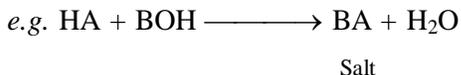


Chapter-5

ANALYTICAL CHEMISTRY

Inorganic salts are considered to be the compounds formed by the acid-base neutralisation reaction.



Any inorganic salt made up of cation, comes from base, hence known as basic radical; By the same way, anion is known as acidic radical. In order to identify a given inorganic compound, following tests characterise different radicals in it.

TEST FOR ACIDIC RADICALS

The methods available for the detection of anions or acidic radicals are not so much systematic since some of the anions belong to more than one of the subdivisions. Essentially the processes employed may be divided into **class A**, those involving the identification by volatile products obtained on treatment with acids and **class B**, those dependent upon reactions in solution. **Class A** is subdivided into (1) gas evolved with dil. HCl or dil. H₂SO₄ and (2) gases or vapours evolved with conc. H₂SO₄. **Class B** is subdivided into (1) precipitation reaction and (2) oxidation and reduction in solution.

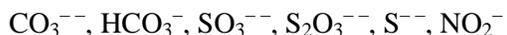
Class A

- Gases evolved with dil HCl or dil. H₂SO₄:** CO₃²⁻, HCO₃⁻, SO₃²⁻, S₂O₃²⁻, S²⁻, NO₂⁻, OCl⁻, CN⁻, CNO⁻, CH₃COO⁻
- Gases or acid vapours evolved with conc. H₂SO₄:** F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, BO₃³⁻, HCOO⁻, C₂O₄²⁻, [SiF₆]⁻, ClO₃⁻, ClO₄⁻, BrO₃⁻, MnO₄⁻, [Fe(CN)₆]³⁻, SCN⁻, Tartarate (C₄H₄O₆²⁻), Citrate [C₆H₅O₇]³⁻.

Class B

- Precipitation reactions:** SO₄²⁻, PO₄³⁻, CrO₄²⁻, CrO₇²⁻, AsO₄³⁻, AsO₃³⁻, S₂O₈²⁻, H₂PO₂⁻, HPO₃²⁻, C₆H₅COO⁻, C₆H₄(OH)COO⁻, C₄H₄O₄²⁻, [SiF₆]²⁻.
- Oxidation/reduction in solution:** CrO₄⁻, Cr₂O₇²⁻, MnO₄⁻, MnO₄²⁻.

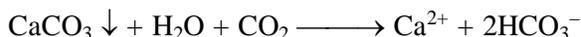
In this chapter, we should concentrate the following radicals *i.e.*



Carbonate and Bicarbonate

Solubility : all normal carbonates, with the exception of those of the alkali metals (except Li₂CO₃) and of ammonium, are *insoluble* in water.

The hydrogen carbonates (or bicarbonates) of Ca, Sr, Ba, Mg and possibly of Fe exist in aqueous solution; they are formed by the action of excess Carbonic acid upon the normal carbonates either in aqueous solution or suspension and are decomposed on boiling the solutions.

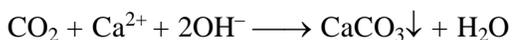


Reactions of CO_3^{2-}

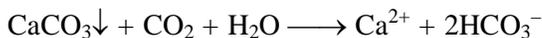
with dil. HCl or dil. H_2SO_4



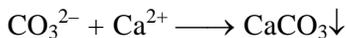
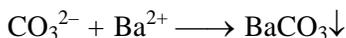
the gas turns lime water milky.



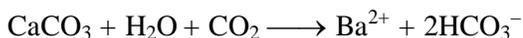
Excess of passage of gas through lime water disappears milkyness



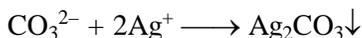
With BaCl_2



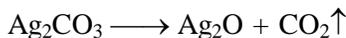
Only normal carbonates react; hydrogen carbonates donot. The precipitate is soluble in mineral acids and carbonic acid



With AgNO_3 solution



the ppt. is soluble in HNO_3 and in NH_3 solution the ppt. becomes yellow or brown upon addition of excess reagent owing to the formation of Ag_2O ; the same happens if the mixture is boiled.



Sulphides, sulphites, thiosulphates, cyanides cyanates, fluorides, nitrites and acetates interfere.

The *Sulphur containing anions* can be quantitatively oxidised by H_2O_2 into sulphates. *Cyanides* are rendered innocuous by treating the test solution with HgCl_2 ; the slightly dissociated $\text{Hg}(\text{CN})_2$ is formed. *Nitrites* can be removed by treatment with Aniline hydrochloride.

Differentiation of CO_3^{2-} and HCO_3^-

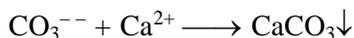
When MgSO_4 is added to a cold solution of Hydrogen carbonate, no ppt. occurs, while a white ppt. of MgCO_3 is formed with normal carbonates.

With HgCl_2 , no ppt. is formed with HCO_3^- , while in a solution of normal carbonates, a reddish brown ppt. of basic Mercury (II) carbonate ($3 \text{HgO} \cdot \text{HgCO}_3$) is formed

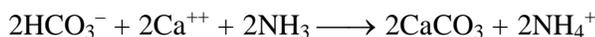


Test for HCO_3^-

In the presence of normal carbonate adding an excess of CaCl_2 to a mixture of CO_3^{2-} and HCO_3^- , the former is precipitated quantitatively.



On filtering the solution rapidly HCO_3^- ion pass into the filtrate. On adding NH_3 to the filtrate, a white ppt or cloudiness is obtained if HCO_3^- present



Sulphites, SO_3^{2-}

Solubility: Only the sulphites of the alkali metals and of ammonium are soluble in water; the sulphites of the other metals are either sparingly soluble or insoluble. The hydrogen sulphites of the alkali metals are soluble in water; the HSO_3^- of alkaline earth metals are known only in solution.

Reactions of SO_3^{2-}

with dil. HCl or dil. H_2SO_4



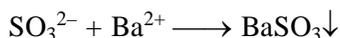
The gas may be identified (i) by its suffocating odour of burning Sulphur, (ii) by the green coloration, due to the formation of Cr^{3+} ions, produced when a filter paper, moistened with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, is held over the mouth of the test tube



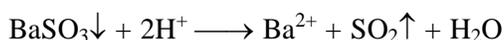
Another method of identifying the gas is (iii) to hold a filter paper, moistened with KIO_3 and starch solution, in the vapour, when a blue colour owing to the formation of iodine, is observable



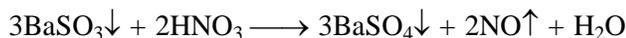
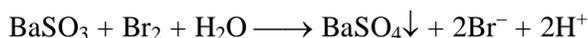
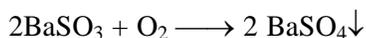
with BaCl_2 or SrCl_2



the ppt. dissolves in dil. HCl , when SO_2 is evolved



On standing, the ppt. is slowly oxidized to the sulphate and is then insoluble in dil mineral acids; this change is rapidly effected by warming with Br_2 water or a little conc. HNO_3 or with H_2O_2

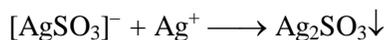


With AgNO_3

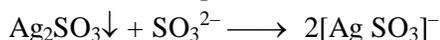
Solution: No visible change occurs initially because of the formation of sulphitoargentate ions



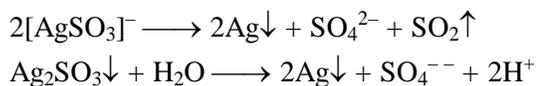
On the addition of more reagent, a white crystalline ppt. of Silver sulphite is formed



the ppt. dissolves if sulphite ions are added in excess;

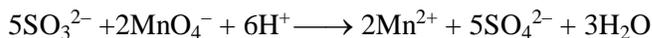


On boiling the solution of complex salt, or an aqueous suspension of the precipitate, grey metallic Silver is precipitated

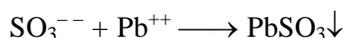


The ppt. also dissolved in NH_3 . The solution obtained after dissolving in NH_3 should be discarded quickly to avoid a serious explosion.

With KMnO_4 solution

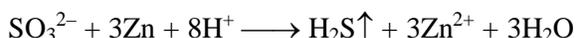


with Lead acetate or Lead nitrate solution

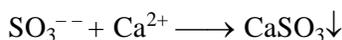


ppt. dissolves in dil. HNO_3 . On boiling, the ppt. is oxidised by atmospheric Oxygen and Lead sulphate is formed.

With Zn and H_2SO_4



With lime water: This test is carried out by adding dilute HCl to the solid sulphite and bubbling the evolved SO_2 through lime water



the precipitate dissolves on prolonged passage of the gas due to the formation of HSO_3^- ion.



Distinction between sulphites and hydrogen sulphite: Solutions of normal alkali sulphites show an alkaline reaction against litmus paper, because of hydrolysis $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$

While the solution of alkali hydrogen sulphite is neutral.

Sulphides S^{2-}

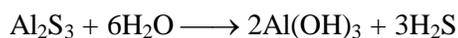
Solubility: The acid, normal and polyphosphides of alkali metals are soluble in water; their aqueous solutions exhibit an alkaline reaction because of hydrolysis



the normal sulphides of most other metals are insoluble; those of the alkaline earths are sparingly soluble, but are gradually changed by contact with water into soluble hydrogen sulphide.

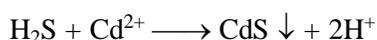
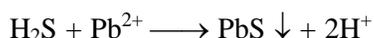
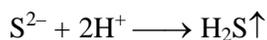


The sulphides of Al, Cr and Mg can only be prepared under dry conditions and they are completely hydrolysed by water.

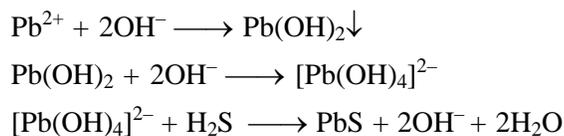


Reaction of S^{2-}

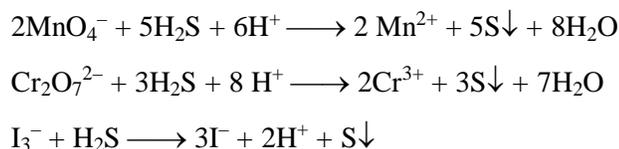
with dil. HCl or dil. H_2SO_4



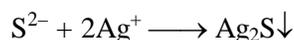
the above tests are with lead acetate and cadmium acetate. A more sensitive test is attained by the use of sodium tetrahydroxoplumbate (II) solutions, prepared by adding NaOH to $(\text{CH}_3\text{COO})_2\text{Pb}$ with the initial ppt. of $\text{Pb}(\text{OH})_2$ has just dissolved:



H_2S is a good reducing agent. It reduces (1) acidified KMnO_4 (2) acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and (3) KI_3 (Iodine) solution.



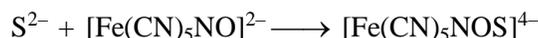
With AgNO_3 Solution



With $(\text{CH}_3\text{COO})_2\text{Pb}$ solution \longrightarrow black ppt of PbS

With $\text{BaCl}_2 \longrightarrow$ no ppt.

