- vii. Wash the precipitate 5–6 times with hot water and transfer into the original beaker carefully with a jet of hot water.
- viii. Dissolve the precipitate in conc. HCl. Wash the sides of the beaker.
- ix. Heat the beaker to 80–90°C on burner (avoid boiling) and add 10% $SnCl_2$ solution (10 g $SnCl_2$ in 90 ml distilled water) dropwise with constant stirring to reduce iron. Yellow colour of FeCl₃ disappears due to conversion of ferric ion to ferrous state. Add 1–2 drops of $SnCl_2$ in excess.
- x. Cool the solution in cold water.
- xi. Add 10 ml HgCl₂ solution and stir. A silky white precipitate of mercurous chloride will appear. If the precipitate is black, discard the solution and repeat the process with a new aliquot. The black colour indicates the reduction of mercurous chloride to elemental mercury that adds inaccuracy to the estimation.
- xii. Add 10–15 ml sulphuric–phosphoric acid mixture and dilute the solution to about 150 ml.
- xiii. Add 2–3 drops of barium diphenylamine sulphonate indicator solution to the solution. Avoid use of excess of indicator as it imparts intense dirty green colour near the end point and confuses the actual end point.
- xiv. Titrate the solution against standard 1N potassium dichromate solution (294.18 g $K_2Cr_2O_7$ in 1 liter distilled water) with constant stirring till a constant stable violet colour appears.
- xv. Estimation of iron is made by following equivalence:

1 ml 1N K₂Cr₂O₇ = 0.05584 g Fe = 0.07185 g FeO = 0.07985 g Fe₂O₃

In most of the rocks, iron is present both in ferrous (FeO) and ferric (Fe₂O₃) states. In the experiment described above, total iron as Fe₂O₃ is found out. In order to determine the exact amount of both the constituents, absolute amount of FeO is determined by potassium permanganate method given below. Amount of Fe₂O₃ is calculated by formula: percent of Fe₂O₃ = percent of total Fe (as Fe₂O₃) – (percent of FeO × 1.1113)

Gravimetric factors:

 $Fe = 0.69944 \times Fe_2O_3$ $Fe = 0.77731 \times FeO$ $FeO = 0.89981 \times Fe_2O_3$ $Fe_2O_3 = 1.11130 \times FeO$

The method of estimation of FeO is given on next page.

3.5.2. Potassium Permanganate Method

Reagent preparation

- *a. Boric acid solution:* Dissolve 100 g boric acid in 1 litre hot distilled water with constant stirring. Cool the solution and dilute to make 2 litres.
- *b. Potassium dichromate solution (0.1 N)*: Take 9.810 g finely ground analar grade $K_2Cr_2O_7$ in a weighing bottle and dry at 110°C in an oven for more than 2 hours. Weigh the bottle with the contents and transfer the content into a 2-litre volumetric flask through a funnel. Weigh the bottle once again to know the true

- iii. Heat the mixture on a burner (boiling is to be avoided).
- iv. Titrate the content of the flask against standard KMnO₄ solution to a permanent pink colour.

 $1 \text{ ml} 1 \text{ N KMnO}_4 = 0.01648 \text{ g of Mn} = 0.02128 \text{ g of MnO}$

3.11. ESTIMATION OF P2O5 BY WILSON METHOD

- i. Dissolve 0.05–0.2 g of sample in 25 ml conc. HCl in a 500 ml conical flask by heating slowly on a burner and add few drops of HNO₃.
- ii. Cool the content and neutralise the acid with 10% NaOH solution. Litmus paper can be used as an indicator.
- iii. Redissolve the precipitate formed in dil. HCl. Add about 5 ml dil. HCl in excess.
- iv. Dilute the solution to 150 ml with demineralised water; add a pinch of citric acid to the solution and boil on a burner.
- v. Add 30 ml of citromolybdate solution to the content and boil.
- vi. Add 25 ml quinoline hydrochloride solution slowly with constant stirring and boil the solution for 5–10 minutes.
- vii. Cool the content by cold-water bath overnight. Precipitation will take place.
- viii. Collect the precipitate on a pad of filter paper pulp under suction.
 - ix. Wash the conical flask thoroughly with cold water and transfer the water to the precipitate collected on the pad.
 - x. Wash the precipitate 8–10 times with cold water till it is free from acid.
 - xi. Transfer the precipitate along with filter paper pad to the original flask.
- xii. Add 50 ml of demineralised water and 0.1N NaOH (4 g NaOH in 1 liter distilled water) solution to the flask to dissolve the yellow precipitate of quinoline phosphomolybdate completely. Add 2–3 drops of phenolphthalein indicator.
- xiii. Titrate the content of the flask against 0.1N HCl till the solution becomes colourless.

1 ml 1N HCl = 0.001193 g of P = 0.002733 g of P₂O₅

3.12. ESTIMATION OF WATER

Water is available in form of water of crystallization within the crystal lattice and in adsorbed (hygroscopic) form.

3.12.1. Estimation of Water of Crystallization (H₂O+) by Penfield's Tube

- i. Dry the sample at 110°C for 1 hour.
- ii. Take a dry Penfield's tube (Fig. 3.2a) and determine its weight (W_1) .
- Pour about 1 g of the sample into the lower bulb through a capillary funnel (Fig. 3.2b).
- iv. Let the weigh of the Penfield's tube with sample is W_2 . The exact weight of the sample is (W_2-W_1) .
- v. Hold the tube horizontally; heat the first bulb on flame to red hot while wrapping the second bulb by a moist filter paper or cloth.
- vi. Pull out and cut off the heated bulb along with the residue from the rest of the tube with flame and seal the cut end of the tube.
- vii. Cool the tube, clean the external portion and weigh (W_3) .

