and  $\text{Sn}^{4+}$  ions respectively. On the other hand, the latter three can be reduced by proper reducing agents. The oxidation reduction potentials of the arsenic (V), arsenic (III) and  $\text{Sb(V)} - \text{Sb(III)}$  systems vary with pH, therefore the oxidation or reduction of the relevant ions can be assisted by choosing an appropriate pH of the reaction.

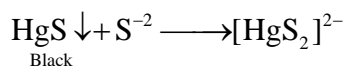
### Reactions of Mercury (II) Ions: ( $\text{HgNO}_3$ )

- Hydrogen Sulphide (Gas or Saturated Aqueous Solutions):** In the presence of dilute (1M)  $\text{HCl}$ , initially a white ppt of mercury (II) chlorosulphide forms, which reacts with further amounts of  $\text{H}_2\text{S}$  and finally a black ppt. of  $\text{HgS}$  is formed.

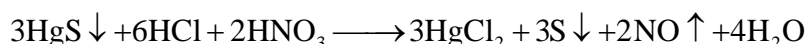


$\text{HgS}$  is one of the least soluble precipitates known ( $K_{\text{sp}} = 4 \times 10^{-54}$ ).

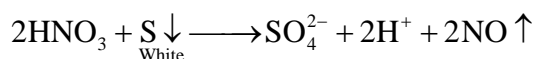
$\text{HgS}$  is insoluble in water, hot dilute  $\text{HNO}_3$ , alkali hydroxides or colourless ammonium sulphide. Sodium sulphides (2M) dissolves the precipitate when the disulphomercurate (II) complex ion is formed:



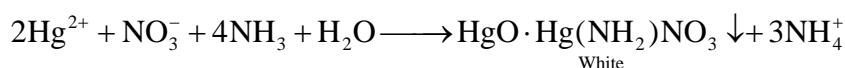
Adding  $\text{NH}_4\text{Cl}$  to the solution,  $\text{HgS}$  precipitates again aqua-regia dissolves the precipitate.



$\text{HgCl}_2$  is practically undissociated under these circumstances. Sulphur remains as a white ppt., which however dissolves readily if the solution is heated, to form  $\text{H}_2\text{SO}_4$ .

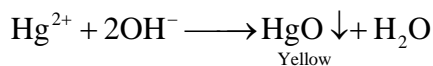


- Ammonia Solution:** White precipitate with a mixed composition is obtained, essentially it consists of  $\text{HgO}$  and mercuryoamidonitrate.



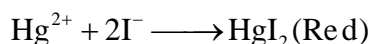
The salt like most of the mercury compounds, sublimes at atmospheric pressure.

3. **Sodium Hydroxide:** When added in small amounts, brownish-red precipitate with varying composition is obtained; if added in stoichiometric amounts, the precipitate turns to yellow when  $\text{HgO}$  is formed.

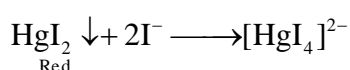


Insoluble in excess  $\text{NaOH}$  soluble in acids.

4. **Potassium Iodide:** When added slowly to the solution, red precipitate of  $\text{HgI}_2$  is obtained..



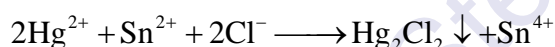
The precipitate dissolves in excess reagent, when colourless tetraiodomercurate (II) ions are formed



An alkaline solution of  $\text{K}_2[\text{HgI}_4]$  serves as a selective and sensitive reagent for  $\text{NH}_4^+$  ion (Nessler's Reagent).

5. **Potassium Cyanide:** Does not cause any change in dilute solutions (difference from other ions of the copper sub-group).

6. **Tin (II) Chloride:** When added I in moderate amounts, white, silky precipitate of  $\text{Hg}_2\text{Cl}_2$  (calomel)

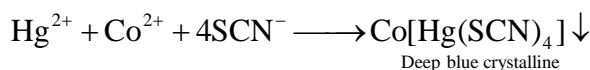


This reaction is widely used to remove the excess of  $\text{Sn}$  (II) ions, used for prior reduction, in oxidation-reduction titrations.

If more reagent is added, mercury (I) chloride is further reduced and black precipitate of mercury is formed.

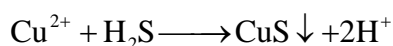


7. **Cobalt (II) Thiocyanate Test:** To the test solution add an equal volume of  $\text{Co}(\text{SCN})_2$  (about 10% freshly prepared), and stir the wall of the vessel with a glass rod. A deep blue crystalline precipitate of cobalt tetrathiocyanatomercurate (II) is formed.



## Reactions of Copper (II) Ions

1. **Hydrogen Sulphide (Gas or Saturated aqueous solution):** Black precipitate of  $\text{CuS}$  is formed.



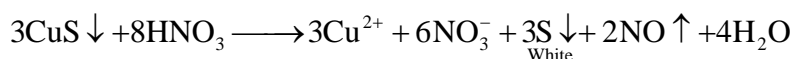
$$K_{\text{sp}} (\text{CuS}) = 10^{-44}$$

The solution must be acidic (1M in  $\text{HCl}$ ) in order to obtain a crystalline, easily filterable precipitate. In the absence of acid, or in very slightly acid solutions a colloidal, brownish black precipitate or colouration is obtained. By adding some acid and boiling, coagulation can be achieved.

