3. Pure sodium carbonate should be used. "Analar" or A.R. grade sodium carbonate is highly satisfactory. Ordinary sodium carbonate contains chloride and sulphate as impurities and responds to tests for these anions. As a consequence, misleading results are encountered.
4. If ammonia is given out on boiling the mixture with sodium carbonate solution, the former must be expelled completely because it tends to complex copper, cadmium, nickel, etc. into the soluble ammine which goes into the filtrate.
5. Some of the cations like As^{3+}, Sb^{3+}, Sn^{2+}, etc. partly go into the filtrate due the amphoteric nature of the parent metals. These should be completely removed by acidifying the "sodium carbonate extract" with pure dil. HCl and passing H_2S gas. Reject the precipitate of their sulphides. Expel H_2S from the filtrate by boiling and use it for the detection of anions.

Na_2CO_3 Neutral Solution

Take 10 cc of the prepared Na_2CO_3 extract. To this add dil. HNO_3 excess of unused Na_2CO_3 (CO_2 is evolved) is neutralised and then render it faintly acidic (test with litmus paper). Heat to boiling for few minutes, allow to cool, then add NH_4OH (dilute) solution until just alkaline and again boil for a few minutes to expel slight excess of ammonia. The clear solution so obtained is practically **Na_2CO_3 neutral solution**. If a ppt. is obtained, it is filtered and the filtrate is used as **Na_2CO_3 neutral solution**. The ppt indicates sulphides of As, Sb and Sn and possible salts of amphoteric bases such as those of Pb, Sn, Al, Zn, etc. The ppt should be rejected.

1. Identification of Carbonate and Bicarbonate

The carbonates of sodium, potassium and ammonium are soluble in water. The remaining carbonates are insoluble in water. All bicarbonates are soluble in water.

Take 0.5 g of the mixture in a test tube containing about 4-5 ml of distilled water. Warm and filter.

Filtrate may have soluble carbonate or bicarbonate. Divide it into two portions. (*i*) To part I add dil. HCl acid. A brisk effervescence due to liberation of CO_2 which turns lime water milky indicates soluble carbonates or bicarbonates. $CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2 \uparrow$ $HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \uparrow$	Residue may have insoluble carbonate. To this add dil. HCl acid. A brisk effervescence with the evolution of CO_2 which turns lime water milky confirms carbonate.

(*ii*) Add $MgSO_4$ solution to part II and shake well. If a white ppt. is obtained in cold, it confirms carbonate. $CO_3^{2-} + Mg^{2+} \longrightarrow MgCO_3$ White ppt. If no ppt. appears in cold, heat it to boiling. Formation of white ppt. confirms bicarbonate $Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2$ $Mg(HCO_3)_2 \longrightarrow MgCO_3\downarrow + H_2O + CO_2\uparrow$	$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$

Test of a bicarbonate in presence of a carbonate

Take 0.5 g of the mixture in a test tube containing about 4-5 ml of distilled water. Warm and filter. To this filtrate, add excess of calcium chloride solution when a white ppt. of $CaCO_3$ is formed indicating the presence of *carbonate*. Calcium bicarbonate formed is soluble in water.

$$Ca^{+2} + CO_3^{2-} \longrightarrow \underset{\text{ppt.}}{CaCO_3}$$

$$Ca^{+2} + 2HCO_3^- \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

Filter the white ppt. and add dilute ammonia solution to the clear filtrate when soluble calcium bicarbonate is converted into $CaCO_3$ and white turbidity appears confirming the presence of a bicarbonate in the test solution.

$$Ca(HCO_3)_2 + 2NH_3 \longrightarrow (NH_4)_2CO_3 + \underset{\text{ppt.}}{CaCO_3}$$

2. Identification of Sulphide

The sulphides of alkali metals are soluble in water whereas the normal sulphides of alkaline earth metals dissolve with difficulty. All the remaining sulphides are insoluble in water. The various tests for sulphide are as follows:

(*i*) *Nitroprusside test*: Add 1–2 ml of freshly prepared sodium nitroprusside solution to 2–3 ml of sodium carbonate extract. A purple or violet colour confirms sulphide.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$$

(*ii*) *Lead acetate test* : Acidify 1–2 ml of the "sodium carbonate extract" with dil. acetic acid and boil the solution to expel CO_2. To this add 1–2 ml of lead acetate solution. If a black ppt. appears, it confirms sulphide.

$$Pb^{2+} + S^{2+} \longrightarrow PbS$$
Black ppt.

