

Qualitative Analysis

Qualitative analysis involves identification of ions (cations and anions) of a salt or a mixture of salts through their characteristic reactions. The process involves

- (i) Analysis of anions and
- (ii) Analysis of cations.

Analysis of Anions (Acidic Radicals)

Analysis of anions can be divided into two groups.

Group 'A' Radicals:

Group 'A' contains anions, which are characterised by volatile products obtained on treatment with acids. It is further divided into two sub groups.

(i) Gases liberated with dilute HCl / dilute H₂SO₄:

Carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), sulphide (S²⁻), sulphite (SO₃²⁻) and nitrite (NO₂⁻).

(ii) Gases or acid vapours evolved with concentrated H₂SO₄:

Fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), nitrate (NO₃⁻), acetate (CH₃COO⁻), borate (BO₃³⁻), oxalate (C₂O₄²⁻), permanganate (MnO₄⁻) plus all anions in (i).

Group 'B' RADICALS:

Group 'B' includes anions that are characterised by their specific reactions in solutions. These reactions may be

- (i) **Precipitation reactions:** SO₄²⁻, PO₄³⁻, CrO₄²⁻, Cr₂O₇²⁻ etc.
- (ii) **Oxidation and reduction in solution:** CrO₄²⁻, Cr₂O₇²⁻ etc.

Group 'A' radicals

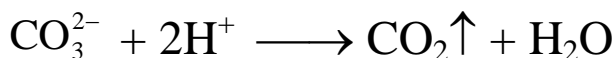
Radicals Detected With Dilute HCl / Dilute H₂SO₄:

1. Carbonate

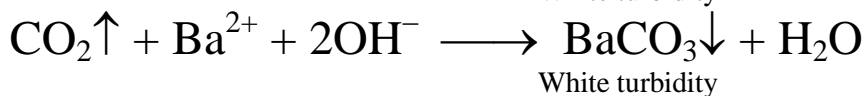
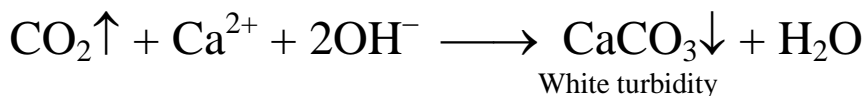
All carbonates (CO_3^{2-}) except those of alkali metals and ammonium are insoluble in H₂O.

(a) Dilute HCl

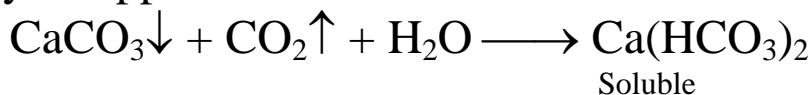
With dilute HCl, it decomposes with effervescences due to the evolution of carbon dioxide.



The gas produces white turbidity with lime water, Ca(OH)₂ or baryta water, Ba(OH)₂.

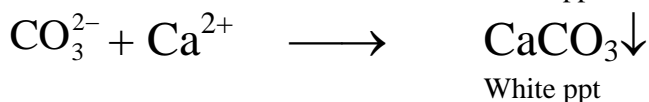
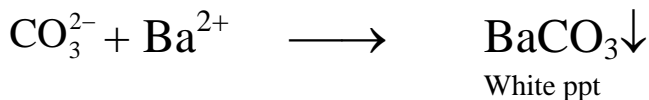


It must be remembered that with prolonged passage of carbon dioxide, the turbidity slowly disappears due to the formation of soluble bicarbonate.



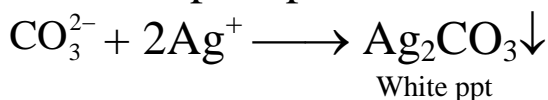
(b) Barium chloride or calcium chloride solution

Carbonates on treatment with BaCl₂ or CaCl₂ gives white precipitate of barium or calcium carbonate, which is soluble in mineral acids and carbonic acid.



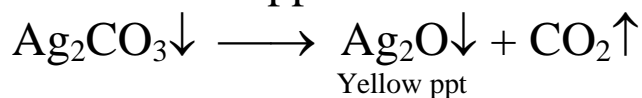
(c) Silver nitrate solution

Carbonates give a white precipitate of silver carbonate with AgNO₃ solution.



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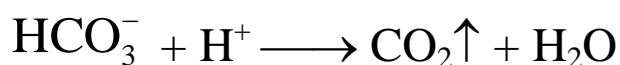
Ag_2CO_3 precipitate is soluble in nitric acid and in ammonia. The precipitate becomes yellow or brown on addition of excess reagent owing to the formation of silver oxide. The same happens if the mixture is boiled.



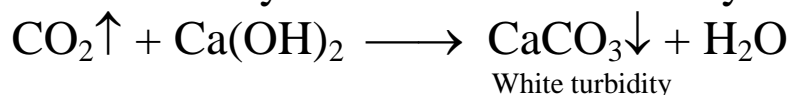
2. Bicarbonate

(a) Dilute HCl

With dilute HCl, all bicarbonates (HCO_3^-) gives effervescence due to the evolution of CO_2 .

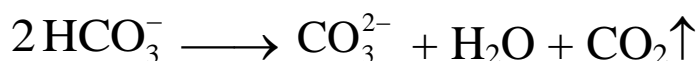


The gas gives white turbidity with lime water or baryta water.



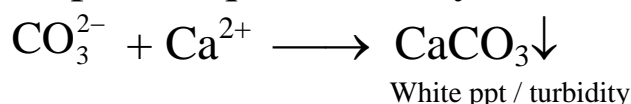
(b) On boiling

When boiled, all bicarbonates decompose to give corresponding carbonates and carbon dioxide, which turns lime water milky.

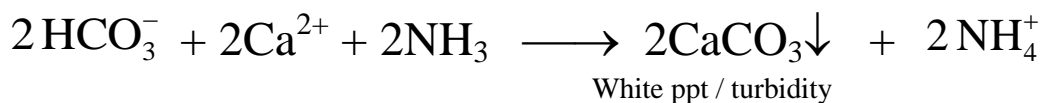


(c) Test for carbonate in the presence of bicarbonate

Adding an excess of calcium chloride to a mixture of carbonate and bicarbonate, the former is precipitated quantitatively.



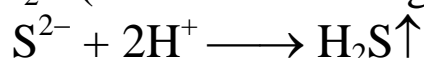
On filtering the solution rapidly, bicarbonate ions pass into the filtrate. On adding ammonia to the filtrate, a white precipitate or cloudiness is obtained.



3. Sulphide

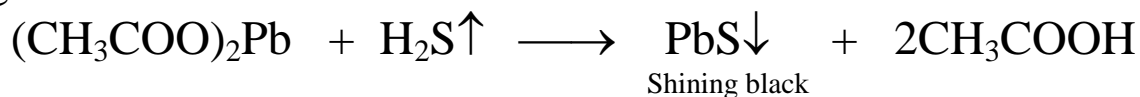
(a) Dilute HCl or dilute H_2SO_4

Sulphide (S^{2-}) on treatment with dilute HCl or dilute H_2SO_4 gives a pungent smelling gas, H_2S (smell of rotten eggs).

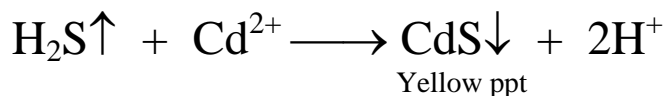


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The blackening of filter paper moistened with lead acetate solution may identify the gas.

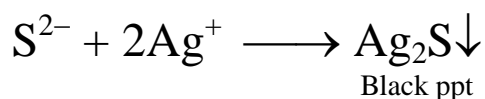


Alternatively, a filter paper moistened with cadmium acetate solution turns yellow.



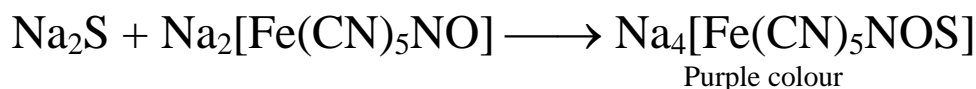
(b) Silver nitrate solution

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



(c) Sodium nitroprusside solution

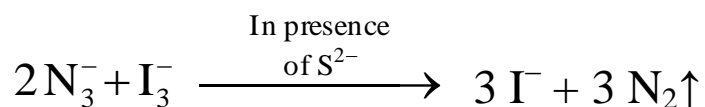
With sodium nitroprusside solution, ionic sulphide gives a purple colour in alkaline medium.



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

(d) Catalysis of iodine-azide reaction test

Solution of sodium azide, NaN_3 and iodine as I_3^- do not react, but on addition of traces of sulphide, (which acts as a catalyst) nitrogen gas is evolved immediately.



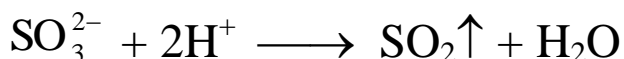
Thiosulphates and thiocyanates behave similarly and hence must be absent for this test.

4. Sulphite

Only the sulphites (SO_3^{2-}) of alkali metals and ammonium are soluble in water.

(a) Dilute HCl or dilute H_2SO_4

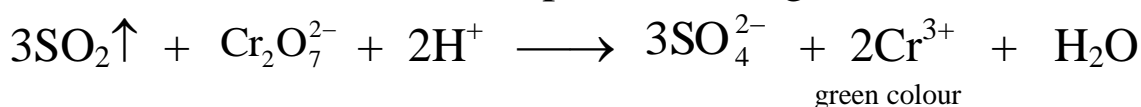
Dilute HCl or H_2SO_4 decomposes sulphites with the evolution of sulphur dioxide.



The gas can be identified

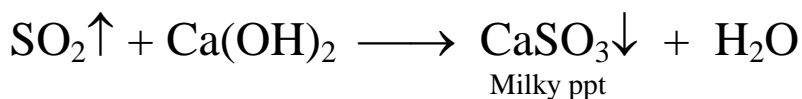
(i) by suffocating odour of burning sulphur.

(ii) by green colour formation, when passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

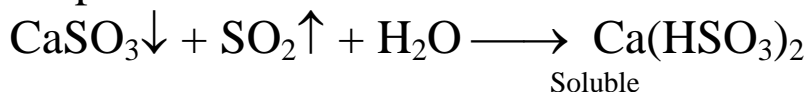


(iii) Lime water test

On passing SO_2 gas through lime water, a milky precipitate of calcium sulphite is formed.

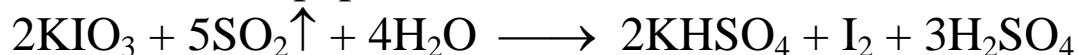


Precipitate dissolves on prolonged passage of the gas, due to the formation of calcium bisulphite.



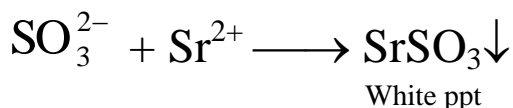
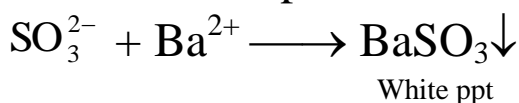
(iv) Potassium iodate-starch paper

When the evolved gas (SO_2) comes in contact with filter paper moistened with KIO_3 and starch solution, the paper turns blue due to iodine–starch complex.



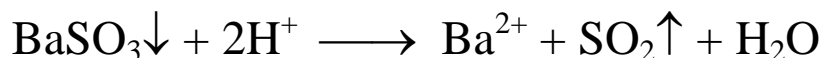
(b) Barium chloride or strontium chloride solution

With BaCl_2 or SrCl_2 solution, sulphites give a white precipitate of barium sulphite or strontium sulphite.



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The precipitate dissolves in dilute hydrochloric acid, when sulphur dioxide is liberated.



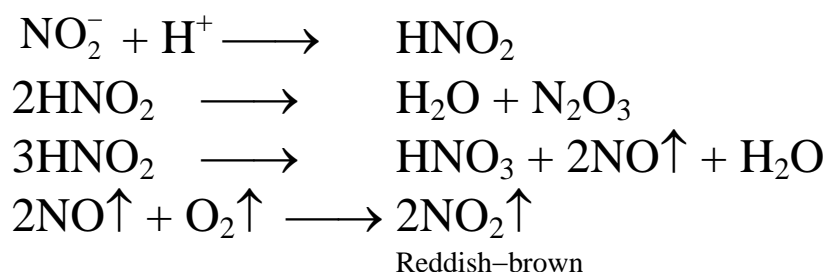
On standing, the precipitate is slowly oxidised to sulphate and is then insoluble in dilute mineral acids.

5. Nitrite

All other nitrites (NO_2^-) except AgNO_2 (sparingly soluble) are soluble in H_2O .

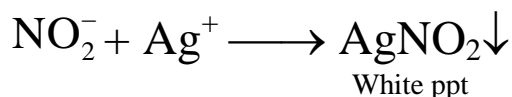
(a) Dilute HCl

On adding dilute HCl to solid nitrite in cold produces a pale blue liquid first (due to the presence of free nitrous acid, HNO_2 or its anhydride N_2O_3) and then evolution of reddish– brown fumes of nitrogen dioxide takes place. The NO_2 is produced by the combination of nitric oxide with oxygen of the air.



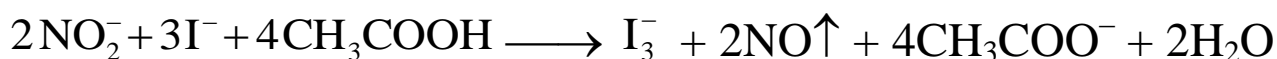
(b) Silver nitrate solution

With silver nitrate solution, a white crystalline precipitate of AgNO_2 is obtained.



(c) Potassium iodide solution:

Addition of a nitrite solution to KI solution followed by acidification with CH_3COOH or dilute H_2SO_4 produces iodine, which turns starch-iodine complex blue.

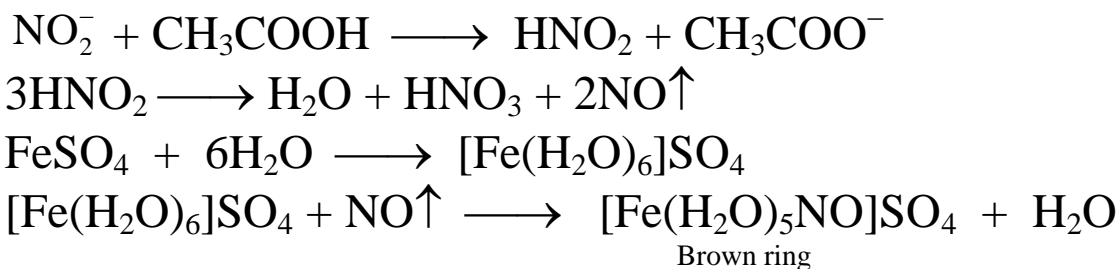


(d) Brown ring test

When the nitrite solution is added carefully to a concentrated solution of iron(II) sulphate acidified with dilute acetic or dilute sulphuric acid, a brown ring appears due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ at the junction of the two

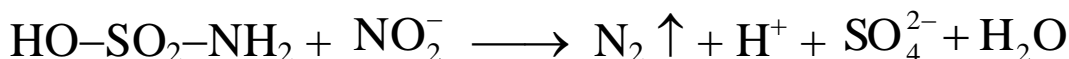
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liquids. If the addition has not been made slowly and cautiously, a brown colouration results.



(e) Sulphamic acid (HO–SO₂–NH₂) test

When a solution of a nitrite is treated with solid sulphamic acid, it is completely decomposed.



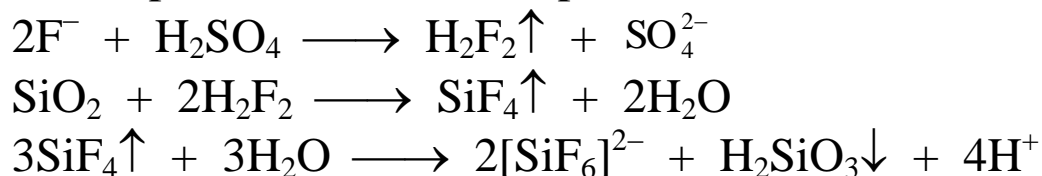
Since no nitrate is formed in this reaction, this is an excellent method for the complete removal of nitrite.

Radicals Detected With Concentrated H₂SO₄

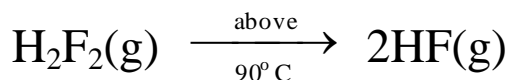
6. Fluoride (F⁻)

(a) Silica and concentrated sulphuric acid

Fluorides on warming with concentrated H₂SO₄ give a colourless, corrosive gas, hydrogen fluoride (H₂F₂). The gas fumes in moist air and the test-tube acquires a greasy appearance as a result of the corrosive action of the vapour on the silica in the glass, which liberates the gas, silicon tetrafluoride, SiF₄. By holding a moistened glass rod in the vapour, gelatinous silicic acid (H₂SiO₃) is deposited on the rod, which is a product of the decomposition of the silicon tetrafluoride.



Note that at room temperature hydrogen fluoride gas is almost completely dimerized, therefore its formula has been written as H₂F₂. At elevated temperatures (say 90°C), it dissociates completely to monomeric hydrogen fluoride.



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(b) The etching test

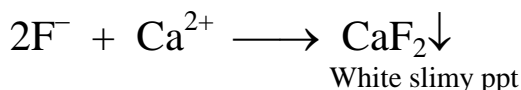
A clean watch glass is coated on the convex side with paraffin wax and scratching a design on the wax with a nail exposes part of the glass. A mixture of fluoride salt and concentrated sulphuric acid is placed in a small lead or platinum crucible and the latter immediately covered with the watch glass, convex side down. A little water should be poured in the upper (concave) side of the watch glass to prevent the wax from melting. The crucible is very gently warmed. After 5–10 minutes, the hydrogen fluoride would etch the glass.

(c) Silver nitrate solution

With silver nitrate solution, no precipitate is obtained, as silver fluoride is soluble in water.

(d) Calcium chloride solution

With calcium chloride solution, a white, slimy precipitate of calcium fluoride (CaF_2), sparingly soluble in acetic acid but slightly more soluble in dilute hydrochloric acid is formed.

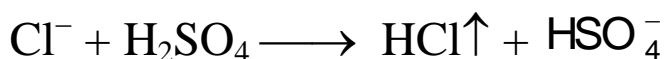


7. Chloride (Cl^-)

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

(a) Concentrated H_2SO_4

With concentrated H_2SO_4 , chlorides gives vapours of HCl .



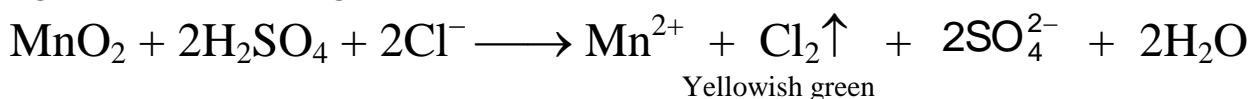
Vapour evolved

(i) turns blue litmus paper red.

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

(b) Manganese dioxide and concentrated sulphuric acid

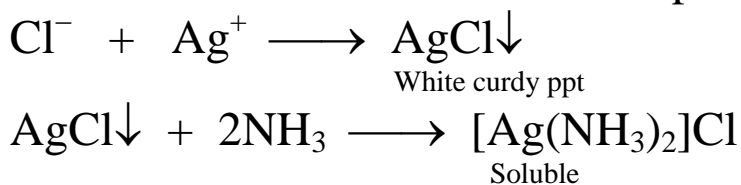
When a solid chloride is treated with MnO_2 and concentrated H_2SO_4 , yellowish–green coloured gas (Cl_2) is evolved.



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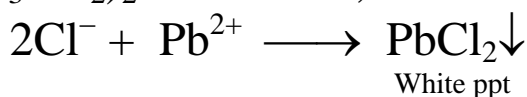
(c) Silver nitrate solution

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



(d) Lead acetate solution

With $(\text{CH}_3\text{COO})_2\text{Pb}$ solution, chlorides gives a white precipitate of lead chloride.

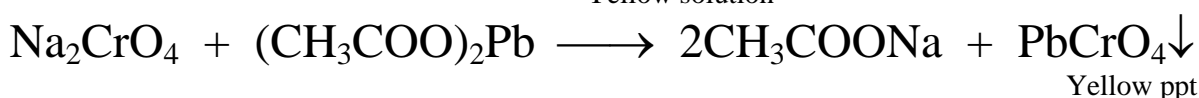
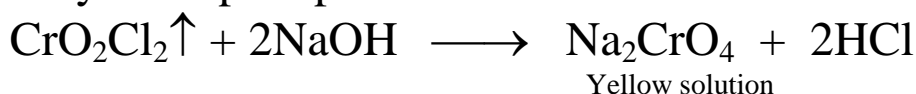


(e) Chromyl chloride test

When a mixture containing chloride ion is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ & concentrated H_2SO_4 , deep orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.



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



This test is given by ionic chlorides only. Chlorides of Hg^{2+} , Pb^{2+} , Ag^+ , Sn^{2+} & Sb^{3+} do not respond to chromyl chloride test due to their covalent character, which allows them to ionise only slightly.

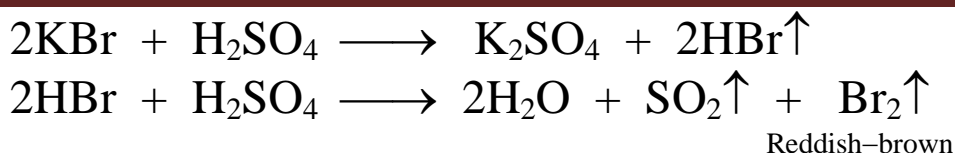
8. Bromide (Br^-)

All bromides are soluble in water except AgBr , Hg_2Br_2 , CuBr and PbBr_2 (soluble in boiling water).

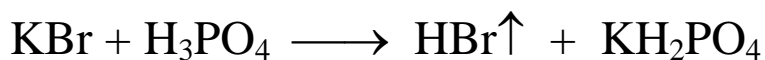
(a) Concentrated H_2SO_4

If concentrated sulphuric acid is poured in a bromide solution, first a reddish-brown solution is formed, later reddish-brown vapours of bromine accompany the hydrogen bromide.

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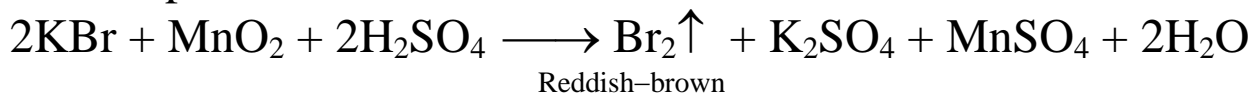


If concentrated H_3PO_4 is used instead of H_2SO_4 and the mixture is warmed, only hydrogen bromide is formed.



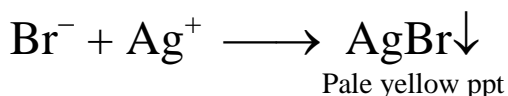
(b) Manganese dioxide and concentrated sulphuric acid

When a mixture of solid bromide, MnO_2 and concentrated H_2SO_4 is heated, reddish-brown vapours of bromine are evolved.