The precipitate is insoluble in boiling dilute (1M)  $\text{H}_2\text{SO}_4$  (distinction from  $\text{Cd}$ ), in sodium hydroxide,  $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$ . It is only very slightly soluble in polysulphides.

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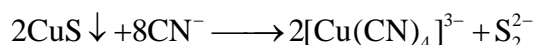
Hot conc.  $\text{HNO}_3$  dissolves the  $\text{CuS}$ , leaving behind sulphur as a white precipitate.



When boiled for longer, sulphur is oxidized to  $\text{H}_2\text{SO}_4$  and a clear solution is obtained.

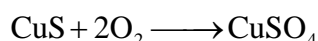


KCN dissolves the ppt., when colourless tetra cyano cuprate (I) ions and disulphide ions are formed.



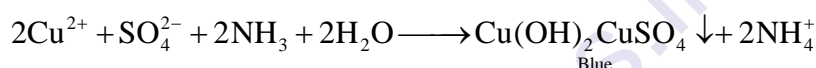
This is an oxidation and reduction reaction (copper is reduced and sulphur is oxidized) coupled with a formation of a complex.

When exposed to air, in the moist state,  $\text{CuS}$  tends to oxidize to  $\text{CuSO}_4$ .

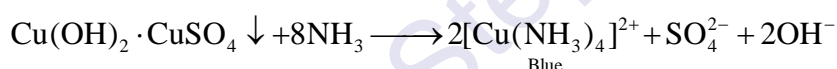


and therefore becomes water soluble. A considerable amount of heat is liberated during this process. A filter paper with  $\text{CuS}$  precipitate on it should never be thrown into a waste container, with paper or other inflammable substances in it. Instead the precipitate should be washed a way first with running water.

2. **Ammonia Solution:** When added slowly blue precipitate of basic copper sulphate is formed.



Which is soluble in excess reagent, when a deep blue colouration is obtained owing to the formation of tetrammine copper (II) complex ion.

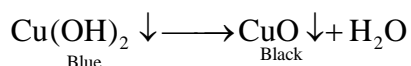


If the solution contains  $\text{NH}_4^+$  salt (or it was highly acidic larger amounts of  $\text{NH}_3$  were used up for its neutralization) precipitation does not occur at all, but the blue colour appears right away. The reaction is characteristic for  $\text{Cu}^{2+}$  ions in the absence of Nickel.

3. **NaOH:** In cold solution blue precipitate of  $\text{Cu}(\text{OH})_2$  is formed..

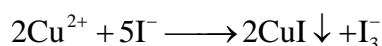


The precipitate is insoluble in excess reagent. When heated, the precipitate is converted to black  $\text{CuO}$  by dehydration.



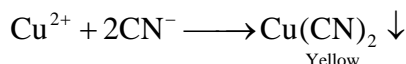
In the presence of a solution of tartaric acid or of nitric acid, copper (II) hydroxide is not precipitated by solutions of caustic alkalis but the solution is coloured, an intense blue. If the alkaline solution is treated with certain reducing agents, such as hydroxyl amine, hydrazine, glucose and acetaldehyde, yellow copper (I) hydroxide precipitated from the warm solution. It is converted into red copper (I) oxide ( $\text{Cu}_2\text{O}$ ) on boiling. The alkaline solution of  $\text{Cu}(\text{II})$  salt containing tartaric solution of  $\text{Cu}(\text{II})$  salt containing tartaric acid is usually known as Fehling solution; it contains the complex ion  $[\text{Cu}(\text{C}_4\text{H}_2\text{O}_6)_2]^{2-}$ .

4. **Potassium Iodide:** Precipitates copper (I) iodide, which is white, but the solution is intensely brown because of formation of triiodide ions.

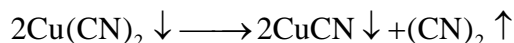


Adding an excess of  $\text{Na}_2\text{S}_2\text{O}_3$  to the solution triiodide ions are reduced to colourless iodide ions and the white colour of ppt. becomes visible. These reactions are used in quantitative analysis for the iodometric determination of copper.

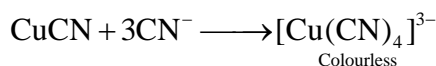
5. **KCN:** When added sparingly forms first a yellow precipitate of copper (II) cyanide.



The precipitate quickly decomposes into copper (II) cyanide and cyanogens (highly poisonous gas) is liberated.

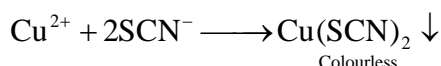


Excess of KCN dissolves the precipitate and the colourless tetracyanocuprate (I) complex is formed.

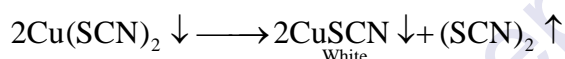


The complex is so stable that  $\text{H}_2\text{S}$  cannot precipitate copper I sulphide from this solution (distinction from Cd).

6. **Potassium Thiocyanate (KSCN):** Black precipitate of copper (II) thiocyanate is obtained.

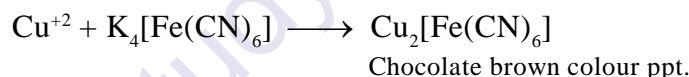


The precipitate decomposes slowly to form white copper (I) thiocyanate and thiocyanogen is formed.



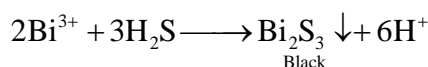
Thiocyanogen rapidly decomposes in aqueous solution.