(iii) *Cadmium carbonate test* : Add 2 ml of "sodium carbonate extract" to 0.2 g of cadmium carbonate in a test tube. Shake the test tube. Appearance of yellow ppt. confirms the presence of sulphide.

$$S^{2-} + Cd^{2+} \longrightarrow CdS \downarrow$$
Yellow ppt.

3. Identification of Sulphite

Sulphites of the alkali metals and of ammonium dissolve readily in water whereas sulphites of other metals are practically insoluble in water. However, all sulphites are soluble in dil. hydrochloric acid. The various tests for the identification of sulphites are:

(i) *$BaCl_2$ test* : To 5 ml of "sodium carbonate extract" add excess of $BaCl_2$ solution. If a white ppt. appears, it may be due to sulphite, sulphate or excess sodium carbonate present in the solution.

$$SO_3^{2-} + Ba^{2+} \longrightarrow BaSO_3 \downarrow$$
$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4 \downarrow$$
$$CO_3^{2-} + Ba^{2+} \longrightarrow BaCO_3 \downarrow$$

Filter the ppt. and divide the ppt. into four parts :

(a) To part I add dil. HCl. If there is evolution of SO_2 which turns acidified dichromate paper green, it confirms sulphite.

$$BaSO_3 + 2H^+ \longrightarrow Ba^{2+} + H_2O + SO_2 \uparrow$$
$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$
Green

(b) To part II add a few drops of potassium permanganate solution followed by the addition of 3 ml of dil. H_2SO_4 acid. If the colour of permanganate gets discharged, the presence of sulphite is confirmed.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$BaSO_3 + H_2O \longrightarrow BaSO_4 + 2H^+ + 2e^-$$
(White ppt.)

(c) To part III add bromine water. On warming this solution, the colour of bromine gets discharged and a white ppt. insoluble in acids is obtained. This confirms sulphite.

$$BaSO_3 + Br_2 + H_2O \longrightarrow BaSO_4 + 2HBr$$
ppt.

(d) To part IV, add I_2 solution. If iodine colour is decolourised, sulphite is confirmed.

$$BaSO_3 + I_2 + H_2O \longrightarrow BaSO_4 + 2H_2O$$

(*ii*) *Sodium nitroprusside test* : This test should not be performed if sulphide is also present.

Take a few drops of "sodium carbonate extract" in a test tube. To this add 2 drops of 1% sodium nitroprusside solution and one drop of saturated zinc sulphate solution. Appearance of a rose red colour confirms the presence of sulphite.

$$Na_2[Fe(CN)_5NO] + SO_3^{2-} + 2Na^+ \xrightarrow{ZnSO_4} \underset{\text{(Rose red colour)}}{Na_4[Fe(CN)_5NO(SO)]}$$

4. Identification of Thiosulphate

The thiosulphates of alkali metals dissolve readily in water while the remaining ones are sparingly solution in water. The various tests for its identification are :

(*i*) *Silver nitrate test* : Add 2–3 ml of $AgNO_3$ solution to 1 ml of "water extract" or "sodium carbonate extract" which is already neutralised with dil. acetic acid. Appearance of white ppt. turning yellow, orange, brown and finally black in quick succession confirms the presence of thiosulphate.

$$S_2O_3^{2-} + 2Ag^+ \longrightarrow \underset{\text{(White ppt.)}}{Ag_2S_2O_3\downarrow}$$

Silver thiosulphate is soluble in excess of thiosulphate. At first a sparingly soluble complex $Na(AgS_2O_3)$ is formed which dissolves in excess of thiosulphate forming a soluble complex.

$$Ag_2S_2O_3 + Na_2S_2O_3 \longrightarrow 2Na[AgS_2O_3]$$

$$2Na[AgS_2O_3] + Na_2S_2O_3 \longrightarrow \underset{\text{Soluble}}{Na_4[Ag_2(S_2O_3)_3]}$$