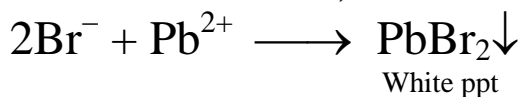
(c) Silver nitrate solution

With AgNO_3 solution, bromide gives a curdy pale yellow precipitate of silver bromide. This precipitate is sparingly soluble in dilute ammonia but readily soluble in concentrated ammonia solution and insoluble in dilute HNO_3 .



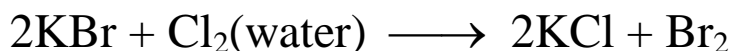
(d) Lead acetate solution

Bromides on treatment with lead acetate solution, gives a white crystalline precipitate of lead bromide, which is soluble in boiling water.

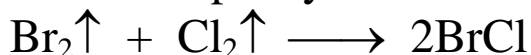


(e) Chlorine water

When chlorine water is added to a solution of bromide, free bromine is liberated, which colours the solution orange-red. If CS_2 , CHCl_3 or CCl_4 is added to the solution and the liquid shaken, the bromine dissolves in the organic solvent and after allowing to stand forms a reddish-brown solution below the colourless aqueous layer.



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



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Pale yellow solution

(f) Potassium dichromate and concentrated H₂SO₄

When a mixture of solid bromide, K₂Cr₂O₇ and concentrated H₂SO₄ is heated and passing the evolved vapours into water, a orange–red solution is obtained.

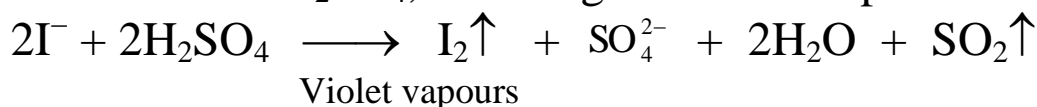


9. Iodide (I[−])

Iodides are generally soluble in water except AgI, Hg₂I₂, HgI₂, CuI and PbI₂.

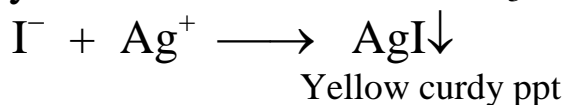
(a) Concentrated H₂SO₄

With concentrated H₂SO₄, iodides gives violet vapours of iodine on warming.



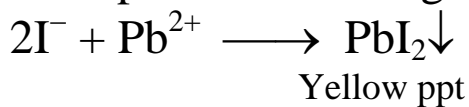
(b) Silver nitrate solution

With AgNO₃ solution, iodides form a yellow curdy precipitate of silver iodide, which is very slightly soluble in concentrated ammonia solution, but is completely insoluble in dilute HNO₃.



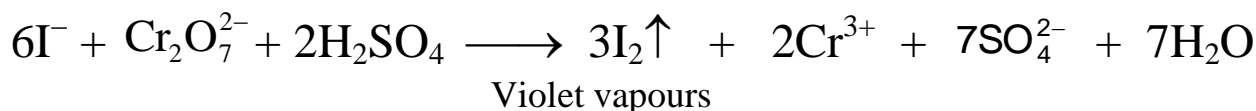
(c) Lead acetate solution

With (CH₃CO₂)₂Pb solution, a yellow precipitate of lead iodide (PbI₂) is formed, which is soluble in hot water forming a colourless solution and yielding golden–yellow plates on cooling.



(d) Potassium dichromate and concentrated sulphuric acid

When iodides are warmed with K₂Cr₂O₇ and concentrated H₂SO₄, iodine is liberated.

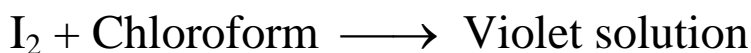
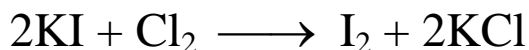


(e) Chlorine water

When this reagent is added dropwise to a solution of an iodide, free iodine is liberated, which colours the solution brown and on shaking with CS₂, CHCl₃ or

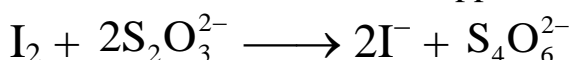
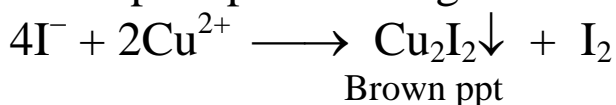
QUALITATIVE ANALYSIS

CCl_4 , it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.



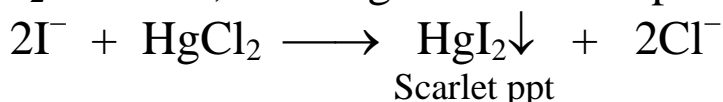
(f) Copper sulphate solution

With CuSO_4 solution, iodide produces a brown precipitate consisting of a mixture of copper(I) iodide and iodine. On addition of hypo ($\text{Na}_2\text{S}_2\text{O}_3$) to the solution, brown precipitate changes to white (colourless).

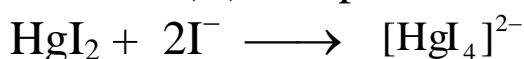


(g) Mercury(II) chloride solution

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



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

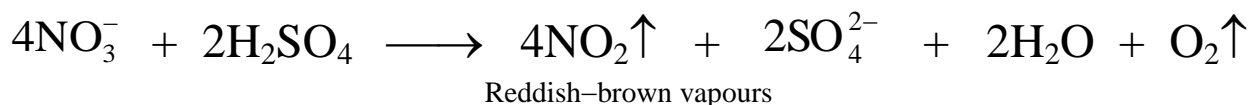


10. Nitrate

All nitrates (NO_3^-) are soluble in water. The nitrates of mercury and bismuth give basic salts on treatment with H_2O but are soluble in dilute nitric acid.

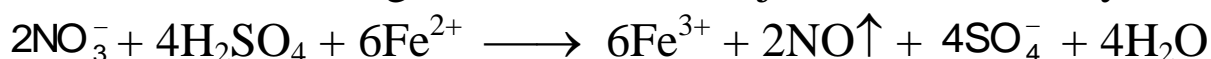
(a) Concentrated H_2SO_4

Nitrates produce reddish-brown vapours of nitrogen dioxide on treatment with concentrated H_2SO_4 .

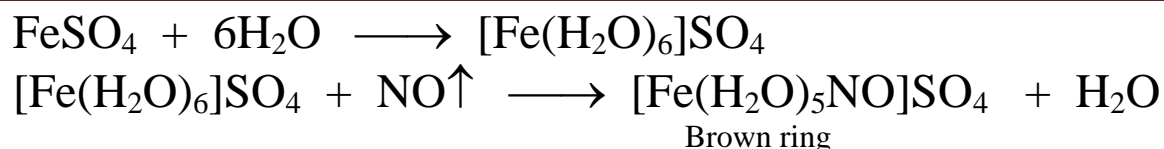


(b) Brown ring test

When a freshly prepared saturated solution of iron(II) sulphate is added to nitrate solution and then concentrated H_2SO_4 is added slowly from the side of the test tube, a brown ring is obtained at the junction of two layers.



QUALITATIVE ANALYSIS



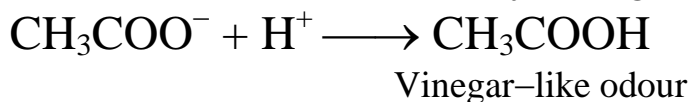
On shaking and warming the mixture the brown colour disappears, nitric oxide is evolved and a yellow solution of iron(III) ions remains.

Bromides and iodides interfere because of the liberated halogen. This test is not trustworthy in the presence of chromates, sulphites, thiosulphates and iodates. All of these anions can be removed by adding an excess of nitrate-free Ag_2SO_4 and filtering the insoluble silver salts.

11. Acetate

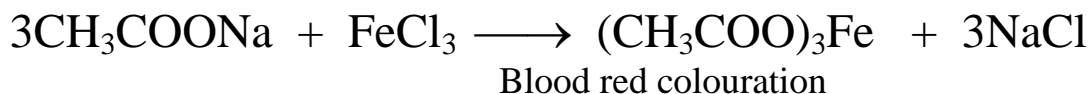
(a) Dilute sulphuric acid

On adding a small quantity of dilute H_2SO_4 to the acetate (CH_3CO_2^-) salt, acetic acid is produced, which can be easily recognized by its vinegar-like odour.



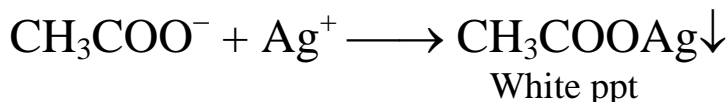
(b) Iron(III) chloride solution

With FeCl_3 solution, acetates give a deep-red colouration due to the formation of ferric acetate.



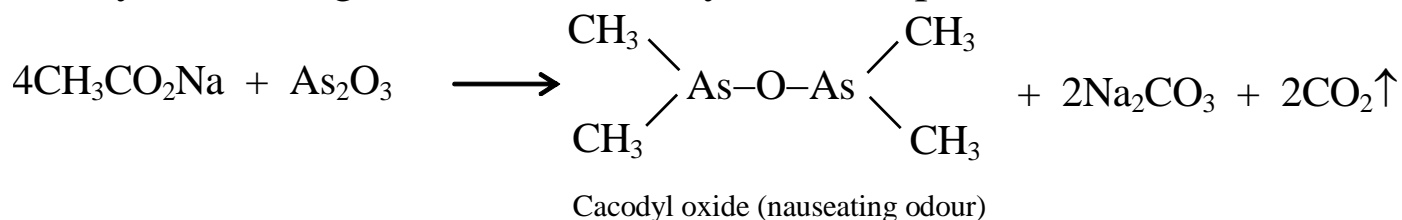
(c) Silver nitrate solution

Acetates on treatment with AgNO_3 solution give a white crystalline precipitate of silver acetate.



(d) Cacodyl oxide reaction

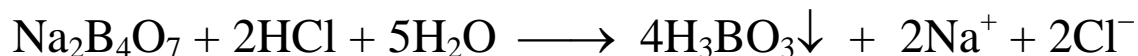
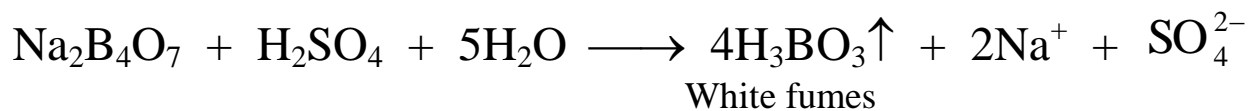
Acetate salt on heating with solid As_2O_3 gives cacodyl oxide, which have an extremely nauseating odour. The cacodyl oxide is poisonous also.



12. Borate

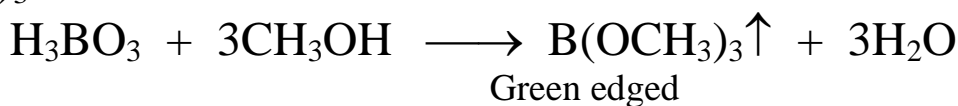
(a) Concentrated H₂SO₄

On heating borate (BO₃³⁻) salts with concentrated sulphuric acid, white fumes of boric acid are evolved. If concentrated hydrochloric acid is added to a concentrated solution of borax, boric acid is precipitated.



(b) Concentrated sulphuric acid and alcohol (flame test)

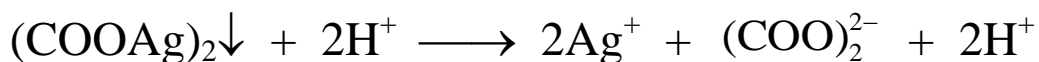
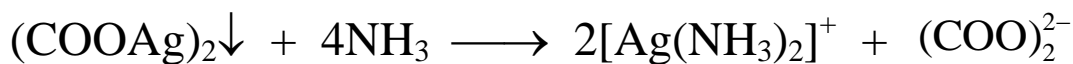
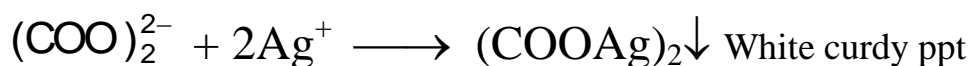
When a little borax is mixed with some concentrated sulphuric acid and methanol or ethanol (the former is preferred because of its greater volatility) in a small porcelain dish and the alcohol ignited, the latter will burn with a green-edged flame, due to the formation of methyl borate, B(OCH₃)₃ or of ethyl borate B(OC₂H₅)₃.



13. Oxalate

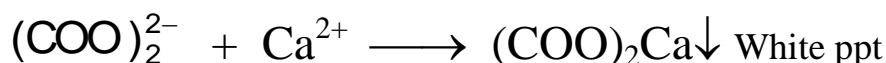
(a) Silver nitrate solution

With silver nitrate solution, a white curdy precipitate of silver oxalate (C₂O₄²⁻) sparingly soluble in water, soluble in ammonia solution and in dilute nitric acid is obtained.



(b) Calcium chloride solution

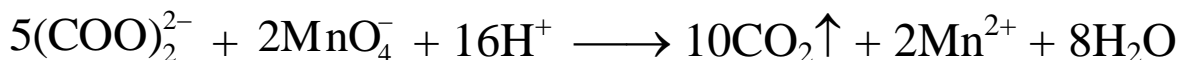
With calcium chloride solution, a white crystalline precipitate of calcium oxalate from neutral solutions is obtained, which is insoluble in dilute acetic acid and oxalic acid but soluble in dilute hydrochloric acid and in dilute nitric acid.



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(c) Potassium permanganate solution

Potassium permanganate solution gets decolourized when warmed in acid solution with an oxalate salt to 60°C. Many other organic compounds also effect the bleaching of permanganate but if the evolved carbon dioxide is tested by the lime water reaction, the test becomes specific for oxalates.

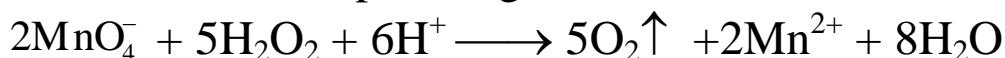


14. Permanganate

All permanganates (MnO_4^-) are soluble in water forming purple solutions.

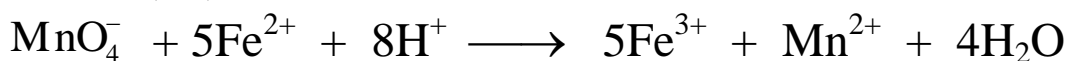
(a) Hydrogen peroxide

H_2O_2 decolourises acidified permanganate solution.



(b) Iron(II) sulphate solution

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



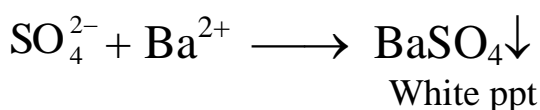
Group 'B' Radicals

15. Sulphate

Sulphates (SO_4^{2-}) of barium, strontium and lead are practically insoluble in water, those of calcium and mercury(II) are slightly soluble and most of the remaining metallic sulphates are soluble.

(a) Barium chloride solution

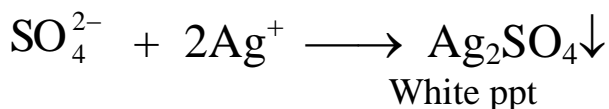
On adding BaCl_2 solution to a sulphate salt solution, a white precipitate of barium sulphate (BaSO_4) insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is formed.



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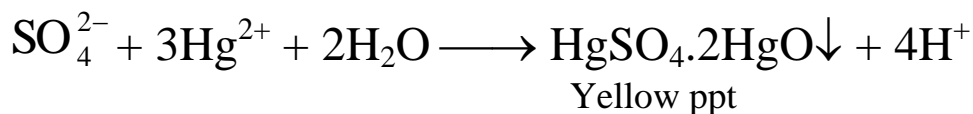
(b) Silver nitrate solution

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



(c) Mercury(II) nitrate solution

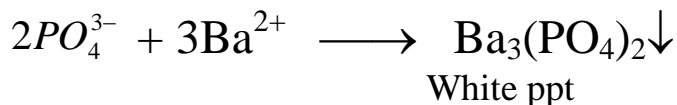
With $\text{Hg}(\text{NO}_3)_2$ solution, sulphates form a yellow precipitate of basic mercury(II) sulphate.



16. Phosphate

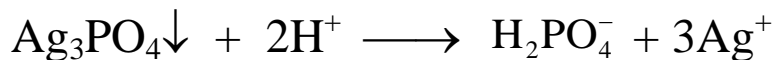
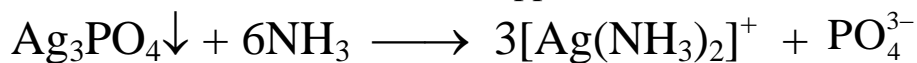
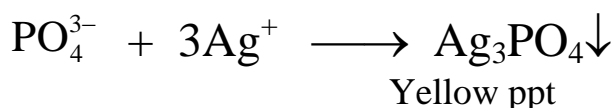
(a) Barium chloride solution

With barium chloride solution, a white amorphous precipitate of barium phosphate, $\text{Ba}_3(\text{PO}_4)_2$ is formed from neutral solutions, soluble in dilute mineral acids and in acetic acid.



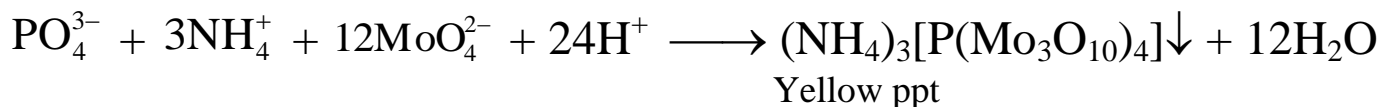
(b) Silver nitrate solution

With silver nitrate solution, a yellow precipitate of silver orthophosphate, Ag_3PO_4 is formed, soluble in dilute ammonia solution and in dilute nitric acid.



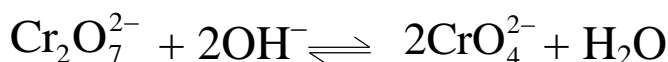
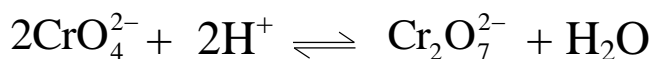
(c) Ammonium molybdate reagent

When ammonium molybdate is treated with a solution containing phosphate, a yellow crystalline precipitate of ammonium phosphomolybdate (ammonium dodecamolybdatophosphate), $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ or $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ is formed. In the compound formed, the Mo_3O_{10} group replaces each oxygen atom in phosphate.



17. Chromate and Dichromate

The chromates (CrO_4^{2-}) of the alkali metals, calcium and magnesium are soluble in water. SrCrO_4 is sparingly soluble. Most other metallic chromates are insoluble in H_2O . Metallic chromates give yellow solution when dissolved in water. In the presence of H^+ ion, chromates are converted into dichromates (orange-red solution). On adding alkalies i.e. hydroxyl ions, the colour again becomes yellow due to the formation of CrO_4^{2-} back.

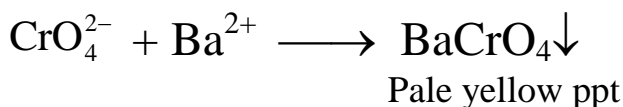


The reaction may also be expressed as

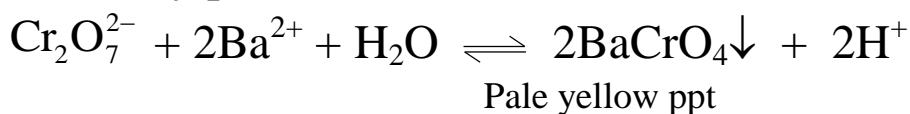


(a) Barium chloride solution

With BaCl_2 solution, CrO_4^{2-} gives a pale yellow precipitate of barium chromate, soluble in dilute mineral acids but insoluble in water and acetic acid.



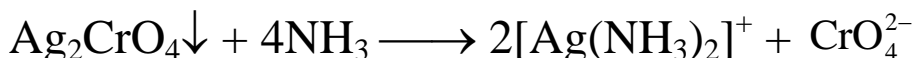
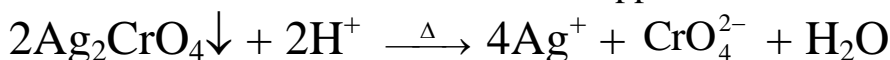
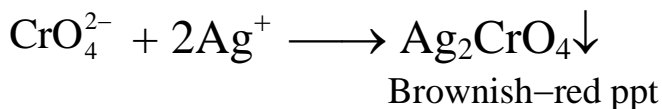
Dichromate ion also gives the same precipitate but as a strong acid is formed, precipitation is only partial.



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

(b) Silver nitrate solution

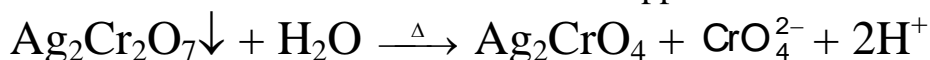
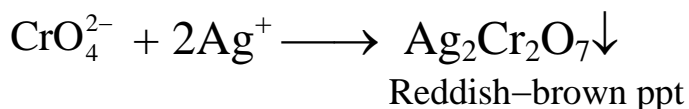
CrO_4^{2-} on treatment with silver nitrate solution gives a brownish - red precipitate of silver chromate, which is soluble in dilute nitric acid and in ammonia solution but is insoluble in acetic acid. HCl converts the precipitate into silver chloride.



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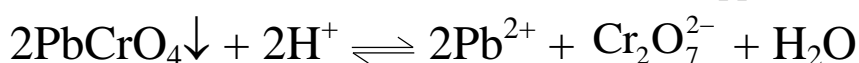
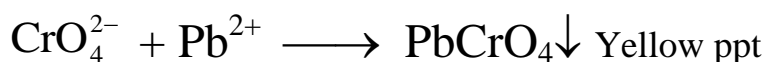


A reddish-brown precipitate of silver dichromate, $\text{Ag}_2\text{Cr}_2\text{O}_7$ is formed with a concentrated solution of a dichromate, which on boiling with water gets converted into less soluble silver chromate.



(c) Lead acetate solution

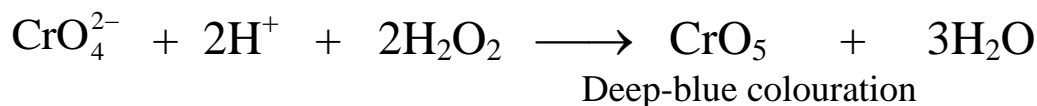
With lead acetate solution, CrO_4^{2-} gives a yellow precipitate of lead chromate (PbCrO_4), insoluble in acetic acid but soluble in dilute nitric acid.



The precipitate is soluble in sodium hydroxide solution and acetic acid reprecipitates lead chromate.

(d) Hydrogen peroxide

If an acidic solution of a chromate is treated with H_2O_2 in the presence of ether/amyl alcohol, a deep-blue solution of chromium pentoxide or chromic peroxide is obtained in ethereal layer.