7. **Potassium Ferrocyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6]$ ) :** Chocolate brown colour precipitate of  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  is obtained.



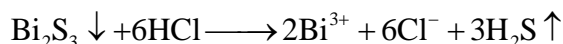
### Reactions of $\text{Bi}^{3+}$ Ions

1. **With  $\text{H}_2\text{S}$  (Gas or saturated aqueous solution):** Blackish brown precipitate of  $\text{Bi}_2\text{S}_3$  is obtained.

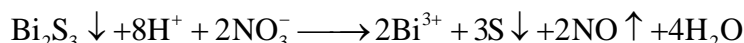


Insoluble in cold. Dilute acid in  $(\text{NH}_4)_2\text{S}$

Boiling conc. HCl dissolves the precipitate when  $\text{H}_2\text{S}$  gas is evolved.

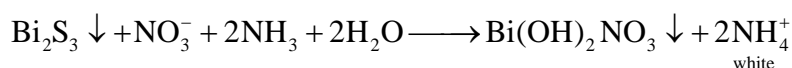


Hot dil.  $\text{HNO}_3$  dissolves  $\text{Bi}_2\text{S}_3$ , leaving behind sulphur in the form of a white precipitate.



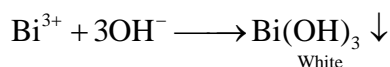
2. **With  $\text{NH}_3$  Solution:** White basic salt of variable composition. The approximate chemical reaction is

## QUALITATIVE ANALYSIS



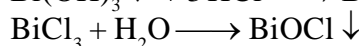
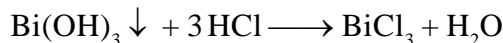
$\text{Bi}(\text{OH})_2\text{NO}_3$  does not dissolve in excess  $\text{NH}_3$  (distinction from Cu and Cd)

3. **With NaOH:** White precipitate of  $\text{Bi}(\text{OH})_3$  is obtained.



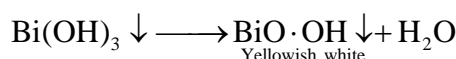
Slightly soluble in excess NaOH

Soluble in conc. HCl and insoluble in dilute HCl



white turbidity

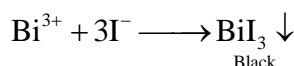
When boiled precipitate loses water and turns yellowish white



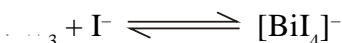
Both the hydrated and the dehydrated precipitate can be oxidised by 4-6 drops of conc.  $\text{H}_2\text{O}_2$  when yellowish brown bismuth ate ions are formed.



4. **Potassium Iodide:** When added drop-wise black precipitate of  $\text{BiI}_3$  is obtained.



The precipitate dissolves readily in excess reagent when orange coloured tetraiodobismuthate ions are formed.

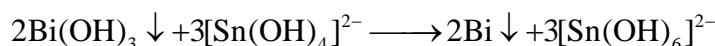
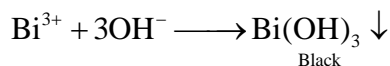


When diluted with  $\text{H}_2\text{O}$ , the above reaction is reversed and black precipitates of  $\text{BiI}_3$  reappear.

5. **KI:** KI forms no precipitate (distinction from copper). Heating the precipitate with  $\text{H}_2\text{O}$ ,  $\text{BiI}_3$  turns orange owing to the formation of bismuthyl iodide.

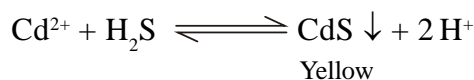


6. **Sodium Tetrahydroxostannate (II) (0.125M freshly prepared):** In cold solution,  $\text{Bi}^{3+}$  ions are reduced to Bismuth metal which separates in the form of a black precipitate. First the sodium hydroxide present in the reagent reacts with  $\text{Bi}^{3+}$  ions,  $\text{Bi}(\text{OH})_3$  is then reduced by tetrahydroxostannate (II) ions to form Bi metal and hexahydroxostannate is formed.



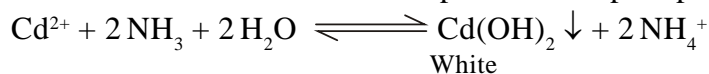
## Reactions of Cadmium (II) Ions [ $\text{Cd}^{2+}$ ]

1. **Reaction with  $\text{H}_2\text{S}$  (Gas or saturated aqueous solution):** Yellow precipitate of CdS is obtained.



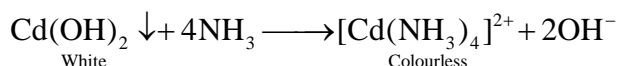
The reaction is reversible, if the conc. of strong acid in the solution is above 0.5M, precipitation is incomplete. Conc. acids dissolve the precipitate for the same reason. The ppt is insoluble in KCN: this distinguishes  $\text{Cd}^{2+}$  ions from  $\text{Cu}^{2+}$ .

2. **Ammonia Solution:** When added drop wise white precipitate of  $\text{Cd}(\text{OH})_2$  is formed.

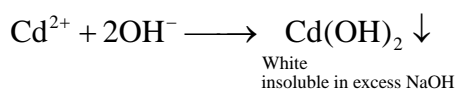


The precipitate dissolves in acid when the equilibrium shifts towards the left.

An excess of  $\text{NH}_3$  dissolves the precipitate, when tetraammine cadmate (II) ions are formed.

