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

Unit-3 Principles involved in Volumetric & Gravimetric estimations.

[By Dr. Birendra Kumar, Maharaja College
email: birendra.kr3956@gmail.com (Mob. 7004602322)]

⟹ **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

$\therefore$ 1mL 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 $K_2Cr_2O_7$ 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

Scanned with CamScanner