Date 8/12/20

Expt. No. 10

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EXPERIMENT: To titrate potentiometrically ferrous ammonium sulphate solution against potassium permanganate and to determine the standard electrode potential of ferrous-ferric system.

THEORY: An electrochemical cell is a device which establishes measurable electrical potential differences and in which flow of electrical current is accompanied by an overall chemical change. A reversible cell is that in which the overall chemical reaction can be reversed in the presence of an opposing external electromotive force of magnitude greater than that of cell itself. An electromotive cell consists of two electrodes or half cells, whose electrolytic solutions are either directly in contact with each other or connected through an intervening electrolytic solution. The net chemical change takes place at the individual electrodes; one of which is oxidation and the other reduction.

At the reversible electrodes, the oxidized and reduced states of a system exist in equilibrium in the solution, where an inert metal electrode (like Pt) is dipped into it e.g. Fe^{3+}/Fe^{2+}, in which the reaction is:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

When potassium permanganate solution is added to Mohr's salt solution, the concentration of Fe^{2+} ions decreases and that of Fe^{3+} ions increases, and as a result the emf of the cell increases slowly. Near to the equivalence point, an inflection is seen due to fall in conc. of Fe^{2+} ions ultimately to 0,

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APPARATUS: Pipette, burette, beaker, funnel, burette stand, clamp, potentiometer, calomel electrode (or Ag/AgCl electrode) and platinum electrode.

CHEMICALS: Mohr's salt solution (Ferrous Ammonium Sulphate; $FeSO_4(NH_4)_2SO_4\ 6H_2O$), potassium permanganate ($KMnO_4$) and sulphuric acid (H_2SO_4).

CHEMICAL REACTIONS and EQUATIONS:

The experimental cell:

$$Hg, Hg_2Cl_2(s)/KCl\ (saturated) \parallel Fe^{3+}/Fe^{2+}/Pt \quad -(1)$$

The emf of the cell:

$$E = E^\circ_{(Fe^{3+}/Fe^{2+})} + \frac{2.303RT}{nF}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} - E_{(calomel)} \quad -(2)$$

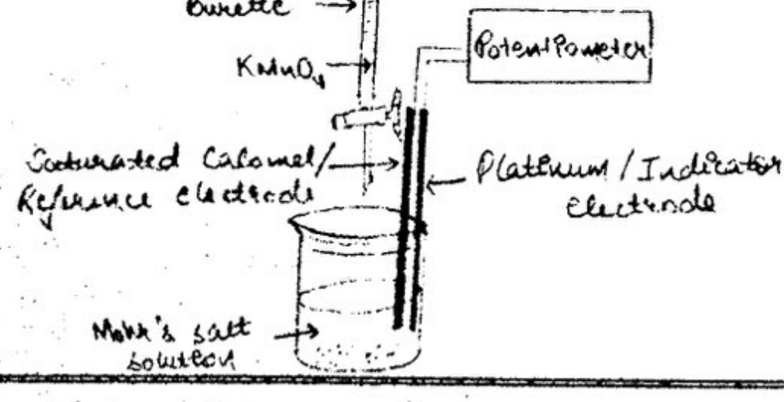
Chemical reaction during potentiometric titration:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+ \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

At half equivalence, eq^n (2) becomes

$$E_{(half\ equivalence)} = E^\circ_{(Fe^{3+}/Fe^{2+})} - E_{(calomel)}$$
$$= E^\circ_{(Fe^{3+}/Fe^{2+})} - 0.242 \quad (at\ 298K)$$
$$\therefore E^\circ_{(Fe^{3+}/Fe^{2+})} = E_{(half\ equivalence)} + 0.242$$

DIAGRAMS:



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resulting in sudden rise in emf of the cell.
At half equivalence,

$$E = E^\circ(Fe^{3+}/Fe^{2+}) - E(\text{calomel})$$

Thus, by noting $E_{(\text{half equivalence})}$ from the graph, $E^\circ_{(Fe^{3+}/Fe^{2+})}$ can be calculated.

PROCEDURE:

1. Take 50ml of 0.1N FAS solution in the beaker and add 5ml of 1N sulphuric acid. Dip the platinum and saturated calomel electrodes in the solution.
2. Connect the indicator and the reference electrodes to the black and red terminals of potentiometer, respectively.
3. Rinse and fill the burette with $KMnO_4$ (0.2N).
4. Note the initial emf of the cell and start addition of the titrant ($KMnO_4$) in portions of 1ml each. Near the equivalence point, decrease the volume of additional titrant to 0.6 ml and later on to 0.2ml and note down the reading after each titration.
5. Continue to take 10-12 readings more, after a sharp change/ increase in emf is noticed.
6. Plot emf (in volts) against the volume of $KMnO_4$ solution added (ml) and note down the equivalence point and the potential at half equivalence point.

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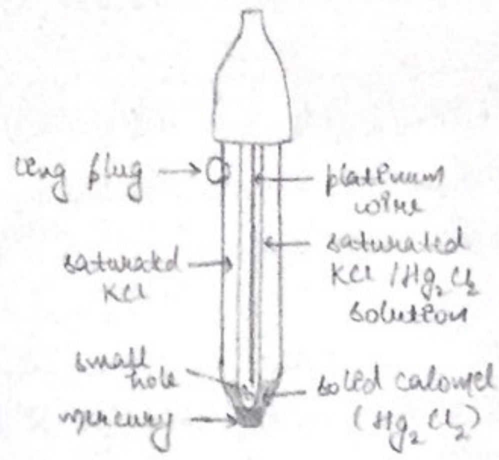
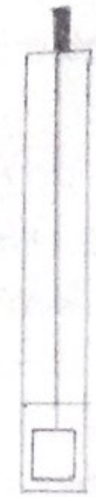