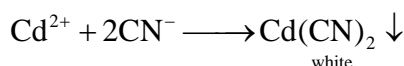


3. **NaOH :** White precipitate of  $\text{Cd}(\text{OH})_2$

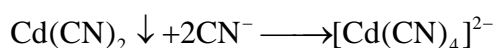


White precipitate dissolves in dilute acids when equilibrium shifts in the backward direction.

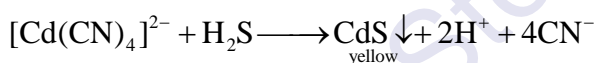
4. **KCN :** White precipitate of  $\text{Cd}(\text{CN})_2$  is obtained when KCN is added slowly to  $\text{Cd}^{2+}$  ions.



An excess of reagent (KCN) dissolves the precipitate with the formation of tetracyanocadmiate ions.



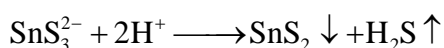
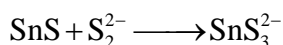
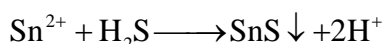
The colourless complex is not very stable; when  $\text{H}_2\text{S}$  gas is introduced,  $\text{CdS}$  is precipitated



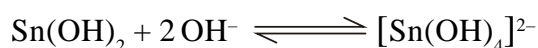
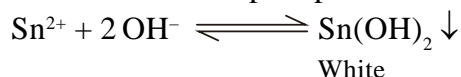
(Difference from copper)

### Reactions of $\text{Sn}^{2+}$ Ions

1.  **$\text{H}_2\text{S}$  (Gas or Saturated Solution):** Brown precipitate of  $\text{SnS}$ , from mildly acidic solutions. The precipitate is soluble in conc.  $\text{HCl}$ . It is also soluble in yellow  $(\text{NH}_4)_2\text{Sn}$  (but not in colourless  $(\text{NH}_4)_2\text{S}$ ) to form a thiostannate treatment of the solution of ammonium thiostannate with an acid yields a yellow precipitate of  $\text{SnS}_2$ .



2. **NaOH Solution:** White precipitate of  $\text{Sn}(\text{OH})_2$ , soluble in excess alkali.

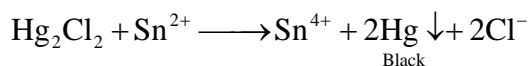
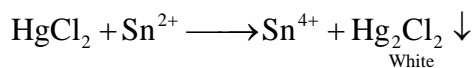


With  $\text{NH}_3$  solution, white  $\text{Sn}(\text{OH})_2$  is precipitated which cannot be dissolved in excess  $\text{NH}_3$ .

3.  **$\text{HgCl}_2$  Solution:** White precipitate of  $\text{Hg}_2\text{Cl}_2$  and finally  $\text{Hg}$  metal (black)

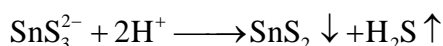
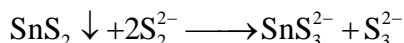
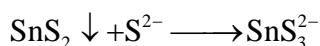
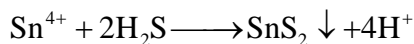


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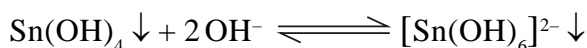
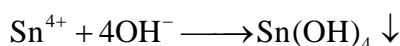


### Reactions of $\text{Sn}^{4+}$ Ions

- Hydrogen Sulphide:** Yellow precipitate of  $\text{Sn(IV)}$  sulphide  $\text{SnS}_2$  from dil. Acid solution. The precipitate is soluble in conc.  $\text{HCl}$  in solution of alkali hydroxide and also in  $(\text{NH}_4)_2\text{S}$  and  $(\text{NH}_4)_2\text{Sn}$ . Yellow  $\text{SnS}_2$  is precipitate upon acidification.

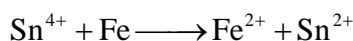


- NaOH:**  $\text{NaOH}$  solution  $\rightarrow$  gelatinous precipitation precipitate (white) of  $\text{Sn(OH)}_4$  soluble in excess of the precipitant forming hexahydroxostannate (VI).



- With  $\text{HgCl}_2$ :** No precipitate (difference from  $\text{Sn(II)}$ )

- Metallic Iron:** Reduces  $\text{Sn}^{4+}$  ions to  $\text{Sn}^{2+}$

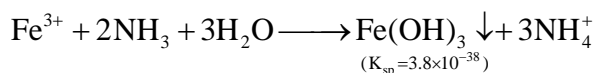


### Third Group of Cations: $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Cr}^{6+}$

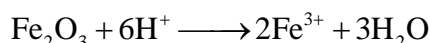
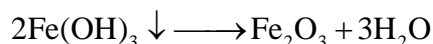
Group Reagent	$\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$
$\text{Fe(OH)}_3$	Red Brown
$\text{Al(OH)}_3$	Gelatinous white
$\text{Cr(OH)}_3$	Green (cotton like)

### Reactions of $\text{Fe}^{3+}$ ions

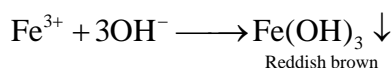
- $\text{NH}_3$  Solution:** Reddish brown, gelatinous precipitate of  $\text{Fe(OH)}_3$  insoluble in excess of the reagent, but soluble in acids.