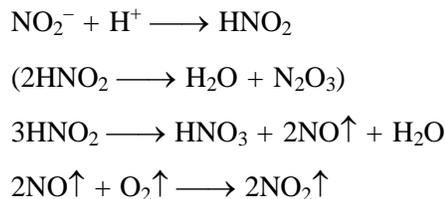
with Sodium nitroprusside solution $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, transient purple colour in the presence of solutions of alkalis. *No reaction occurs with the solutions of H_2S or with the free gas.* If, however filter paper moistened with a solution of the reagent made alkaline with NaOH or ammonia solution, a purple coloration is produced with free H_2S



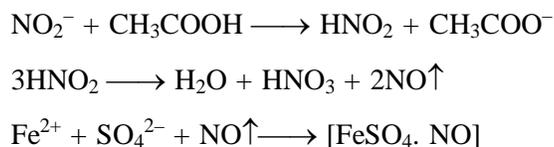
Nitrites

Solubility: Silver nitrite is sparingly soluble in water. All other nitrites are soluble in water

Reaction of Nitrites, NO_2^-



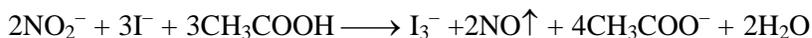
Brown ring test: When the nitrite solution is added carefully to a saturated solution of iron (II) sulphate acidified with dil. CH_3COOH or with dil. H_2SO_4 , a brown ring due to the compound $[\text{FeSO}_4.\text{NO}]$ is formed at the junction of the two liquids. If the addition has not been made, a brown coloration results. *This reaction is similar to brown ring test for nitrates.* For which a stronger acid (Conc. H_2SO_4) must be employed.



Iodides, bromides, coloured ions and anions that give coloured compounds with Iron (II) ions must be absent.

With BaCl_2 solution \longrightarrow no ppt.

With AgNO_3 Solution : $\text{NO}_2^- + \text{Ag}^+ \longrightarrow \text{AgNO}_2 \longrightarrow$ white ppt



With acidic KMnO_4 solution



With NH_4Cl



With Urea

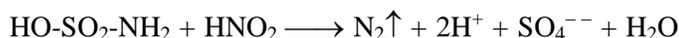


With thiourea



SCN^- and I^- interfere and, if present, must be removed either with excess of solid Ag_2SO_4 or with dil. AgNO_3 solution before adding the acetic acid and thiourea.

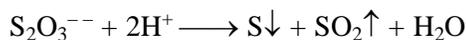
with Sulphamic acid $\text{HO-SO}_2\text{-NH}_2$)



Thiosulphates, $\text{S}_2\text{O}_3^{--}$

Most of the thiosulphates that have been prepared are soluble in water; those of Pb, Ag and Ba are very sparingly soluble. Many of them dissolves in excess $\text{Na}_2\text{S}_2\text{O}_3$ solution forming complex salts.

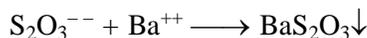
Reactions of $\text{S}_2\text{O}_3^{--}$ with dil. HCl or dil. H_2SO_4



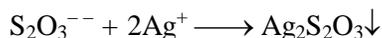
With KI_3 solution



With BaCl_2 Solution.



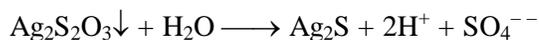
With AgNO_3 solution



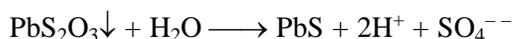
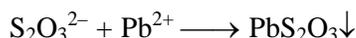
At first, no ppt occurs due to complex formation.



the ppt is unstable, turning dark on standing, when Ag_2S is formed



With $(\text{CH}_3\text{COO})_2\text{Pb}$ solution



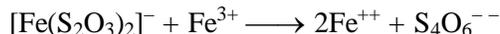
With KCN Solution



With Iron (III) chloride solution: a dark violet colouration appears probably due to the formation of dithiosulphate Iron (III) complex.



on standing, the colour disappears rapidly, while tetrathionate and iron (II) ion are formed.



the overall reaction can be written as



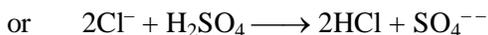
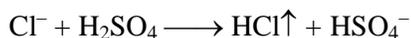
Catalytic test : NaN_3 and I_3^- do not react but in the presence of thiosulphate, which acts as a catalyst, there is an immediate vigorous evolution of N_2



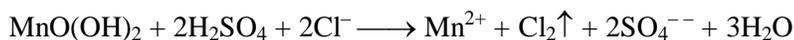
Chlorides. Cl^-

Solubility: Most chlorides are soluble in water. Mercury (I) chloride, Hg_2Cl_2 , Silver chloride, AgCl , Lead chloride, PbCl_2 (this is sparingly soluble in cold but readily soluble in boiling water). Copper (I) chloride, BiOCl , SbOCl , Mercury (II) Oxochloride are insoluble in water.

Reactions of Cl^-



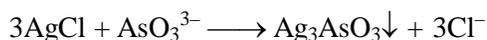
Reaction with Manganese dioxide and conc. H_2SO_4



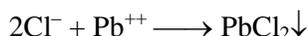
With AgNO_3 Solution



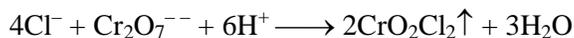
Silver chloride ppt. when shaken with sod. arsenite solution, it is converted into yellow Silver arsenite (distinction from AgBr and AgI , which are unaffected by this treatment)



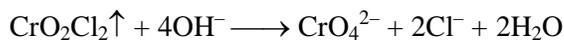
With lead acetate solution



With $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ (Chromyl chloride test)



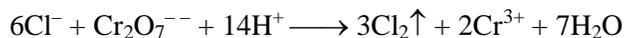
or



orange red vapours yellow ppt.



Some Cl_2 may also be liberated, owing to the reaction



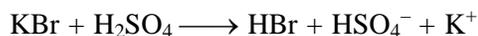
Note: Chlorides of Hg, Ag, Pb and Sn do not give chromyl chloride test.

Bromides, Br^-

Solubility: Silver, Mercury (I) and Copper (I) bromide are *insoluble* in water, lead bromide is sparingly soluble in cold, but more soluble in boiling water. All other bromides are soluble

Reactions of Br^-

With Conc. H_2SO_4

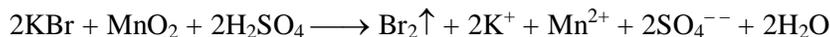


or

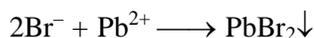


The properties of HBr are similar to those of HCl

With $\text{MnO}_2 + \text{H}_2\text{SO}_4$



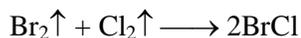
With AgNO_3 solution



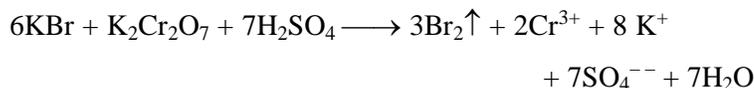
With Cl_2 water



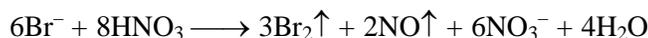
with an excess of chlorine water



With $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$



With HNO_3 acid

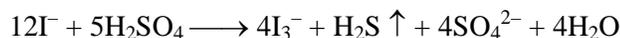
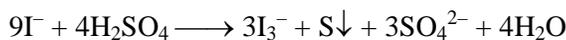
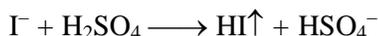
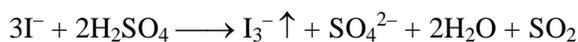


Iodides, I^-

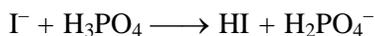
Solubility: The solubilities of the iodides are similar to Cl^- and Br^- ; silver, Mercury (I), Mercury (II) copper (I) and lead iodides are the least soluble salts

Reactions of iodides

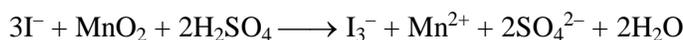
With conc. H₂SO₄



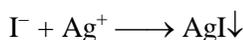
Pure HI is formed on warming with conc. H₃PO₄



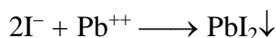
With MnO₂ + H₂SO₄ (conc.)



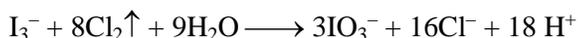
With AgNO₃ Solution



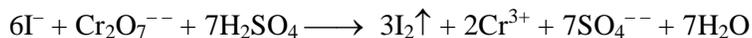
With lead acetate solution



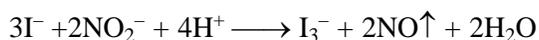
With Cl₂ water



With K₂Cr₂O₇ + H₂SO₄



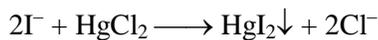
With KNO₂ solution



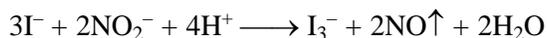
With CuSO₄ solution



With Mercury (II) chloride solution



Starch test: Iodides are readily oxidised in acid solution to free iodine by a number of oxidising agents; the free iodine may then be identified by the deep-blue colouration produced with starch solution



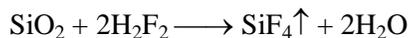
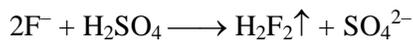
Some anions are identified by their characteristic chemical reactions. These radicals are *fluoride, oxalate, sulphate, borate and phosphate*.

Fluorides, F⁻

Solubility: the fluorides of the common alkali metals and of Ag, Hg, Al and Ni are readily soluble in water, those of Pb, Cu, Iron (III) Barium and Lithium are slightly soluble and those of the other alkaline earth metals are insoluble.

Reactions of F⁻

With conc. H₂SO₄



Note that at room temperature, HF gas is almost completely dimerized, therefore its formula has been written as H₂F₂. At elevated temperatures (say 90° C) it dissociates completely to monomer hydrogen fluoride $\text{H}_2\text{F}_2 \rightleftharpoons 2\text{HF}$.

Oxalate

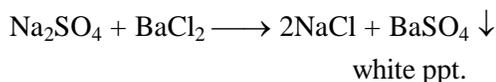
When oxalate is heated with conc. H₂SO₄, a mixture of CO and CO₂ is given off. The CO burns with blue flame.



Sulphate

Dissolve a little amount of the substance (salt or mixture) and add Barium chloride solution. A white precipitate insoluble in conc. HNO₃ is formed.

Reactions: White precipitate of Barium sulphate is obtained when soluble sulphate is treated with Barium chloride solution.



The white precipitate is insoluble in conc. HNO₃. Certain chlorides, e.g., NaCl and BaCl₂ when present in large quantities, may form a white precipitate which dissolves on dilution with water.

Silver and lead, if present, may be precipitated as Silver chloride and lead chloride by the addition of barium chloride. To avoid it, barium nitrate may be used in place of barium chloride.

Borate

To a small quantity of the substance (salt or mixture), add a few mL of ethyl alcohol and conc. H₂SO₄. Stir the contents with a glass rod. Heat the test tube and bring the mouth of the test tube near the flame. The formation of green edged flame indicates the presence of borate.

Reactions with explanations: When borate is heated with ethyl alcohol and H₂SO₄, ethyl borate vapours come out which burn with green colour in oxidative flame.



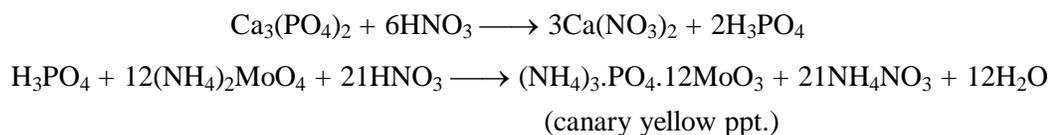
Ethyl borate

In place of ethyl alcohol, methyl alcohol can also be used. This test should be performed in a test tube and not in a porcelain basin because copper or barium salts, if present, will come in contact with the flame which also give green flame.

