

Dr. Debranjana Ghosh

Instruction sheet for
practical classes.

Physical chemistry

Semester - 4 (H), CC-8 (Prac.)

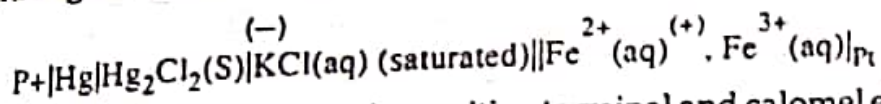
and

Semester - 4 (G), GE-4 (Prac.)

Topic: potentiometric titration

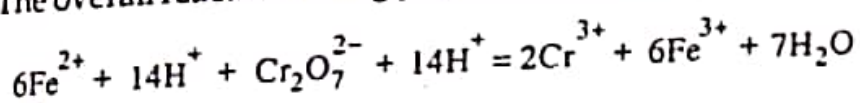
1.12.2 Potentiometric Titration of Ferrous Iron in Mohr's Salt against a Standard Solution of $K_2Cr_2O_7$ or $KMnO_4$

Principle: It is a redox titration in which ferrous iron is oxidised to ferric iron by the oxidant $K_2Cr_2O_7$ or $KMnO_4$. In this titration the indicator electrode is a platinum electrode dipped into a standard solution of Mohr's salt. To complete the cell, this electrode is connected with a saturated calomel electrode through KCl salt-bridge. The electrochemical cell thus formed is



The platinum electrode is connected to the positive terminal and calomel electrode is attached to the negative terminal of the potentiometer.

A known volume of acidified Mohr's salt solution is taken in a beaker and to it platinum wire is inserted. From the burette, standard solution of $KMnO_4$ or $K_2Cr_2O_7$ is added to this Mohr's salt solution. At any instant during the titration the solution contains a mixture of Fe^{2+} and Fe^{3+} ions with a platinum-wire in it and this forms a reversible electrode (indicator electrode). The progressive addition of $K_2Cr_2O_7$ or $KMnO_4$ will cause a change in E.M.F. of the cell because the ratio Fe^{3+}/Fe^{2+} increases. If the E.M.F. of the cell is plotted against the titre added, the curve that is obtained shows its greatest slope when the equivalence point is reached. Thus from the slope, equivalence point can be determined. The overall reaction taking place when $K_2Cr_2O_7$ is used as oxidant is as below:



The E.M.F. of the cell is given by the following equation.

$$E_{cell} = E_{Fe^{3+}/Fe^{2+}} - E_{calomel}$$

$$E_{cell} = E^0_{Fe^{3+}/Fe^{2+}} + 0.591 \log_{10} \frac{Fe^{3+}}{Fe^{2+}} - E_{calomel}$$

At the mid-point of the titrations, $[Fe^{2+}] = [Fe^{3+}]$, so the above equation stands as

$$E_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E_{calomel} \quad (A)$$

Thus from the volume of titrant required at the equivalence point and knowing the potentials of reference calomel electrode and standard electrode, concentration of ferrous iron in the solution can be estimated. Again, from the value of E.M.F. at the mid-point of titration standard redox potential of Fe^{3+}/Fe^{2+} system can be evaluated putting value of potential of reference electrode in equation (A).

Apparatus Required:

- (i) Potentiometer
- (ii) Platinum electrode
- (iii) Calomel electrode
- (iv) Beaker, burette and pipette
- (v) Salt-bridge.

Chemicals Required:

- (i) (N/10) Mohr's salt solution
- (ii) (2N) H₂SO₄
- (iii) (N/2) K₂Cr₂O₇ / (N/2) KMnO₄

Procedure: 20 ml of (N/10) Mohr's salt solution is taken in a beaker. A clean platinum electrode is inserted into it. This beaker is connected with a saturated calomel electrode through a salt-bridge. The two electrodes are connected to the two terminals of the potentiometer. From a burette, K₂Cr₂O₇ or KMnO₄ solution is added to the solution of Mohr's salt, 4 drops at a time. The solution is stirred well and the E.M.F. is noted. Finally the graph of E.M.F. versus volume of oxidant (K₂Cr₂O₇ or KMnO₄) added is plotted (figure below). The equivalence point and mid-point of the titrations are recorded.

Results and Calculations

At Room Temperature:

Volume of Mohr's salt solution taken	Volume of K ₂ Cr ₂ O ₇ or KMnO ₄ added	E.M.F.
20 ml	0.0	
20 ml	0.2	
20 ml	0.4	
20 ml	0.6	

Calculations

Let S_1 be the strength of oxidant and V_1 be its volume at equivalence point. Thus

$$S_1 (N/2) K_2Cr_2O_7 \text{ or } KMnO_4 \times V_1 = 20 \times S_2,$$

where S_2 is the strength of Mohr's salt solution.

$$S_2 = \frac{S_1 \times V_1}{20}.$$

From the graph, E.M.F. at mid-point of titration ($V_1/2$) is calculated and from equation (A) standard redox potential ($E^0_{Fe^{3+}/Fe^{2+}}$) is calculated.

