Potentiometric Redox Titration of Fe^{2+} by standard Ce^{4+} solution

- A *potentiometric titration* belongs to chemical methods of analysis in which the endpoint of the titration is monitored with an indicator electrode that records the change of the potential as a function of the amount (usually the volume) of the added titrant of exactly known concentration

- Provide more reliable data than data from titrations that use chemical indicators

- Particularly useful with colored or turbid solutions

Potentiometric redox titration of Fe^{2+} *vs.* Ce^{4+} solution

- The reference electrode used here is saturated calomel electrode (SCE). It consists of mercury metal covered with a paste of Hg + $Hg_2Cl_2\downarrow$ in contact with saturated KCl solution and Pt Wire for electrical contact. The reduction potential of this electrode is 0.244 V. This saturated calomel electrode functions as ANODE.

- The Indicator electrode is a platinum electrode which responds rapidly to oxidation-reduction couples and senses the potential which depends upon the concentration ratio of the reactants & products of redox reactions. Here, the Pt electrode is in contact with a Ferrous-Ferric couple. This electrode functions as CATHODE.

Cell Representation:

$$(-)\ Pt \mid Hg_{(l)}, Hg_2Cl_2(s) \mid KCl_{(sat)} \parallel Fe^{3+}, Fe^{2+} \mid Pt\ (+)$$

Cell Reaction:

Anode:- $2\,Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

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

Cell E.m.f.:

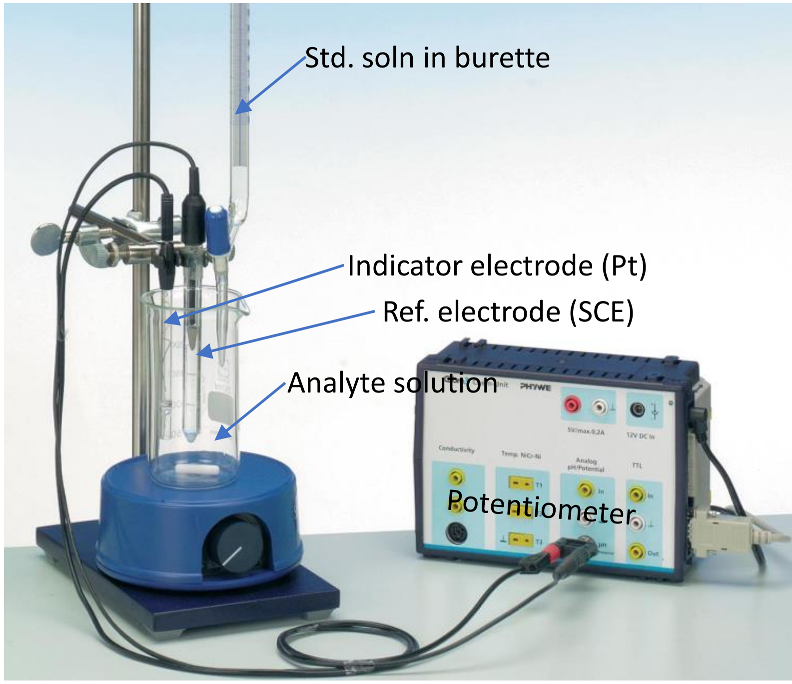
$$E_{cell} = E^{\circ}\,(Fe^{3+} / Fe^{2+}) + \frac{2.303RT}{F} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} - E_{SCE}$$

- The cell potential is measured during the course of reaction and graphs are plotted
- From the graphs end point of the titration is located and concentration is calculated

Experiment

Requirements:

Potentiometer, Platinum electrode, Saturated calomel electrode (SCE), Ferrous ammonium sulfate and 0.25 M Ceric ammonium sulphate (both prepared in 2N H_2SO_4)



Procedure:

- Pipette out 25 ml of test solution (ferrous solution) in a clean 100 ml beaker, place the platinum electrode & SCE in the solution, which creates a Fe^{+2}/Fe^{+3} couple. Connect the electrodes to the potentiometer and measure the EMF of the of the cell

- Add cerric sulfate from burette in small portions to the ferrous solution, stir it and note the EMF

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

- Continue the titration till a sudden inflextion in EMF occurs. Then take about 6 to 8 readings after inflexion

- Draw a graph of E_{cell} Vs volume of cerric sulfate added; the inflexion point gives an approximate equivalence