Phosphate

Take about 0.2 g of the substance in a test tube and add 2 mL conc. HNO_3 . Heat and add 2 mL ammonium molybdate solution. Again heat. A canary yellow precipitate indicates the presence of phosphate.

Reactions: The canary yellow precipitate is due to the formation of ammonium phosphomolybdate.



Arsenic under similar conditions also yields a yellow precipitate of $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$ (Ammonium arsenomolybdate). So, in presence of As, phosphate is tested in the filtrate of second group.

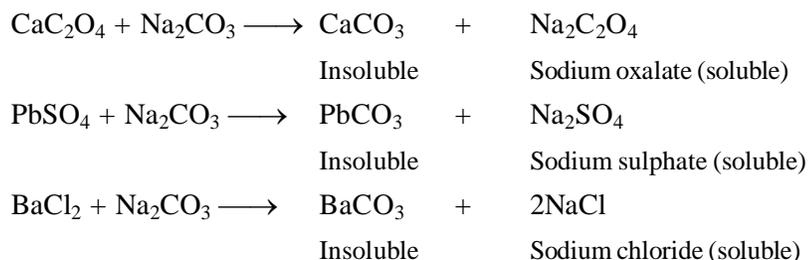
- The precipitate of ammonium phosphomolybdate dissolves in excess of phosphate. Thus, the reagent (ammonium molybdate) should always be added in excess.
- HCl interferes in this test. Hence, if the test of phosphate is to be performed with the solution containing HCl, the solution should be boiled to remove HCl.
- Reducing agents such as sulphites, sulphides, etc., interfere as they reduce Mo(VI) to molybdenum blue ($\text{Mo}_3\text{O}_8 \cdot x\text{H}_2\text{O}$). The solution, therefore, turns blue. In the presence of reducing agents, the solutions should be boiled with HNO_3 as to oxidise them before the addition of ammonium molybdate.

Identification of acidic radicals with sodium carbonate extract

A large number of acidic radicals can be confirmed by using sodium carbonate extract of the mixture.

During the heating of mixture with sodium carbonate, double decomposition takes place, *i.e.*, exchange of ions takes place.

For example,



Thus, carbonates of the cations of the mixture are formed which are mostly insoluble in water and are obtained in the residue. On the other hand, sodium salts of the anions (acidic radicals) of the mixture are formed which being soluble in water are obtained in the filtrate.

Advantage of preparing sodium carbonate extract

- Many salts are insoluble in water and dilute acids. The preparation of sodium carbonate extract affords a convenient method for bringing the anions of the mixture in solution.
-

- (b) It removes the basic radicals (usually coloured) which could have interfered in the usual tests of some of the acidic radicals.
- (c) The residue can be used for the tests of basic radicals of I to VI groups as it can be easily dissolved in dil. HCl or conc. HCl. Such a solution does not involve the problem of removing interfering radicals like oxalate, fluoride, borate and phosphate.

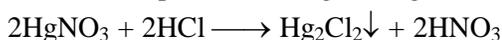
On passing H₂S through the filtrate of the third group, sulphides of fourth group are precipitated. NiS and CoS are black and insoluble in concentrated HCl while MnS (buff coloured). ZnS (colourless) are soluble in conc. HCl.

Test for Basic radicals or cations

[A] I group **Hg⁺ or Hg₂⁺⁺, Pb²⁺, Ag⁺**

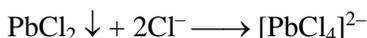
Group reagent **dil. HCl.**

White ppt. indicates the presence of Hg⁺ or Hg₂⁺⁺, Pb⁺⁺, Ag⁺

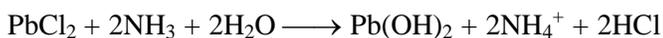


Reactions of lead (II) ions

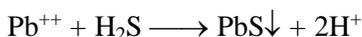
PbCl₂ is soluble in hot water. It is also soluble in conc. HCl or conc. KCl when the tetrachloroplumbate (II) ion is formed.



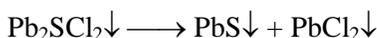
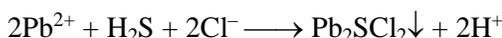
If the ppt. is washed by decantation and dilute ammonia is added, no visible change occurs [difference from Hg₂⁺⁺ and Ag⁺], though a ppt. exchange reaction takes place and Pb(OH)₂ is formed



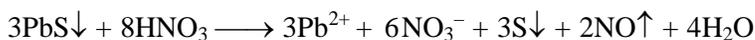
With H₂S



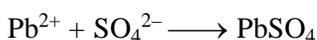
If test is carried out in presence of larger amounts of a chloride, initially a red ppt. of lead sulphochloride is formed



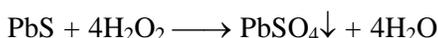
lead sulphide decomposes when conc. HNO₃ is added and white finally divided elemental Sulphur is precipitated.



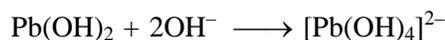
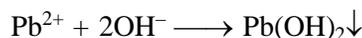
If the mixture is boiled, Sulphur is oxidised by HNO₃ to sulphate, which immediately forms white lead sulphate precipitate with the lead ions in the solution.



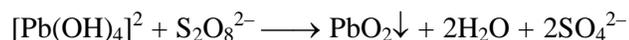
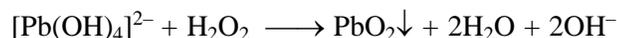
On boiling PbS with 3% H₂O₂ solution, the black ppt. turns white owing to the formation of lead sulphate



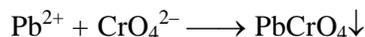
With NaOH solution



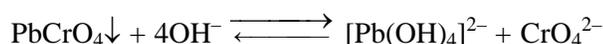
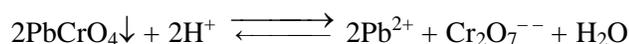
Hydrogen peroxide or ammonium peroxodisulphate, when added to a solution of tetrahydroxoplumbate (II), forms a black ppt. of PbO_2 by oxidising bivalent lead to tetravalent lead.



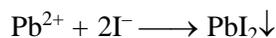
With Potassium chromate



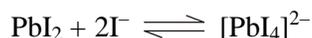
Nitric acid or sodium hydroxide dissolve the precipitate:



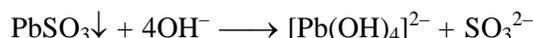
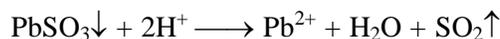
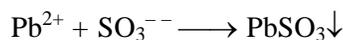
With KI



in excess of I^-

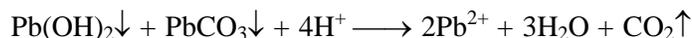


With sodium sulphite

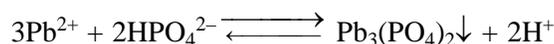


With Na_2SO_3 solution

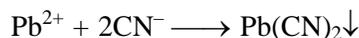
$2\text{Pb}^{2+} + 2\text{CO}_3^{2-} + \text{H}_2\text{O} \longrightarrow \text{Pb}(\text{OH})_2\downarrow + \text{PbCO}_3\downarrow + \text{CO}_2\uparrow$ ppt. dissolves in dil. HNO_3 and even in acetic acid and CO_2 gas is liberated.



With disodium Hydrogen phosphate

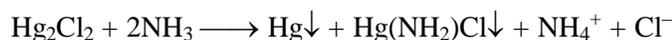
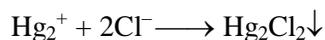


With Potassium cyanide

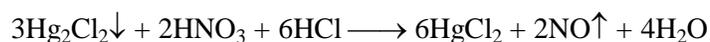


Reactions of Mercury (I) ion

with dil. HCl



Hg_2Cl_2 dissolves in aqua regia forming undissociated soluble Mercury (II) chloride



With H₂S ion neutral or in dil. acidic medium



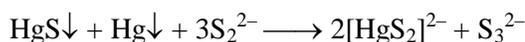
Sodium sulphide (colourless) dissolves the Mercury (II) sulphide (but leaves Hg metal) and a disulphomercurate (II) complex is formed



After removing the Mercury metal by filtration, black Mercury (II) sulphide can be again pptd. by acidification with dil. mineral acids:



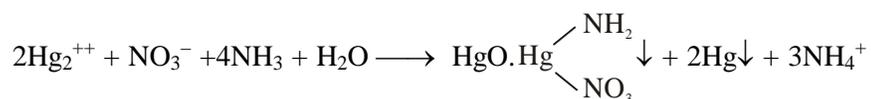
Sodium disulphide (yellow) dissolves both Mercury and Mercury (II) sulphide



Aqua regia dissolves the ppt. yielding undissociated Mercury (II) chloride and Sulphur



With Ammonia solution



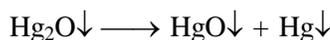
This reaction is used to differentiate between Mercury (I) and Mercury (II) ions.

With NaOH



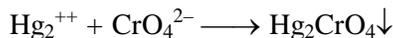
the ppt. is insoluble in excess reagent, but dissolves readily in dil. HNO₃.

When boiling, the colour of the ppt. turns to grey, owing to disproportionation, when Hg(II) oxide + Hg are formed.

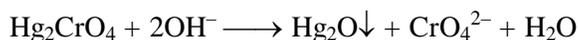


With Potassium Chromate Solution

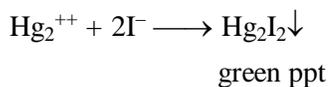
If the test is carried out in cold, a brown amorphous ppt. is formed with an undefined composition. When heated the ppt. turns to red crystalline Mercury (I) chromate



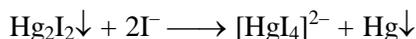
NaOH turns the ppt. into black Mercury (I) oxide



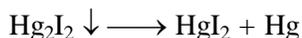
With KI



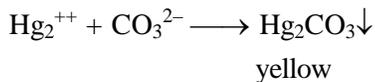
in excess of reagent



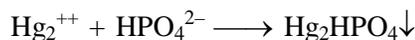
When boiling the Mercury (I) iodide ppt. with water, disproportionation again takes place, and a mixture of red Mercury (II) iodide and finely distributed black Mercury is formed



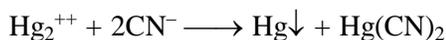
With Na_2CO_3



With disodium hydrogen phosphate



With KCN



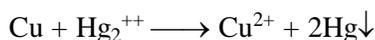
mercury (II) cyanide, though soluble, is virtually undissociated.

With Tin (II) chloride

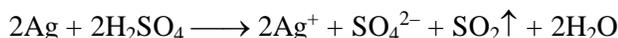
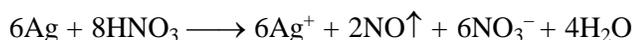


mercury (II) ions react in a similar way.

With Cu

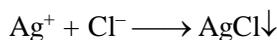


With Al

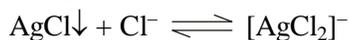


Reactions of Ag^+ ion

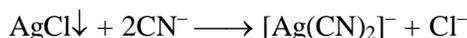
With dil. HCl



with conc. HCl, ppt. dissolves



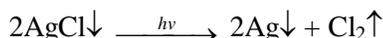
dilute ammonia solution dissolves the AgCl ppt.



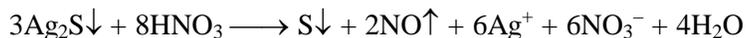
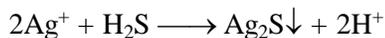
With $\text{Na}_2\text{S}_2\text{O}_3$ solution



Sunlight or ultraviolet irradiation decomposes the Silver chloride precipitate, which turns to greyish or black owing to the formation of Silver metal.



