B.Sc.-I (Hons.&Sub.), Paper-IB (Inorganic Chemistry)

Unit-3 Principles involved in Volumetric & Gravimetric estimations.

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⟹ **Volumetric estimation of Cu^{2+}:**

Principle: When potassium iodide (KI) solution is added in excess to a Cu^{2+} solution, KI is quantitatively oxidised to liberate I_2. The amount of liberated I_2 is equivalent to the Cu^{2+} present in the solution. The liberated I_2 can be titrated with a standard (N/10) sodium thiosulphate ($Na_2S_2O_3$) solution using 1% starch solution as an indicator.

$$2Cu^{2+} + 4KI \longrightarrow Cu_2I_2 + I_2 + 4K^+ \quad \text{——} (1)$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6 \quad \text{——} (2)$$

Equivalence relation from equation (1) & (2);

$2Na_2S_2O_3$	$\equiv I_2$	$\equiv 2Cu^{2+}$
2 Moles		2 Moles
Or, 2gm equivalent		2gm ion
Or, 2000 mL N Sol.		127.14 gm

$\therefore$ 1 mL N $Na_2S_2O_3$ solution $\equiv$ 0.06357 gm Cu^{2+} or Cu.

⟹ **Volumetric estimation of Iron (Fe):**

Principle: Iron (Fe^{2+}) is estimated in given sample of Mohr's salt/iron ores by an oxidising agent $KMnO_4$ or $K_2Cr_2O_7$ in presence of dilute (2N) H_2SO_4. The ore is usually dissolved in HCl, the Fe^{3+} reduced to Fe^{2+}. The solution is titrated with standard $KMnO_4$/$K_2Cr_2O_7$ solution in acidic medium using 1% N-phenylanthranilic acid solution in 0.005 M NaOH as an external indicator in case of $K_2Cr_2O_7$ titration. Determination/estimation of Fe^{2+} with $K_2Cr_2O_7$ solution preferred over $KMnO_4$ solution due to (i) an excellent primary standard (ii) its aqueous solution stable indefinitely (iii) it is used only in acidic medium, and is reduced rapidly at RT to a green Cr^{3+} salt (iv) less easily reduced by organic matter, and stable towards light.

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$[Fe^{2+} \longrightarrow Fe^{3+} + e] \times 6$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

i.e; $K_2Cr_2O_7 \equiv 6Fe^{2+} \equiv 6Fe$ (in ore) $\equiv 6FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt)

1 Mole	6 Moles	6 Moles
Or, 6 gm equivalent	6 × 55.85 gm	6 × 391.85 gm
Or, 1000 mL N Sol.	55.85 gm	391.85 gm

$\therefore$ 1 mL N $K_2Cr_2O_7$ solution $\equiv$ 0.056 gm Fe/Fe^{2+} ion $\equiv$ 0.392 gm Mohr's Salt.

The green colour due to formation of Cr^{3+} ions by reduction of $K_2Cr_2O_7$ solution makes it impossible to ascertain the end point, so a redox indicator (1% N-phenylanthranilic acid in 0.005 M NaOH used.

⟹ **Volumetric estimation of Calcium (Ca^{2+}):**

Calcium (Ca^{2+}) is estimated in given sample of limestone/Ca-ore/Ca^{2+} salts/sol by permanganatometry (using standard $KMnO_4$ sol.). The Ca-ore/limestone ($CaCO_3$) is first treated with dilute HCl to give $CaCl_2$ solution. When $CaCl_2$ (Ca^{2+}) solution is treated

with hot ammonium oxalate solution, calcium oxalate (CaC_2O_4) is formed. The calcium oxalate is decomposed by dilute H_2SO_4 to free oxalic acid ($H_2C_2O_4$), which is then titrated with standard (N/10) $KMnO_4$ solution.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$
$$CaCl_2 + (NH_4)_2SO_4 \longrightarrow CaC_2O_4 + 2NH_4Cl$$
$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$
$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2\uparrow$$

From above equations, equivalence relation:

$2KMnO_4 \equiv 5H_2C_2O_4 \equiv 5CaCl_2 \equiv 5CaCO_3 \equiv 5Ca$ or Ca^{2+}

2 Moles or, 10 gmequ. or, 1 gmequivalent or, 1000 mL N solution

5 Moles or, 0.5 mole or, 20.04 gm

$\therefore$ 1 mL N $KMnO_4$ solution = 0.0204 gm Ca or Ca^{2+}.