Saturated calomel electrode
(Reference electrode)



Platinum electrode

OBSERVATIONS:

S.No.	Volume of $KMnO_4$ added (mL)	EMF (Volts)	S.No.	Volume of $KMnO_4$ added (mL)	EMF (Volts)
1.	0.0	0.299	17.	8.0	0.440
2.	0.5	0.340	18.	8.5	0.445
3.	1.0	0.360	19.	9.0	0.450
4.	1.5	0.371	20.	9.5	0.455
5.	2.0	0.379	21.	10.0	0.463
6.	2.5	0.387	22.	10.5	0.474
7.	3.0	0.393	23.	11.0	0.482
8.	3.5	0.399	24.	11.5	0.498
9.	4.0	0.404	25.	12.0	0.545
10.	4.5	0.409	26.	12.5	1.008
11.	5.0	0.414	27.	13.0	1.049
12.	5.5	0.418	28.	13.5	1.062
13.	6.0	0.422	29.	14.0	1.064
14.	6.5	0.426	30.	14.5	1.066
15.	7.0	0.431	31.	15.0	1.070
16.	7.5	0.435			

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RESULT: The standard half-cell potential of Fe^{3+}/Fe^{2+} couple is 0.662 V.

PRECAUTIONS: 1. After each addition of titrant, the contents of the beaker should be stirred gently.
2. Electrodes should not be used as stirrer.

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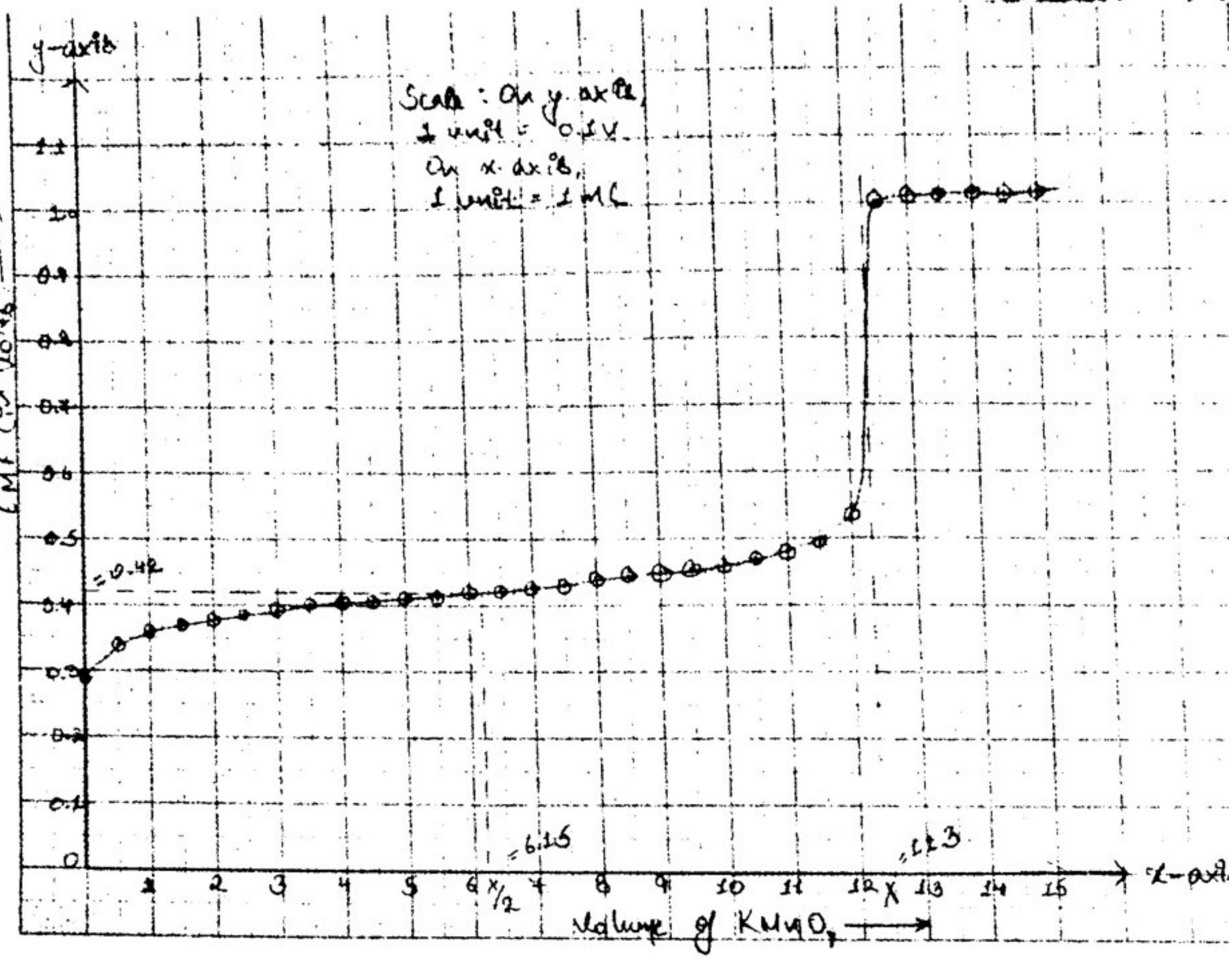
GRAPH:



CALCULATIONS:

$$E^\circ(Fe^{3+}/Fe^{2+}) = E + E\,(\text{calomel})$$
$$= 0.42 + 0.242$$
$$= 0.662\,V$$

RESULT: The standard half-cell potential of Fe^{3+}/Fe^{2+} couple is 0.662V.

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