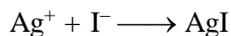
With H_2S



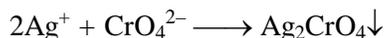
With NaOH Solution



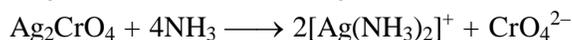
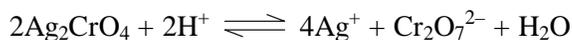
With KI



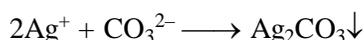
With K_2CrO_4



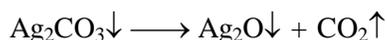
the ppt. is soluble in dil. HNO_3 and in ammonia



With Na_2CO_3



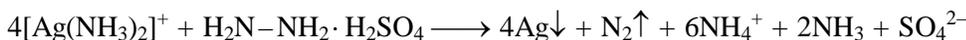
yellowish white ppt.



With Na_2HPO_4



With Hydrazine sulphate (saturated)



(B) II group: Hg^{2+} , Pb^{2+} , Cu^{2+} , Bi^{3+} , As^{3+} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+}

group reagent: $\text{HCl} + \text{H}_2\text{S}$

Black ppt. : HgS , PbS , Bi_2S_3 , CuS

Yellow ppt. : CdS , As_2S_3 , As_2S_5 , SnS_2

Orange ppt. : Sb_2S_3 , Sb_2S_5

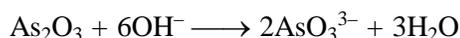
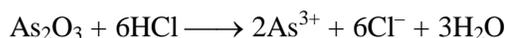
Brown ppt. : SnS

Cations of the IInd gp. are traditionally divided into two sub-groups, the copper subgroup and the arsenic subgroup. The basis of this division is the *solubility of the sulphide precipitates in ammonium polysulphide*. While sulphides of the copper sub-group are insoluble in this reagent, those of the arsenic groups dissolve with the formation of thiosalts.

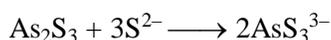
Copper sub group, Mercury (II), Lead(II), Bismuth (III) Copper (II) and Cadmium (II): The chlorides, nitrates and sulphates of the cations of the copper subgroup are quite soluble in water. The sulphides, hydroxides and carbonates are insoluble. Some of the cations of the copper sub-group (mercury (II) copper (II) and cadmium (II) tend to form complexes (ammonia, cyanide ions etc.)

Arsenic sub-group: Arsenic (III), Arsenic (V), Antimony (III), Antimony (V), Tin (II), Tin (IV).

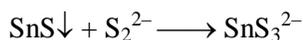
These ions have amphoteric character, their oxides form salts both with acids and bases.



The dissolution of sulphides in ammonium polysulphide can be regarded as the formation of thiosalts from anhydrous thioacids

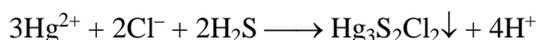


All the sulphides of the Arsenic sub-group dissolve in (colourless) ammonium sulphide except Tin (II) sulphide: to dissolve the latter, ammonium polysulphide is needed, which acts partly as an oxidizing agent, thiostannate ions being formed

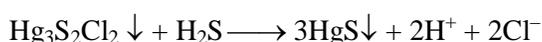


Reactions of Mercury (II) ions

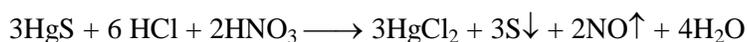
With H₂S



white



Black



aquoregia



With Ammonia solution



white



yellow ppt.

With KI

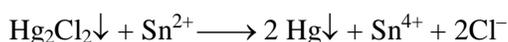
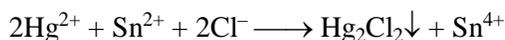


red ppt.

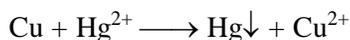


With KCN: does not cause any change in dil. solutions (difference from other ions of the Copper subgroup)

With SnCl₂



With Cu

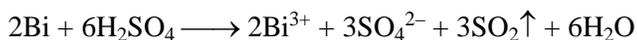
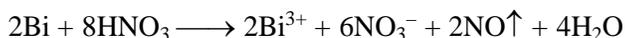


With Cobalt (II) thiocyanate

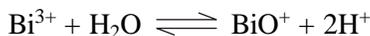


deep blue

Bismuth, Bi: brittle, crystalline, reddish white metal



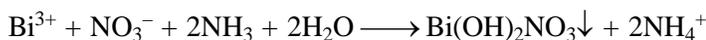
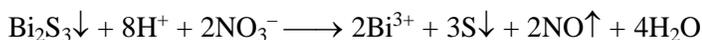
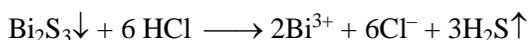
Bismuth forms trivalent and pentavalent ions, Bi^{3+} is most common



the bismuthyl ion, BiO^+ , forms insoluble salts, like bismuthyl chloride, with most ions. If we want to keep Bismuth in the solution we must acidify the solution when the above equilibrium shifts towards the left.

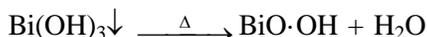
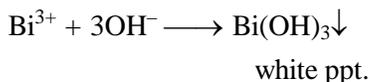
Pentavalent Bismuth forms the bismuthate BiO_3^- ion. Most of its salts are insoluble in water reactions

With H_2S

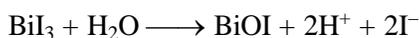
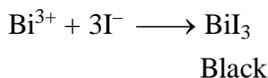


white basic salt

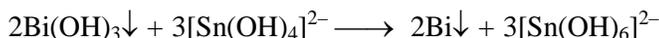
With NaOH



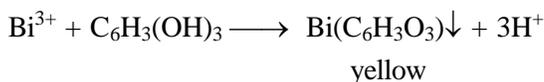
With KI



With Sodium tetrahydroxostanate (II)

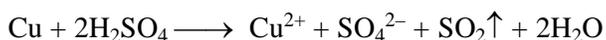
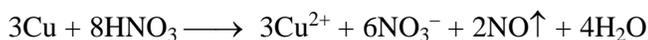


With Pyrogallol reagent



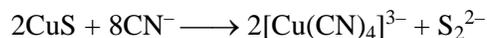
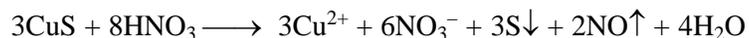
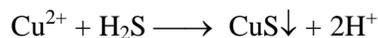
Copper (Cu)

light red metal which is soft, malleable and ductile

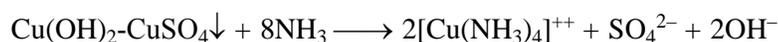
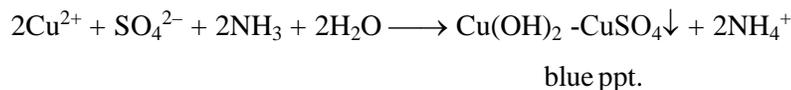


Reactions

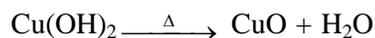
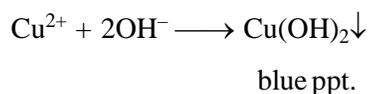
With H₂S



With Ammonia solution



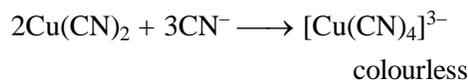
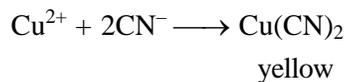
With NaOH solution



With KI

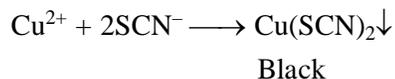


With KCN



The complex is so stable (*i.e.*, the conc. of copper (I) ions is – so low) that H₂S cannot ppt. copper (I) sulphide from this solution.

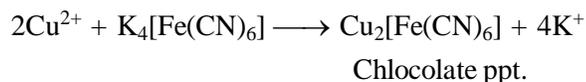
With potassium thiocyanate



it turns slowly white

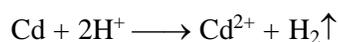


With K₄[Fe(CN)₆]



Cadmium, Cd

Silver-white, malleable and ductile

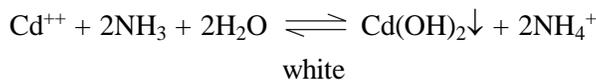


Reaction

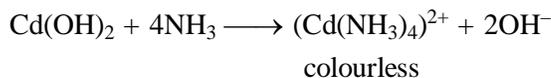
With H₂S



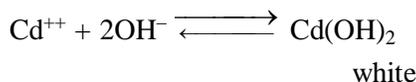
With Ammonia solution



in excess of Ammonia solution



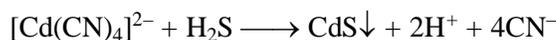
With NaOH



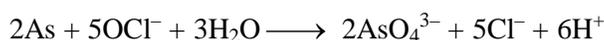
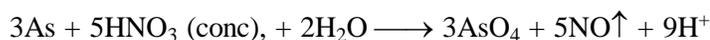
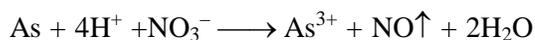
With KCN



The colourless complex is not very stable; when H₂S is introduced, CdS is precipitated.



Arsenic, As : It is a steel grey, brittle solid with a metallic lustre

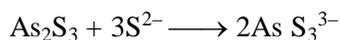


Reactions of Arsenic (III) ions

With H₂S



Ammonium sulphide also dissolves the precipitate



on re-acidifying



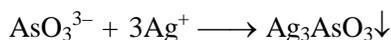
Yellow Ammonium sulphide (ammonium polysulphide) (NH₄)₂S₂ dissolves the precipitate, and thioarsenate AsS₄³⁻ ions are formed



on acidifying



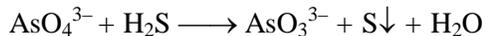
With Silver nitrate



With KI₃



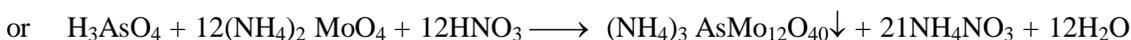
Reaction of Arsenate ions



If a large excess of conc. HCl is present and H₂S is passed rapidly into the cold solution



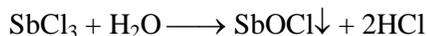
With Ammonium molybdate solution



Antimony Sb

Reactions are almost similar as that of Arsenic (III) and (V)

Sb³⁺ ions in solution as SbCl₃ on addition of water give white ppt.



Tin, (Sn)

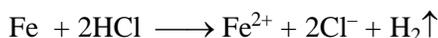
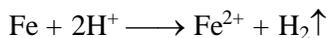
Reactions are almost as that of Arsenic and Antimony.

ppt. of SnS is soluble in yellow ammonium sulphide not in colourless Ammonium sulphide.

With Mercury (II) chloride, SnCl₂ reacts but not SnCl₄ (Reactions are already discussed previously in this chapter).

(c) third group of cations Iron (III), Aluminium (III), Chromium (III) group reagent in presence of NH₄Cl, NH₄OH is added.

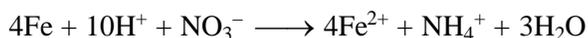
Iron, Fe (II): Chemically pure iron is a Silver white, tenacious and ductile metal. Dilute or conc. HCl and dilute H₂SO₄ dissolve Iron when iron (II) salts and H₂ gas produced



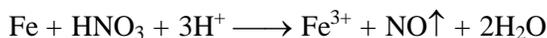
Hot, conc. H₂SO₄ yields iron (III)



with cold dilute nitric acid, Iron (II) and Ammonium ions are formed



Cold, concentrated nitric acid renders iron passive 8M or hot conc. HNO₃ dissolves iron with the formation of nitrogen oxide gas and iron (III) ions.