By warming or exposing to sunlight, As_2S is precipitated.

$$2NaAg[S_2O_3] \longrightarrow Ag_2S + S + SO_2 + Na_2SO_4$$

$$Na_4[Ag_2(S_3O_3)_3] \longrightarrow Ag_2S + S + SO_2 + Na_2S_2O_3 + Na_2SO_4$$

(*ii*) *Ferric chloride test* : Take 1–2 ml of sodium carbonate extract neutralised by dil. acetic acid or 1–2 ml of water extract in a test tube. To this add a few drops of ferric chloride solution. A violet red colour which soon fades away confirms the presence of thiosulphate.

$$2S_2O_3^{2-} + Fe^{3+} \longrightarrow [Fe(S_2O_3)_2]^-$$

$$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$$

5. Identification of Nitrite

All nitrites except silver nitrite are soluble in water. However, the silver salt being the least soluble in water. The various tests for identification of nitrites are as follows :

(*i*) *Starch-iodide test* : Acidify 1–2 ml of the "sodium carbonate extract" with dil. acetic or dil. sulphuric acid and boil the solution to expel CO_2

Then add a crystal of KI and 1 ml of starch solution. Also, add a few drops of dil. H_2SO_4. A deep blue coloration confirms nitrite.

$$2NO_2^- + 4H^+ + 2I^- \longrightarrow 2NO + I_2 + 2H_2O$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue coloured complex}$$

The blue colour is due to the liberation of iodine from hydroiodic acid by nitrous acid.

(*ii*) *Thiourea test*: Acidify 2–3 ml of "sodium carbonate extract" with dilute acid. Boil off CO_2. To this add a pinch of thiourea and a few drops of dil. HCl and ferric chloride solution. A characteristic blood red colouration indicates the presence of nitrite.

$$NO_2^- + H_2NCSNH_2 \longrightarrow N_2 \uparrow + CNS^- + H_2O$$

$$CNS^- + Fe^{+3} \longrightarrow [Fe(CNS)]^{2+}$$

(Blood red colour)

NOTE *As thiocyanates and iodides interfere in this test, these must be removed by precipitation with silver nitrate solution before doing thiourea test for nitrite.*

(*iii*) *Brown ring test* : Acidify "Na_2CO_3 extract with dil. acetic acid or dil. sulphuric acid. Add this solution carefully to a concentrated solution of ferrous sulphate acidified with acetic acid or dil. sulphuric acid. If a brown ring due to the compound [Fe, NO] SO_4 is formed at the junction of the two liquids, it confirms the presence of nitrite.

$$3NO_2^- + 2H^+ \longrightarrow NO_3^- + 2NO + H_2O$$

$$FeSO_4 + NO \longrightarrow [FeNO]SO_4$$

(Brown ring)

NOTE *Nitrate gives a corresponding reaction only when conc. sulphuric acid is added in place of dil. sulphuric acid.*

(*iv*) *m-phenylenediamine rest* : Acidify 1–2 ml of the sodium carbonate extract with dil. acetic acid and boil to expel CO_2. To this add a few drops of *m*-phenylene diamine hydrochloride solution followed by a few drops of hydrochloric acid, brown ppt. confirms nitrite.

$$NO_2^- + H^+ \longrightarrow HNO_2$$

$$2C_6H_4\begin{matrix}NH_2\\NH_2\end{matrix} + HNO_2 \longrightarrow C_6H_4\begin{matrix}NH_2\\N{=}N{-}C_6H_3\begin{matrix}NH_2\\NH_2\end{matrix}\end{matrix} + H_2O$$

(Bismark brown)

6. Identification of Acetate

All acetates, except the silver salts, are readily soluble in water. Owing to the feeble nature of the acid, some of its salts are easily hydrolysed with the formation of insoluble basic salts. However, the various tests for its identification are as follows :

(*i*) *Ester test* : Heat a pinch of dry mixture with a few drops of conc. H_2SO_4 and 0.5 ml of ethyl alcohol. A pleasant pear-like fruity smell shows the presence of acetate.

