Expt. No.: 8

Date: 18.2.2020

Experiment	Iron in carbon steel by potentiometry
Problem definition	Mechanical properties of steel depend on its composition. Hence, it is important to analyze the amount of Iron in steel for industrial applications.
Methodology	Potentiometric method using $KMnO_4$ (oxidizing agent) to oxidize Fe(II) in steel to Fe(III) facilitates the estimation of Iron in steel.
Solution	Estimation of iron (%) in different steel samples.
Student learning outcomes	Students will learn to a) perform potentiometric method b) analyze the composition of iron in different grades of steel

Principle:

Potassium permanganate ($KMnO_4$) oxidizes ferrous ion to ferric ion in the presence of acid as per the reaction:

$$5Fe^{+2} \rightarrow 5Fe^{+3} + 5e^- \text{.......(1)}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \text{.......(2)}$$

$$\text{Overall, } 5Fe^{+2} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+3} + Mn^{2+} + 4H_2O$$

Electrode potential (oxidation potential) in the titration depends upon the concentration of Fe^{2+}, Fe^{3+} and H^+ ions. To avoid the effect of the change in H^+ ion concentration, the titration is usually carried out in large excess of acid. Oxidation potential of this redox system is given by

$$E = E_0 + \frac{RT}{nF}\ln\left(\frac{Fe^{3+}}{Fe^{2+}}\right)$$

Connecting the redox electrode (Platinum) with a saturated calomel electrode (SCE) completes the necessary cell as indicated below:

$$\mathbf{Hg \,|\, Hg_2Cl_2\ (s),\ Saturated\ KCl \ ||\ Fe^{3+}, Fe^{2+} \,|\, Pt}$$

When $KMnO_4$ is added, Fe^{2+} is oxidized to Fe^{3+} whose concentration increases with progressive addition of $KMnO_4$. The observed EMF gradually increases. At the end point, there will be a sharp increase due to the sudden removal of all Fe^{2+} ions. Plot-1: EMF measured (E) *vs* Volume of $KMnO_4$ added and Plot-2: $\Delta E/\Delta V$ *vs* Average volume of $KMnO_4$ was drawn. End point of the titration is measured from the Plot-2 graph.

Requirements:

Reagents and solutions: 100 mL of $KMnO_4$ (0.05 N) solution, 100 mL of steel solution, 2 N H_2SO_4.

Apparatus: Calomel electrode, Platinum electrode, Potentiometer, Volumetric flasks, Burette, Pipette, Beakers.

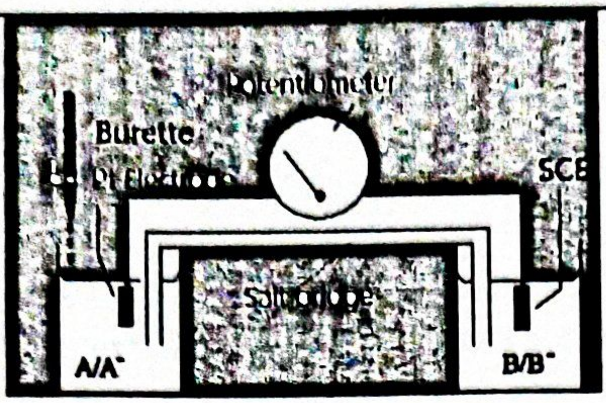

Fig. 1: Typical apparatus for potentiometric titrations.

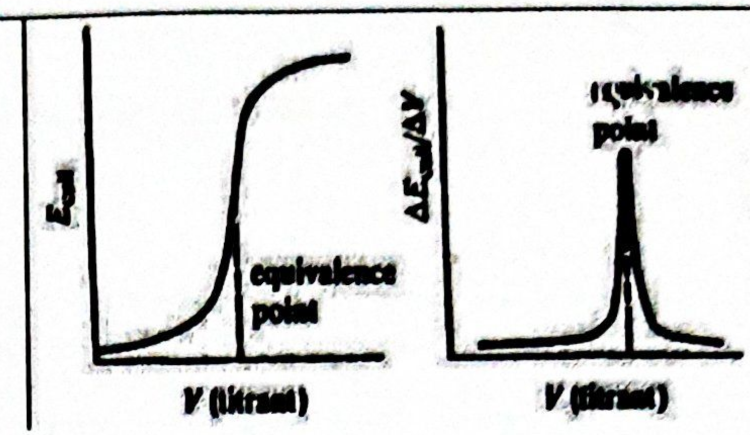

Fig. 2: Typical Potentiometric titration curves. (a) Normal curve and (b) First derivative curve.