CrO_5 is unstable and it decomposes yielding oxygen and a green solution of Cr^{3+} in the absence of ether /amyl alcohol.

Analysis of Cations (Basic Radicals)

Classification of cations

For the purpose of systematic qualitative analysis of cations, they are divided into five groups and the classification is based on whether a cation reacts with the given group reagent by the formation of a precipitate or not.

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Group reagents

Hydrochloric acid, hydrogen sulphide, ammonium hydroxide and ammonium carbonate.

Group	Group Reagent	Ions	Nature of precipitate and their colour
Group I	dilute HCl	Pb^{2+} , Hg_2^{2+} , Ag^+	PbCl_2 , HgCl_2 , AgCl - white
Group II A	H_2S in dilute HCl	Pb^{2+} , Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+}	As_2S_3 , As_2S_5 , CdS , SnS_2 —Yellow HgS , CuS , PbS —Black Sb_2S_3 , Sb_2S_5 —Orange Bi_2S_3 , SnS —Brown
Group II B		As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+}	
Group III A	NH_4OH in presence of NH_4Cl	Fe^{3+} , Al^{3+} , Cr^{3+}	$\text{Fe}(\text{OH})_3$ —Brown, $\text{Al}(\text{OH})_3$ —White, $\text{Cr}(\text{OH})_3$ —Green
Group III B	H_2S in presence of NH_4OH & NH_4Cl	Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+}	ZnS —White, MnS – Buff, CoS , NiS —Black
Group IV	$(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4Cl and NH_4OH	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 , SrCO_3 , CaCO_3 —White
Group V	No common group reagent	Mg^{2+} , Na^+ , K^+ , NH_4^+	—

It should be noted that:

- (i) Group I radicals (Ag^+ , Pb^{2+} , Hg_2^{2+}) are precipitated as chlorides because the solubility product of these chlorides (AgCl , PbCl_2 , Hg_2Cl_2) is less than the solubility products of chlorides of all other metal ions, which remain in solution.
- (ii) Group II radicals are precipitated as sulphides because of their low solubility, whereas sulphides of other metals remain in solution because of

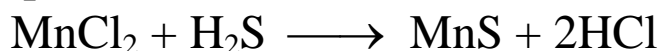
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their high solubility products. HCl acts as a source of H^+ , which decreases the concentration of S^{2-} due to common ion effect. Hence, the decreased concentration of S^{2-} is only sufficient to precipitate the Group II metals ions as sulphides.

- (iii) Group III A radicals are precipitated as hydroxides and the NH_4Cl suppresses the ionisation of NH_4OH so that only the group III A cations are precipitated as hydroxides because of their low solubility product.
- (a) Excess of NH_4Cl should not be added, else manganese will precipitate as $MnO_2.H_2O$.
- (b) $(NH_4)_2SO_4$ cannot be used in place of NH_4Cl because the SO_4^{2-} will give precipitate of $BaSO_4$.
- (c) NH_4NO_3 cannot be used in place of NH_4Cl as NO_3^- ions will oxidise Mn^{2+} to Mn^{3+} and thus, $Mn(OH)_3$ will be precipitated in III A group.
- (iv) Ammonium hydroxide increases the ionisation of H_2S by removing H^+ from H_2S as unionised water.



Now the excess of S^{2-} ions is available and hence the ionic product of group III B exceeds their solubility product and will be precipitated. In case H_2S is passed through a neutral solution, incomplete precipitation will take place due to the formation of HCl, which decreases the ionisation of H_2S . For example,



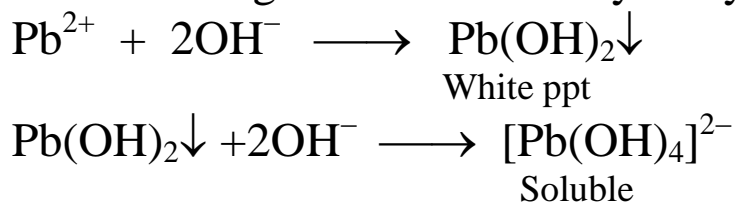
Group - I Radicals (Pb^{2+} , Ag^+ , Hg_2^{2+})

On adding dilute HCl to the salt solution if white precipitate is obtained, it indicates the presence of Pb^{2+} , Ag^+ or Hg_2^{2+} ion in the solution.

18. Lead (II)

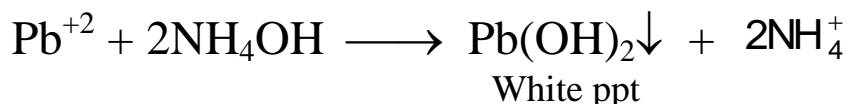
(a) Sodium hydroxide solution

With NaOH, Pb^{2+} forms a white precipitate of lead hydroxide. The precipitate dissolves in excess reagent to form tetrahydroxoplumbate(II) ions.



(b) Ammonia solution

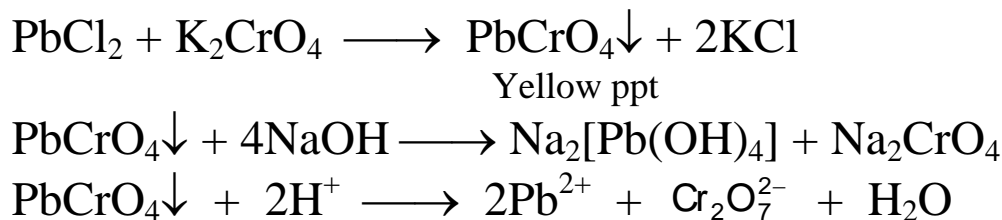
With ammonia solution, Pb^{2+} gives a white precipitate of lead hydroxide.



The precipitate is insoluble in excess reagent.

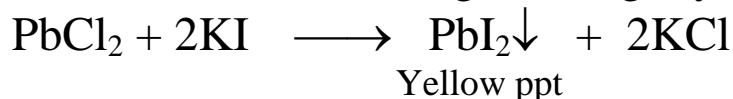
(c) Potassium chromate solution

PbCl_2 is soluble in hot water and gives a yellow precipitate with K_2CrO_4 . The precipitate obtained is insoluble in acetic acid but soluble in NaOH & nitric acid.



(d) Potassium iodide solution

PbCl_2 on addition of KI solution gives bright yellow precipitate of PbI_2 .



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

Yellow precipitate dissolves on adding excess of potassium iodide solution.

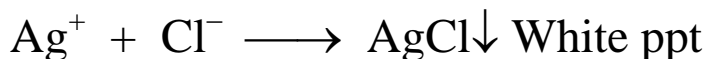


The reaction is reversible and on diluting with H_2O , the precipitate reappears.

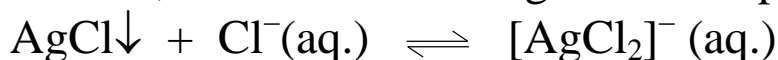
19. Silver (I)

(a) Dilute hydrochloric acid

With dilute hydrochloric acid (or soluble chlorides), a white precipitate of silver chloride is formed.



With concentrated hydrochloric acid, precipitation does not occur. After decanting the liquid from over the precipitate, it can be dissolved in concentrated hydrochloric acid, when a dichloroargentate complex is formed.



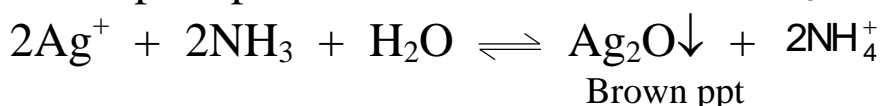
On dilution with water, the equilibrium shifts back to the left and the precipitate reappears. Dilute ammonia solution dissolves the precipitate to form the diammineargentate(I) complex ion.



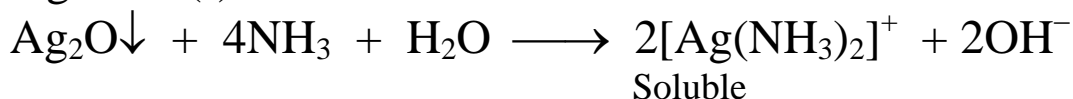
Dilute nitric acid or hydrochloric acid neutralizes the excess ammonia and the precipitate reappears because the equilibrium is shifted backwards.

(b) Ammonia solution

Ag^+ give brown precipitate of silver oxide with NH_3 solution.

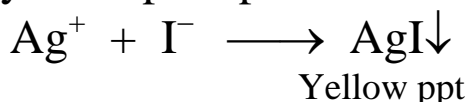


The reaction reaches equilibrium, thus the precipitation is incomplete at any stage. The precipitate dissolves in excess of the reagent forming diammineargentate(I) ion.

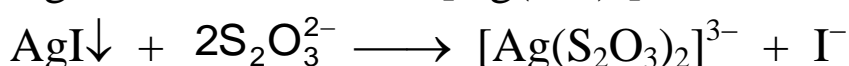
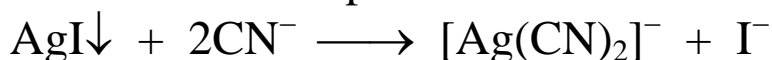


(c) Potassium iodide solution

Ag^+ give yellow precipitate of silver iodide on reaction with KI solution.



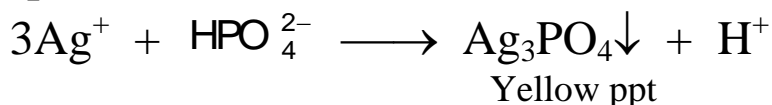
The precipitate is insoluble in dilute or concentrated ammonia but dissolves in KCN and in sodium thiosulphate.



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(d) Disodium hydrogen phosphate solution

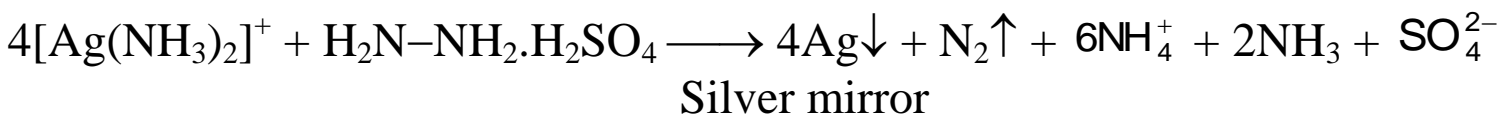
With disodium hydrogen phosphate in neutral solution, a yellow precipitate of silver phosphate is obtained.



Nitric acid and ammonia solution dissolves the precipitate.

(e) Hydrazine sulphate (saturated)

When hydrazine sulphate is added to a solution of diammineargentate ions, it forms finely divided silver metal and gaseous nitrogen is evolved.

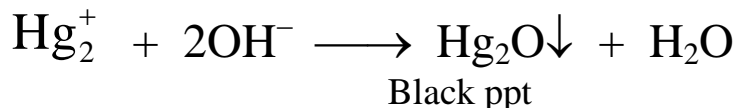


If the vessel in which the reaction is carried out is clean, silver adheres to the glass walls forming an attractive mirror.

20. Mercury (II)

(a) Sodium hydroxide solution

With NaOH, Hg_2^+ forms a black precipitate of mercury(I) oxide.

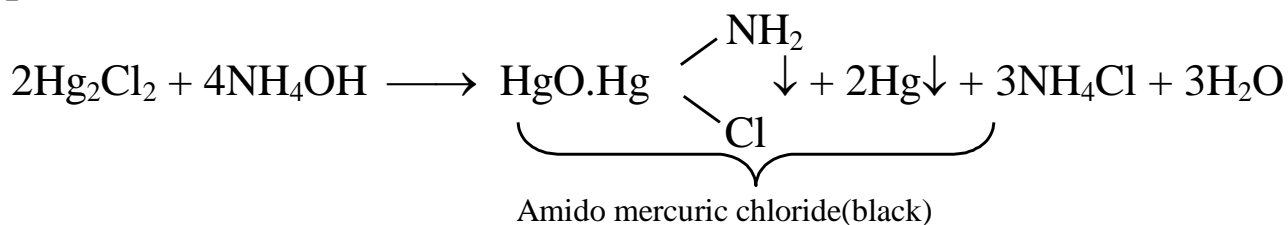


The precipitate is insoluble in excess reagent but dissolves in dilute nitric acid. When the solution is boiled, the colour of precipitate changes to grey owing to the disproportionation, when mercury(II) oxide and mercury metal are formed.



(b) Ammonia solution

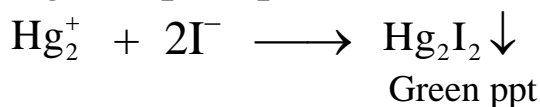
HgCl_2 on treatment with NH_4OH results in giving black precipitate, which is a mixture of mercury metal and basic mercury(II) amido chloride (white precipitate).



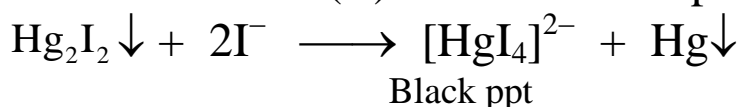
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(c) Potassium iodide solution

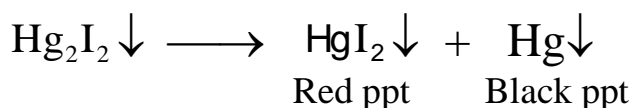
Hg_2^+ give a green precipitate of mercury(I) iodide on reaction with KI solution.



If excess reagent is added, a disproportionation reaction takes place and a soluble tetraiodomercurate(II) ions and black precipitate of mercury is formed.

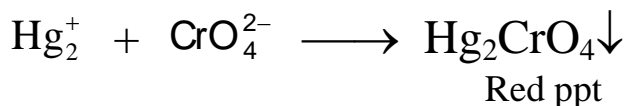


Boiling the mercury(I) iodide precipitate with water, disproportionation again takes place and a mixture of red mercury(II) iodide precipitate and black mercury is formed.

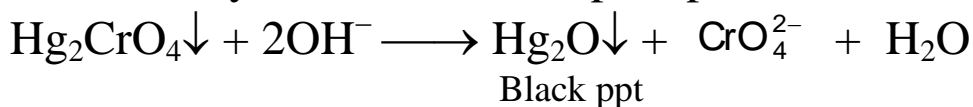


(d) Potassium chromate solution

Hg_2^+ give a red crystalline precipitate of mercury(I) chromate with potassium chromate solution in hot.



Addition of sodium hydroxide turns the precipitate into black mercury(I) oxide.

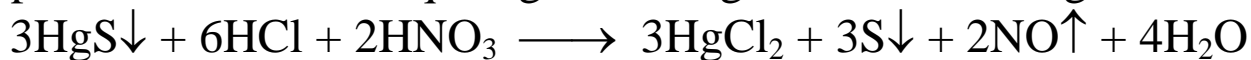


Group II-A Radicals (Pb^{2+} , Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+})

The precipitates of group II-A are insoluble in yellow ammonium sulphide.

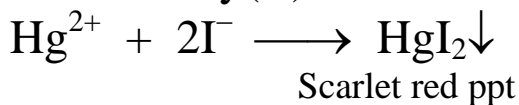
21. Mercury (II)

HgS precipitated dissolves in aquaregia forming undissociated HgCl_2 .



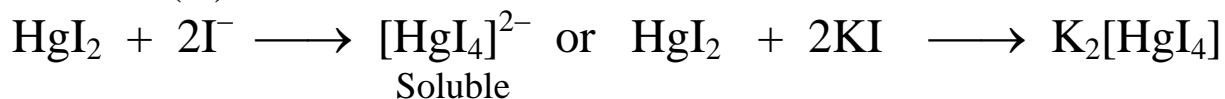
(a) Potassium iodide solution

Potassium iodide when added slowly to the solution of Hg^{2+} , a scarlet red precipitate of mercury(II) iodide is formed.



QUALITATIVE ANALYSIS

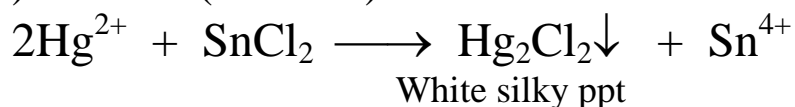
The precipitate dissolves in excess reagent, when colourless tetraiodomercurate(II) ions are formed.



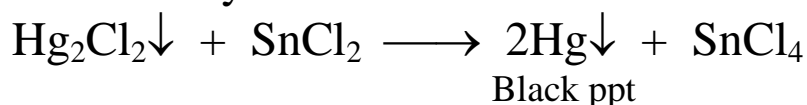
An alkaline solution of potassium tetraiodomercurate(II) serves as a selective and sensitive reagent for ammonium ions (Nessler's reagent).

(b) Tin(II) chloride solution

When SnCl_2 solution is added to a solution of Hg^{2+} , a white silky precipitate of mercury(I) chloride (calomel) is obtained.

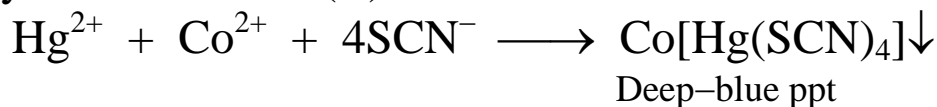


If more reagent is added, mercury(I) chloride is further reduced and black precipitate of mercury is formed.



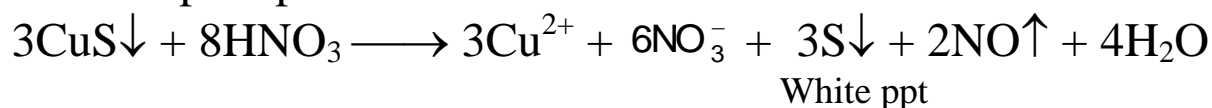
(c) Cobalt(II) thiocyanate test

When $[\text{Co}(\text{SCN})_4]^{2-}$ is added to the solution of Hg^{2+} and walls of the vessel are stirred with a glass rod, a deep-blue crystalline precipitate of cobalt tetrathiocyanatomercurate(II) is formed.



22. Copper (II)

Hot, concentrated nitric acid dissolves copper(II) sulphide, leaving behind sulphur as a white precipitate.



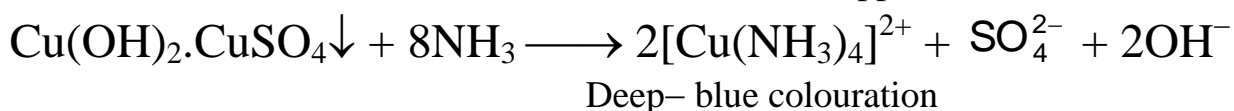
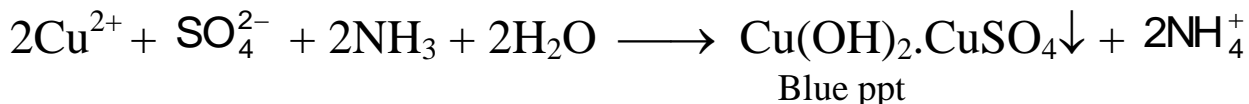
When boiled for long sulphur is oxidised to H_2SO_4 and a clear blue solution is obtained.



QUALITATIVE ANALYSIS

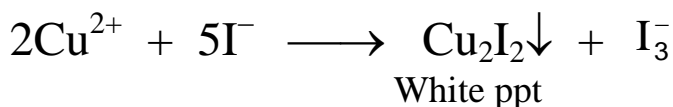
(a) Ammonia solution

When ammonia solution is added to solution of Cu^{2+} , a blue precipitate of a basic copper sulphate is obtained, which is soluble in excess reagent giving deep-blue colouration of tetraamminecopper(II) sulphate.

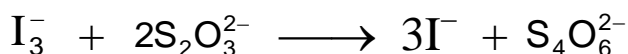


(b) Potassium iodide

Potassium iodide with Cu^{2+} gives a white precipitate of copper(I) iodide but the solution is intensely brown because of the formation of tri-iodide ions (or iodine).



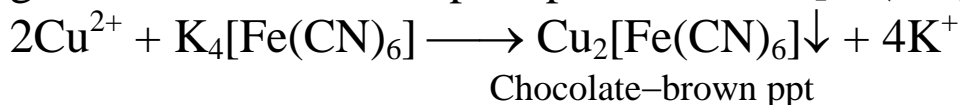
Adding an excess of sodium thiosulphate to the solution, tri-iodide ions are reduced to colourless iodide ions and the white colour of the precipitate becomes visible. The reduction with thiosulphate yields tetrathionate ions.



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

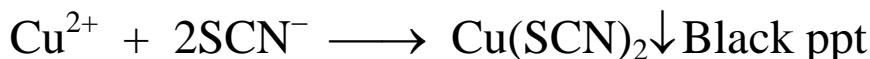
(c) Potassium hexacyanoferrate(II) solution

Cu^{2+} ions give chocolate-brown precipitate with $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution.



(d) Potassium thiocyanate solution

With potassium thiocyanate, a black precipitate of copper(II) thiocyanate is obtained.



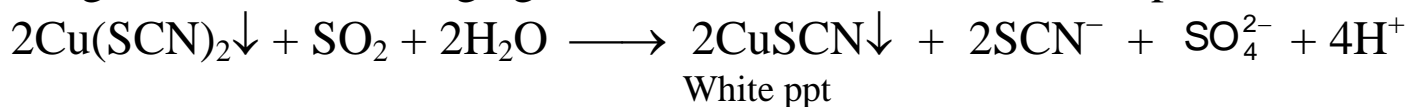
The precipitate decomposes slowly to form white copper(I) thiocyanate and thiocyanogen is formed.



QUALITATIVE ANALYSIS

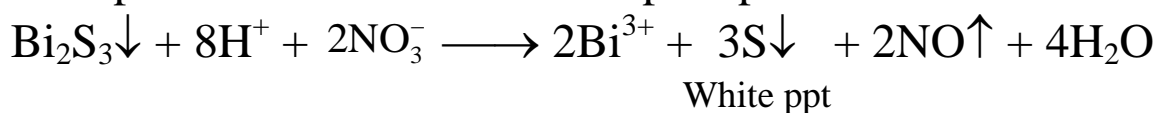
Thiocyanogen decomposes rapidly in aqueous solutions.

Copper(II) thiocyanate can be transformed to copper(I) thiocyanate immediately by adding a suitable reducing agent like saturated solution of sulphur dioxide.



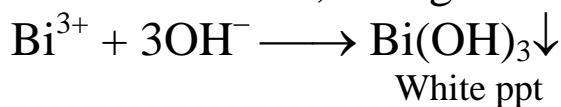
23. Bismuth(III)

Black precipitate of Bi_2S_3 so obtained dissolves in hot dilute nitric acid, leaving behind sulphur in the form of a white precipitate.

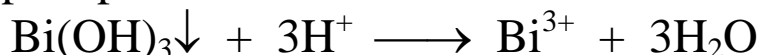


(a) Sodium Hydroxide

With NaOH solution, Bi^{3+} give a white precipitate of bismuth(III) hydroxide.



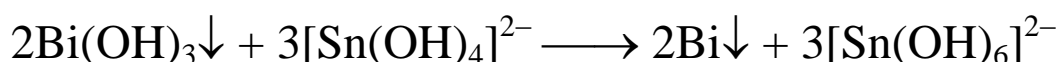
The precipitate is soluble in acids.