$$CH_3COOH + C_2H_5OH \rightleftharpoons \underset{\text{(Fruity odour)}}{CH_3COOCH_5} + H_2O$$

(*ii*) *Ferric chloride test* : To 1 ml of water extract (for 1 ml of sodium carbonate extract neutralised with dil. acetic acid) add carefully neutral ferric chloride solution. Appearance of red colour may be due to the presence of acetate. Now dilute and boil the liquid. A dark-red precipitate of basic ferric acetate is formed.

$$3CH_3COO^- + Fe^{3+} \longrightarrow \underset{\substack{\text{Ferric acetate}\\\text{(red colour)}}}{(CH_3COO)_3Fe}$$

$$(CH_3COO)_3Fe + 2H_2O \xrightarrow{\text{Boil}} \underset{\substack{\text{Basic ferric acetate}\\\text{(Brown ppt.)}}}{Fe(OH)_2(O.COCH_3)} + 2CH_3COOH$$

NOTE

(*a*) *Thiocyanate if present in the mixture interferes in the test as it also gives red coloration with ferric chloride solution.*

(*b*) *Bench $FeCl_3$ solution is acidic, due to the hydrolysis which results in the formation of free HCl acid. In order to prepare a neutral solution of ferric chloride, take 5 ml of bench $FeCl_3$ solution. To this add dilute ammonia solution dropwise till a slight ppt. persists. Then boil till a clear reddish brown solution of neutral ferric chloride is obtained.*

(*iii*) *Cocodyl test* : On heating a pinch of the dry mixture with an equal amount of arsenic oxide in a test tube, an extremely unpleasant smell of cocodyl oxide is obtained which confirms acetate.

$$4CH_3COOK + As_2O_3 \longrightarrow \underset{\text{Cocodyl oxide}}{(CH_3)_2AsO(CH_3)_2As} + 2K_2CO_3 + 2CO_2$$

(*iv*) *Lanthanum nitrate test* : This is a very sensitive test for acetate. Take 0.5 ml of a 6% lanthanum nitrate solution followed by the addition of 0.5 ml of iodine solution in KI and a few drops of dilute ammonia solution and heat to boiling. A blue colour is obtained. This confirms acetate.

(*v*) *D.N.P. Test* : Mix a pinch of solid mixture with equal volume of pure calcium hydroxide in a test tube. Heat the test tube strongly. Pass the evolved vapours into a solution of 2 : 4 dinitrophenyl hydrazine. The formation of a yellow ppt. or turbidity confirms acetate.

$$Ca(OH)_2 + 2CH_3COOH \longrightarrow (CH_3COO)Ca \xrightarrow{-CaCO_3} CH_3COCH_3$$

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>\!C{=}O + H_2N.NHC_6H_3(NO_2)_2 \longrightarrow$$

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>\!C{=}N.NHC_6H_3(NO_2)_2$$

Yellow coloured compound

NOTE *2 : 4 dinitrophenyl hydrazine can be prepared by dissolving 0.25 g solid 2 : 4 dinitrophenyl hydrazine in a mixture of 42 ml of conc. HCl and 50 ml of water by warming on a water bath, then diluting it to 250 ml with water.*

(*vi*) *Oxalic acid test* : Take a small quantity of the mixture on the plam. To this add a small quantity of oxalic acid and moisten it with water and then rub between the thumb and the fore finger. If a characteristic vinegar smell is given out, it confirms acetate.

$$2CH_3COONa + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2CH_3COOH$$

Acetic acid vapours (Vinegar-like smell)

7. Identification of Nitrate

All normal nitrates are soluble in water, except that a few by hydrolysis yield insoluble basic salts, which, however, dissolve in dil. nitric acid. Its various tests are :

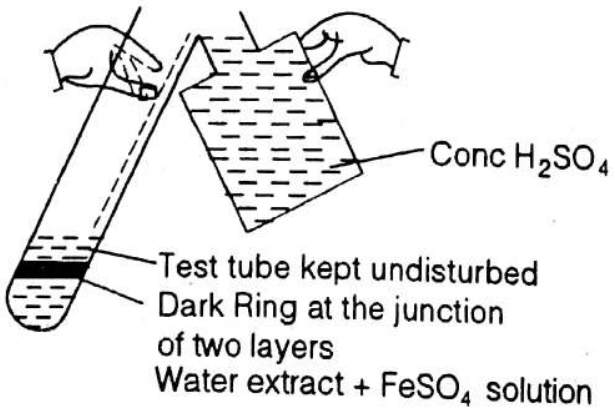

Fig. 3.1. How to perform ring test ?