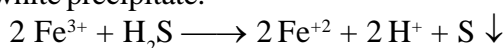
Iron (III) hydroxide is converted during strong heating into  $\text{Fe}_2\text{O}_3$  the ignited oxide is soluble with difficulty in dilute acids, but dissolves in vigorous boiling with conc.  $\text{HCl}$ .



- NaOH Solution:** Reddish brown precipitate of  $\text{Fe(OH)}_3$  in solute in excess of  $\text{NaOH}$ .



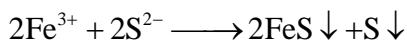
- Hydrogen Sulphide:** In acidic solution reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and sulphur is formed as a milky white precipitate.



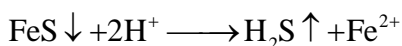
White

If a neutral solution of  $\text{FeCl}_3$  is added to a freshly prepared, saturated solution of  $\text{H}_2\text{S}$ , a bluish colouration appears first, followed by the precipitation of sulphur. The blue colour is due to a colloidal solution of sulphur of extremely small particle size.

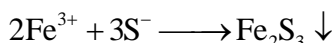
4. **Ammonium Sulphide:** A black precipitate, consisting of Fe and sulphur is formed.



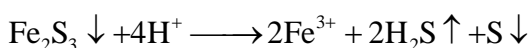
In HCl and black FeS precipitate dissolves and white colour of sulphur becomes visible.



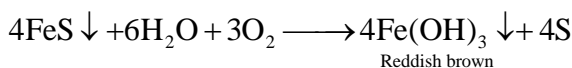
From alkaline solution black iron (II) sulphide is obtained.



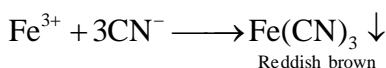
On acidification with HCl,  $\text{Fe}^{3+}$  ions are reduced to  $\text{Fe}^{2+}$  and sulphur is formed.



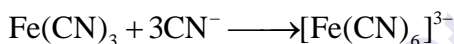
The damp iron (II) sulphide precipitate, when exposed to air, is slowly oxidized to brown  $\text{Fe}(\text{OH})_3$ .



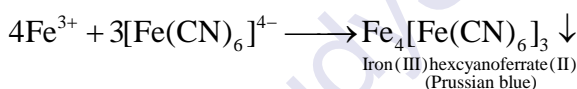
5. **KCN:** When added slowly, produces a reddish brown precipitate of  $\text{Fe}(\text{CN})_3$ .



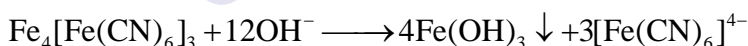
In excess, reagent dissolves giving a yellow solution, when hexacyanoferrate (III) ions are formed.



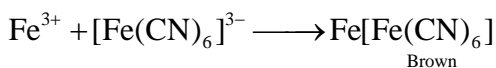
6.  **$\text{K}_4[\text{Fe}(\text{CN})_6]$ :** Solution intense blue precipitate of Fe(III) hexacyanoferrate (Prussian blue)



The precipitate is insoluble in dilute acids, but decomposes in conc. HCl. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. NaOH turns the precipitate red as  $\text{Fe}_2\text{O}_3$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  ions are formed.



7.  **$\text{K}_3[\text{Fe}(\text{CN})_6]$ :** A brown colouration is produced due to the formation of an undissociated complex, Iron (III) hexacyanoferrate (III).

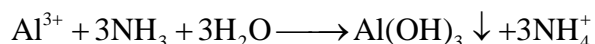


### Reactions of $\text{Al}^{3+}$ Ions

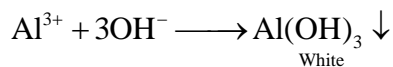
1. **Ammonia Solution:** White gelatinous precipitate of  $\text{Al}(\text{OH})_3$ , slightly soluble in excess of reagent. The solubility is decreased in presence of  $\text{NH}_4^+$  ions. A small proportion of the precipitate passes into the solution as colloidal  $\text{Al}(\text{OH})_3$  ( $\text{Al}(\text{OH})_3$  solution), the solution is coagulated on boiling the solution or upon the addition of soluble salts (e.g.  $\text{NH}_4\text{Cl}$ ) yielding a precipitate of  $\text{Al}(\text{OH})_3$ , known as  $\text{Al}(\text{OH})_3$  gel. To ensure complete precipitation of  $\text{NH}_3$  solution is added in slight excess and the mixture is boiled until the liquid has a slight odour of  $\text{NH}_3$ . When

## QUALITATIVE ANALYSIS

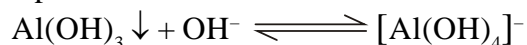
freshly precipitated, it dissolves readily in strong acids and bases, but after boiling it becomes sparingly soluble.



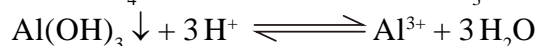
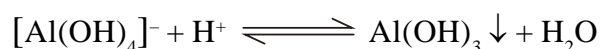
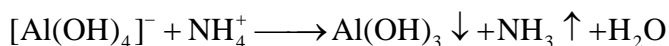
2. **Sodium Hydroxide:** White precipitate of  $\text{Al}(\text{OH})_3$  is obtained.



The precipitate dissolves in excess NaOH forming tetrahydroxoaluminate (III) ion.