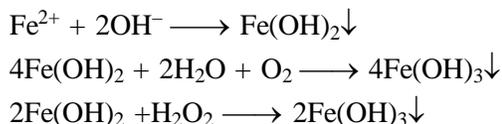


Iron forms two important series of salts.

Fe (II) salts and Fe (III) salts

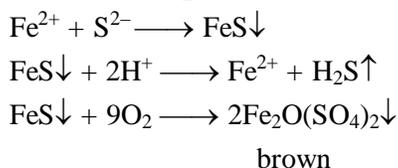
Reactions of Iron (II) ion.

With NaOH

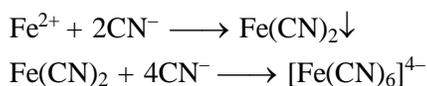


With H₂S : No precipitation takes place in acid solution since the [S²⁻], is insufficient to exceed the solubility product of Iron (II) sulphide. If the H⁺ conc. is reduced, and the sulphide ion conc. correspondingly increased, by the addition of sodium acetate solution, partial precipitation of black iron (II) sulphide, FeS occurs.

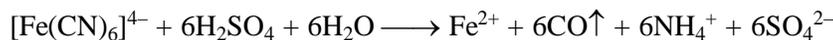
With Ammonium Sulphide



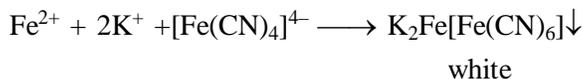
With KCN



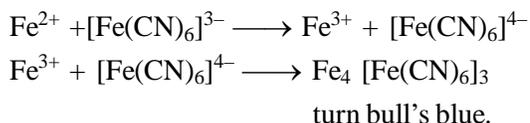
Iron present in this complex can be detected by decomposing the complex by boiling the solution with conc. H₂SO₄



With potassium hexacyano ferrate (II) solution

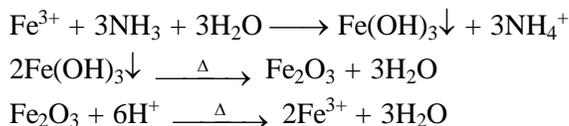


With potassium hexacyano ferrate (III) solution



Iron (III)

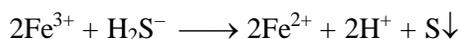
With Ammonia Solution



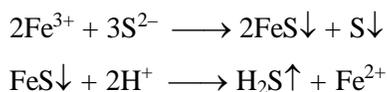
With NaOH solution



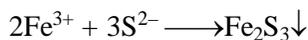
With H₂S



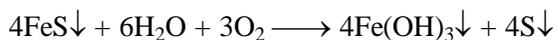
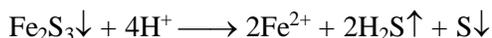
With Ammonium sulphide



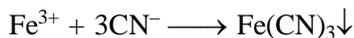
from alkaline solution, black Iron (III) sulphide is obtained



on acidification with HCl, Fe^{3+} gets converted into Fe^{2+}

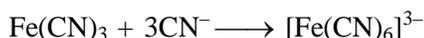


With potassium cyanide



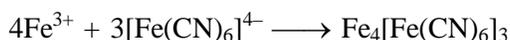
reddish brown ppt.

In excess of reagent

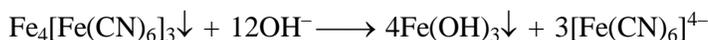


With potassium hexacyano ferrate (II)

Intense blue ppt. of iron (III) hexacyanoferrate (Prussian blue)

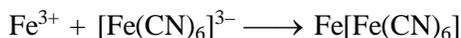


The precipitate is insoluble in dil. acids, but decomposes in conc. HCl. A large excess of reagent dissolves in partly or entirely, when an intense blue solution is obtained. NaOH turns the ppt. red as iron (III) oxide hexacyanoferrate (II) ions are formed

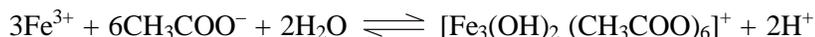


If iron (III) chloride is added to an excess of potassium hexacyanoferrate (II), a product with the composition $\text{KFe}[\text{Fe}(\text{CN})_6]$ is formed. This tends to form colloidal solution (soluble Prussian blue) and cannot be filtered.

With potassium hexacyanoferrate (III): A brown colouration is produced upon adding Hydrogen peroxide or some Tin (II) chloride solution, the hexacyanoferrate (III) part of the compound is reduced and *prussian blue* is precipitated.



With sodium acetate solution: A reddish brown colouration is formed

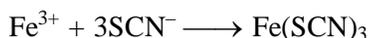


the reaction is complete only if the strong acid, which is formed, is removed by the addition of an excess of the reagent, which acts as a buffer.

If solution is diluted and boiled, a reddish brown ppt. of basic Iron (III) acetate is formed.



With Ammonium thiocyanate



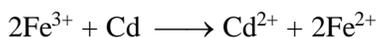
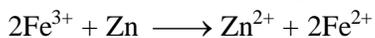
deep red coloured solution

Fluorides and Mercury (II) ions bleach the colour because of the formation of the more stable hexafluoroferrate (III) $[\text{FeF}_6]^-$ complex and the nondissociated Mercury (II) thiocyanate species

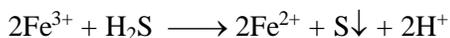
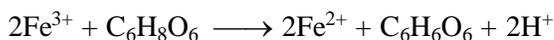
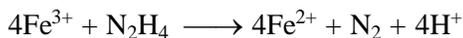
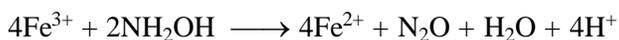


Reduction of Iron (III) to Iron (II)

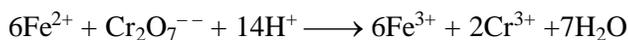
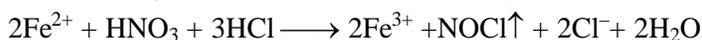
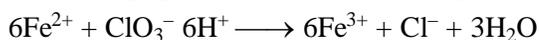
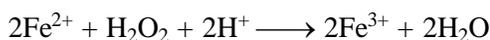
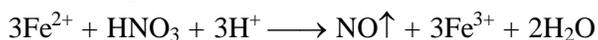
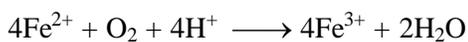
May be accomplished by various reagents, Zinc or Cadmium metal, or their amalgams (*i.e.*, Alloys with Hg)



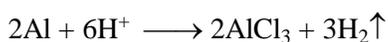
Tin (II) chloride, KI, NH_2OH , HCl , N_2H_4 sulphate or Ascorbic acid may be used.



Oxidation of Iron (II) to iron (III) : Oxidation occurs slowly upon exposure to air. Rapid oxidation is effected by conc. HNO_3 , H_2O_2 , conc. HCl with KClO_3 , aqua regia, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and Cerium (IV) sulphate in acid solution.



Aluminium, Al: Aluminium is a white ductile and malleable metal; the powder is grey

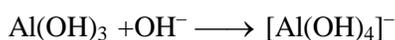
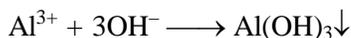


Reactions of Aluminium (III) ions

With Ammonia solution



With NaOH



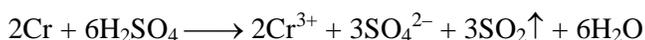
With sodium acetate solution



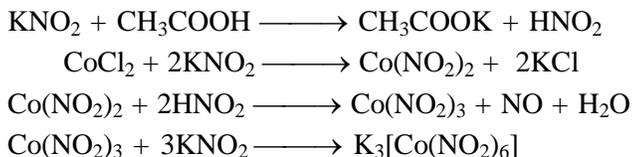
Chromium, Cr

It is a white crystalline metal and is not appreciably ductile or malleable. It melts at 1765° . The metal is soluble in dilute or concentrated hydrochloric acid. If air is excluded, Chromium (II) ions are formed.

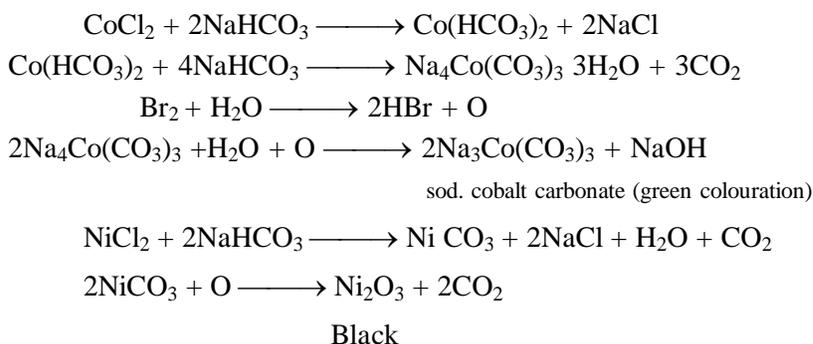
Dilute H_2SO_4 attacks Chromium slowly, with the formation of hydrogen. In hot, conc. H_2SO_4 , chromium dissolves readily to form chromium (III) ions and SO_2



Part II: Add CH_3COOH in excess and KNO_2 . The appearance of yellow precipitate confirms the presence of Cobalt.



Part III: Solution containing either nickel or cobalt is treated with NaHCO_3 and bromine water. Appearance of apple green colour confirms the presence of cobalt. If no apple green colour is observed, the solution is heated when black precipitate is formed, which shows the presence of nickel.

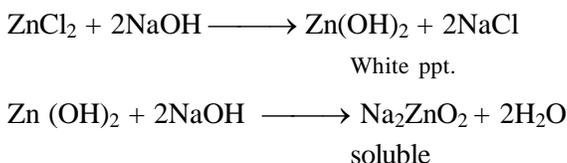


Zn^{2+} (Zinc)

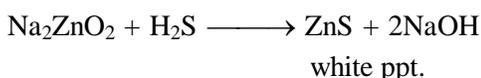
The sulphide dissolves in HCl.



When the solution is treated with NaOH , first a white precipitate appears which dissolves in excess of NaOH .



On passing H_2S , white precipitate of zinc sulphide is formed.

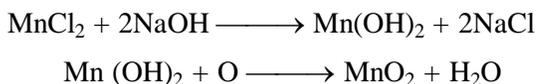


Mn^{2+} (Manganese)

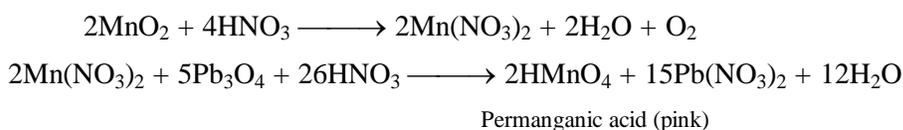
Manganese sulphide dissolves in HCl.



On heating the solution with NaOH and Br_2 -water, Manganese dioxide gets precipitated.

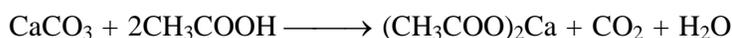
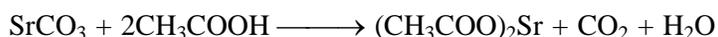
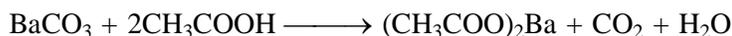


The precipitate is treated with excess of nitric acid and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.