- viii. Neutralise the solution by Na₂CO₃ solution and boil to remove all CO₂.
 - ix. Add zinc oxide suspension to the solution till the precipitate becomes coffee coloured.
 - x. Boil the mixture, cool and filter through Whatman No. 40 filter paper with some pulp.
 - xi. Add 10 ml conc. HCl to clear the solution.
- xii. Dilute the solution to 200 ml, heat to about 60°C and add α nitroso β napthol slowly with constant stirring.
- xiii. Cool the solution for several hours to bring it to room temperature.
- xiv. Filter the content through Whatman No. 42 filter paper, using pulp, and wash the precipitate several times with warm dilute HCl.
- xv. Transfer the paper and precipitate to a deep type weighed 30 ml porcelain crucible.
- xvi. Ignite the paper and precipitate gently at first and finally to constant weight at 750 to 850°C.
- xvii. Cool the resultant solid in a desiccator and weigh (W₂).

Co (%) =
$$\frac{73.42 \times W_2}{W_1}$$

4.4. ESTIMATION OF CHROMIUM IN CHROMITE

Chromite is the most important ore of chromium. Chemically, it is represented by $FeCr_2O_4$, but Mg and Al are found in the lattice replacing Fe and Cr, respectively. The procedure of estimation of Cr_2O_3 is given below.

- i. Take 0.2 g of finely grinded chromite powder in a nickel crucible.
- ii. Add about 1 g of sodium peroxide to the mineral powder and mix both thoroughly with a glass rod.
- iii. Heat the crucible gently over a low flame till the mass melts.
- iv. Cool the crucible and place it in a 500 ml beaker containing a little water. Cover the beaker by a watch glass.
- v. Add nearly 100 ml of water to the beaker and after completion of the violent reaction remove the crucible with a glass rod and wash thoroughly. Pour the washed water into the same beaker.
- vi. Boil the solution, cool to room temperature and filter through Whatman No. 40 filter paper.
- vii. Wash the residue with hot water till it is free from chromate ions.
- viii. As there are chances of some chromium being held up by the residue, dissolve the residue in the filter paper by minimum amount of HCl.
- ix. Dilute the solution and add sodium peroxide slowly with constant stirring till a permanent precipitate is obtained.
- x. Boil the content, cool and filter through Whatman No. 40 filter paper.
- xi. Wash the residue 5–6 times with hot water.
- xii. Mix the filtrate with the filtrate obtained in step (vi) above.
- xiii. Boil the filtrate for half an hour to decompose hydrogen peroxide.
- xiv. Cool the filtrate, acidify with 1:1 H₂SO₄ and add measured amount of ferrous ammonium sulphate solution till the solution becomes green.

- v. Close the mouth of the flask with the rubber stopper and through one hole allow a slow stream of CO_2 from a Kipp's apparatus to pass into the flask. The other hole serves as an outlet.
- vi. Boil the solution in the flask for more than half an hour to expel excess hydrogen gas. Maintain a slow stream of CO₂ throughout the boiling process.

vii. Cool the flask and remove the stopper and the delivery tube.

- viii. Add 5 ml ammonium thiocyanate solution that serves as an indicator and titrate quickly with ferric ammonium sulphate [FeNH₄(SO₄)₂.12H₂O] solution to a faint red colour.
- ix. Calculate TiO₂ from the following factor:

1 ml 1 N FeNH₄(SO₄)₂.12H₂O = 0.08 g TiO₂ = 0.04795 g Ti

4.13. ESTIMATION OF VANADIUM IN VANADIUM ORE

Important vanadium minerals are patronite (VS₄), vanadinite [Pb₄(PbCl)(VO₄)₃], carnotite (K₂O.2U₂O₃.V₂O₅.3H₂O) and titaniferous vanadium ores. The procedure of estimation of vanadium is as follows:

- i. Fuse 0.2 to 0.5 g of finely ground ore with 5 times of its weight of sodium peroxide in an iron or nickel crucible.
- ii. Transfer the product into a 500 ml beaker, add water and boil.
- iii. Filter through Whatman No. 41 filter paper adding some pulp.
- iv. Reject the residue and proceed with the filtrate (sodium vanadate).
- v. Boil the solution for 30 minutes to expel H_2O_2 .
- vi. Transfer the solution into a 500 ml beaker, neutralise with 1:1 H_2SO_4 and add 4–6 ml of acid in excess.
- vii. Add ferrous ammonium sulphate solution until a drop of the solution shows blue in a spot test with potassium ferricyanide solution.
- viii. Add 10–15 ml H_3PO_4 and cool to room temperature.
 - ix. Add 0.1 N KMnO₄ until a light pink colour appears. Allow the solution to stand still for few minutes so that all vanadium is oxidised.
 - x. Destroy the excess KMnO₄ by 0.05 N NaNO₂ solution.
 - xi. Add 2 g of urea and stir. Allow it to stand for 5 minutes.
- xii. Add 15 g of sodium acetate and stir to dissolve. If any precipitate is formed, add a drop of H_2SO_4 to clear it.
- xiii. Add 8 drops of diphenylamine barium sulphonate indicator; allow 2–3 minutes for the development of full colour of the indicator.
- xiv. Titrate with 0.1 N ferrous ammonium sulphate solution until the disappearance of blue colour.
- xv. Calculate V or V_2O_5 from the following factors.

1 ml of 1 N Fe(SO₄).(NH₄)₂SO₄ = 0.05094 g V = 0.09094 g V₂O₅

4.14. ESTIMATION OF TUNGSTEN IN TUNGSTEN ORE

The important tungsten-bearing minerals are wolframite (FeMn)WO₄, scheelite (CaWO₄), tungstenite (WS₂), tungstite (WO₃), etc. Estimation of WO₃ is made by gravimetric analysis by the procedure given below.