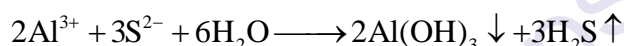


The reaction is a reversible one, and any reagent which will reduce the  $\text{OH}^-$  concentration sufficiently should cause the reaction to proceed from right to left with the consequently precipitation of  $\text{Al}(\text{OH})_3 \downarrow$ . This may be effected by  $\text{AlCl}_3$  or by adding the acid; in the latter case, a large excess of acid, in the latter case, a large excess of acid causes the precipitated hydroxide to redissolve.



The precipitation of  $\text{Al}(\text{OH})_3$  by solutions of NaOH and  $\text{NH}_3$  does not take place in the presence of tartaric acid, citric acid because of the formation of soluble complex salt.

3. **Ammonium Sulphide Solution:** A white precipitate  $\text{Al}(\text{OH})_3$  is obtained.

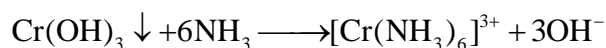
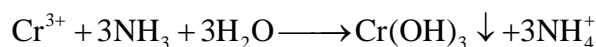


4. **Sodium Acetate Solution:** No precipitate is obtained in cold, neutral solution, but on boiling with excess reagent, a voluminous precipitate of basic aluminium acetate  $\text{Al}(\text{OH})_2(\text{CH}_3\text{COO})$  is formed



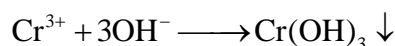
## Reactions of $\text{Cr}^{3+}$ Ions

1. **Ammonia Solution:** Green-grey or grey-blue gelatinous precipitate of  $\text{Cr}(\text{OH})_3$ , slightly soluble in excess of reagent in cold forming a violet or pink solution containing complex hexamine chromium (III) ion; upon boiling the solution,  $\text{Cr}(\text{OH})_3$  is precipitated. Hence for complete precipitation of chromium as the hydroxide, it is essential that the solution be boiling and excess aqueous ammonia solution be avoided.

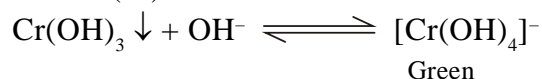


In the presence of acetate ions and the absence of other trivalent metal ions,  $\text{Cr}(\text{OH})_3$  is not precipitated. The precipitation of  $\text{Cr}(\text{OH})_3 \downarrow$  is also prevented by tartarates and citrates.

2. **Sodium Hydroxide Solution:** The green-grey or grey blue precipitates of  $\text{Cr}(\text{OH})_3$  is obtained..



The reaction is reversible; the addition of the acids, the precipitates readily, tetrahydroxochromate (III) ions are formed

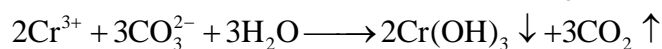


The solution is green. The reaction is reversible on (slight) acidification and also on boiling  $\text{Cr}(\text{OH})_3$  precipitates again.

On adding  $\text{H}_2\text{O}_2$  to alkaline solution of  $[\text{Cr}(\text{OH})_4]^-$ , a yellow solution is obtained, owing to the oxidation of  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$ .



3. **Sodium Carbonate Solution:** Precipitate of  $\text{Cr}(\text{OH})_3$  is obtained.

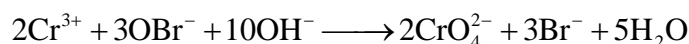


4. **Chromate Test:**  $\text{Cr}^{3+}$  ions can be oxidized to  $\text{CrO}_4^{2-}$  in several ways

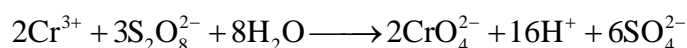
(a) Adding an excess of  $\text{NaOH}$  to a  $\text{Cr}^{3+}$  salt followed by a few ml of 10%  $\text{H}_2\text{O}_2$ . The excess of  $\text{H}_2\text{O}_2$  can be removed by boiling the solution for few minutes.



(b) Oxidation can be carried out by  $\text{Br}_2/\text{H}_2\text{O}$  in alkaline solution (i.e. by  $\text{OBr}^-$ ).



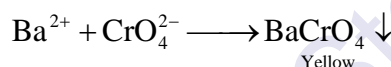
(c) In acid solution  $\text{Cr}^{3+}$  ions can be oxidized by potassium (or ammonium) peroxodisulphate.



### Identification of $\text{CrO}_4^{2-}$ :

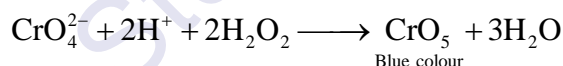
Having carried out the oxidation with one of the methods are described above,  $\text{CrO}_4^{2-}$  ions can be identified by anyone of the following methods.

- (a)  **$\text{BaCl}_2$  Test:** After acidifying the solution with  $\text{CH}_3\text{COOH}$  and adding  $\text{BaCl}_2$ , a yellow precipitate of  $\text{BaCrO}_4$  is formed.

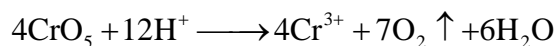


- (b) **Chromium Pentoxide (or Peroxide) Test :**

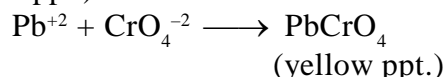
On acidifying the solution with dil.  $\text{H}_2\text{SO}_4$  adding 2 to 3 ml of ether or amyl alcohol to the mixture and finally adding some  $\text{H}_2\text{O}_2$ , a blue coloration is formed. During the reaction  $\text{CrO}_5$  is formed.