GROUP V (Ba (II), Sr (II), Ca (II))

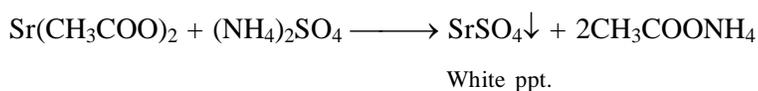
Ammonium carbonate precipitates V group radicals in the form of carbonates. These carbonates are soluble in acetic acid.



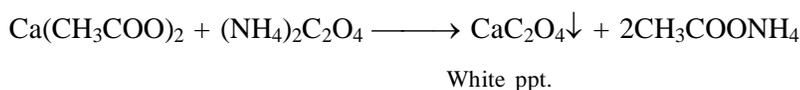
Ba²⁺ (Barium): Barium chromate is insoluble and precipitated by the addition of potassium chromate solution



Sr²⁺ (strontium): Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution



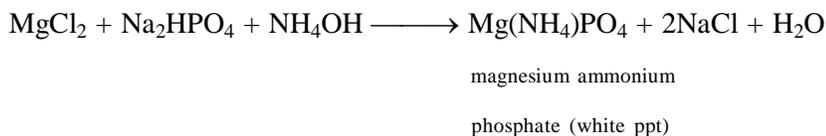
Ca²⁺ (Calcium): Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.



Calcium chlorate and calcium sulphate are soluble

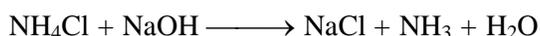
GROUP VI

In the filtrate of V group, some quantity of ammonium oxalate is added as to remove Ba, Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH₄OH. Disodium hydrogen phosphate is now added, a white precipitate is formed.

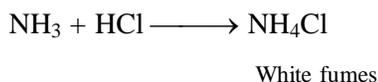


Group Zero

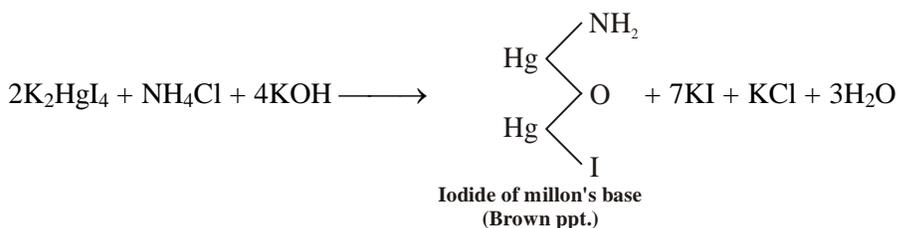
NH₄⁺ (ammonium) : The substance (salt or mixture) when heated with NaOH solution evolves ammonia



When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonium chloride are formed.



To the aqueous solution of ammonium salt when Nessler's reagent is added, brown coloured precipitate is formed.



DRY TESTS

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

- (i) Flame test
- (ii) Borax bead test
- (iii) Micro-cosmic salt bead test
- (iv) Charcoal cavity test
- (v) Cobalt nitrate charcoal test.

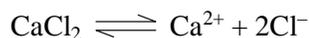
(i) Flame Test: Carefully clean a platinum wire by dipping it into dilute nitric acid and heating it in the Bunsen flame. Repeat until the flame is colourless. Dip the heated wire into the substance being tested (either solid or solution), and then hold it in the hot outer part of the Bunsen flame.

Compound of	Colour of flame
Sodium	Yellow
Potassium	Violet
Lithium	Crimson
Calcium	Orange-red
Barium	Green
Strontium	Bright-red

Note: In testing for Potassium salt when a Sodium salt is also known to be present, a Cobalt glass must be used. This glass absorbs the yellow Sodium light, but transmits the violet Potassium light.

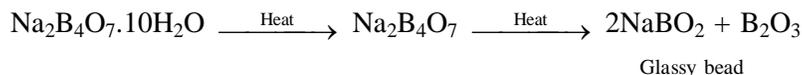
In the flame test, electrons are raised to higher energy levels and when they drop back they emit radiation of characteristic wave length.

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

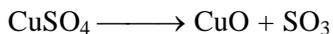


The cations impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light of characteristic colour.

(ii) Borax Bead test: On heating the colourless glassy bead formed consists of sodium metaborate and boric anhydride.



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

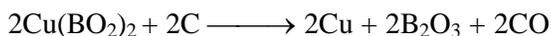
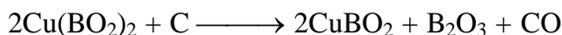


copper metaborate

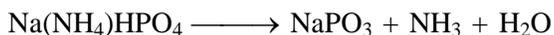
(blue)

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

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



(iii) **Microcosmic salt bead test:** This test is similar to borax bead test. When microcosmic salt is heated, a colourless transparent bead of sodium metaphosphate is formed.



Sodium metaphosphate

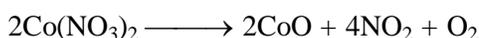
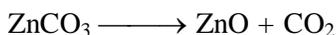
Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured. The shade of the colour gives a clue regarding the presence of metal. Like borax bead test, colours are noted both in oxidising and reducing flames in hot and cold conditions.

(iv) **Charcoal cavity test:** This test is carried out on a charcoal block in which a small cavity has been made by a knife. About 0.1 g of the substance is mixed with 0.2 g of anhydrous Na_2CO_3 or fusion mixture and the mixture is placed in the cavity. The mass is moistened with a drop of water and heated in a reducing flame with the blow pipe. The Bead or incrustation formed is observed. When metallic salt is heated with Na_2CO_3 , the metal carbonate is formed which decomposes into oxide. The carbon of the block reduces the oxide into metal. For example,



(v) **Cobalt nitrate charcoal test:** A small amount of the substance and twice its bulk of sodium carbonate is placed in the charcoal cavity. A drop of water is added and the mass is heated in an oxidising flame with the help of blow pipe. After cooling, one or two drops of cobalt nitrate solution are added and the mass is again heated in the oxidising flame. The colour produced in the cavity is noted.

By heating the salt with sodium carbonate, the oxide is formed which on heating with cobalt nitrate form a mixed oxide of a characteristic colour.



Rinmann green

	Observation	Inference
(a)	Blue mass	Aluminium
(b)	Green residue	Zinc
(c)	Pink residue	Magnesium
(d)	Bluish-green	Tin

Dry Heat

A white sublimate: **Ammonium** (usually NH_3 also)

A white or grey sublimate: **Mercury, Arsenic** or **Antimony**

A yellow sublimate (S): a **Sulphur** compound

A yellow residue (PbO) : a **Lead** compound perhaps

A residue yellow when hot, white when cold (ZnO): a **Zinc** compound

$\text{O}_2\uparrow$ (glowing splint): a **Chlorate** or **peroxide** perhaps

$\text{CO}_2\uparrow$ (lime water test) : a **Bicarbonate** or **Carbonate**

SO_2 (smell and KMnO_4) : a **Thiosulphate, Bisulphate** or occasionally a **Sulphate**

$\text{SO}_3\uparrow$ (white fumes): some **Sulphates**

$\text{I}_2\uparrow$ (violet vapour) : an **Iodate** or possibly **iodide**

$\text{Br}_2\uparrow$ (red vapour) : a **Bromate** or possibly **Bromide**

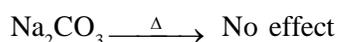
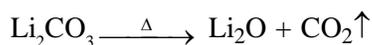
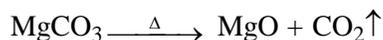
General Solubility Rules: (Solubility in water)

1. All nitrates, nitrites bicarbonates, acetates, thiosulphate, chlorates are soluble. KClO_3 and KClO_4 are sparingly soluble.
2. All chlorides, bromides and iodides are soluble, except those of lead, mercurous and Silver ions. Lead chloride is only slightly soluble in cold water but more soluble in hot water. Antimony and bismuth salts hydrolyse in the absence of acids to the insoluble oxychlorides SbOCl and BiOCl .
3. All carbonates and phosphates are insoluble, except those of Na^+ , K^+ and NH_4^+ and Ag^+ are moderately soluble.
4. All carbonates and phosphates are insoluble, except those of Na^+ , K^+ and NH_4^+ .
5. All hydroxides, oxides and sulphides except those of Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Sr^{2+} are insoluble.

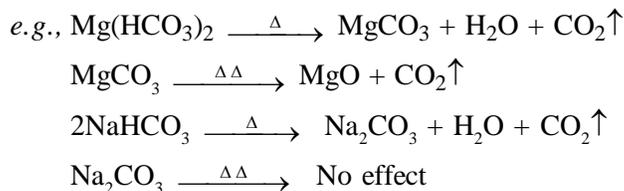
Heating Effect

Bicarbonates and Carbonates:

1. Generally carbonates on heating give metal oxide and CO_2
2. Except Li_2CO_3 , all alkalimetal carbonates are thermally stable.
3. Silver and Mercury carbonates on heating precipitates metal, CO_2 and O_2

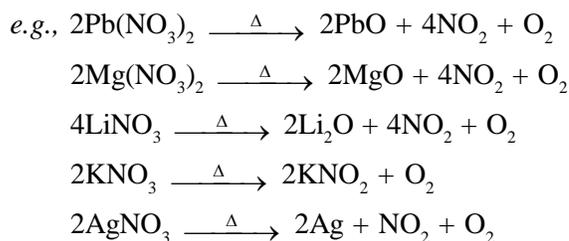


All bicarbonates on heating first give carbonate. Water and CO₂ and an strong heating carbonate formed is further decomposed into metal oxide and CO₂.



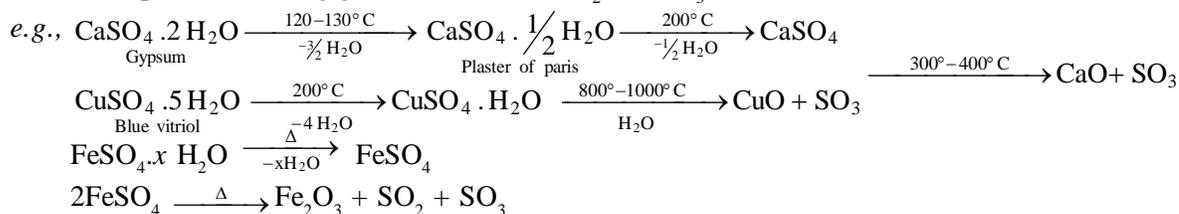
Nitrates

1. Generally nitrates on heating give metal oxide, NO₂ and O₂
2. Except LiNO₃, all alkali metal nitrates decomposed into metal nitrite and O₂.
3. Silver and Mercury nitrates on heating precipitates metal, NO₂ and O₂



Sulphates

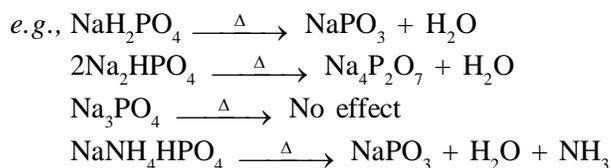
1. Sulphates of Ba, Pb, Na etc. are quite stable and loose water of crystallization on heating.
2. On strong heating sulphates give metal oxide and SO₃ (some times into SO₂ and O₂)
3. Ferrous sulphate on heating gives ferric oxide, SO₂ and SO₃ both



Phosphates

Phosphoric acid (H₃PO₄) forms three series of phosphates *i.e.* 1° phosphate (H₂PO₄⁻); 2° phosphate (HPO₄⁻); and 3° phosphate (PO₄⁻)

- 1° phosphate on heating give metaphosphate and H₂O
- 2° phosphate on heating give pyrophosphate and H₂O
- 3° phosphate are thermally stable



Sodium ammonium Hydrogen phosphate is 2° phosphate however it behaves as 1° phosphate because NH₄⁺ is treated like Hydrogen on heating.