Procedure:

Calibration of Potentiometer: Switch on the potentiometer and connect the standard cell terminals to either channel A (move channel switch to position A) or channel B (move the channel switch to position B). The meter should read 1.018 V. In case it is not 1.018 V, adjust the std. knob to obtain reference value.

Estimation of Fe(II) in steel: Transfer the given unknown steel [containing Fe(II)] solution into a clean 100 mL standard flask and make the solution up to the mark with distilled water and mix well. Pipette out 20 mL made up steel sample solution into a clean 100 mL beaker and add one test tube of dil. H_2SO_4 (2 N). Place Pt electrode in the beaker and connect to the +ve terminal of the potentiometer. In another beaker, place 50 mL of saturated KCl solution and dip the SCE in the solution and connect to the -ve terminal of the potentiometer. Place a salt bridge to complete the cell. Read the EMF of the cell and note down the value. Add 1 mL of $KMnO_4$ solution from the burette to the beaker containing steel sample solution. Stir the solution carefully and measure the EMF. Continue the addition of $KMnO_4$ solution and record the EMF for every 1 mL addition as per procedure till the potential shows a tendency to increase rapidly. After the abrupt change in cell EMF is observed, continue the titration to take 5 more reading by adding 1 mL burette solution every time. Plot EMF (ordinate) *vs.* volume of $KMnO_4$ added (abscissa) to get S-shaped curve which indicate the volume range of the end point.

To find out the volume of end point more precisely, carry out the 2nd titration in similar way but by adding 1 mL aliquots of $KMnO_4$ initially and then 0.1 mL aliquots between the two volumes where the end point is detected. Continue the titration beyond the end point as done above. The exact end point is determined by differential method i.e. by plotting $\Delta E/\Delta V$ *vs* average volume of $KMnO_4$ added. Calculate the normality strength of the Fe(II) in the given solution.

OBSERVATION AND CALCULATIONS

Potentiometric Titration-I:

Burette: $KMnO_4$ solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

S. No.	Volume of $KMnO_4$ (mL)	EMF (volts)	S. No.	Volume of $KMnO_4$ (mL)	EMF (volts)
1	0	0.379	11	10	0.982
2	1	0.405	12	11	0.982
3	2	0.424	13		
4	3	0.439	14		
5	4	0.455	15		
6	5	0.478	16		
7	6	0.515	17		
8	7.	0.938	18		
9	8.	0.987	19		
10	9	0.984	20		