In aqueous solution blue colour fades speedily, because  $\text{CrO}_5$  decomposes to  $\text{Cr}^{3+}$  and oxygen.



- (c)  **$\text{Pb}(\text{OAc})_2$  Test :** On acidification with acetic acid, followed by addition of lead acetate gives  $\text{PbCrO}_4$  (yellow ppt.)



### Radicals of Group IV

Radicals	$\text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}$
Group Reagent	$\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$ and $\text{NH}_4\text{Cl}$
Black	$\text{CoS}, \text{NiS}$
Pink	$\text{MnS}$
White	$\text{ZnS}$

### Group V of Cations

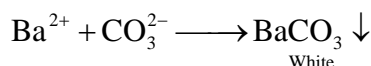
## QUALITATIVE ANALYSIS

Radicals	Ba <sup>2+</sup> , Sr <sup>2+</sup> , Ca <sup>2+</sup>
Group Reagent	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> in presence of NH <sub>4</sub> OH
Precipitates as	Carbonates
White	BaCO <sub>3</sub> , SrCO <sub>3</sub> , CaCO <sub>3</sub>

### Reactions of Ba<sup>2+</sup> ions

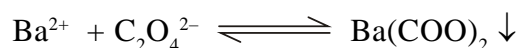
- Reactions with NH<sub>3</sub> Solution:** No precipitate OF Ba(OH)<sub>2</sub> is obtained because of its relatively high solubility. If the alkaline solution is exposed to the atmosphere some CO<sub>2</sub> gas is absorbed and a turbidity due to BaCO<sub>3</sub> is produced.

- (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> Solution:** White precipitate of BaCO<sub>3</sub>, soluble in acetic acid and dilute mineral acids

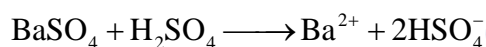
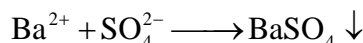


The precipitate is slightly soluble in ammonium salts of strong acids.

- (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> Solution:** A white precipitate of Ba(C<sub>2</sub>O<sub>4</sub>) is obtained slightly soluble in water (0.09 g L<sup>-1</sup>) but readily dissolved by hot dilute acetic acid (distinction from Ca<sup>2+</sup>) and by mineral acid.



- Dilute Sulphuric Acid:** Heavy, white, finely divided precipitate of BaSO<sub>4</sub>, practically insoluble in water (2.5 × 10<sup>-3</sup> g/L), almost insoluble in dilute acids and in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, but appreciably soluble in boiling conc. H<sub>2</sub>SO<sub>4</sub>. By precipitation in boiling solution, or preferably in the presence of NH<sub>4</sub>OOCCH<sub>3</sub>, a more readily filterable form is obtained.



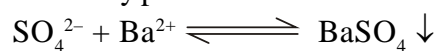
If BaSO<sub>4</sub> is boiled with a conc. solution of Na<sub>2</sub>CO<sub>3</sub> partial transformation into the less soluble BaCO<sub>3</sub> occurs in accordance with the equation.



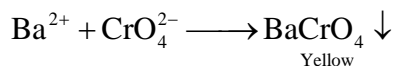
Owing to the reversibility of the reaction, the transformation is incomplete. BaSO<sub>4</sub> precipitate may also be dissolved in a hot 5% solution disodium ethylene diamine tetracetate (Na<sub>2</sub>EDTA) in the presence of NH<sub>3</sub>.

- Saturated CaSO<sub>4</sub> Solution:** Immediate white precipitate of BaSO<sub>4</sub>. A similar phenomenon occurs if saturated SrSO<sub>4</sub> is used.

This is because of the three alkaline earth metal sulphates, BaSO<sub>4</sub> is the least soluble. In the solutions of saturated CaSO<sub>4</sub> or SrSO<sub>4</sub> the concentration of SO<sub>4</sub><sup>2-</sup> ion is high enough to cause precipitation with larger amounts of Ba<sup>2+</sup>, because the product of ionic concentrations exceeds the value of the solubility product.

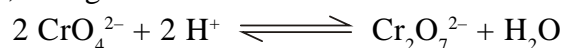


- K<sub>2</sub>CrO<sub>4</sub> Solution:** A yellow precipitate of BaCrO<sub>4</sub>, practically insoluble in water (3.2 mg L<sup>-1</sup>)



The precipitate is insoluble in dilute CH<sub>3</sub>COOH (distinction from Ca<sup>2+</sup> and Sr<sup>2+</sup> ions), but readily soluble in mineral acids.

The addition of acid to K<sub>2</sub>CrO<sub>4</sub> solution causes the yellow colour of the solution to change to reddish orange, owing to the formation of dichromate.

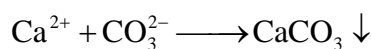


The solubility products for SrCrO<sub>4</sub> and CaCrO<sub>4</sub> are much larger than for BaCrO<sub>4</sub> and hence

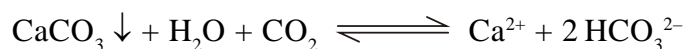
they require a larger  $\text{CrO}_4^{2-}$  ion concentration to precipitate them. The addition of acetic acid to the  $\text{K}_2\text{CrO}_4$  solution lowers to the  $\text{CrO}_4^{2-}$  ion concentration sufficiently to prevent the precipitation of  $\text{SrCrO}_4$  and  $\text{CaCrO}_4$  but it is maintained high enough to precipitate  $\text{BaCrO}_4$ .