(a) *Ring test* : To 2–3 ml of water extract (or 2–3 ml of sodium carbonate extract neutralised with dilute sulphuric acid), add 2–3 ml of freshly prepared ferrous sulphate solution. Then, pour the conc. sulphuric acid

slowly in a thin stream along the sides of the test tube. A brown black ring at the junction of the two layers confirms nitrate.

$$3Fe^{+2} + NO_3^- + 4H^+ \longrightarrow 3Fe^{+3} + NO + 2H_2O$$

$$Fe^{+2} + NO \longrightarrow [Fe(NO)]^{+2}$$

Brown complex ion

NOTE

(*i*) This test fails when nitrite is present even in traces. This happens because nitrite forms a black solution when ferrous sulphate solution is added.

(*ii*) This test also fails in the presence of bromide or iodide or both when present along with nitrate in the mixture.

(b) *The Lunge test or Diphenylamine test* : To the water extract or sodium carbonate extract neutralised with dil. H_2SO_4 acid, add a few ml of the diphenylamine reagent in a test tube. If a blue ring is formed at the zone of contact of the two liquids, it confirms nitrate.

This reaction is also given by many other oxidising agents such as nitrites, chromates, chlorates, permanganate and ferric salts.

NOTE Diphenylamine reagent is prepared by dissolving 0.4 g of diphenylamine in 80 ml of conc. sulphuric acid followed by the addition of 20 ml of water.

(c) *Zinc or aluminium and sodium hydroxide test* : Take about 2 ml of sodium carbonate extract and add 0.5 g of sodium hydroxide. Boil the solution for few second. Cool and add a pinch of aluminium powder or zinc dust. Heat the contents of the test tube and pass the vapours in the Nessler's reagent. If a brown ppt. is formed, it confirms nitrate. The formation of brown ppt. is due to the action of ammonia produced during the reaction on Nessler's reagent.

$$NO_3^- + Al + OH^- \not\longrightarrow NH_3 + AlO_2^-$$

$$NO_3^- + Zn + OH^- \longrightarrow NH_3 + ZnO_2^{2-}$$

$$NH_3 + \text{Nessler's reagent} \longrightarrow \text{Brown ppt.}$$

NOTE This test is interfered by nitrites, cyanides, thiocyanates, ferrocyanides and ferricyanides because these also evolve ammonia under the above conditions. Nitrite is removed by boiling the sodium carbonate extract with ammonium chloride whereas all other nitrogenous anions are removed by warming the sodium carbonate extract with silver sulphate to about 60°C and shaking vigorously for about 4–5 minutes when the silver salts of these anions are precipitated which are removed by filtration. The excess silver is removed from the filtrate by adding NaOH solution and filtering the black ppt. of silver oxide. In the filtrate, nitrate is tested as above.

8. Identification of Chloride

All chlorides are soluble in water, except the silver, mercurous and cuprous salts. Lead chloride is sparingly soluble in cold water but readily dissolves in hot water. Chlorides of antimony, bismuth and tin salts are hydrolysed by water. The various tests for the identification of chlorides are as follows :

(a) *Silver nitrate test* : Acidify 2–3 ml of "sodium carbonate extracts" with dil. HNO_3. Boil the solution to expel CO_2. To this add $AgNO_3$ solution; if a whie ppt. soluble in ammonia but insoluble in HNO_3 is obtained, it confirms chloride.

$$Ag^+ + Cl^- \longrightarrow AgCl$$

$$AgCl + 2NH_3 \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]_2^+} + Cl^-$$

(b) *Chromyl chloride test* : Take 0.5 g of the dry mixture in a test tube. To this add 0.5 g powdered $K_2Cr_2O_7$ and 5 ml conc. H_2SO_4. Heat the test tube and pass the red vapours of chromyl chloride through dil. NaOH solution. If a yellow colour is obtained, acidify the yellow solution with acetic acid and then add 1–2 ml of lead acetate solution. A yellow ppt. of lead chromate, soluble in NaOH, identifies chloride.