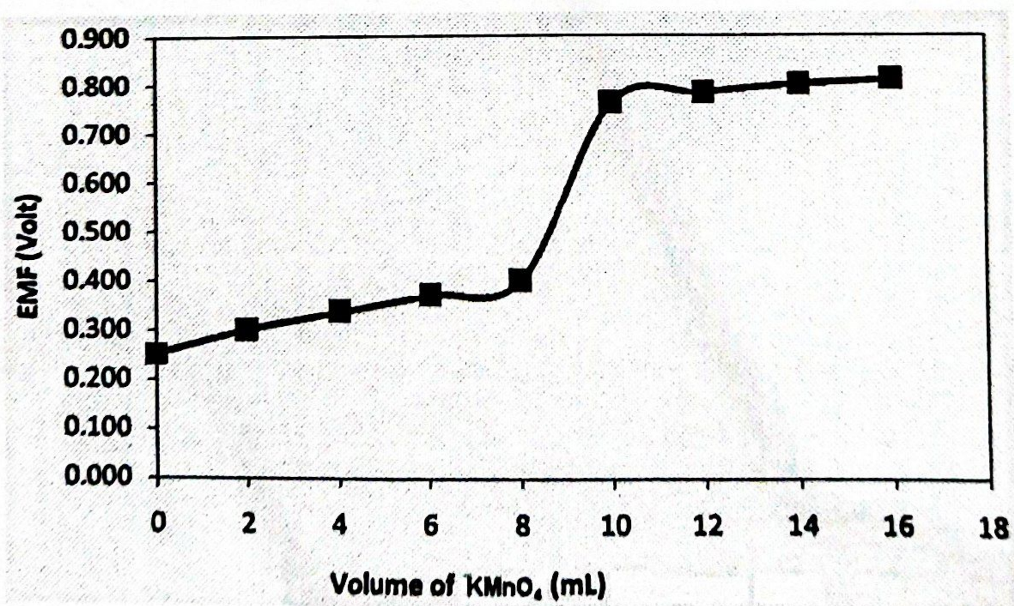

Fig. 3: Plot of EMF *vs* Volume of $KMnO_4$ added (mL)

Potentiometric Titration-II:

Burette: $KMnO_4$ solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

Sl. No.	Vol. of $KMnO_4$ (mL)	EMF (Volt)	ΔE (Volt)	ΔV (mL)	ΔE/ΔV (Volt/mL)	Average Volume (mL)
1	3.6	0.423				
2	3.7	0.424				
3	3.8	0.425				
4	3.9	0.426				
5	4.0	0.441				
6	4.1	0.447				
7	4.2	0.450				
8	4.3	0.449				
9	4.5	0.452				
10	4.7	0.531				
11	4.8	0.821				
12	4.9	0.502				
13	5.0	0.453				
14	5.1	0.424				
15	5.2	0.422				

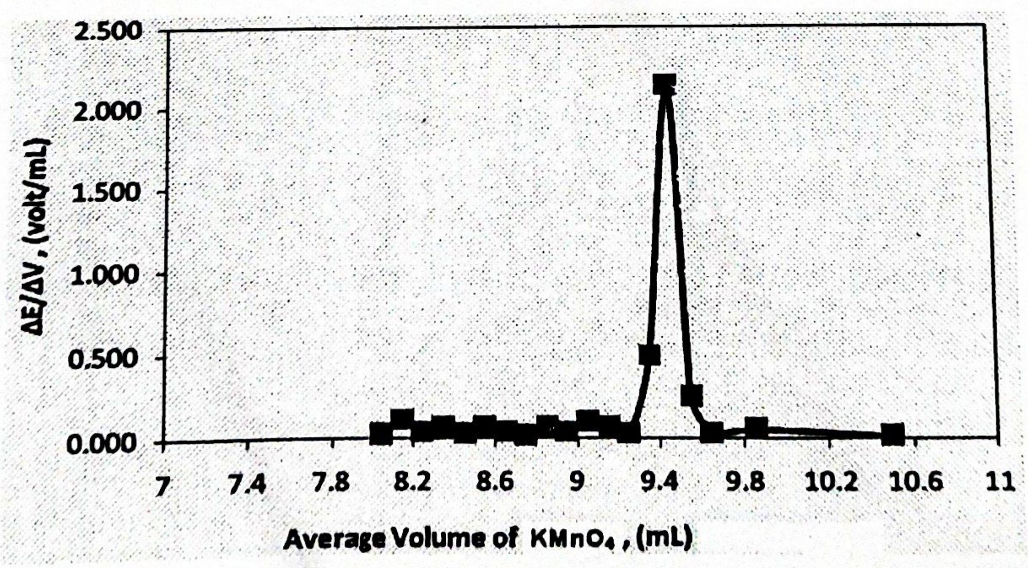

Fig. 4: Plot of ΔE/ΔV *vs* Average volume of $KMnO_4$ added.

Calculation:

$$(N \times V) \text{ of steel sample solution} = (N \times V) \text{ of } KMnO_4$$

$$N \text{ of steel sample solution} = \frac{0.05\,N \times \text{Volume of } KMnO_4 \text{ from Plot-2}}{20 \text{ mL of steel sample}}$$

= ____________N

Amount of Fe present in 1L of sample solution = Normality of steel sample x Atomic weight of Fe (55.85)

$$\text{Amount of Fe present in given sample solution} = \frac{\text{Normality of steel sample} \times 55.85 \times 100}{1000}$$

= ________________grams in 100 mL

Result: The amount of Iron present in given steel sample is found to be =_________ grams.

Evaluation of Result:

Sample number	Experimental value	Actual Value	Percentage of error	Marks awarded