### Reactions of $\text{Ca}^{2+}$ Ions

1. **Ammonia Solution:** No precipitate as  $\text{Ca}(\text{OH})_2$  is fairly soluble. With an aged precipitant a turbidity may occur owing to the formation of  $\text{CaCO}_3$ .
2.  **$(\text{NH}_4)_2\text{CO}_3$  Solution:** White amorphous precipitate of  $\text{CaCO}_3$  is obtained..



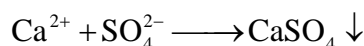
On boiling the precipitate becomes crystalline. The precipitate is soluble in water which contains excess carbonic acid (freshly prepared soda water) because of the formation of soluble  $\text{Ca}(\text{HCO}_3)_2$ .



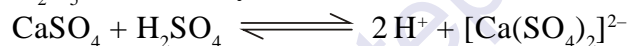
On boiling, precipitate appears again, because  $\text{CO}_2$  is removed during the process and the reaction proceeds towards the left.  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions react in a similar way.

The precipitate is soluble in acids, even in  $\text{CH}_3\text{COOH}$ .

3. **Dilute Sulphuric Acid:** White precipitate of  $\text{CaSO}_4$  is obtained.



The precipitate is appreciably soluble in water, i.e., more soluble than  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . In the presence of  $\text{C}_2\text{H}_5\text{OH}$  solubility is much less.



The same complex is formed if a precipitate is heated with a 10% of  $(\text{NH}_4)_2\text{SO}_4$ , leading to partial dissolution.

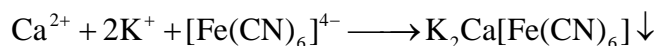
4.  **$(\text{NH}_4)_2\text{C}_2\text{O}_4$  Solution:** White precipitate of  $\text{CaC}_2\text{O}_4$ , immediately from concentrated and slowly from dilute solution.



Precipitation is facilitated by making the solution alkaline by  $\text{NH}_3$ . The precipitate is practically insoluble in  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{COH}$  but readily soluble in mineral acids.

5.  **$\text{K}_2\text{CrO}_4$  Solution:** No precipitate from dilute solution nor from conc. solution in the presence of  $\text{CH}_3\text{COOH}$ .

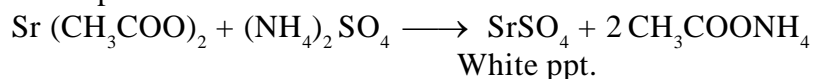
6.  **$\text{K}_4[\text{Fe}(\text{CN})_6]$  Solution:** White precipitate of a mixed salt is obtained..



In the presence of  $\text{NH}_4\text{Cl}$  the test is more sensitive. In this case potassium is replaced by ammonium ions in the precipitate. The tests can be used to distinguish calcium from strontium, barium and  $\text{Mg}^{2+}$  ions however interfere.

**Reaction of  $\text{Sr}^{2+}$  (strontium) :** Strontium sulphate is insoluble and precipitated by the addition of

ammonium sulphate solution.

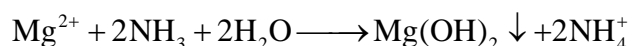


## Sixth Group of Cations : $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$

Group Reagent No common group reagent

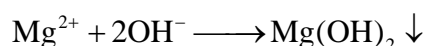
### Reaction of $\text{Mg}^{2+}$ ions

1. **Ammonium Solution:** Partial precipitation of white gelatinous  $\text{Mg}(\text{OH})_2$ .



The precipitate is very sparingly soluble in water ( $1.2 \times 10^{-2}\text{g/L}$ ) but readily soluble in ammonium salts.

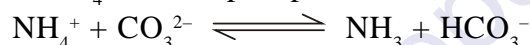
2. **NaOH Solution:** White precipitate of  $\text{Mg}(\text{OH})_2$ , insoluble in excess NaOH, but readily soluble in  $\text{NH}_4^+$  salts.



3.  **$(\text{NH}_4)_2\text{CO}_3$  Solution:** In the absence of  $\text{NH}_4^+$  salts, a white precipitate of basic magnesium carbonate is obtained..

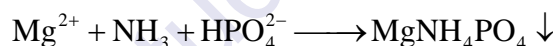


In the presence of  $\text{NH}_4^+$  salts, no precipitation occurs, because the equilibrium is shifted to left



4.  **$\text{Na}_2\text{CO}_3$  Solution:** White voluminous precipitate of basic carbonate as above is formed, insoluble in bases but readily soluble in acids and in solutions of  $\text{NH}_4^+$  ions.

5.  **$\text{Na}_2\text{HPO}_4$  Solution:** White crystalline precipitate of  $\text{Mg}(\text{OH})_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  in the presence of  $\text{NH}_4\text{Cl}$  (to prevent precipitation of  $\text{Mg}(\text{OH})_2$ ) and  $\text{NH}_3$  solution).



The precipitate is sparingly soluble in water, soluble in  $\text{CH}_3\text{COOH}$  and in mineral acids. The precipitate separates slowly from dilute solutions because of its tendency, to form supersaturated solutions, this may usually be overcome by cooling and by rubbing the test tube or beaker beneath the surface of the liquid with a glass rod.

A white flocculants precipitate of  $\text{MgHPO}_4$  is produced in neutral solutions.