SOLVED EXAMPLES

Example 1 : An aqueous solution of gas (X) shows the following reactions

- It turns red litmus blue.
- When added in excess to a copper sulphate solution, a deep blue colour is obtained.
- On addition of FeCl_3 solution, a brown precipitate, soluble in dilute HNO_3 is obtained.

Identify (X) and give equations for the reactions at step (b) and (c).

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



(tetra-amine cupric
sulphate) deep blue

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



Brown precipitate)

Brown precipitate is soluble in HNO_3



Soluble complex)

Example 2 : A compound (A) on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure of HCl . Heating it continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B) when heated with zinc powder. However the compound (A), when heated alone does not give nitrogen. Identify (A) and (B)

Solution : Gas (B) gives white fumes with HCl hence it should be NH_3 . Thus, compound (A) must be an ammonium salt.

We know that nitrates and nitrites on heating with Zn and alkali liberate NH_3 gas. Hence the compound (A) should be ammonium nitrate or nitrite. But compound (A) does not give N_2 on heating hence it may not be ammonium nitrite.

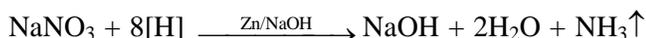
Reactions involved:



(A)



(White fumes)



Example 3 : (a) The yellow coloured precipitate of compound (A) is formed on passing H_2S through a neutral solution of salt (B).

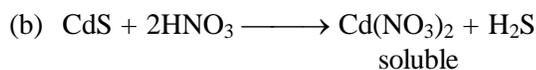
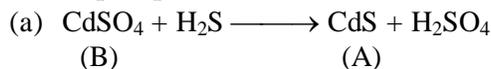
(b) (A) is soluble in hot dilute HNO_3 but insoluble in yellow ammonium sulphide.

(c) 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).

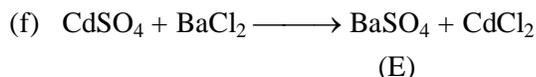
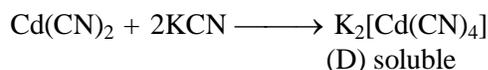
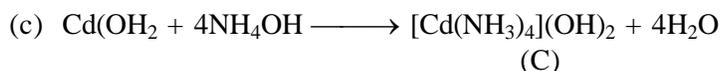
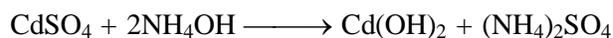
- (d) The solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).
- (e) The solution of (D) on treatment with H₂S gives (A).
- (f) The solution of (B) in dil. HCl on treatment with a solution of BaCl₂ gives white precipitate of compound (E) which is insoluble in conc. HNO₃.

Identify (A) to (E) and give chemical equations for the reactions at steps (a) to (c) to (f)

Solution : Yellow precipitate of CdS is (A)



CdS \longrightarrow Insoluble in yellow ammonium sulphide



- Which of the following gives a suffocating gas when treated with dilute HCl?
 - carbonate
 - sulphite
 - sulphate
 - borate
- The acidic solution of a salt produces blue colour with KI starch solution. the salt may be
 - sulphite
 - bromide
 - nitrite
 - chloride
- Sulphite on treatment with dil. H₂SO₄ liberates a gas which
 - turns lead acetate paper black
 - burns with blue flame
 - smells like vinegar
 - turns acidified K₂Cr₂O₇ paper green
- A gas is evolved which burns with blue flame when the mixture is heated with conc. H₂SO₄. The mixture contains:
 - carbonate
 - oxalate
 - nitrate
 - nitrite
- Mercurous chloride turns black on treatment with ammonium hydroxide. This is due to the formation of
 - Hg(NH₂)Cl
 - Hg₂Cl₂.NH₄OH

-
- (d) heated with HNO_2
16. A white solid is first heated with dilute H_2SO_4 and then with concentrated H_2SO_4 . No action is observed in either case. The solid contains:
- (a) sulphide (b) sulphite
(c) sulphate (d) thiosulphate
17. The salt used for performing 'bead test' in qualitative inorganic analysis is
- (a) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
(b) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
(c) $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$
(d) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
18. The only cations present in a slightly acidic solution are Fe^{3+} , Zn^{2+} and Cu^{2+} . The reagent which when added in excess to this solution would identify and separate Fe^{3+} in one step is
- (a) 2M HCl (b) 6 M NH_3 (c) 6 M NaOH (d) H_2S gas
19. Concentrated aqueous sodium hydroxide can separate a mixture of
- (a) Al^{3+} and Sn^{2+} (b) Al^{3+} and Fe^{3+}
(c) Al^{3+} and Zn^{2+} (d) Zn^{2+} and Pb^{2+}
1. Sometimes, a white precipitate is obtained even in the absence of members of Ist group on the addition of HCl. Explain it.
2. Give examples and explain with equations:
- (a) Two colourless solutions give a black precipitate on mixing.
(b) Two colourless solutions give a red precipitate on mixing, soluble in excess of one of them.
(c) Two colourless solutions give a white precipitate on mixing, soluble in ammonium hydroxide.
(d) Two colourless solutions give a yellow precipitate on mixing.
3. What is yellow ammonium sulphide? Why is yellow ammonium sulphide and not ordinary ammonium sulphide used for the separation of II A and II B sub-groups?
4. Explain, while performing qualitative analysis of basic radicals of third group, why ammonium chloride is added in excess before adding ammonium hydroxide?
5. What happens when
- (a) Copper sulphate is treated with excess of NH_4OH
(b) Bismuth chloride is treated with sodium stannite solution in presence of NaOH
-

MISCELLANEOUS ASSIGNMENT

Comprehension

The following observations were made on Na_2CrO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$.

- When CO_2 was passed over Na_2CrO_4 , then $\text{Na}_2\text{Cr}_2\text{O}_7$ was formed.
- When Zn is added to acidic solution of $\text{Na}_2\text{Cr}_2\text{O}_7$, the colour changes from orange to green, then to blue and then back to green.
- Na_2CrO_4 when added to a nitrate salt solution gave a yellow coloured precipitate which after separation and drying followed by flame test gave a green coloured flame.

- What is the function of CO_2 in the first observation?
 - Acts as an oxidising agent
 - Acts as a reducing agent
 - Produces chromium and oxygen
 - Makes the solution acidic
 - The reason for the colour $\text{Na}_2\text{Cr}_2\text{O}_7$ solution to first change from orange to green on adding Zn is because
 - Zn is reducing agent and changes Cr^{+4} to Cr^{+3}
 - Zn is a reducing agent and changes Cr^{+6} to Cr^{+3}
 - Zn is a reducing agent and it reduces Ca^{+6} to Cu^{+2}
 - None of these
 - The second change in colour in the solution that is from green to blue is due to the conversion of
 - Cr^{+3} to Cr^{+1}
 - Cr^{+3} to Cr
 - Cr^{+3} to Cr^{+2}
 - Cr^{+3} to Cr^{+4}
 - The extent of splitting in *d*-orbitals is more when the chromium in the solution is in
 - +1 oxidation state
 - +2 oxidation state
 - +3 oxidation state
 - +6 oxidation state
 - The nitrate salt which gives a yellow precipitate with Na_2CrO_4 and the yellow precipitate gives greenflame with bunsen burner
 - Pb^{2+}
 - Ca^{2+}
 - Mg^{2+}
 - Ba^{2+}
-

PREVIOUS YEAR QUESTIONS

IIT-JEE/JEE-ADVANCE QUESTIONS

1. A substance on treatment with dilute H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. These reactions indicate the presence of
(a) CO_3^{2-} (b) S^{2-} (c) SO_3^{2-} (d) NO_2^-
2. A metal nitrate gives black ppt. with KI and on adding excess of KI it gives orange colour. It is
(a) Hg^{+2} (b) Bi^{+3} (c) Sn^{+2} (d) Pb^{+2}
3. Which of the following hydrogen halides react(s) with AgNO_3 (aq) to give a precipitate that dissolves in $\text{Na}_2\text{S}_2\text{O}_3$ (aq)?
(a) HCl (b) HF (c) HBr (d) HI
4. The compound that does **NOT** liberate CO_2 , on treatment with aqueous sodium bicarbonate solution, is
(a) Benzoic acid (b) Benzenesulphonic acid
(c) Salicylic acid (d) Carboic acid (Phenol)
5. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are)
(a) Ba^{2+} , Zn^{2+} (b) Bi^{3+} , Fe^{3+} (c) Cu^{2+} , Pb^{2+} (d) Hg^{2+} , Bi^{3+}

Paragraph for Question 5 to 6

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (**P**) and a filtrate (**Q**). The precipitate **P** was found to dissolve in hot water. The filtrate (**Q**) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (**R**) with H_2S in an ammoniacal medium. The precipitate **R** gave a coloured solution (**S**), when treated with H_2O_2 in an aqueous NaOH medium.

5. The precipitate **P** contains
(a) Pb^{2+} (b) Hg_2^{2+} (c) Ag^+ (d) Hg^{2+}
6. The coloured solution **S** contains
(a) $\text{Fe}_2(\text{SO}_4)_3$ (b) CuSO_4 (c) ZnSO_4 (d) Na_2CrO_4

DCE QUESTIONS

1. The brown ring complex compound is formulated as $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$. The oxidation state of iron is
(a) 1 (b) 2 (c) 3 (d) 0
-

-
2. When a colourless gas is passed through bromine water only decolourisation takes place. The gas is
(a) SO_2 (b) HBr (c) HCl (d) H_2S
3. $\text{K}_2\text{Cr}_2\text{O}_7$ gets oxidized in which medium
(a) Acidic (b) Neutral (c) basic (d) All of these
4. In an alkaline condition KMnO_4 reacts as follows: $2\text{KMnO}_4 + 2\text{KOH} \longrightarrow 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + \text{O}$. Its equivalent weight is
(a) 31.6 (b) 52.7 (c) 49 (d) 158
5. The brown ring complex compound is formulated as $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$. The oxidation state of iron is
(a) 1 (b) 2 (c) 3 (d) 0
6. The brown ring complex compound is formulated as $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$. The oxidation state of iron is
(a) 1 (b) 2 (c) 3 (d) 0
7. Which do not decolourise KMnO_4 aq. solution
(a) $\text{C}_2\text{O}_4^{2-}$ (b) HSO_3^- (c) CO_3^{2-} (d) SO_3^{2-}

AIEEE/JEE-MAINS QUESTIONS

1. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is
(a) +4 (b) +6 (c) +2 (d) +3
2. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives
(a) HgNH_2Cl (b) $\text{NH}_2\text{-Hg-Hg-Cl}$ (c) Hg_2O (d) HgO
3. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is
(a) +4 (b) +6 (c) +2 (d) +3
4. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl because HCl
(a) furnishes H^+ ions in addition to those from oxalic acid
(b) reduces permanganate to Mn^{2+}
(c) oxidises oxalic acid to carbon dioxide and water
(d) gets oxidised by oxalic acid to chlorine
-