When boiled, the precipitate loses water and turns yellowish–white.

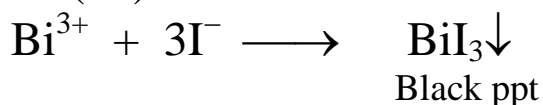


$\text{Bi}(\text{OH})_3$ when reduced by tetrahydroxostannate(II) ions give black precipitate of bismuth metal.

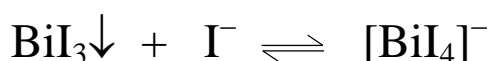


(b) Potassium iodide

When KI solution is added dropwise to Bi^{3+} solution, a black precipitate of bismuth(III) iodide is obtained.



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



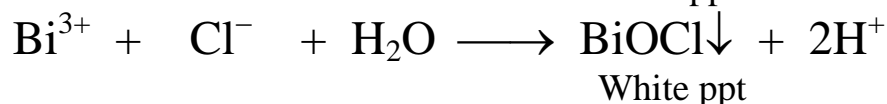
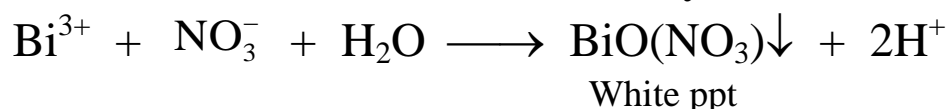
Heating the precipitate of BiI_3 with water, it turns orange due to the formation of bismuthyl iodide.

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(c) Water

When a solution of a bismuth salt is poured into a large volume of water, a white precipitate of the corresponding basic salt is produced. This is soluble in dilute mineral acids but is insoluble in alkali hydroxides.

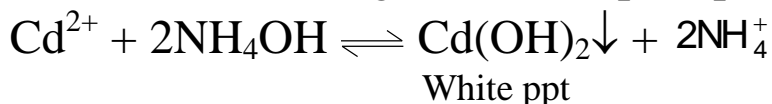


24. Cadmium (II)

Yellow precipitate of CdS dissolves in hot dilute nitric acid giving Cd^{+2} ions.

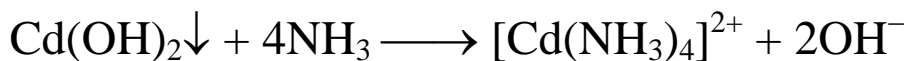
(a) Ammonium Hydroxide

With NH_4OH solution, Cd^{2+} give a white precipitate of cadmium hydroxide.



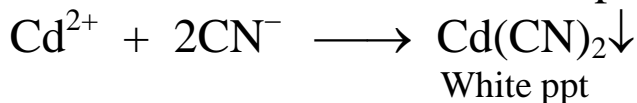
The precipitate dissolves in acid when the equilibrium shifts towards the left.

An excess of reagent dissolves the precipitate, when tetramminecadmate(II) ions are formed.



(b) Potassium cyanide

With KCN solution, Cd^{2+} forms a white precipitate of cadmium cyanide.



An excess of reagent dissolves the precipitate due to the formation of tetracyanocadmiate(II) ions.

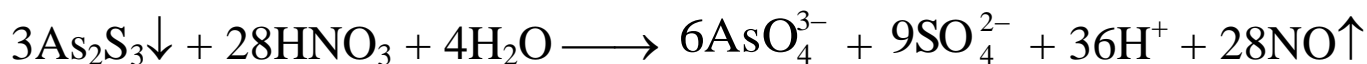


Group II - B Radicals (As^{3+} , Sb^{3+} , Sn^{2+} , Sn^{4+})

The precipitates of group II B as As_2S_3 , Sb_2S_3 , SnS and SnS_2 are soluble in yellow ammonium sulphide, $(\text{NH}_4)_2\text{S}_2$.

25. Arsenic (III)

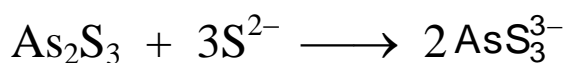
Yellow precipitate of As_2S_3 is insoluble in concentrated hydrochloric acid but dissolves in hot concentrated nitric acid.



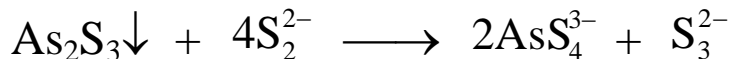
As_2S_3 also dissolves readily in sodium hydroxide and NH_4OH .



Ammonium sulphide also dissolves the precipitate of As_2S_3 , forming thioarsenite AsS_3^{3-} .

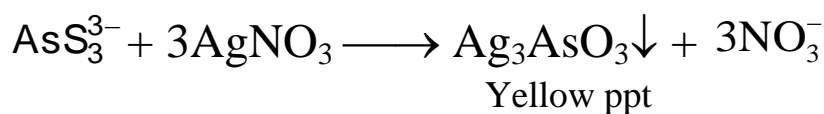


Yellow ammonium sulphide also dissolves the precipitate forming thioarsenate 2AsS_4^{3-} .



(a) Silver nitrate solution

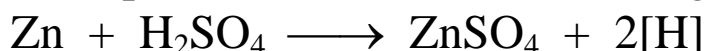
With AgNO_3 solution, AsS_3^{3-} gives a yellow precipitate of silver arsenite in neutral solution.



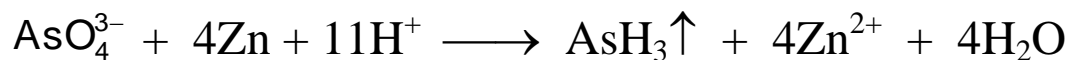
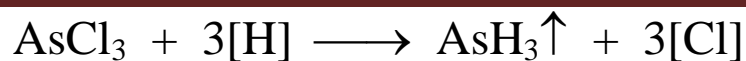
The precipitate is soluble in both nitric acid and ammonia.

(b) Marsh's test

This test is based on the fact that all soluble compounds of arsenic are reduced by 'nascent' hydrogen in acid solution to arsine (AsH_3), a colourless, extremely poisonous gas with a garlic-like odour. If the gas, mixed with hydrogen, is conducted through a heated glass tube, it is decomposed into hydrogen and metallic arsenic, which is deposited as a ***brownish-black 'mirror'*** just beyond the heated part of the tube. The following reactions take place during the test.

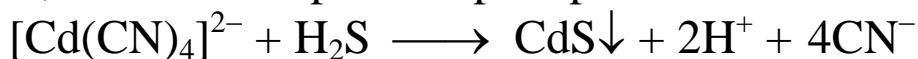


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Brownish-black mirror

The colourless complex is not too stable. Thus, when hydrogen sulphide gas is passed, cadmium sulphide is precipitated.



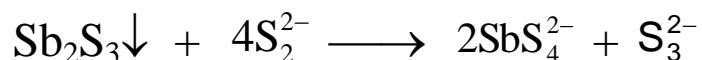
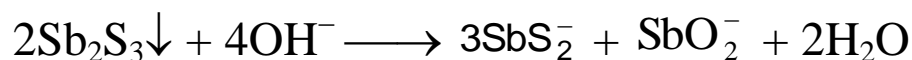
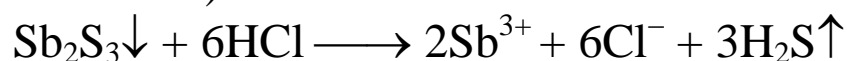
The marked difference in the stabilities of the copper and cadmium tetracyanato complexes serves as the basis for the separation of Cu^{2+} and Cd^{2+} ions.

(c) Potassium iodide

With KI solution, no precipitate is formed (distinction from copper).

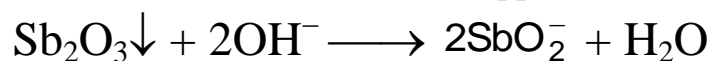
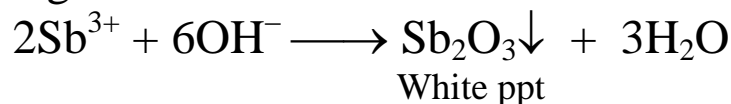
26. Antimony (III)

Orange-red precipitate of Sb_2S_3 is soluble in warm concentrated hydrochloric acid, in NaOH solution and in yellow ammonium sulphide (forming a thioantimonate).



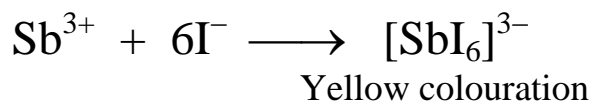
(a) Sodium Hydroxide or Ammonia Solution

With NaOH or NH_3 solution, Sb^{3+} forms a white precipitate of antimony(III) oxide $\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which is soluble in concentrated solution of caustic alkali forming antimonites.



(b) Potassium iodide solution

With KI solution, Sb^{3+} gives a yellow colouration due to the formation of complex salt.



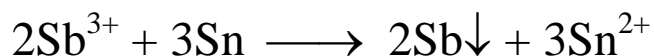
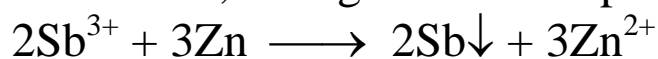
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(c) Water

When water is poured in a solution of soluble SbCl_3 , a white precipitate of antimonyl chloride (SbOCl) is formed, soluble in HCl . With a large excess of water, the hydrated oxide $\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ is produced.

(d) Zinc or Tin

With zinc or tin, Sb^{3+} gives a black precipitate of antimony.

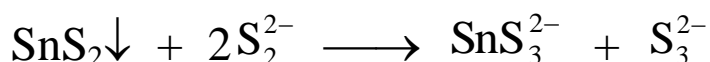
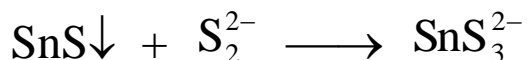


(e) Marsh's test

Marsh's test is carried out exactly as described for arsenic. The stibine (SbH_3), which is evolved, burns with a faintly bluish-green flame. The gas is decomposed by passage through a tube heated to dull redness. A "***lustrous black mirror***" of antimony is formed in a similar manner to the arsenic mirror, but it is deposited on both sides of the heated portion of the tube because of the greater instability of the stibine.

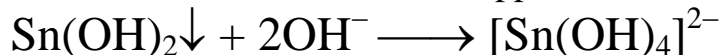
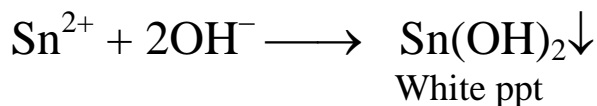
27. Tin (II) And Tin (IV)

SnS (brown precipitate) and SnS_2 (yellow precipitate), both are soluble in concentrated HCl and yellow ammonium sulphide.

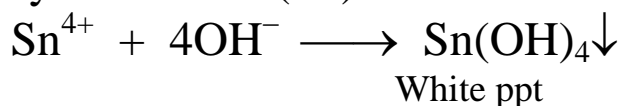


(a) Sodium hydroxide solution

With NaOH , Sn^{2+} gives a white precipitate of tin(II) hydroxide, which is soluble in excess alkali.



With NaOH solution, Sn^{4+} give a gelatinous white precipitate of tin(IV) hydroxide, which is soluble in excess of precipitant forming hexahydrostannate(IV).

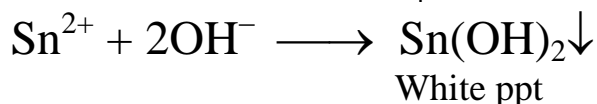


QUALITATIVE ANALYSIS

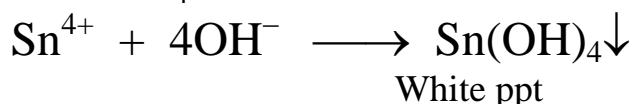


(b) Ammonia solution

With NH_4OH , Sn^{2+} forms a white precipitate of Sn(OH)_2 but the precipitate is insoluble in excess of NH_4OH .

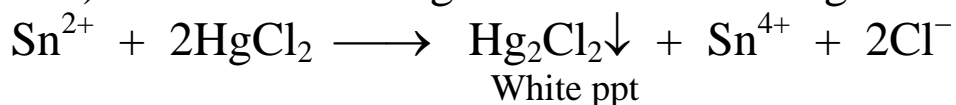


With NH_4OH , Sn^{4+} gives a white precipitate of Sn(OH)_4 , which is insoluble in excess of NH_4OH .

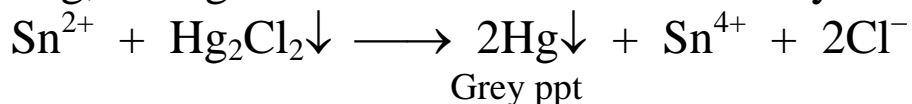


(c) Mercury(II) chloride solution

With mercury(II) chloride solution, a white precipitate of mercury(I) chloride (calomel) is formed if a large amount of the reagent is added quickly.



If however, tin(II) ions are in excess, the precipitate turns grey, especially on warming, owing to further reduction to mercury metal.



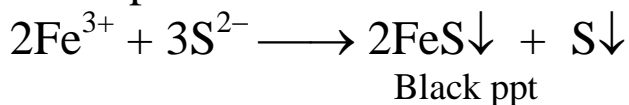
Sn^{4+} gives no precipitate with mercury(II) chloride solution.

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

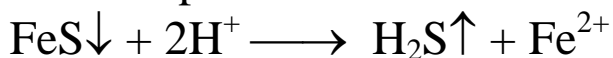
28. Iron (III)

(a) Ammonium sulphide solution

With ammonium sulphide solution, Fe^{3+} gives a black precipitate of iron(II) sulphide and sulphur.



In hydrochloric acid, the black iron(II) sulphide precipitate dissolves and the white colour of sulphur becomes visible.

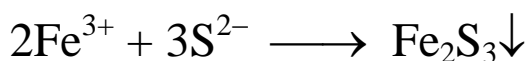


The damp iron(II) sulphide precipitate, when exposed to air, is slowly oxidized to brown iron(III) hydroxide.

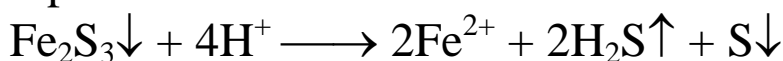
QUALITATIVE ANALYSIS



From alkaline solutions of ammonium sulphide, black iron(III) sulphide is obtained.

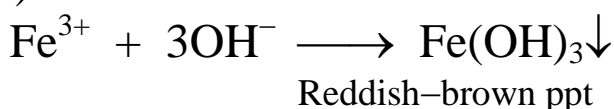


On acidification with hydrochloric acid, iron(III) ions are reduced to iron(II) ions and sulphur is formed.



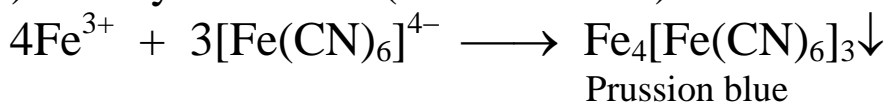
(b) Sodium hydroxide solution

With sodium hydroxide solution, a reddish-brown precipitate of iron(III) hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium) is obtained.

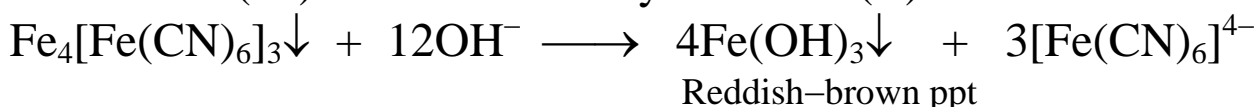


(c) Potassium hexacyanoferrate(II)

With potassium hexacyanoferrate(II) solution, Fe^{3+} gives intense blue precipitate of iron(III) hexacyanoferrate (Prussian blue).



The precipitate is insoluble in dilute acids but decomposes in concentrated hydrochloric acid. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. Sodium hydroxide turns the precipitate red as iron(III) oxide and hexacyanoferrate(II) ions are formed.



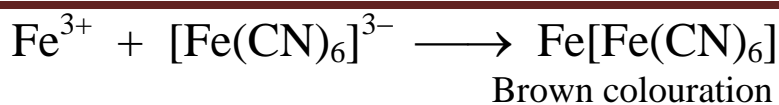
Oxalic acid also dissolves Prussian blue forming a blue solution. This process was once used to manufacture blue writing inks.

If iron(III) chloride is added to an excess of potassium hexacyanoferrate(II), a product with the composition $\text{KFe}[\text{Fe}(\text{CN})_6]$ is formed. This tends to form colloidal solutions ('Soluble Prussian Blue') and cannot be filtered.

(d) Potassium hexacyanoferrate(III)

With potassium hexacyanoferrate(III), a brown colouration is produced, due to the formation of an undissociated complex, iron(III) hexacyanoferrate(III).

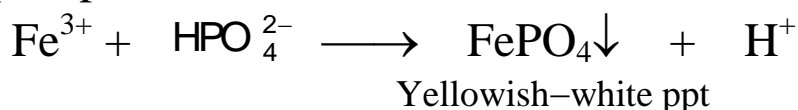
QUALITATIVE ANALYSIS



Upon adding hydrogen peroxide or some tin(II) chloride solution, the hexacyanoferrate(III) part of the compound is reduced and Prussian blue is precipitated.

(e) Disodium hydrogen phosphate solution

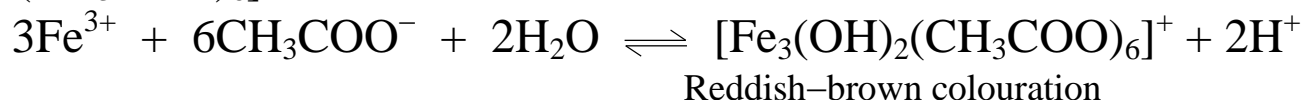
With disodium hydrogen phosphate solution a yellowish–white precipitate of iron(III) phosphate is formed.



The reaction is reversible, because a strong acid is formed which dissolves the precipitate. It is advisable to add small amounts of sodium acetate, which acts as a buffer.

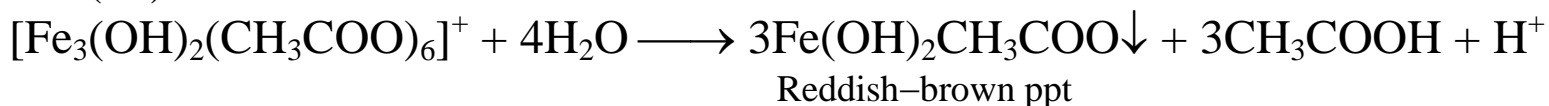
(f) Sodium acetate solution

With sodium acetate solution, a reddish–brown colouration is obtained, attributed to the formation of a complex ion with the composition $[\text{Fe}_3(\text{OH})_2(\text{CH}_3\text{COO})_6]^+$. The reaction



becomes complete only if the strong acid, which is formed, is removed by the addition of an excess of the reagent, which acts as a buffer.

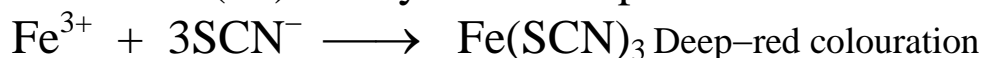
If the solution is diluted and boiled, a reddish–brown precipitate of basic iron(III) acetate is formed.



The excess of acetate ion acts as a buffer and the reaction goes to completion.

(g) Ammonium thiocyanate solution

With ammonium thiocyanate solution in slightly acidic medium, a deep–red colouration is produced (difference from iron(II) ions), due to the formation of a non-dissociated iron(III) thiocyanate complex.



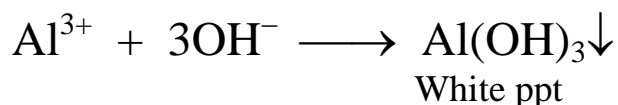
This neutral molecule can be extracted by ether or amyl alcohol.

29. Aluminium (III)

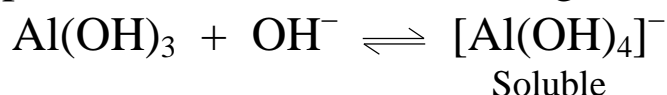
Halides, nitrates, sulphates of Al are water soluble and the aqueous solutions display acidic character owing to hydrolysis.

(a) Sodium hydroxide solution

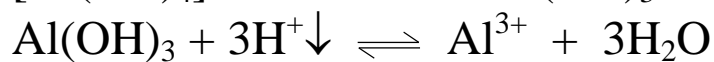
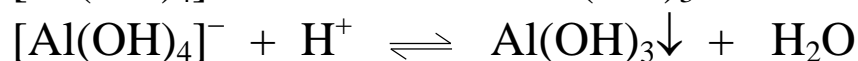
With sodium hydroxide solution, Al^{3+} gives a white precipitate of aluminium hydroxide.



The precipitate dissolves in excess reagent, forming tetrahydroxoaluminate ions.

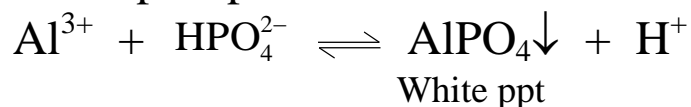


The reaction is reversible and any reagent, which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration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



(b) Disodium hydrogen phosphate solution

With disodium hydrogen phosphate solution, a white gelatinous precipitate of aluminium phosphate is obtained.

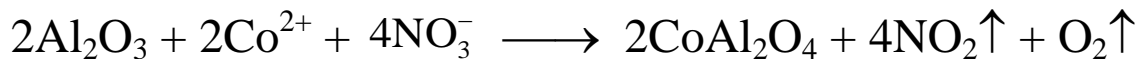


The reaction is reversible; strong acids dissolve the precipitate. However, the precipitate is insoluble in acetic acid (difference from phosphates of alkaline earths, which are soluble). The precipitate can also be dissolved in sodium hydroxide.

QUALITATIVE ANALYSIS

(c) Cobalt nitrate solution

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



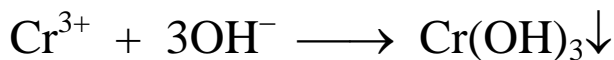
Blue infusible mass

Use of excess cobalt nitrate solution should be avoided since this will produce black cobalt oxide (Co_3O_4) upon ignition, which will mask the blue colour.

30. Chromium (III)

(a) Sodium hydroxide solution

With sodium hydroxide solution, a green precipitate of chromium(III) hydroxide is formed.



Green ppt

The reaction is reversible; on the addition of acids the precipitate dissolves. In excess reagent, the precipitate dissolves readily, tetrahydroxochromate(III) ions (or chromite ions) are formed.

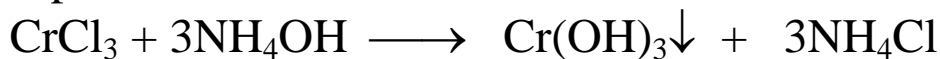


Soluble

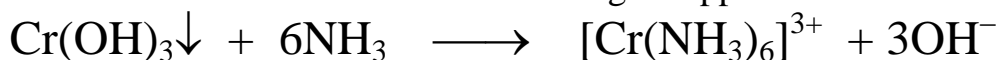
The solution is green. The reaction is reversible; on (slight) acidification and also on boiling chromium(III) hydroxide precipitates again.