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2Na_2SO_4 + 3H_2O + \underset{\text{(Red)}}{2CrO_2Cl_2}$$

$$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$$

$$CrO_4^{2-} + Pb^{2+} \longrightarrow \underset{\text{(Yellow ppt.)}}{PbCrO_4 \downarrow}$$

$$PbCrO_4 + 4OH^- \longrightarrow \underset{\text{(Soluble)}}{CrO_4^{2-}} + PbO_2^{2-} + 2H_2O$$

(*i*) This test fails in such mixtures which contain heavy metal chlorides such as chlorides of Hg, Sn, Pb or Ag. In such cases, chromyl chloride test can be performed from the residue obtained after evaporating 10 ml of sodium carbonate extract in a china dish.

(*ii*) The mixture which contains iodide does not respond to this test. In such cases only the liberation of chlorine will occur which confirms the presence of chloride.

(c) *Sodium arsenite test*: Acidify 2–3 ml of 'sodium carbonate extract" with dil. HNO_3. Boil the solution to expel CO_2. To this add $AgNO_3$ solution. If a white ppt. is obtained, it means that chloride may be present. Filter the ppt. and treat this ppt. with sodium arsenite solution. The formation of yellow ppt. confirms chloride.

$$Na_3AsO_3 + 3AgCl \longrightarrow \underset{\text{Yellow ppt.}}{Ag_3AsO_3} + 3NaCl$$

This test serves as a distinctive test for chloride because silver bromide and silver iodide are not affected by sodium arsenite solution.

9. Identification of bromide

All bromides are soluble in water, except the silver, mercurous and cuprous salts. All the bromides dissolve in dil. or conc. hydrochloric acid or nitric acid except the silver salts. The various tests for the identification of bromide in mixture are as follows :

(a) *Silver nitrate test* : Acidify 2–3 ml of "sodium carbonate extract" with dil. HNO_3. Boil off CO_2. To this add $AgNO_3$ solution. The formation of light yellow ppt. sparingly soluble in dil. ammonia solution confirms bromide.

$$Ag^+ + Br^- \longrightarrow AgBr\downarrow$$
(Light yellow ppt.)

(b) *Carbon disulphide test* : Neutralise 2 ml of sodium carbonate extract with HCl acid. Boil off CO_2. To this add 2 ml of CS_2 or CCl_4 of $CHCl_3$. Then to this add chlorine water dropwise and shake. The formation of orange colour in CS_2 or CCl_4 or $CHCl_3$ layer confirms bromide.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$
$$Br_2 + CS_2 \longrightarrow \text{Orange colour}$$

10. Identification of Iodide

The solubilities of the iodides are analogous to the corresponding chlorides and bromides. The iodides of silver, mercury, cuprous and lead are much less soluble than the corresponding chlorides and bromides. However, the various tests for the identification of iodide in a mixture are :

(a) *Silver nitrate test* : Neutralise 2 ml of "sodium carbonate extract" with dil. HNO_3 and boil off CO_2. Then add $AgNO_3$ solution. The formation of pale yellow ppt. insoluble in ammonia solution and conc. HNO_3 confirms iodide.

$$Ag^+ + I^- \longrightarrow AgI\downarrow$$
(Pale yellow ppt.)

(b) *Carbon disulphide test* : Acidify 2 ml of "sodium carbonate extract" with dil. HCl acid. Boil off CO_2. To this add 2 ml of CS_2 (or $CHCl_3$ or CCl_4) and chlorine water dropwise. Shake the test tube. The formation of violet colour in CS_2 layer which disappears on the addition of excess of chlorine water identifies iodide.

$$2I^- + Cl_2 \longrightarrow 2Cl^- + I_3$$
$$I_2 + CS_2 \longrightarrow \text{Violet colour}$$
$$5Cl_2 + I_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

NOTE When both I^- and Br^- are present, the organic layer at first turns violet and then the violet colour disappears to give a yellowish brown colour.