SUBJECTIVE PROBLEM

- (c) Stannous chloride is treated with mercuric chloride.
- (d) Excess of water is added to concentrated solution of antimony chloride.
6. (a) What is the function of concentrated HNO_3 in third group?
(b) Will you add HNO_3 in third group even if iron is given in ferric state in the mixture?
(c) Can you use NaCl and NaOH instead of NH_4Cl and NH_4OH in third group?
7. Identify the unknown species and complete the following:
- (a) $(A) + \text{BaCl}_2 \longrightarrow$ White precipitate
(b) $\text{NaOH} + (B) \longrightarrow$ NH_3 gas
(c) $(C) + \text{MnO}_2 + \text{H}_2\text{SO}_4 \longrightarrow$ Violet vapours
(d) $(D) + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$ Green coloured solution
(e) $(E) \xrightarrow{\text{Heat}}$ Yellow compound
Colourless
8. Fill in the ^{solid} blanks
- (a) Lime water is used for the test of
- (b) Acetates are in water.
- (c) Nitrates when treated with conc. H_2SO_4 evolve gas.
- (d) Chromyl chloride test is performed for
- (e) Chlorides of are insoluble in dilute HCl .
- (f) H_2S is used as a group reagent in group in medium while in group in medium.
- (g) HgS is in dilute HNO_3
- (h) Yellow ammonium sulphide dissolves sulphides of
- (i) Group reagent for third group radicals is
- (j) If metal ions of group III are precipitated by NH_4Cl medium and NH_4OH without prior oxidation by concentrated HNO_3 is not completely precipitated.
- (k) colour of zinc sulphide is
- (l) In V group, K_2CrO_4 is used for the test of
- (m) precipitate is formed when Na_2HPO_4 is added to magnesium salt in presence of NH_4OH .
- (n) Ammonium thiocyanate is used in the detection of
9. State, whether the following statements are **True** or **False**:
- (a) AgCl dissolves in NH_4OH .
- (b) Sb_2S_3 is yellow in colour.
- (c) Copper sulphate forms a violet colour with potassium ferrocyanide solution.
- (d) Both phosphate and arsenic ions give yellow precipitate when heated with nitric acid and ammonium molybdate.
- (e) Addition of ammonium chloride to a sodium containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia.
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- (f) Ammonium sulphate can be used in place of ammonium chloride in third group.
 - (g) Iodine is liberated when an iodide is heated with conc. H_2SO_4 .
 - (h) It is not necessary to use HNO_3 in the third group if ferric compound is given in a mixture.
 - (i) In the test of acetate radical, neutral ferric chloride is used.
 - (j) Nessler's reagent is the alkaline solution of K_2HgI_4 .
 - (k) The solubility product of cadmium sulphide is highest amongst the sulphides of second group.
 - (l) Cobalt can be tested with dimethyl glyoxime.
 - (m) Cobalt salt with KNO_2 and acetic acid gives yellow precipitate.
 - (n) The carbonates of barium, strontium and calcium are soluble in acid.

10. Explain with proper reasoning:

- (a) The aqueous solution of ferric chloride can not be stored. It is always acidified with hydrochloric acid.
- (b) The aqueous solution of FeCl_3 possesses yellow colour. The colour becomes green on passing H_2S gas.
- (c) The aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is orange. On adding an alkali, it turns yellow.
- (d) In the test of oxalate, the evolved gas burns with blue flame only initially.
- (e) Why yellow ammonium sulphide is used in group (II) sulphides separation?
- (f) Why zinc sulphide is not precipitated when H_2S is passed through ZnCl_2 solution?
- (g) CaSO_4 is insoluble but is not precipitated when excess of $(\text{NH}_4)_2\text{SO}_4$ is added to CaCl_2 .
- (h) Why $(\text{NH}_4\text{Cl} + \text{NH}_4\text{OH})$ and not $[(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{OH}]$ is used in group (III) analysis?
- (i) Why is it necessary to add few drops of conc. HNO_3 to the filtrate of group (II) before the use of $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$.
- (j) Why NaOH cannot be used to separate $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$?

11. An aqueous solution of salt (A) gives a white precipitate (B) with NaCl solution. The filtrate gives a black precipitate, (C) when H_2S is passed into it. Compound (B) dissolves in hot water and the solution gives a yellow precipitate (D) on treatment with sodium iodide and cooling. The compound (A) does not give any gas with dilute HCl but liberates a reddish-brown gas on heating. Identify the compounds (A) to (D)

12. A mixture of two salts was treated as follows:

- (a) The mixture was heated with manganese dioxide and concentrated H_2SO_4 , when yellowish green gas was liberated.
- (b) The mixture on heating with NaOH solution gave a gas which turned red litmus blue.
- (c) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with NH_4CNS .
- (d) 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 (a), (b), (c) and (d)

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

Identify (A) to (E) and give chemical equations for the reactions at steps (a) to (e)

14. A colourless solid (A) on hydrolysis produces a heavy white precipitate (B). Solid (A) gives a clear solution in conc. HCl ; however, when added to large amount of water, it again gives precipitate of (B). When H_2S is passed through a suspensions of (A) or (B), a brown black precipitate of (C) is obtained. compound (A) liberates a gas (D) on treating with H_2SO_4 . The gas (D) is water soluble and gives white precipitate (E) with solution of mercurous salt but not with mercuric salt. Identify (A) to (E). Also report (A), (B) and (C) if (C) is orange precipitate.
15. An inorganic compound (A) in its aqueous solution produced a white ppt. with NaOH , which gets dissolved in excess of NaOH . The aqueous solution of (A) also produced white ppt. with NH_4OH which also dissolved in excess of NH_4OH . Also its aqueous solution produced light yellow ppt. with AgNO_3 solution, soluble in dil. HNO_3 . Identify (A).
16. A colourless solid (A) on heating gives a white solid (B) and a colourless gas (C). (B) gives a reddish brown gas on treatment with dil. acids. When (B) is heated with solid NH_4Cl , a colourless gas (D) and a residue (E) are obtained. When (A) is heated with $(\text{NH}_4)_2\text{SO}_4$ a colourless gas (F) is obtained along with a white residue (G). Both (E) and (G) imparts yellow colour to flame. The gas (C) reacts with Mg to give white powder. The gas (D) is heated with calcium and the product on hydrolysis gives NH_3 . Identify (A) to (G).
17. 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). The gases when passed through an acidified KMnO_4 solution discharges the pink colour and when passed through acidified BaCl_2 solution gave a white precipitate. Identify (A), (B), (C), (D), (E) and (F).
18. An aqueous solution of salt gave the following reactions:
- (a) With barium chloride solution, white precipitate insoluble in HCl is obtained.
- (b) Addition of excess KI gives a brown precipitate which turns white on addition of excess of hypo.
- (c) With potassium ferrocyanide solution, chocolate coloured precipitate is formed. Identify the salt.
-

-
- 19.** (a) The solution of salt (A) in dilute HCl gives a dirty yellow precipitate on passing H_2S gas. The precipitate dissolves in yellow ammonium sulphide.
- (b) The salt (A) gives chromyl chloride test.
- (c) (A) first forms a white precipitate with NaOH which dissolves in excess of NaOH forming a compound (B).
- (d) The alkaline solution of (B) when added to bismuth chloride gives a black precipitate (C),
- (e) (A) reduces $HgCl_2$ in solution to a white precipitate (D) which changes to grey. Identify (A), (B), (C) and (D). Give reactions at steps (a) to (e)
- 20.** (a) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of (A) in NH_4OH
- (b) (B) on treatment with aqua-regia gives (A).
- (c) The solution of (A) is treated with excess of sodium bicarbonate and then with NaOH and bromine water. No apple green colour is observed. The solution is heated, when a black precipitate (C) is obtained.
- (d) (A) on treatment with potassium cyanide give a buff coloured precipitate which dissolves in excess of this reagent forming a compound (D)
- Identify (A) to (D) and give chemical equations for the reactions at steps (a) to (d)
-

ANSWERS

Objective Questions

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (d) | 4. (b) | 5. (c) |
| 6. (d) | 7. (c) | 8. (a) | 9. (b) | 10. (d) |
| 11. (c) | 12. (b) | 13. (a) | 14. (c) | 15. (b) |
| 16. (c) | 17. (c) | 18. (b) | 19. (b) | |

Miscellaneous Assignment

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (d) | 2. (b) | 3. (c) | 4. (d) | 5. (d) |
|--------|--------|--------|--------|--------|

Previous Year Questions

- | | | | | |
|--------|--------|------------|--------|--------|
| 1. (c) | 2. (b) | 3. (a,c,d) | 4. (d) | 5. (a) |
| 6. (d) | | | | |

DCE QUESTIONS

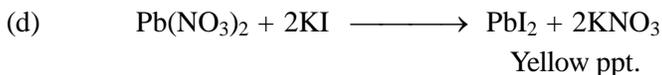
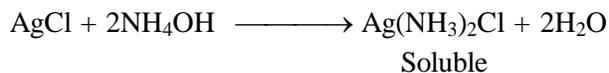
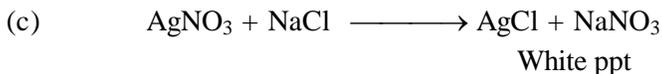
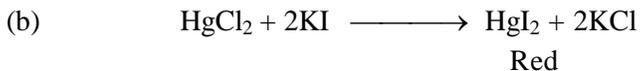
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|--------|--------|--------|--------|--------|
| 1. (b) | 2. (a) | 3. (a) | 4. (d) | 5. (b) |
| 6. (b) | 7. (c) | | | |

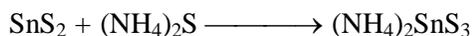
MAINS QUESTIONS

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|--------|--------|--------|--------|
| 1. (d) | 2. (a) | 3. (d) | 4. (b) |
|--------|--------|--------|--------|

Subjective Problems

2. (a) Lead salt + sodium sulphide.





- (f) The reaction of ZnCl_2 and H_2S produces HCl which dissolves ZnS .



- (g) The precipitate of CaSO_4 dissolves in $(\text{NH}_4)_2$ forming a complex (double sulphate).



Soluble

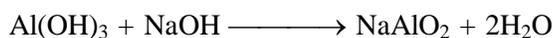
- (h) The presence of sulphate ions brings precipitation of various basic ions such as Ca^{2+} , Ba^{2+} , Sr^{2+} , etc.

- (i) The addition of few drops of conc. HNO_3 serves two purposes.

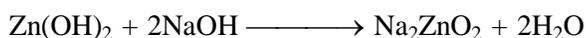
(a) It precipitates the dissolved H_2S .

(b) It converts ferrous ion into ferric ion if iron is present

- (j) Both the hydroxides dissolve in NaOH .



Soluble



Soluble

11. (A) $\text{Pb}(\text{NO}_3)_2$; (B) PbCl_2 ; (C) PbS ; (D) PbI_2

12. Test (b) and (d) show the presence of NH_4^+ test (a) shows the presence of Cl^- ion and test (c) shows the presence of Fe^{2+} and Fe^{3+}

13. (A) CoCl_2 ; (B) CoS ; (C) $\text{K}_4[\text{Co}(\text{CN})_6]$ (D) $\text{K}_3[\text{Fe}(\text{CN})_6]$

14. (A) BiCl_3 ; (B) BiOCl ; (C) Bi_2S_3 ; (D) HCl ; (E) AlBr_3

15. AlBr_3

16. (A) NaNO_3 ; (B) NaNO_2 ; (C) O_2 ; (D) N_2 ; (E) NaCl ;
(F) N_2O ; (G) Na_2SO_4

17. (A) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; (B) FeSO_4 ; (C) Fe_3O_4 ; (D) Fe_2O_3 ;
(E) SO_2 ; (F) SO_3

18. CuSO_4

19. (A) SnCl_2 ; (B) Na_2SnO_2 ; (C) Bi (D) Hg_2Cl_2

20. (A) MnO_2 ; (B) K_2MnO_4 ; (C) KMnO_4 ; (D) Cl_2
-