(b) Ammonia solution

Bluish-green gelatinous precipitate of $\text{Cr}(\text{OH})_3$ is obtained when treated with ammonia solution but dissolves in excess of ammonia due to the formation of a soluble complex.



Bluish-green ppt



Excess

Pink colouration

(c) Chromium pentoxide (chromium peroxide, peroxochromic acid) Test

On acidifying the solution with dilute sulphuric acid, adding few drops of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, blue

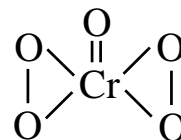
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colouration is formed, which can be extracted into the organic phase by gently shaking. During the reaction, chromium pentoxide is formed.



Blue colouration
in ether layer

Chromium pentoxide has the following structure:



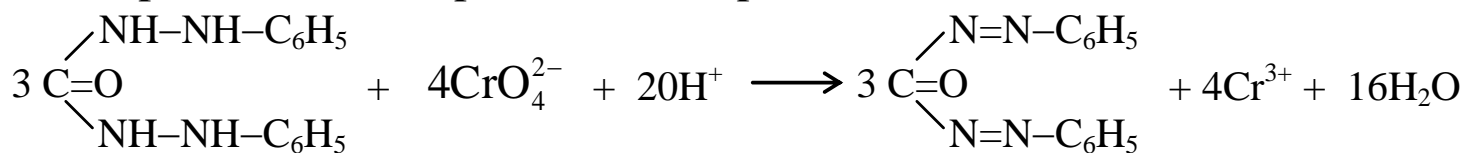
Because of the two peroxide groups, the compound is often called chromium peroxide.

The name peroxochromic acid is less appropriate, because the compound does not contain hydrogen at all. In aqueous solution, the blue colour fades rapidly, because chromium pentoxide decomposes to chromium(II) and oxygen.



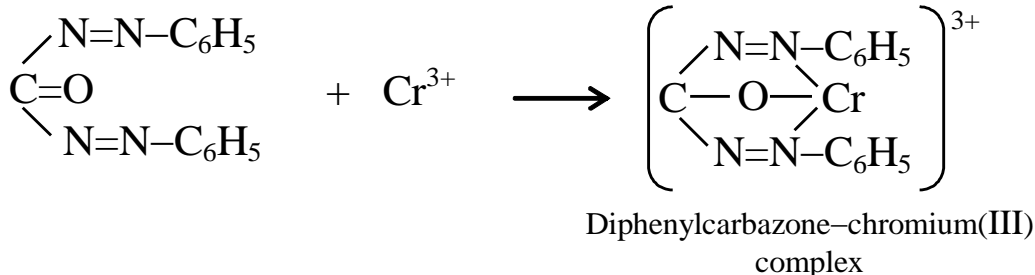
(d) 1,5-Diphenylcarbazide test

In dilute mineral acid solution, diphenylcarbazide produces a soluble violet colour, which is a characteristic test for chromium. During the reaction, chromate is reduced to chromium(III) and diphenylcarbazone is formed. These reaction products in turn produce a complex with the characteristic colour.



Diphenylcarbazide

Diphenylcarbazone

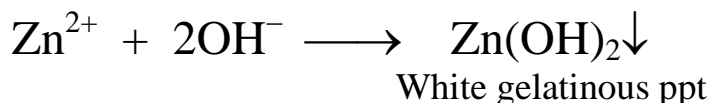


Group III B (Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+})

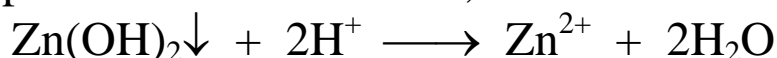
31. Zinc (II)

(a) Sodium hydroxide solution

With sodium hydroxide solution, a white gelatinous precipitate of zinc hydroxide is formed.



The precipitate is soluble in acids,



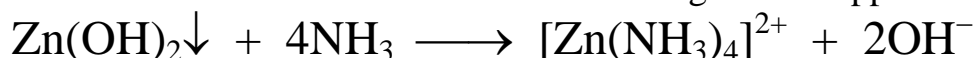
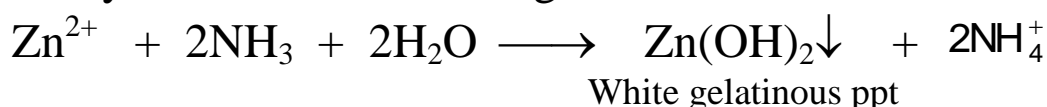
and also in the excess of the reagent.



Zinc hydroxide is thus an amphoteric compound.

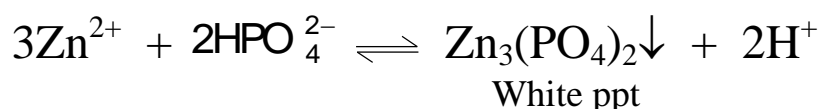
(b) Ammonia solution

With ammonia solution, Zn^{2+} forms a white gelatinous precipitate of Zn(OH)_2 , which is readily soluble in excess reagent.

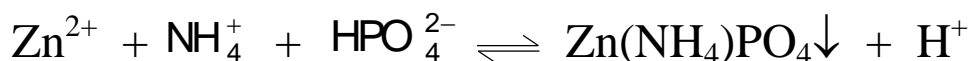


(c) Disodium hydrogen phosphate solution

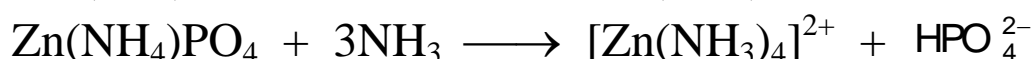
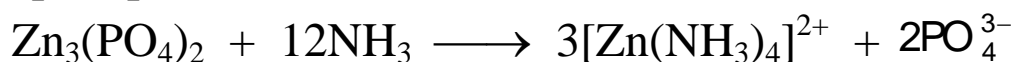
With disodium hydrogen phosphate solution, a white precipitate of zinc phosphate is formed.



In the presence of ammonium ions, zinc ammonium phosphate is formed.



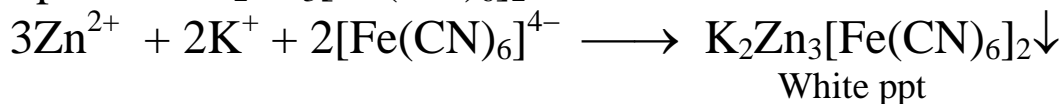
Both precipitates are soluble in dilute acids, when the reactions are reversed. Also, both precipitates are soluble in ammonia.



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(d) Potassium hexacyanoferrate(II)

With potassium hexacyanoferrate(II) solution, a white precipitate of variable composition is obtained. If the reagent is added in some excess, the composition of the precipitate is $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.



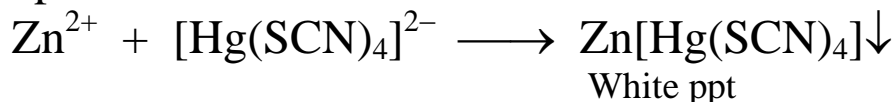
The precipitate is insoluble in dilute acids but dissolves readily in sodium hydroxide.



This reaction can be used to distinguish zinc from aluminium.

(e) Ammonium tetrathiocyanatomercurate(II)

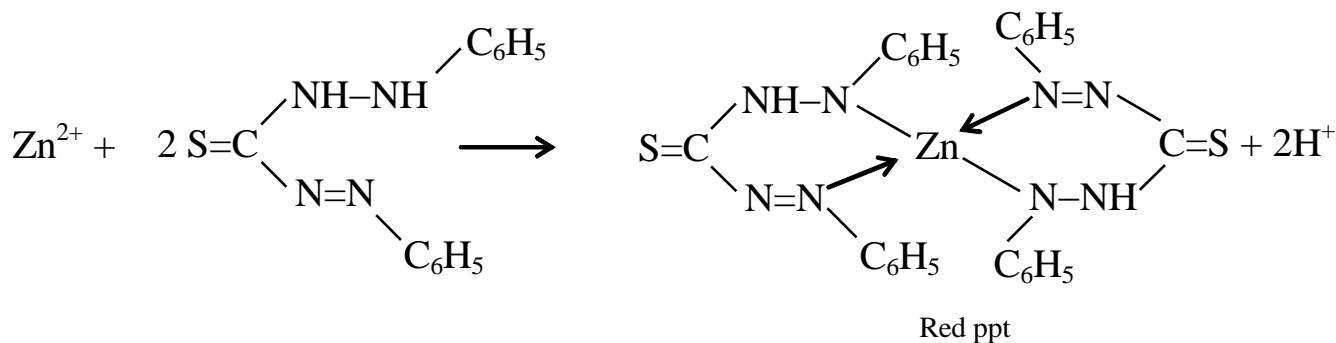
Copper salts alone do not form a precipitate with the ammonium tetrathiocyanatomercurate(II) reagent while zinc ions, if present alone, forms a white precipitate.



In the presence of copper ions, the copper complex coprecipitates with that of zinc and the violet (or blackish–purple) precipitate consisting of mixed crystals of $\text{Zn}[\text{Hg}(\text{SCN})_4] + \text{Cu}[\text{Hg}(\text{SCN})_4]$ is obtained.

(f) Diphenylthiocarbazone(dithiazone) test

Dithiazone forms complexes with a number of metal ions, which can be extracted with chloroform. The zinc complex, formed in neutral, alkaline or acetic acid solutions, is red in colour.

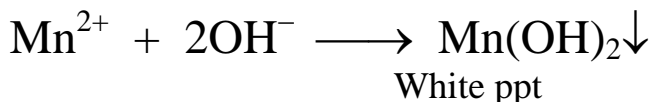


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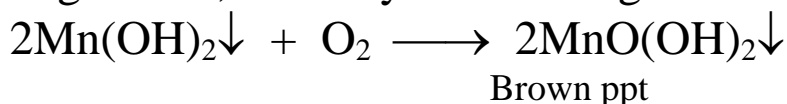
32. Manganese (II)

(a) Sodium hydroxide solution

With sodium hydroxide solution, an initially white precipitate of manganese(II) hydroxide is obtained.

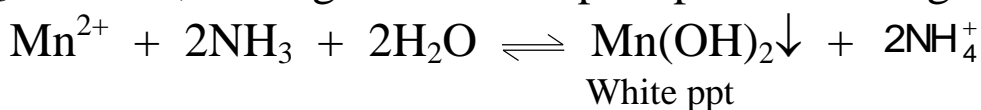


The precipitate is insoluble in excess reagent. It rapidly oxidizes on exposure to air, becoming brown, when hydrated manganese dioxide, MnO(OH)_2 , is formed.



(b) Ammonia solution

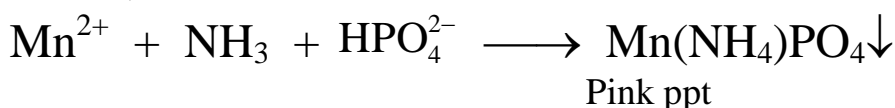
With NH_3 solution, Mn^{2+} gives a white precipitate of manganese(II) hydroxide.



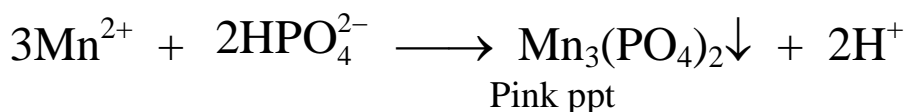
The precipitate is soluble in ammonium salts, when the reaction proceeds towards the left.

(c) Disodium hydrogen phosphate solution

With disodium hydrogen phosphate solution, a pink precipitate of manganese ammonium phosphate $\text{Mn(NH}_4\text{)PO}_4 \cdot 7\text{H}_2\text{O}$, in the presence of ammonia (or ammonium ions) is obtained.



If ammonium salts are absent, pink precipitate manganese(II) phosphate is formed.



Both precipitates are soluble in acids.

(d) Lead dioxide and concentrated nitric acid

On boiling a dilute solution of manganese(II) ions with lead dioxide and a little concentrated nitric acid and allowing the suspended solid containing unattacked lead dioxide to settle, the supernatant liquid acquires a violet-red (or purple) colour due to permanganic acid.

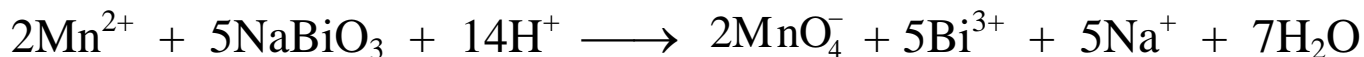
QUALITATIVE ANALYSIS



Purple colour

(e) Sodium bismuthate (NaBiO_3) solution

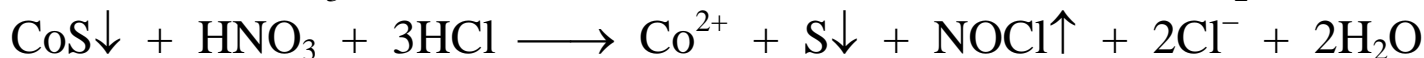
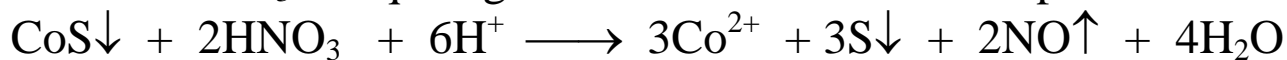
When sodium bismuthate (NaBiO_3) is added to a cold solution of manganese(II) ions in dilute nitric acid or in dilute sulphuric acid, the mixture stirred and excess reagent filtered off, a violet-red (or purple) solution of permanganate is produced.



Purple colour

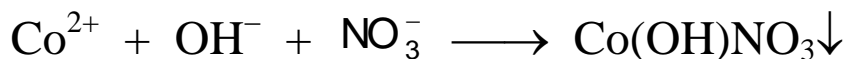
33. Cobalt (II)

The black precipitate of CoS is insoluble in dilute HCl or acetic acid but hot concentrated HNO_3 or aquaregia dissolves it and white sulphur remains.



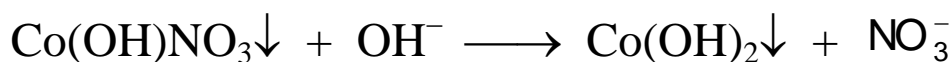
(a) Sodium hydroxide solution

Cobalt(II) nitrate in cold gives a blue basic salt with NaOH solution.



Blue ppt

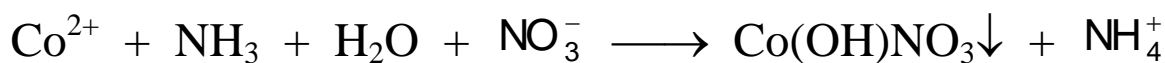
Upon warming with excess alkali, the basic salt is converted into a pink precipitate of Co(II) hydroxide.



Pink ppt

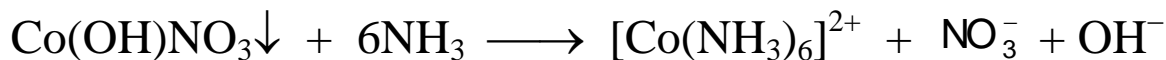
(b) Ammonia solution

When cobalt(II) nitrate is treated with ammonia solution, a blue basic salt is precipitated.



Blue ppt

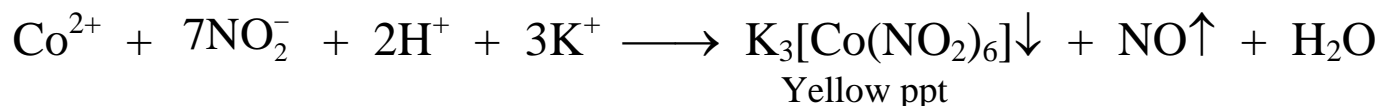
The excess of the reagent dissolves the precipitate, when hexamminecobaltate(II) ions are formed.



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(c) Potassium nitrite solution

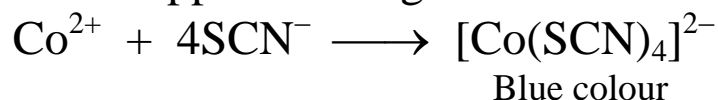
To a neutral solution of cobalt(II), add acetic acid, then a freshly prepared saturated solution of potassium nitrite, if the concentration of cobalt(II) in the test solution is high enough, a yellow precipitate of potassium hexanitritocobaltate(II), $K_3[Co(NO_2)_6] \cdot 3H_2O$ appears immediately. Otherwise, the mixture should either be slightly heated or the wall of the vessel should be rubbed with a glass rod.



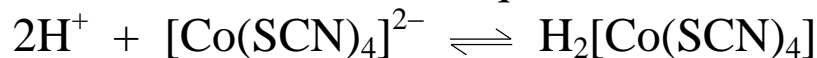
The reaction can also be used for testing for potassium and for nitrite ions. Nickel ions do not react if acetic acid is present.

(d) Ammonium thiocyanate test (Vogel reaction)

On adding ammonium thiocyanate to a neutral or acid solution of cobalt(II), a blue colour appears owing to the formation of tetrathiocyanatocobaltate(II) ions.



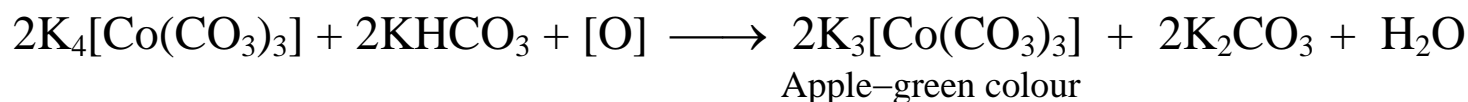
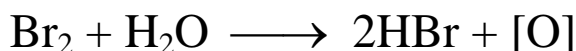
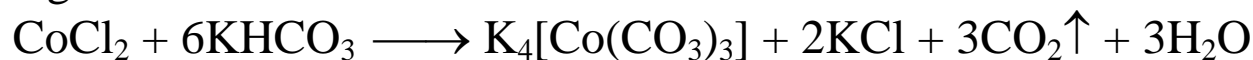
In amyl alcohol or diethyl ether is added, the free acid $H_2[Co(SCN)_4]$ is formed and dissolved by the organic solvent (distinction from nickel). The test is rendered more sensitive if the solution is acidified with concentrated hydrochloric acid, when the equilibrium



shifts towards the formation of the free acid, which then can be extracted with amyl alcohol or ether.

(e) $KHCO_3$ and Br_2 water

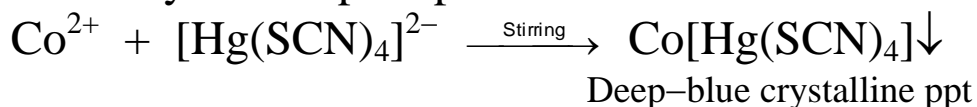
On addition of $KHCO_3$ and Br_2 water to a solution of Co^{2+} , the solution turns apple-green in colour.



QUALITATIVE ANALYSIS

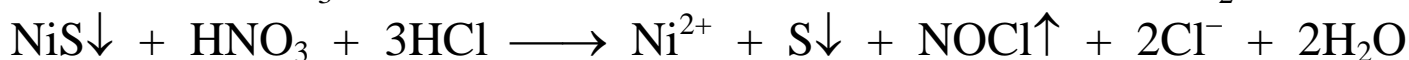
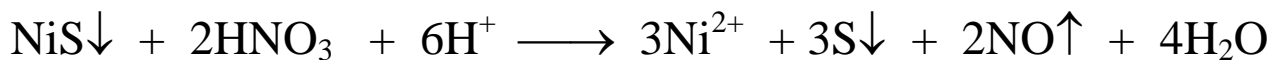
(f) Ammonium tetrathiocyanatomercurate(II)

With Co^{2+} ion, ammonium tetrathiocyanatomercurate(II) solution form a deep-blue crystalline precipitate.



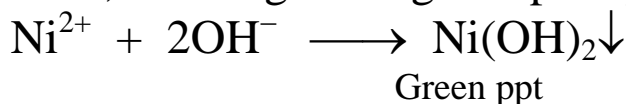
34. Nickel (II)

The black precipitate of NiS is insoluble in cold dilute HCl and in acetic acid but dissolves in hot concentrated nitric acid and in aquaregia with the separation of sulphur.

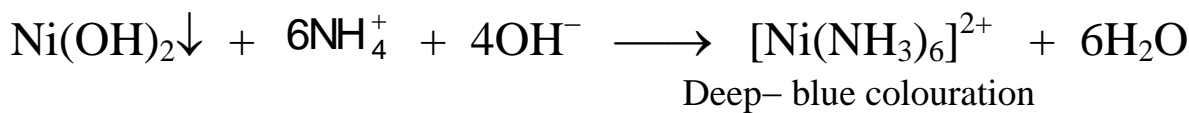
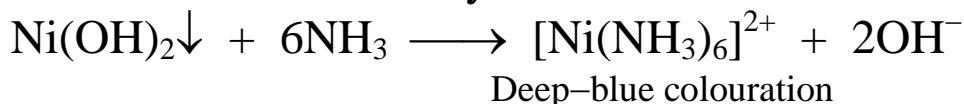


(a) Sodium hydroxide solution

With Ni^{2+} , NaOH gives a green precipitate of $\text{Ni}(\text{OH})_2$.

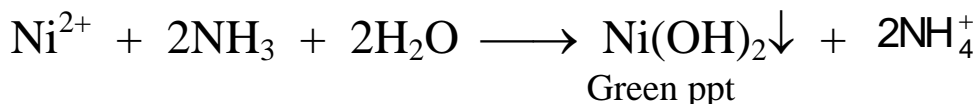


The precipitate is insoluble in excess reagent. The precipitate dissolves in ammonia and excess alkali hydroxide.

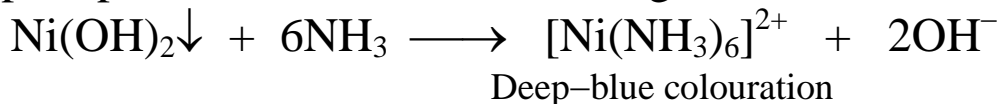


(b) Ammonia solution

With ammonia solution, Ni^{2+} give a green precipitate of nickel(II) hydroxide.



The precipitate dissolves in excess reagent and the solution turns deep blue.



If ammonium salts are present, no precipitation occurs, but the complex is formed immediately.