(c) Take 2 cc of soda extract, acidify with either dil. H_2SO_4 or dil., CH_3COOH, followed by addition of crystals of solid $NaNO_2$ slowly. Free iodine vapours recognised by their colour are given out confirming the presence of an iodide.

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$
$$2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$$
$$2HNO_2 + 2HI \longrightarrow I_2 + 2NO + 2H_2O$$

11. Identification of Fluoride

The solubilities of fluorides in water. in the case of silver and the alkaline earth metals, are reciprocal of those of the other halides. Alkali, silver, aluminium and stannous fluorides are soluble in water, other fluorides are insoluble in water. The various tests for the identification of fluoride in a mixture are as follows :

(a) *Water drop test* : Take a small amount of the original mixture in a dry test tube. To this add an equal amount of sand and 1 ml of conc. H_2SO_4. Heat the test tube and hold a moistened glass rod over the mouth of it. A white gelatinous deposit on this glass rod confirms fluoride.

$$4F^- + SiO_2 + 4H^+ \longrightarrow \underset{\text{(White fumes)}}{SiF_4\uparrow} + 2H_2O$$

$$3SiF_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{H_4SiO_4} + \underset{\text{Hydrofluosilicic acid}}{2H_2SiF_6}$$

(White waxy ppt.)

(b) *Calcium chloride test* : Acidify 2–3 ml of "sodium carbonate extract" with very dil. acetic acid. Boil off CO_2. To this add $CaCl_2$ solution. In case a white ppt. is formed, add dil. H_2SO_4 acid. If this ppt. does not dissolve, it means fluoride is confirmed (See oxalate also).

$$Ca^{2+} + 2F^- \longrightarrow \underset{\text{(White ppt.)}}{CaF_2\downarrow}$$

12. Identification of Oxalate

The oxalates of the alkali metals and magnesium are soluble in water while other oxalates are nearly or quite insoluble in water, but dissolve in dilute hydrochloric acid. The various tests for the identification of oxalate in a mixture are as follows :

(a) *Calcium chloride test*: Acidify 2–3 ml "sodium carbonate extract" with very dil. acetic acid; boil off CO_2. To this add $CaCl_2$ solution. If a white ppt. is obtained, dissolve it in minimum quantity of dil. H_2SO_4 acid and to this add potassium permanganate solution dropwise. If pink colour gets discharged, it identifies oxalate.

$$C_2O_4^{2-} + Ca^{2+} \longrightarrow \underset{\text{(White ppt.)}}{CaC_2O_4\downarrow}$$

$$CaC_2O_4 + 2H^+ \longrightarrow Ca^{2+} + H_2C_2O_4$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2C_2O_4 \longrightarrow 2CO_2 + 2H^+ + 2e^-] \times 5$$

$$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2\uparrow$$

(b) *Ferrous sulphate test* : Acidify "Sodium carbonate extract" with dil. acetic acid. Boil off CO_2. To this add ferrous sulphate solution. If a yellow precipitate appears, it identifies oxalate.

$$\begin{matrix} COO^{2-} \\ 2| \\ COO \end{matrix} + Fe^{2+} \longrightarrow \underset{\text{(Yellow)}}{Fe(C_2O_4)_2]^{2-}}$$

13. Identification of Tartrate

Normal tartrates of the alkali metals are soluble in water; other simple tartrates are slightly soluble in water. Its various tests are :

(a) *Silver mirror test* : Carefully clean a test tube, then thoroughly rinse the tube with water, and place in it a little silver nitrate solution. Add to this solution very dilute ammonia until the precipitated silver oxide is nearly, but not quite redissolved.

In another test tube, take 2–3 ml of sodium carbonate extract. Neutralise it with dil. acetic acid. Boil off CO_2. Then add dil. NH_3 solution dropwise till it smells of ammonia. Boil the solution for some time to expel excess of NH_3.