⟹ **Gravimetric estimation of Ba^{2+}**

When an excess of dilute H_2SO_4 is slowly added to a solution of Ba^{2+} salt (e.g. $BaCl_2$), barium is quantitatively precipitated as $BaSO_4$ (Barium sulphate). Knowing the weight of Ba^{2+} salt and $BaSO_4$ precipitate, barium (Ba^{2+}) is estimated in barium salt.

$$BaCl_2 \text{ or } Ba^{2+} + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HCl \text{ or } 2H^+$$

i.e; $BaSO_4 \equiv Ba$ or Ba^{2+}

1 Mole — 1 Mole

233.42 gm — 137.36 gm

$$\% \text{ of } Ba^{2+} = \frac{137.36 \times W'}{233.42 \times W} \times 100$$

(where W, W' = weights of Ba^{2+} salt & $BaSO_4$ respectively).

⟹ **Gravimetric estimation of SO_4^{2-}:**

When an excess of a dilute solution of $BaCl_2$ is slowly added to a hot solution of a soluble sulphate (e.g. K_2SO_4 or H_2SO_4) solution containing a little conc. HCl or H_2SO_4, the sulphate (SO_4^{2-}) present in solution quantitatively precipitated as $BaSO_4$. Knowing the weights of $BaSO_4$ & soluble sulphate salt, SO_4^{2-} in soluble sulphate can be estimated. The precipitation is done at boiling temp. and weakly acidic medium in order to prevent the possible formation of Ba^{2+} salts as CrO_4^{2-}, CO_3^{2-} & PO_4^{3-}.

$$K_2SO_4 \text{ or } H_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2KCl \text{ or } 2HCl$$

i.e; $BaSO_4 \equiv SO_4^{2-}$

1 Mole — 1 Mole.

or, 233.42 gm — 96 gm.

$$\% \text{ of } SO_4^{2-} = \frac{96 \times W'}{233.42 \times W} \times 100$$

(where W & W' are weights of soluble sulphate & $BaSO_4$ respectively)

⟹ **Gravimetric estimation of Ni^{2+}:**

When an alcoholic solution of dimethylglyoxime (H_2DMG) is added to neutral or faintly acidic hot solution of Ni^{2+} salt, nickel is quantitatively precipitated as inner complex, nickel dimethylglyoximate (scarlet red). A slight excess of aqueous ammonia (NH_4OH) free from CO_3^{2-} added during precipitation of Ni^{2+}, since precipitate is insoluble in its amm. salts. only a slight of the reagent should be used, since (H_2DMG is not very soluble in water or in very dilute ethanol and may precipitate, if a very large excess is added, some of the precipitate may dissolve. Knowing weights (W, W') of Ni^{2+} salt & nickel dimethylglyoximate ppt; Ni^{2+} is estimated.

$$Ni^{2+} + 2\ H_3C-C=N-OH \ (H_3C-C=N-OH) \xrightarrow[\Delta]{+2NH_4OH} \text{Ni(DMG)}_2 + 2NH_4^+ + 2H_2O$$

(Nickeldimethylglyoximate) or $Ni(DMG)_2$

$Ni(DMG)_2 \equiv Ni \equiv Ni^{2+}$ salt.

1 Mole — 1 Mole

288.71 gm — 58.71 gm

$$\% \text{ of } Ni = \frac{58.71 \times W'}{288.71 \times W} \times 100$$