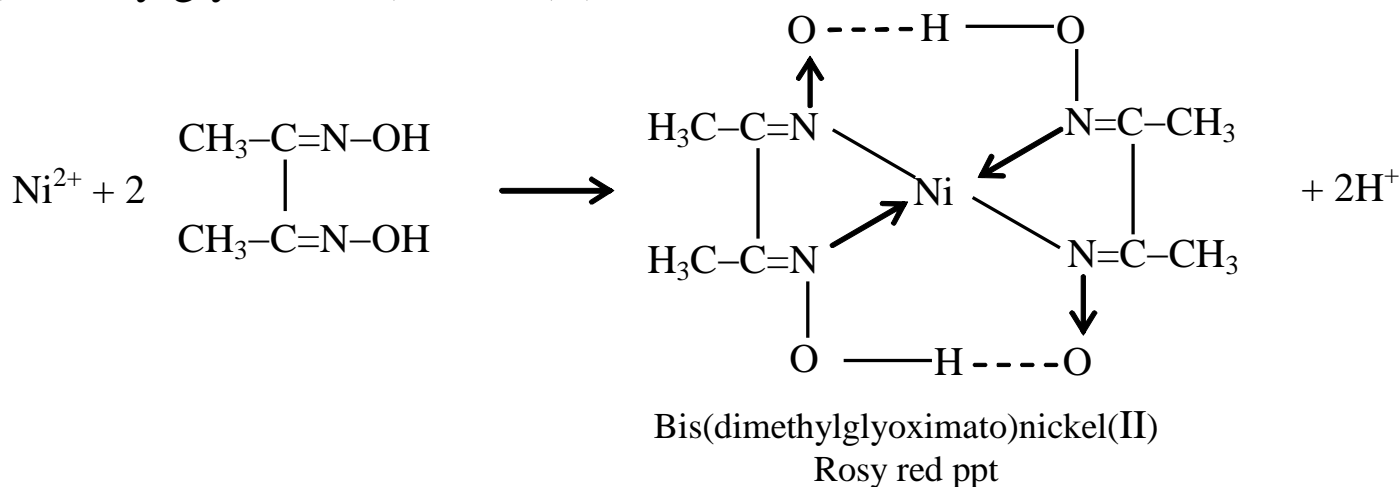
QUALITATIVE ANALYSIS

(c) Potassium nitrite solution

No precipitate is produced in the presence of acetic acid (difference from cobalt).

(d) Dimethylglyoxime reagent ($\text{C}_4\text{H}_8\text{O}_2\text{N}_2$)

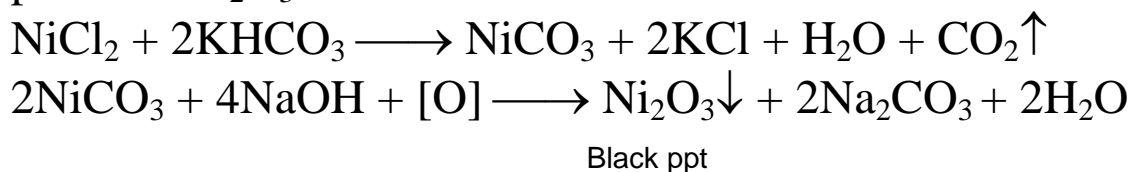
Ni^{2+} in presence of ammonia gives a rosy red precipitate of bis(dimethylglyoximate) nickel(II).



Iron(II) (red colouration), bismuth (yellow precipitate) and larger amounts of cobalt (brown colouration) interfere in ammoniacal solution.

(e) KHCO_3 , NaOH and Br_2 water

On addition of KHCO_3 , NaOH and Br_2 water to solution of Ni^{2+} , a black precipitate of Ni_2O_3 is formed.

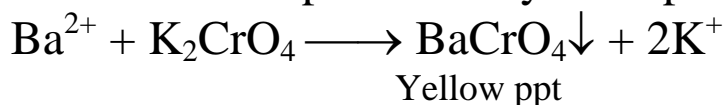


Group IV (Ba^{2+} , Sr^{2+} , Ca^{2+})

35. Barium (II)

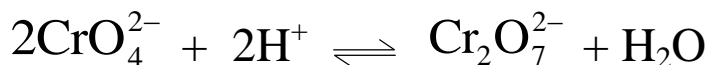
(a) Potassium chromate solution

Ba^{2+} ion in solution produces a yellow precipitate with K_2CrO_4 solution.



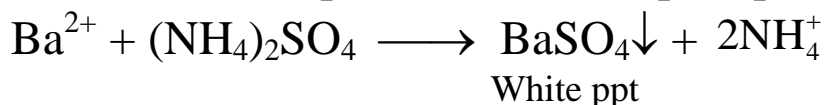
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The precipitate is insoluble in dilute acetic acid but readily soluble in mineral acids. Addition of acid to K_2CrO_4 solution causes the yellow colour of the solution to change to reddish–orange due to formation of $\text{Cr}_2\text{O}_7^{2-}$.

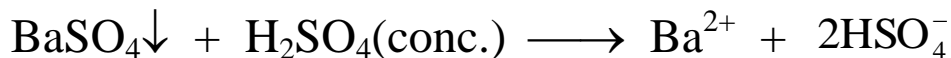


(b) Ammonium sulphate solution

Ba^{2+} ions in solution produces a white precipitate with $(\text{NH}_4)_2\text{SO}_4$ solution.

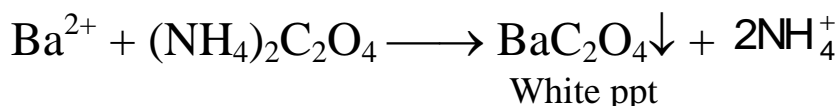


The precipitate is insoluble in dilute acids and in ammonium sulphate solution but appreciably soluble in boiling concentrated H_2SO_4 .



(c) Ammonium oxalate solution

Ba^{2+} ions in solution produces a white precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.

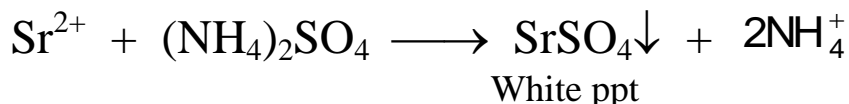


The precipitate readily dissolves in hot dilute acetic acid and in mineral acids.

36. Strontium (II)

(a) Ammonium sulphate solution

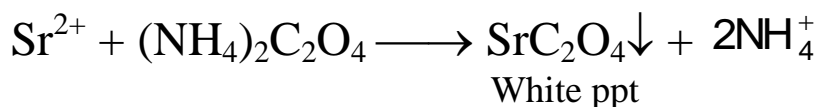
Sr^{2+} ions give a white precipitate with $(\text{NH}_4)_2\text{SO}_4$ solution.



The precipitate is slightly soluble in boiling hydrochloric acid.

(b) Ammonium oxalate solution

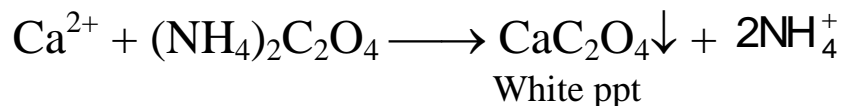
Sr^{2+} ions give a white precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.



The precipitate is insoluble in acetic acid but soluble in mineral acids.

37. Calcium (II)**(a) Ammonium oxalate solution**

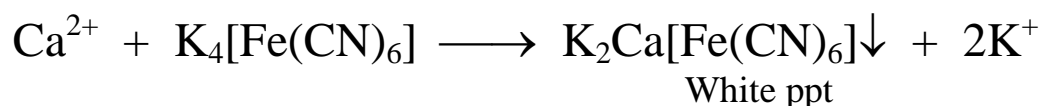
Ca^{2+} ions give a white precipitate with concentrated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution immediately.



The precipitate is insoluble in acetic acid but soluble in mineral acids.

(b) Potassium hexacyanoferrate(II) solution

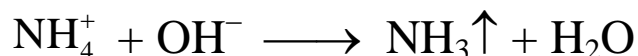
With potassium hexacyanoferrate(II) solution, Ca^{2+} ions give a white precipitate of a mixed salt.



The test can be used to distinguish calcium ion from strontium and barium ions.

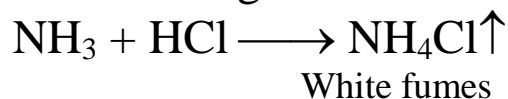
Group V (NH_4^+ , Na^+ , K^+ , Mg^{2+})**38. Ammonium****(a) Sodium hydroxide solution**

All ammonium salts on heating with alkali (NaOH) gives smell of NH_3 .

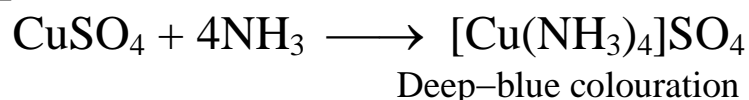


(i) The gas evolved can be detected by its smell.

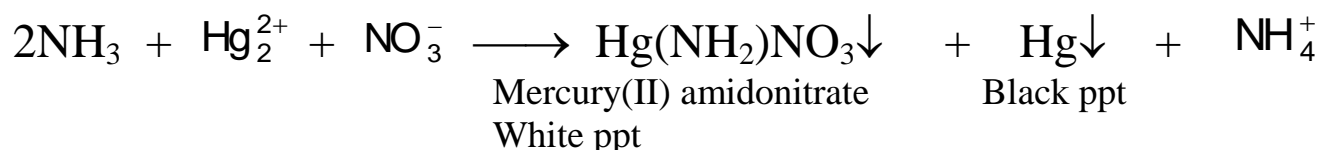
(ii) Gas evolved gives white fumes of NH_4Cl with HCl .



(iii) Paper soaked in CuSO_4 solution, becomes deep-blue by NH_3 due to the complex formation.



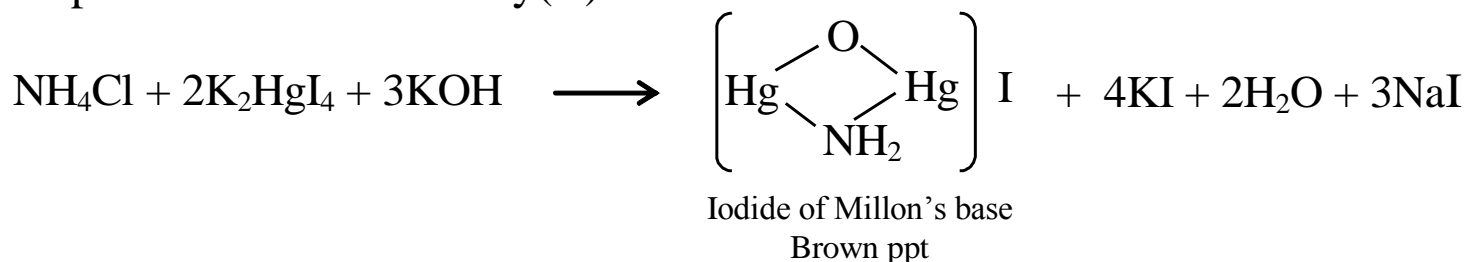
(iv) Gas can be identified by its ability to turn filter paper moistened with mercury(I) nitrate solution black.



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(b) Nessler's reagent

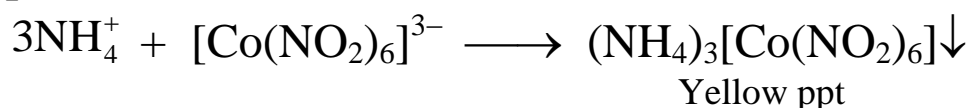
With Nessler's reagent (an alkaline solution of potassium tetraiodomercurate(II)), ammonium salts form a brown precipitate or brown or yellow colouration is produced depending on the amount of NH_4^+ ions present in the solution. The precipitate is a basic mercury(II) amido-iodine.



This test can detect even traces of NH_3 present in a sample.

(c) Sodium hexanitritocobaltate(III) solution

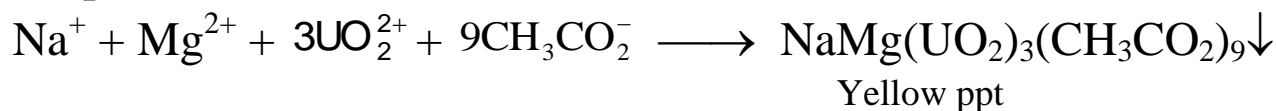
With NH_4^+ ions, sodium hexanitritocobaltate(III) solution gives a yellow precipitate of ammonium hexanitritocobaltate(III).



39. Sodium (Na^+)

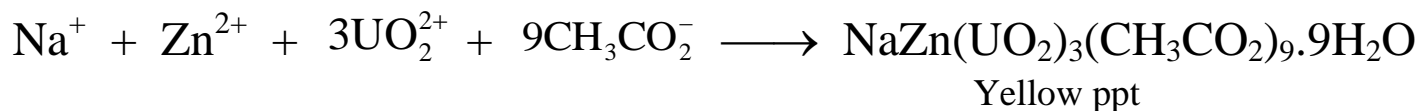
(a) Uranyl magnesium acetate solution

Sodium ions with uranyl magnesium acetate solution gives a yellow crystalline precipitate of sodium magnesium uranyl acetate $\text{NaMg}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}$ from concentrated solution. Addition of about one-third volume of alcohol helps the precipitation.



(b) Uranyl zinc acetate reagent

Na^+ ions on reaction with uranyl zinc acetate solution gives a yellow crystalline precipitate of sodium zinc uranyl acetate, $\text{NaZn}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}$.

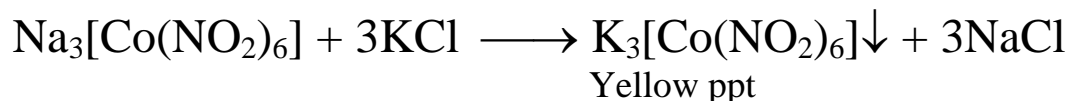


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40. Potassium (K^+)

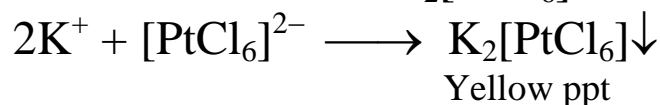
(a) Sodium hexanitritocobaltate(III) solution

Potassium salts gives yellow precipitate with sodium hexanitritocobaltate(III) solution.



(b) Hexachloroplatinic(IV) acid reagent

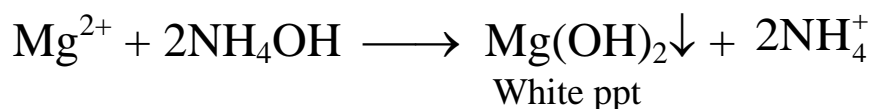
Yellow precipitate of potassium hexachloroplatinate(IV) is obtained by the reaction of K^+ ions with $H_2[PtCl_6]$.



41. Magnesium (II)

(a) Ammonia solution

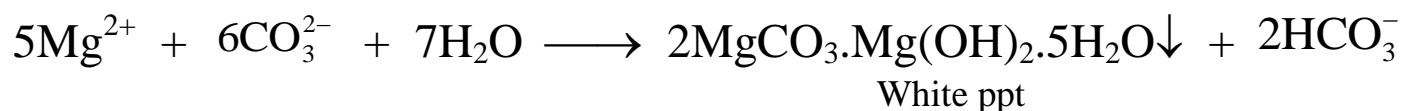
Mg^{2+} gives white gelatinous precipitate of magnesium hydroxide on reaction with ammonium hydroxide,



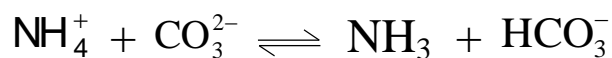
The precipitate obtained is sparingly soluble in water but readily soluble in ammonium salts.

(b) Ammonium carbonate solution

Mg^{2+} reacts with ammonium carbonate solution in the absence of NH_4^+ salts to give a white precipitate of basic magnesium carbonate.



In the presence of NH_4^+ salts no precipitation occurs, because the equilibrium

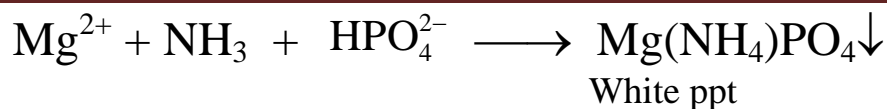


is shifted towards the formation of HCO_3^- ions.

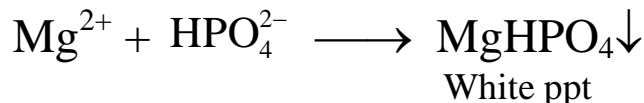
(c) Disodium hydrogen phosphate solution

With disodium hydrogen phosphate solution, Mg^{2+} gives a white crystalline precipitate magnesium ammonium phosphate in the absence of NH_4Cl and ammonia solution.

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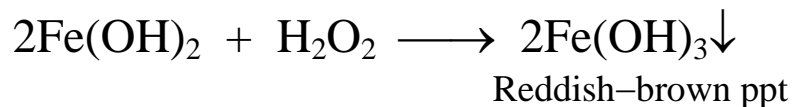
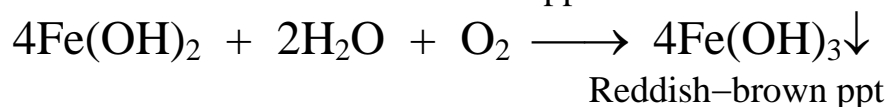
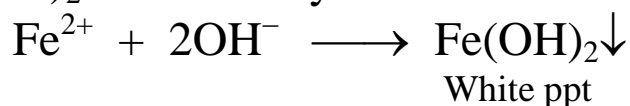
A white flocculent precipitate of magnesium hydrogen phosphate (MgHPO_4) is obtained in neutral solutions.



42. Iron (II)

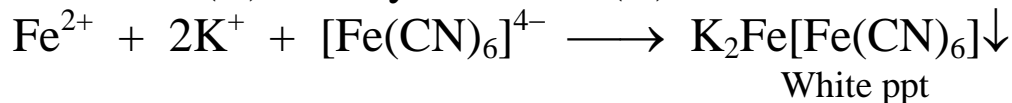
(a) Sodium hydroxide solution

With sodium hydroxide, Fe^{2+} forms a white precipitate of iron(II) hydroxide, $[\text{Fe}(\text{OH})_2]$ in the complete absence of air, insoluble in excess but soluble in acids. Upon exposure to air, iron(II) hydroxide is rapidly oxidized, yielding ultimately reddish-brown iron(III) hydroxide. Under ordinary conditions, it appears as a dirty-green precipitate. The addition of hydrogen peroxide to $\text{Fe}(\text{OH})_2$ immediately oxidizes it to iron(III) hydroxide.



(b) Potassium hexacyanoferrate(II) solution

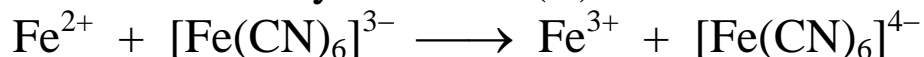
With potassium hexacyanoferrate(II) solution, Fe^{2+} forms a white precipitate of potassium iron(II) hexacyanoferrate(II) in the absence of air.



Under ordinary atmospheric conditions, a pale-blue precipitate is obtained.

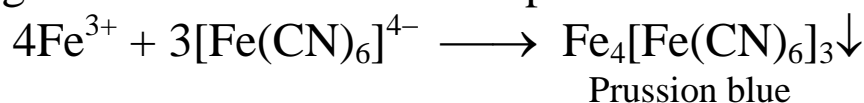
(c) Potassium hexacyanoferrate(III) solution

With potassium hexacyanoferrate(III) solution, a dark-blue precipitate is obtained. First hexacyanoferrate(III) ions oxidise iron(II) to iron(III) and itself get reduced to hexacyanoferrate(II).



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Fe^{3+} and $[\text{Fe}(\text{CN})_6]^{4-}$ ions combine to give a precipitate called Turnbull's blue, which is same as Prussian blue. Earlier Turnbull's blue and Prussian blue were thought to be two different complexes.



The identical composition and structure of Turnbull's blue and Prussian blue has recently been proved by Mossbauer spectroscopy.

(d) Ammonium thiocyanate solution

With ammonium thiocyanate solution, no colouration is obtained with pure iron(II) salts (distinction from(III) ions).

(e) Dimethylglyoxime reagent

With dimethylglyoxime reagent soluble red iron(II) dimethyl glyoxime is obtained in ammonical solution. Iron(III) salts give no colouration, but nickel, cobalt and large quantities of copper salts interfere and must be absent.

Some Important Observations During Qualitative Analysis

Residue and its Colour after Heating

S. No.	RESIDUE	COLOUR
(i)	ZnO	Yellow (hot) and white (cold)
(ii)	PbO	Reddish brown (hot) and yellow (cold)
(iii)	HgO, Pb ₃ O ₄	Black (hot) and red (cold)
(iv)	Fe ₂ O ₃	Black (hot) and red brown (cold)

Flame Test

Compounds of certain metals are volatilised in a non-luminous Bunsen burner flame and impart characteristic colours to the flame. The chlorides are among the most volatile compounds and these are prepared *in situ* by mixing the compound with a little concentrated hydrochloric acid before carrying out the

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test. A thin platinum wire about 5 cm long and 0.03–0.05 mm diameter, fused into the end of a glass rod (which serves as a handle) is employed for the flame test. This is first thoroughly cleaned by dipping it into concentrated hydrochloric acid contained in a watch glass and then heating it in the fusion zone of the Bunsen burner flame; the wire is clean when it imparts no colour to the flame. The wire is dipped into concentrated hydrochloric acid on a watch glass, then into a little of the substance being investigated so that a little amount of it adheres to the wire. It is then introduced into the lower oxidizing zone of the flame and the colour imparted to the flame is observed. The colours imparted to the flame by salts of different metals are shown in table given below.

Metal ion	Colour observed
Sodium	Persistent golden–yellow flame
Potassium	Violet (lilac) flame
Lithium	Carmin–red flame
Calcium	Brick–red flame
Strontium	Crimson flame
Barium	Yellowish–green(apple green) flame
Borates, copper	Green flame
Lead, arsenic, antimony, bismuth	Blue flame (wire slowly corroded)

Borax Bead Test

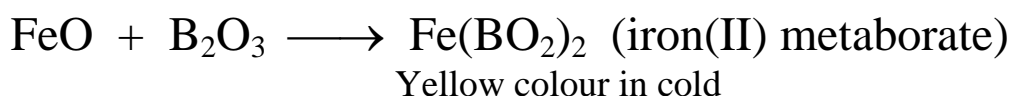
Platinum wire is also used for the borax bead test. The free end of the platinum wire is coiled into a small loop through which an ordinary matchstick will barely pass. The loop is heated in the Bunsen burner flame until it is red hot and then quickly dipped into powdered borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. 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.



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The bead is 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 the substance as otherwise the bead will become dark and opaque in the subsequent heating. The bead and adhering substance are heated in the lower oxidizing flame, allowed to cool and then the colour is observed.

Characteristic coloured beads are produced with salts of copper, iron, chromium, manganese, cobalt and nickel. The coloured borax beads are due to the formation of coloured borates.