Mix the two solutions. Now gradually warm the solution by placing the test tube containing it in a beaker of cold water, which is then heated nearly to the boiling point. A bright silver mirror will be deposited on the inner surface of the test tube.

$$2Ag^+ + 2OH^- \longrightarrow Ag_2O + H_2O$$

$$\underset{\text{Tartrate ion}}{C_4H_4O_6^{2-}} + 5Ag_2O \longrightarrow \underset{\text{(Silver mirror)}}{10Ag} + 2OH^- + 4CO_2 + HO$$

(b) *Fenton's test* : Neutralise the "sodium carbonate extract" in a similar manner as given in "silver mirror test". To this add a drop of saturated ferrous sulphate solution followed by the addition of 2 drops of 20 volume hydrogen peroxide. Also, add excess of sodium hydroxide solution and a drop of ferric chloride. If a deep-violet or blue colour is produced it identifies tartrate.

14. Identification of Citrate

Citrates of alkali metals are soluble in water whereas the remaining citrates are sparingly soluble in water. Its various tests are :

(*i*) *Calcium chloride test* : Prepare a neutral solution of "sodium carbonate extract" as given in the silver mirror test of tartrate. To this add calcium chloride solution. No precipitation occurs in the cold. However, on boiling the solution for several minutes a crystalline white ppt. of calcium citrate is obtained. (Distinction from tartrate in which precipitate appears in cold). This white precipitate is insoluble in caustic alkali but soluble in ammonium chloride.

$$2Na_3C_6H_5O_7 + 3CaCl_2 \longrightarrow Ca_3(C_6H_5O_7)_2 + 6NaCl$$

(*ii*) *Silver mirror test* : Prepare a neutral solution of "sodium carbonate extract" as given in the silver mirror test of tartrate. To this add silver nitrate solution. A white ppt. of silver citrate (which is soluble in dil. ammonia solution) is obtained. If the ammoniacal solution of silver citrate is put in a hot water bath maintained at 60°C, no silver mirror is obtained. If, however, the ammoniacal solution of silver citrate is boiled, silver mirror is gradually produced (In tartrates, silver mirror is readily obtained).

(*iii*) *Deniges test* : Acidify "sodium carbonate extract" with dil. acetic acid. Boil off CO_2. To this add 0.5 ml of **Deniges** reagent. Heat the solution to boiling. Then add a few drop of 0.1 N potassium permanganate solution. The purple colour gets discharged rapidly and a white crystalline ppt. is obtained.

The ppt. is a mixture of basic mercuric sulphate and the mercuric salt of acetone dicarboxylic acid.

$$HgSO_4.2HgO.2[CO(CH_2COO)_2Hg]$$

This test is very sensitive but the interference is caused by the presence of halides.

Deniges reagent can be prepared by dissolving 1 g of mercuric oxide in 20 ml of water and 4 ml of conc. sulphuric acid.

15. Identification of Cyanide

All metallic cyanides are insoluble in water except those of the alkaline earths and mercury. Cyanide in solution is best identified by the following tests :

(*i*) *Prussian blue test* : Acidify "sodium carbonate extract" with dil. acetic acid. To this add sodium hydroxide solution and a little dilute ferrous sulphate solution and boil the solution. Now acidify the solution with hydrochloric acid followed by the addition of ferric chloride. If a blue ppt. or colour is formed, it confirms cyanide.

The blue colour or ppt. is due to the formation of Prussian blue.

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

$$[Fe(CN)_6]^{4-} + 4Fe^{3+} \longrightarrow \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3}$$

(*ii*) *Ferric-thiocyanate test* : Neutralise the sodium carbonate extract with dil. acetic acid. To this add a little yellow ammonium sulphide solution. Evaporate the solution to dryness in a china dish. Acidify the solution with dil. hydrochloric acid. Now add few drops of ferric chloride. If a blood red colour appears, it identifies cyanide.

$$CN^- + (NH_4)_2S_x \longrightarrow CNS^- + (NH_4)_2S_{x-1}$$

$$Fe^{3+} + CNS^- \longrightarrow [Fe(CNS)]^{2+}$$