	Oxidizing flame	
Metal	Hot	Cold
Copper	Green	Blue
Iron	Yellow–brown	Yellow
Chromium	Yellow	Green
Manganese	Violet (amethyst)	Amethyst
Cobalt	Blue	Blue
Nickel	Violet	Reddish–brown

Coloured Compounds

In dry state:

Colour	Compounds/ions
Black	(a) Sulphides: Ag_2S , PbS , HgS , CuS , NiS , CoS (b) Oxides: FeO , Fe_3O_4 , CuO , Ag_2O , Ni_2O_3 , Co_2O_3 , MnO
Brown	Dark: Fe_2O_3 , PbO_2 , Cu_2O , CdO , SnS , Fe(OH)_3 , SnS , Ag_2O , Bi_2S_3 , CuCrO_4 Light: MnCO_3

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Red	Pb ₃ O ₄ (red lead) HgI ₂ , HgO, Cu ₂ O
Pink	Co(II) salt, Mn(II) salt
Orange	Sb ₂ S ₃ , Sb ₂ S ₅ , Dichromate (Cr ₂ O ₇ ²⁻)
Green	Dark: Cr(III) salts Light: Ni(II) salts, Mohr's salt, Fe(II) salts, CuCl ₂
Yellow	Fe(III) salts ; Chromate (CrO ₄ ²⁻), Ferrocyanide [Fe(CN) ₆] ⁴⁻ , CdS, As ₂ S ₃ , PbI ₂ , AgI, SnS ₂ , NiCl ₂ , hot ZnO.
Blue	Cu(II) salts (Hydrated), anhydrous Co(II) salt
Purple	Permanganate (MnO ₄ ⁻), Solid Iodine
Buff Colour	MnS

In solution:

Colour	Ions
Pink	Co ²⁺ (II), Mn ²⁺ (II)
Orange	dichromate ion (Cr ₂ O ₇ ²⁻)
Green	Cr(III), Ni(II), Fe(II) In decreasing order of intensity of colour
Yellow	Chromate (CrO ₄ ²⁻), Fe(III), Ferrocyanide [Fe(CN) ₆] ⁴⁻
Blue	Cu(II)
Purple	MnO ₄ ⁻

Colour of Gases

Coloured gases	Colourless gases
1. Reddish brown: Br ₂ and NO ₂	H ₂ , CO, CO ₂ , N ₂ , N ₂ O, NO, NH ₃ , SO ₂ , HCl, H ₂ O, O ₂ , H ₂ S, PH ₃
2. White: SO ₃	
3. Greenish & yellow: F ₂ and Cl ₂	
4. Violet (Purple): I ₂	
5. Light Blue: O ₃	

Fundamental Solved Examples

Example 1.

- (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH_4OH .
- (ii) (B) on treatment with hydrochloric acid and KClO_3 gives (A).
- (iii) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).
- (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.
- (v) The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green colour of compound (E) is formed. No change is observed on heating.

Identify (A) to (E) and give chemical equations for reactions at steps (i) to (v).

Solution:

The compound (A) is a cobalt(II) salt (CoCl_2).

- (i)
$$\underset{\text{(A)}}{\text{CoCl}_2} + 2\text{NH}_4\text{OH} + \text{H}_2\text{S} \longrightarrow \underset{\text{Black (B)}}{\text{CoS}\downarrow} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$$
- (ii)
$$\text{CoS}\downarrow + 2\text{HCl} + \text{O (from KClO}_3\text{)} \longrightarrow \text{CoCl}_2 + \text{H}_2\text{O} + \text{S}$$
- (iii)
$$\text{CoCl}_2 + 2\text{KCN} \longrightarrow \underset{\text{Buff coloured ppt}}{\text{Co(CN)}_2\downarrow} + 2\text{KCl}$$
- (iv)
$$2\text{K}_4[\text{Co(CN)}_6] + \text{H}_2\text{O} + \text{O (from air)} \longrightarrow \underset{\text{(D)}}{2\text{K}_3[\text{Co(CN)}_6]} + 2\text{KOH}$$
- (v)
$$\begin{aligned} \text{CoCl}_2 + 6\text{NaHCO}_3 &\longrightarrow \text{Na}_4[\text{Co(CO}_3\text{)}_3] + 2\text{NaCl} + 3\text{CO}_2 + 3\text{H}_2\text{O} \\ 2\text{Na}_4[\text{Co(CO}_3\text{)}_3] + \text{H}_2\text{O} + \text{O} &\longrightarrow \underset{\text{(E)}}{2\text{Na}_3[\text{Co(CO}_3\text{)}_3]} + 2\text{NaOH} \end{aligned}$$

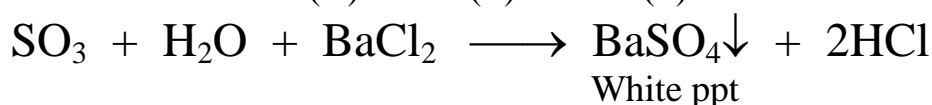
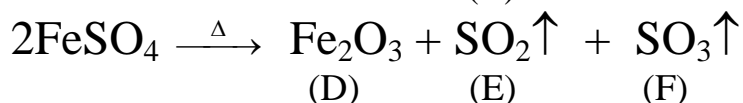
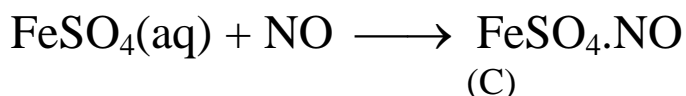
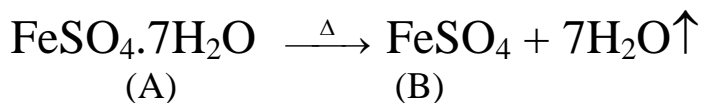
Example 2:

A hydrated metallic salt (A), light green in colour, on careful heating gives a white anhydrous residue (B). (B) is soluble in water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) gives a brown residue (D) and a mixture of two gases (E) and (F) upon strong heating. The gases when

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passed through an acidified BaCl_2 solution gave a white precipitate. Identify (A), (B), (C), (D), (E) and (F).

Solution:

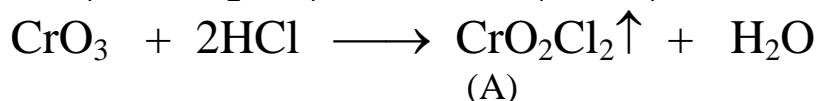
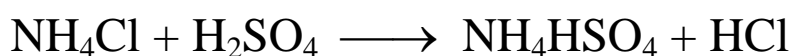
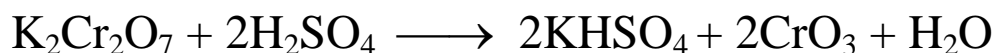


Example 3:

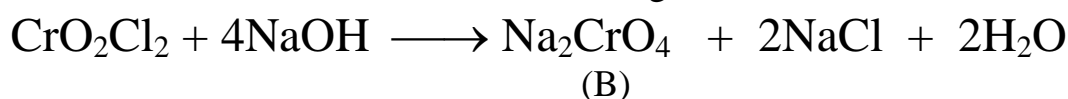
When a crystalline compound (X) is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 , a reddish-brown gas (A) is evolved. On passing (A) into caustic soda, a yellow coloured solution of (B) is obtained. Neutralizing the solution of (B) with acetic acid and on subsequent addition of lead acetate, a yellow precipitate of (C) is obtained. When (X) is heated with NaOH , a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish-brown precipitate (D) is formed. Identify (A), (B), (C), (D) and (X). Write the equation of reactions involved.

Solution:

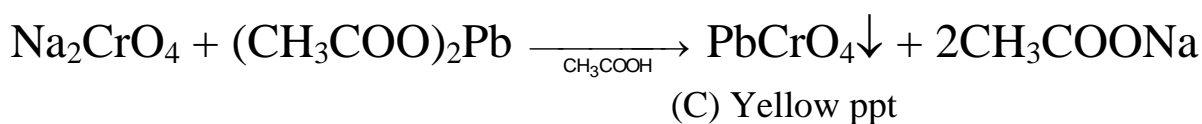
The given information in the question infers that compound (X) should be NH_4Cl .



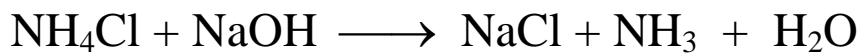
Reddish-brown gas



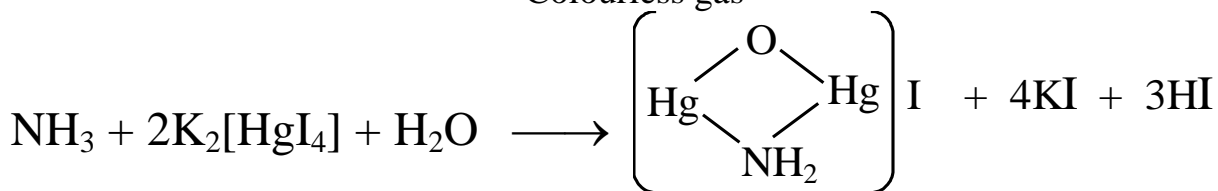
Yellow coloured solution



QUALITATIVE ANALYSIS



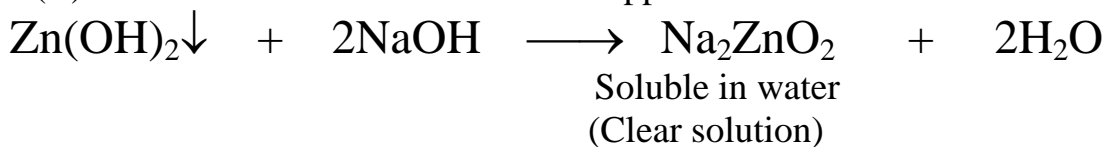
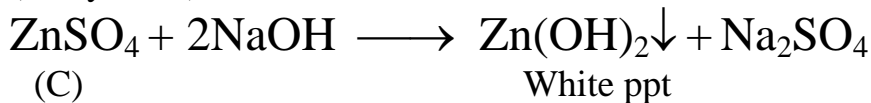
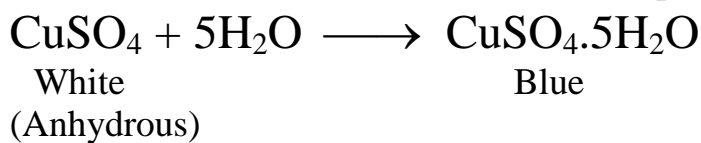
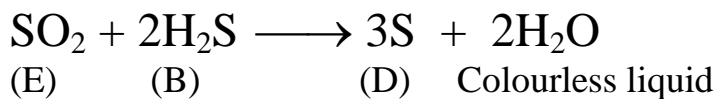
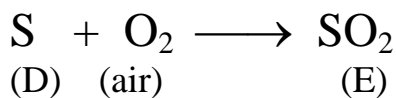
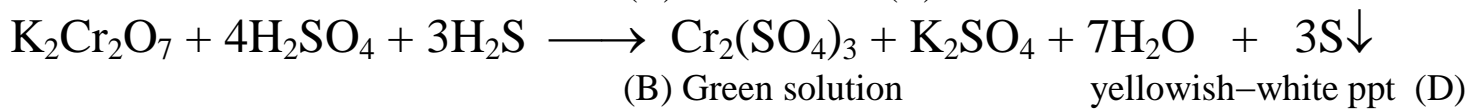
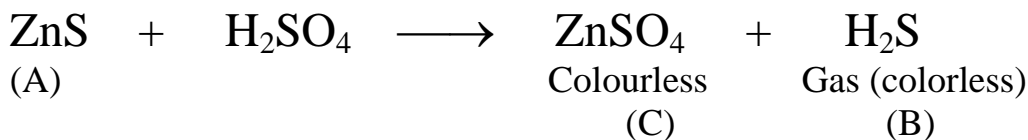
Colourless gas



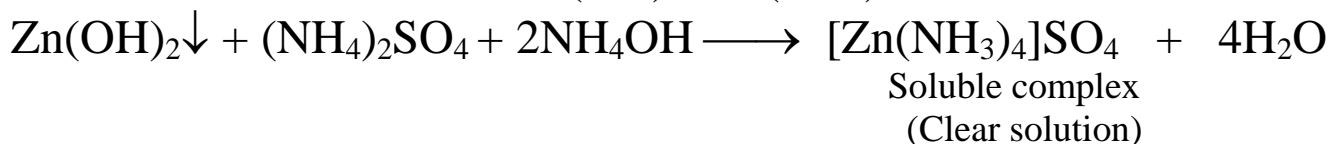
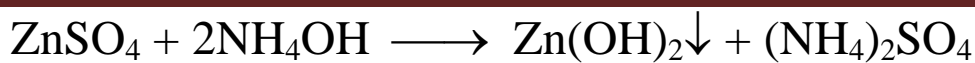
Example 4:

A white substance (A) reacts with dilute H_2SO_4 to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E), which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to (C) produces first a white precipitate, which dissolves in the excess of respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D), (E) and write the equations of the reactions involved.

Solution:



QUALITATIVE ANALYSIS



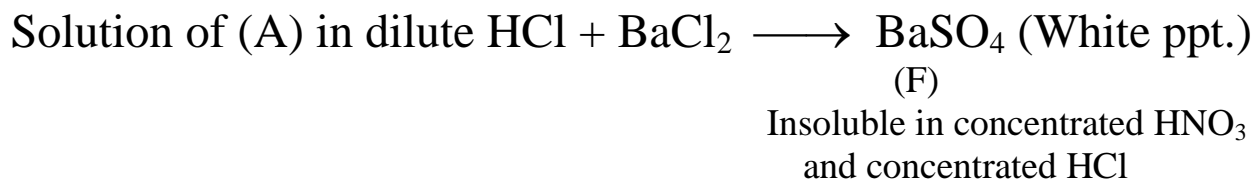
Example 5:

- (i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).
- (ii) The solution of (B) in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound (C).
- (iii) The aqueous solution of (A) on treatment with excess of NaOH and bromine water gives a compound (D).
- (iv) A solution of (D) in concentrated HNO_3 on treatment with lead peroxide at boiling temperature produced a compound (E), which was of the same colour as that of (C).
- (v) A solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (F), which was insoluble in concentrated HNO_3 and concentrated HCl .

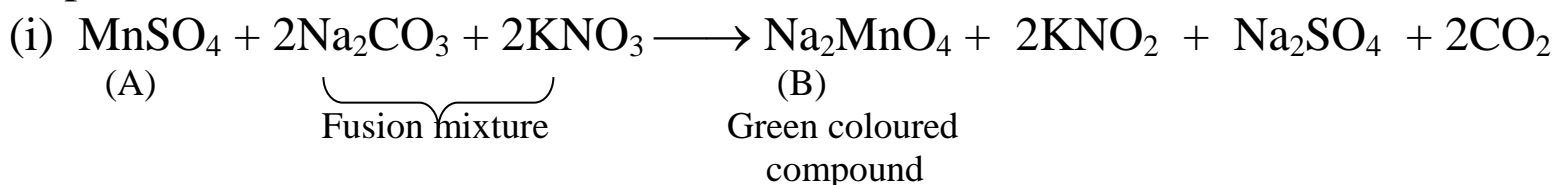
Identify (A) to (F) and give balanced chemical equations for the reactions at steps (i) to (v).

Solution:

The compound (A) is a sulphate as its solution in dilute HCl on treatment with barium chloride solution gives a white precipitate of barium sulphate (F), which is insoluble in concentrated HNO_3 and concentrated HCl .



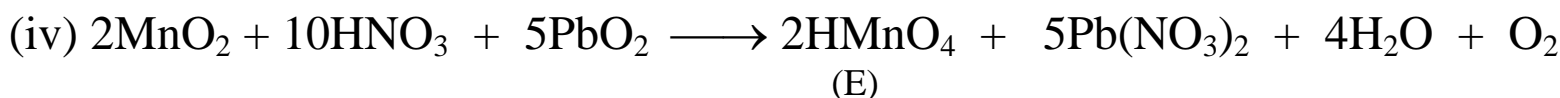
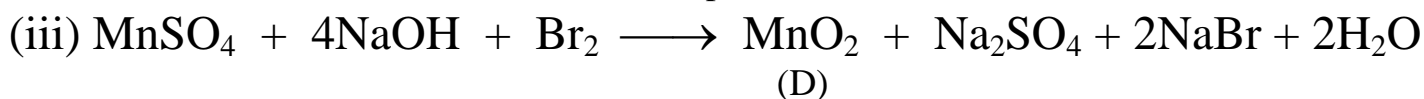
From reactions (i) and (ii), it is clear that the compound (A) is manganese sulphate.



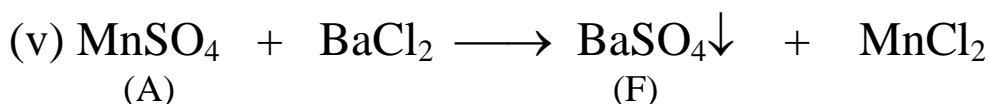
QUALITATIVE ANALYSIS



Pink coloured
compound



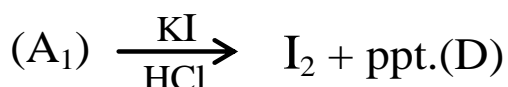
Pink coloured solution



White ppt

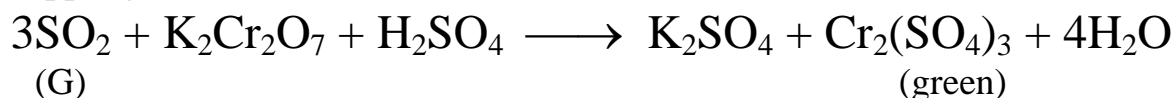
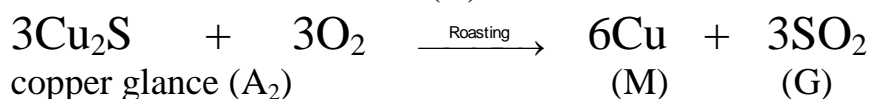
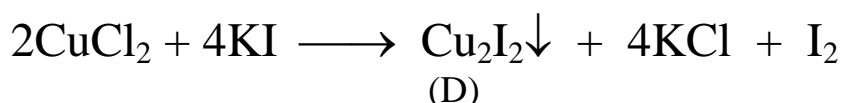
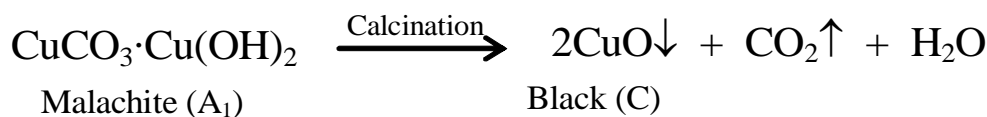
Example 6:

Two ores of the same metal (M) are (A₁) and (A₂).



Identify (M), (A₁), (A₂), (C), (D) and (G).

Solution:



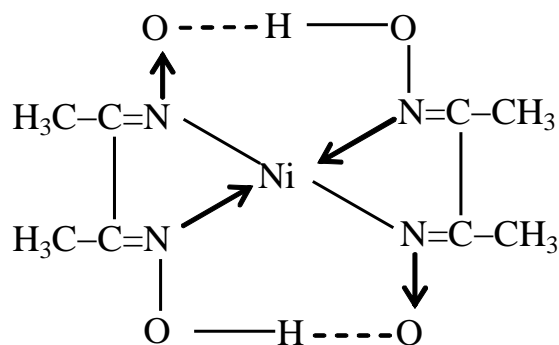
QUALITATIVE ANALYSIS

Example 7.

Nickel chloride is mixed with dimethyl glyoxime. When ammonium hydroxide is slowly added, a shining red precipitate is formed.

- Give the structure of complex showing hydrogen bonds.
- Give the charge and the state of hybridization of the central metal ion.
- Predict the magnetic behaviour of the complex.

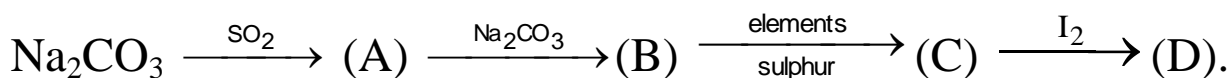
Solution:



- The charge on Ni in the complex is +2.
- The hybridisation of Ni in the complex is dsp^2 and its structure is square planar.
- The complex is diamagnetic.

Bis(dimethylglyoximate)nickel(II)

Example 8:



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

Solution:

(A) : NaHSO_3 (B) : Na_2SO_3
(C) : $\text{Na}_2\text{S}_2\text{O}_3$ (D) : $\text{Na}_2\text{S}_4\text{O}_6$

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

Example 9:

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

- Mixture gives black precipitate C on passing H_2S gas in acidic medium.
- C is soluble in aqua-regia and on adding SnCl_2 , it gives white precipitate, which finally turns to greyish black precipitate D.

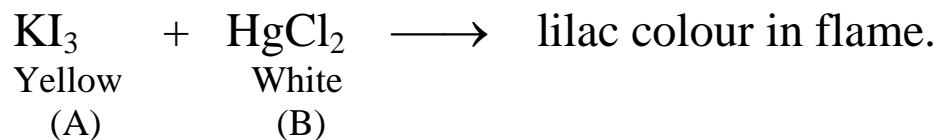
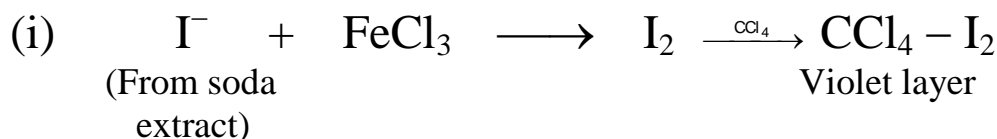
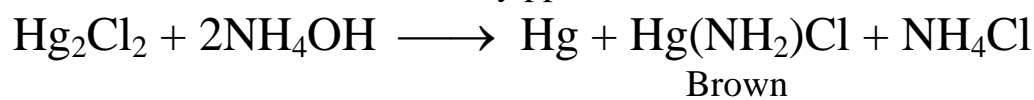
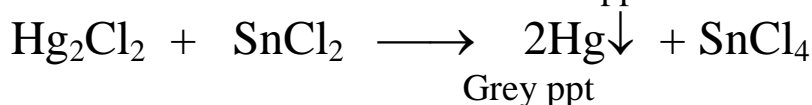
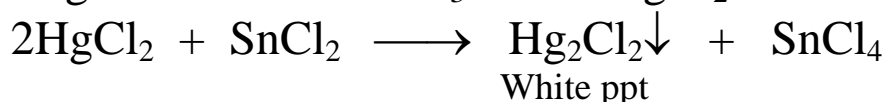
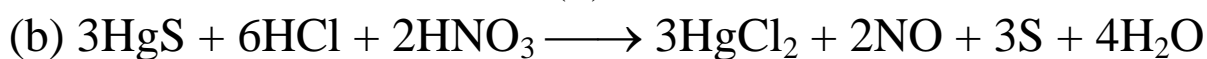
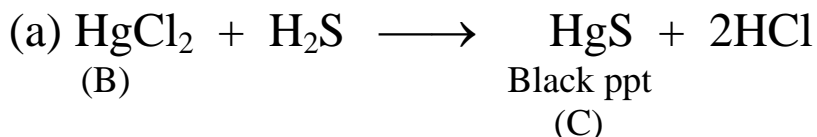
The white precipitate on treatment with NH_4OH gives a brown precipitate.

QUALITATIVE ANALYSIS

- (i) The sodium carbonate extract of the salt A with $\text{CCl}_4/\text{FeCl}_3$ gives a violet layer.
- (ii) The sodium carbonate extract of the salt A gives yellow precipitate in AgNO_3 solution, which is insoluble in NH_3 . Identify A and B and the precipitate C and D.

Solution:

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



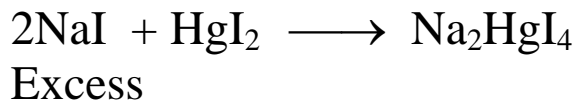
Example 10.

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

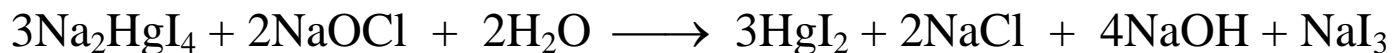
QUALITATIVE ANALYSIS

Solution:

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



The Na_2HgI_4 on addition of NaOCl , oxidises as:



Thus, colour of partially soluble HgI_2 is restored.

Example 11.

Two solid laboratory reagents (A) and (B) give the following reactions:

Compound (A)

- (i) On strongly heating it gives two oxides of sulphur.
- (ii) On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained, which starts turning brown on exposure to air.

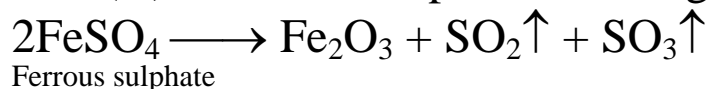
Compound (B)

- (iii) It imparts green colour to the flame.
- (iv) Its solution does not give a precipitate on passing H_2S .
- (v) When it is heated with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 , a red gas is evolved. Gas when passed in an aqueous solution of NaOH , turns it yellow.

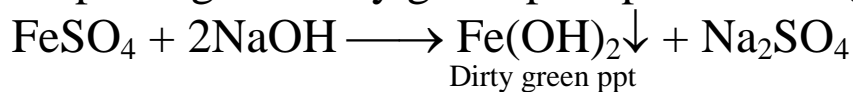
What are (A) and (B)?

Solution:

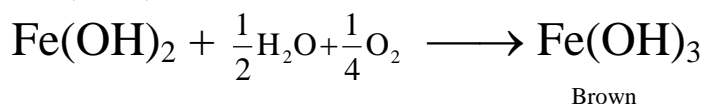
Compound (A) is ferrous sulphate, which give SO_2 and SO_3 on heating



Ferrous sulphate gives dirty green precipitate of $\text{Fe}(\text{OH})_2$ with aqueous NaOH .



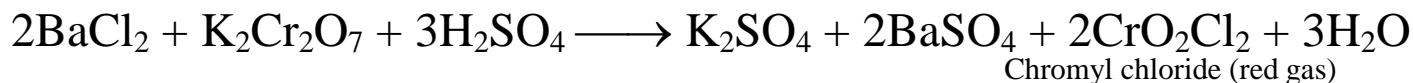
$\text{Fe}(\text{OH})_2$ turns brown on oxidation, when exposed to atmosphere.



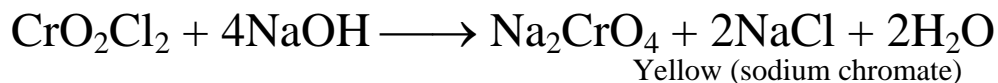
QUALITATIVE ANALYSIS

Compound (B) is BaCl_2 which imparts green colour to flame and does not give any precipitate with H_2S .

BaCl_2 forms chromyl chloride, when treated with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 .



Chromyl chloride forms, yellow coloured Na_2CrO_4 with aqueous NaOH .



Example 12.

A light green crystalline (X) compound responds to the following test:

- (i) Its aqueous solution gives a brown precipitate or colouration with alkaline $\text{K}_2[\text{HgI}_4]$ solution.
- (ii) Its aqueous solution gives a blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution.
- (iii) Its solution in hydrochloric acid gives a white precipitate with BaCl_2 solution. Identify the ions present and suggest the formula of the compound, (X).

Solution:

- (i) K_2HgI_4 is called Nessler's reagent. it is specially used to test the presence of NH_4^+ ; giving brown precipitate. Hence, compound contains NH_4^+ .
- (ii) With $\text{K}_3[\text{Fe}(\text{CN})_6]$, only Fe^{2+} ion gives blue colour called turnbull's/prussion blue.
- (iii) BaCl_2 gives white precipitate with SO_4^{2-} ions. Hence, compound (X) would be Mohr' salt. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ which contains all the three ions.

Example 13.

An unknown solid mixture contains one or two of the following: CaCO_3 , BaCl_2 , AgNO_3 , Na_2SO_4 , ZnSO_4 and NaOH . The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to above solution, a precipitate is formed, which dissolves with further addition of the acid. What is/are present in the solid mixture?

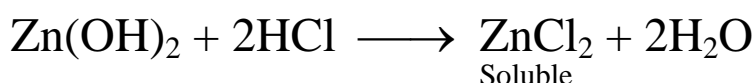
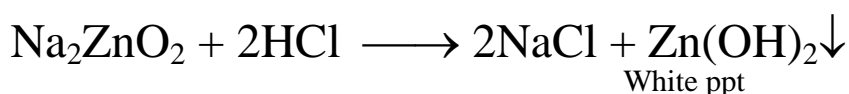
QUALITATIVE ANALYSIS

Solution:

- (i) Mixture gives pink colour with phenolphthalein, hence it should contain NaOH.
- (ii) Aqueous solution gives precipitate with dilute HCl, which dissolves in excess HCl. It means that compound is zinc salt.

Thus, the solid mixture should be of NaOH and ZnSO₄.

Reactions involved are:

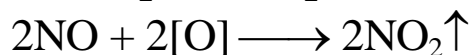
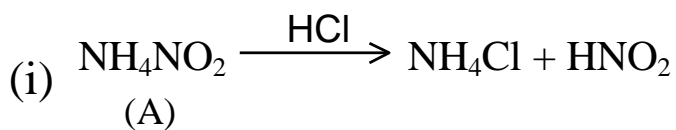


Example 14.

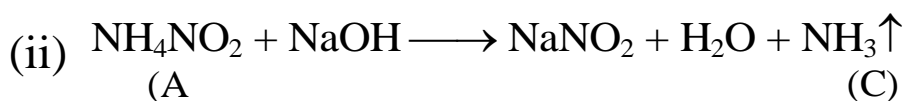
A colourless solid (A) liberates a brown gas (B) on acidification, a colourless alkaline gas (C) on treatment with NaOH and a colourless non-reactive gas (D) on heating. If heating of the solid is continued, it completely disappears. Identify the compounds (A) to (D).

Solution:

Alkaline gas (C) with NaOH indicate that solid should be ammonium salt. Heating the salt, a colourless non-reactive gas (D) is formed. The gas (D) may be nitrogen. The compound may thus be NH₄NO₂. Reactions involved are as follows:



(B) Brown gas



QUALITATIVE ANALYSIS



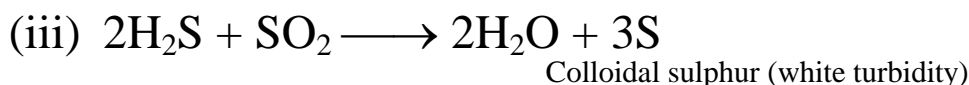
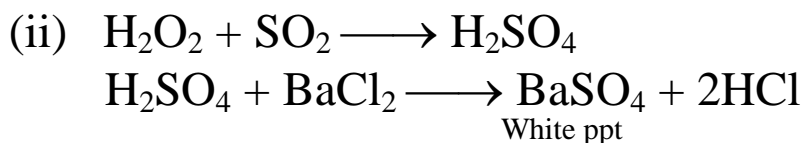
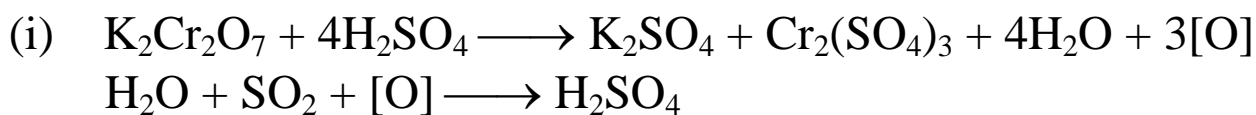
Example 15.

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

- (i) It decolourizes an acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
 - (ii) On boiling it with H_2O_2 , cooling it and then adding an aqueous solution of BaCl_2 a precipitate insoluble in dil. HCl is obtained.
 - (iii) On passing H_2S in the solution, a white turbidity is obtained.
- Identify the compound (X).

Solution:

The reactions given in (i), (ii) and (iii) may be explained if we consider the gas (X) to be SO_2 .



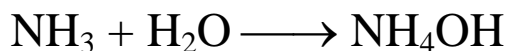
Example 16.

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

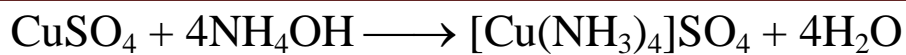
- (i) It turns red litmus blue.
- (ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
- (iii) On addition of FeCl_3 solution, a brown precipitate, soluble in dilute HNO_3 is obtained. Identify the compound (X).

Solution:

Gas (X) is soluble in water forming basic solution because it turns red litmus blue. Hence, the gas may be NH_3 .

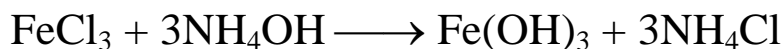


QUALITATIVE ANALYSIS



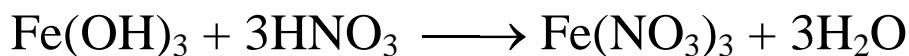
(Tetra-amine
cupric sulphate)
Deep blue complex

Ferric chloride gives brown precipitate of $\text{Fe}(\text{OH})_3$.



Brown ppt

Brown precipitate is soluble in HNO_3



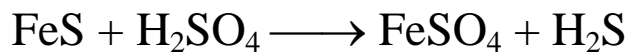
Soluble salt

Example 17.

A black coloured compound (A) on reaction with dil. H_2SO_4 gives a gas (B) which on passing in a solution of an acid (C) gives a white turbidity (D). Gas (B) when passed in acidified solution of (E) gives a precipitate (F) soluble in dilute HNO_3 . After boiling this solution when excess of NH_4OH is added, a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate coloured precipitate (H) is obtained. On addition of an aqueous solution of BaCl_2 to an aqueous solution of (E), a white precipitate insoluble in HNO_3 is obtained. Identify the compounds (A) to (H).

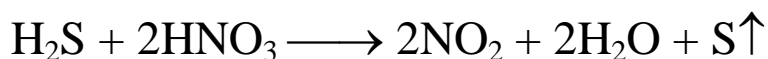
Solution:

Reactions involved may be given as



Ferrous sulphide
Black (A)

(B)



(B)

(C)

Colloidal sulphur
(D) (Turbid)



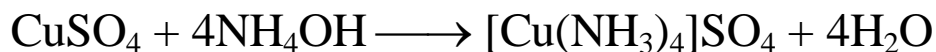
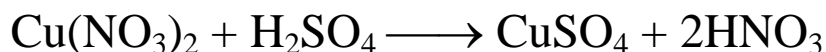
(E)

Black ppt
(F)

QUALITATIVE ANALYSIS

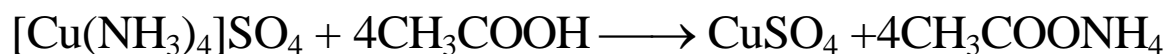


(F)

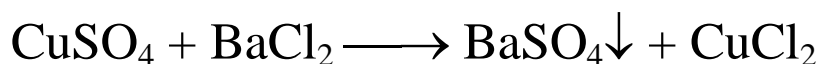


(Deep blue)

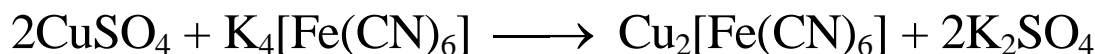
(G)



(E)



White ppt
insoluble in HNO_3



Cupric ferrocyanide
(Chocolate precipitate)

Example 18.

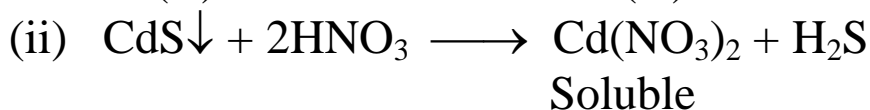
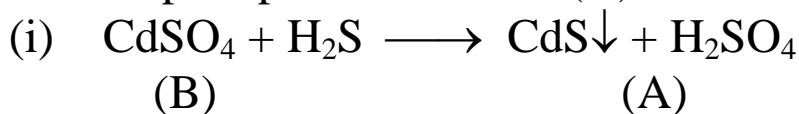
- (i) The yellow coloured precipitate of compound (A) is formed on passing H_2S through a neutral solution of salt (B).
- (ii) (A) is soluble in hot dilute HNO_3 but insoluble in yellow ammonium sulphide.
- (iii) The solution of (B) on treatment with small quantity of NH_3 gives white precipitate which becomes soluble in excess of it forming a compound (C).
- (iv) Solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).
- (v) The solution of (D) on treatment with H_2S gives (A).
- (vi) The solution of (B) in dilute HCl when treated with solution of BaCl_2 gives white precipitate of compound (E) which is insoluble in conc. HNO_3 .

Identify the compounds (A) to (E).

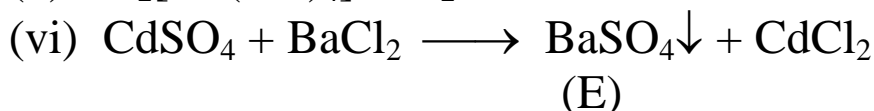
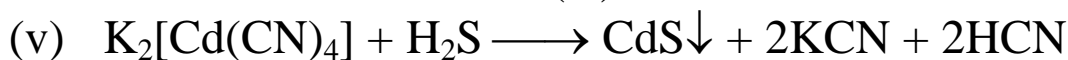
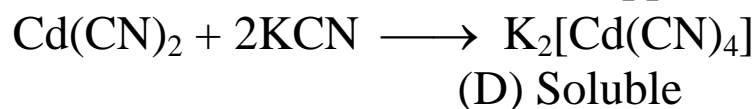
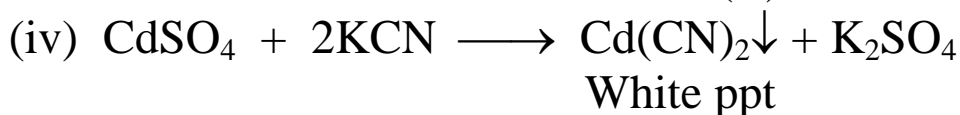
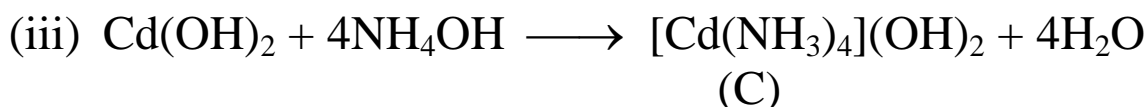
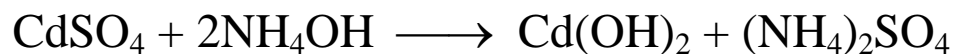
QUALITATIVE ANALYSIS

Solution:

Yellow precipitate of CdS is (A).



$\text{CdS}\downarrow \longrightarrow$ Insoluble in yellow ammonium sulphide



White precipitate of BaSO₄ is insoluble in HNO₃.

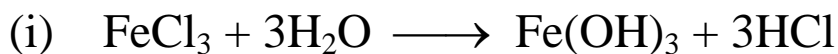
Example 19.

- (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.
- (ii) (A) on treatment with an excess of NH₄SCN gives a red coloured compound (B) and on treatment with a solution of K₄[Fe(CN)₆] gives a blue coloured compound (C).
- (iii) (A) on heating with excess of K₂Cr₂O₇ in presence of concentrated H₂SO₄ evolves deep red vapours of (D).
- (iv) On passing the vapours of (D) into a solution of NaOH and then adding the solutions of acetic acid and lead acetate, a yellow precipitate of compound (E) is obtained.

Identify the compounds (A) to (E) and give chemical equations for the reactions at steps (ii) to (iv).

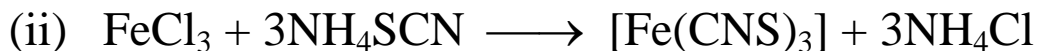
QUALITATIVE ANALYSIS

Solution:



(A)

Solution becomes acidic due to hydrolysis. FeCl_3 sublimes at 300°C .

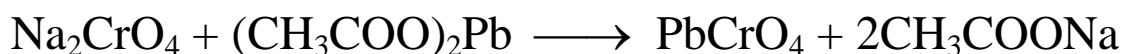
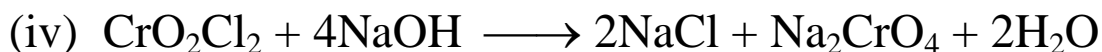


(C) Blood-red



(D)

Chromyl chloride



(E) Yellow ppt

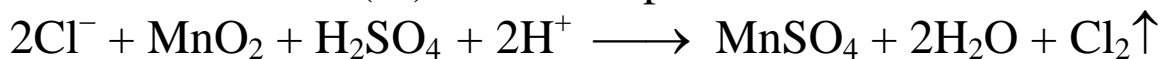
Example 20.

A mixture of two salts was treated as follows:

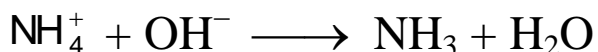
- (i) The mixture was heated with manganese dioxide and concentrated H_2SO_4 , when yellowish green gas was liberated.
- (ii) The mixture on heating with NaOH solution gave a gas, which turned red litmus blue.
- (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with NH_4CNS .
- (iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.
- Identify the two salts. Give ionic reactions involved in the tests (i), (ii) and (iii).

Solution:

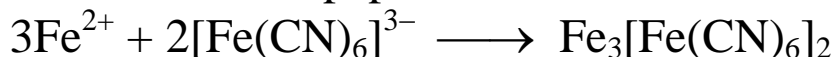
Test (ii) and (iv) show the presence of ammonium radical. Test (i) shows the presence of Cl^- ion and test (iii) shows the presence of Fe^{2+} and Fe^{3+} ion.



Yellowish-green



NH_3 turns red litmus paper blue.



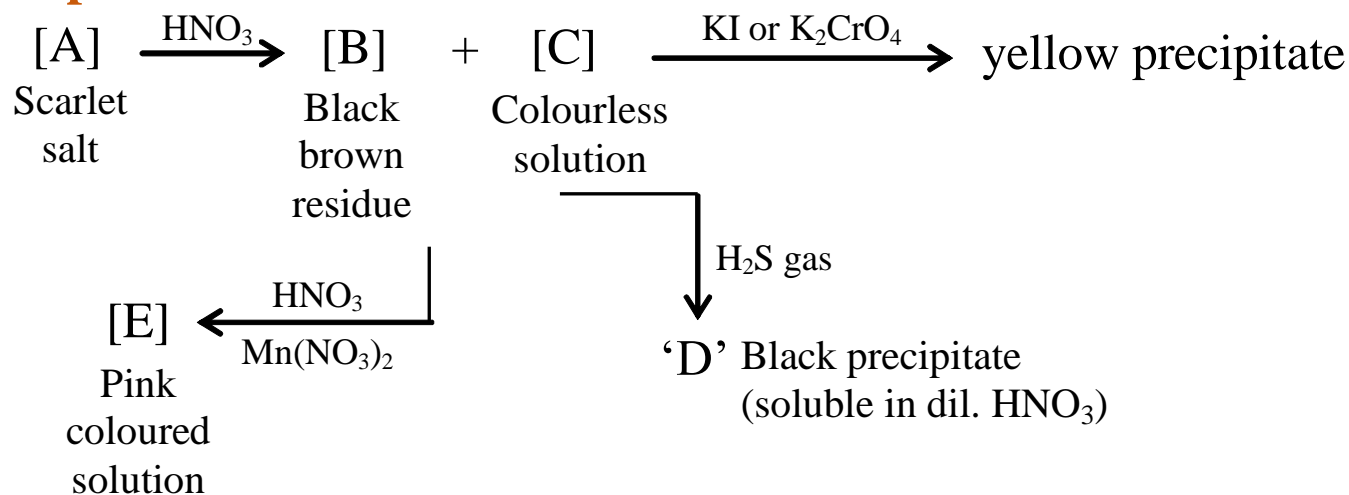
Blue colouration



QUALITATIVE ANALYSIS

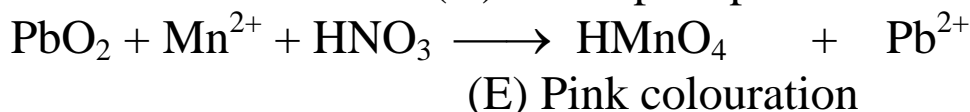
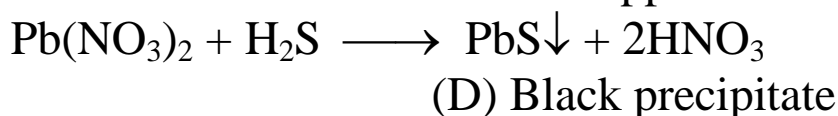
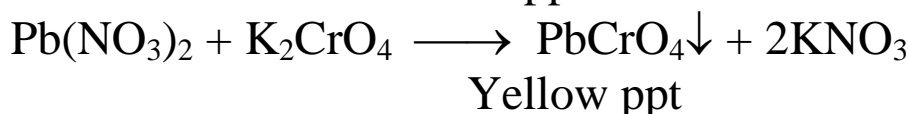
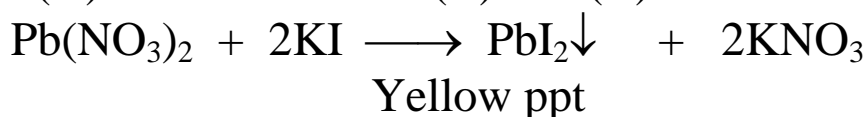
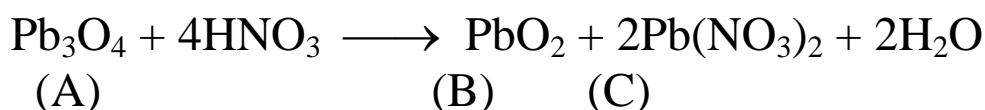
Thus, the mixture consists of FeCl_2 and NH_4Cl . Some of FeCl_2 has undergone oxidation into FeCl_3 with atmospheric oxygen.

Example 21.



What are the compound (A) to (E) in above road map problem? Give the reactions involved.

Solution:



Example 22.

Compound (A) reduces HgCl_2 to a white precipitate, turning to gray. Solution of (A) turns yellow coloured solution of FeCl_3 to a green coloured solution. Solution of (A) gives white precipitate with NaOH , which dissolves in excess of NaOH . Moreover, the solution of (A) gives yellow precipitate, when H_2S gas is passed through it. This precipitate dissolves in yellow ammonium sulphide.

QUALITATIVE ANALYSIS

Compound (A) is found to give chromyl chloride test. Identify the compound (A) and give the reactions involved.

Solution:

Compound (A) is SnCl_2 .