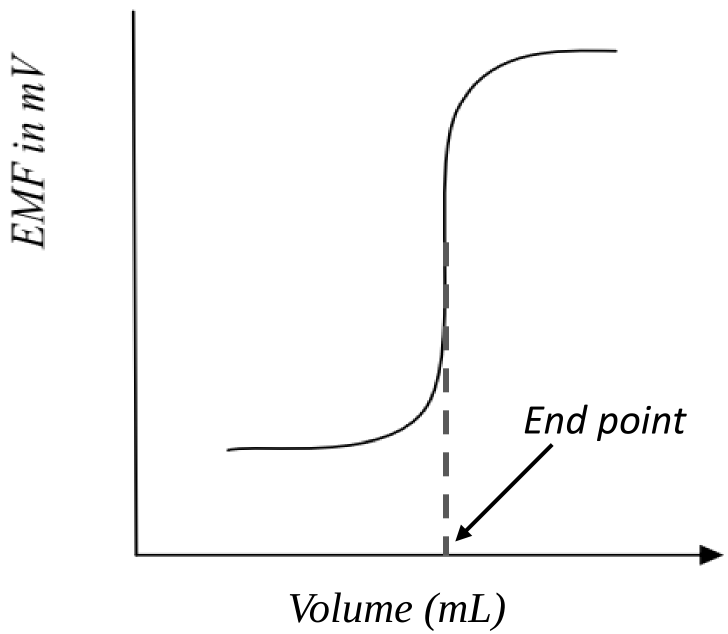
- Differential graph is drawn by plotting $\Delta E/\Delta V$ (Y-axis) *vs.* volume of cerric sulfate (X-axis) to get a sharp peak, which corresponds to the precise equivalence point of titration

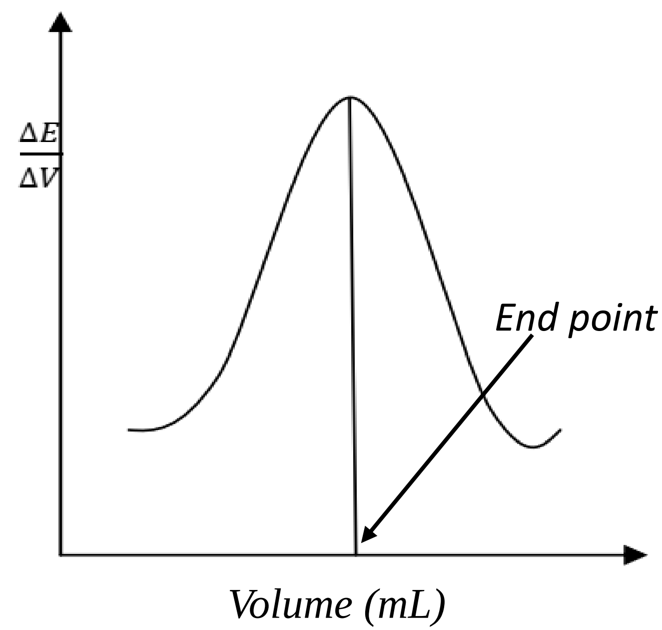
- From the titration curve, volume of cerric sulfate required is found out and concentration of ferrous sulphate can be calculated

Observation table

S.No.	V Ce^{4+} (mL)	Ecell (mv)	ΔE	$\frac{\Delta E}{\Delta V}$
1	V1	E1		
2	V2	E2	E2-E1	V2-V1
3	V3	E3	E3-E2	V3-V2

Graphs





CALCULATION:

From the graph:

The volume at equivalent point = ... mL.

Volume of $FeSO_4(NH_4)_2SO_4 = N_1V_1 = N_2V_2$

$\therefore$ $N_2 = N_1V_1 / V_2 =$ .... N

N_1 = Normality of $Ce(SO_4)_2 = 0.25N$

N_2 = Normality of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = ? N

V_1 = Volume of $Ce(SO_4)_2$ = ... mL (from the graph)

V_2 = Volume of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = 25 mL.

Amt. of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = Normality x Eq. Wt. [M.W. = Eq. Wt. for FAS]

RESULT:

(1) Amount of Ferrous sulphate/Ferrous ammonium sulphate in the given solution = ...g/L

(2) Volume of Ceric sulphate (ceric ammonium sulphate) for the end point = ...mL

For example

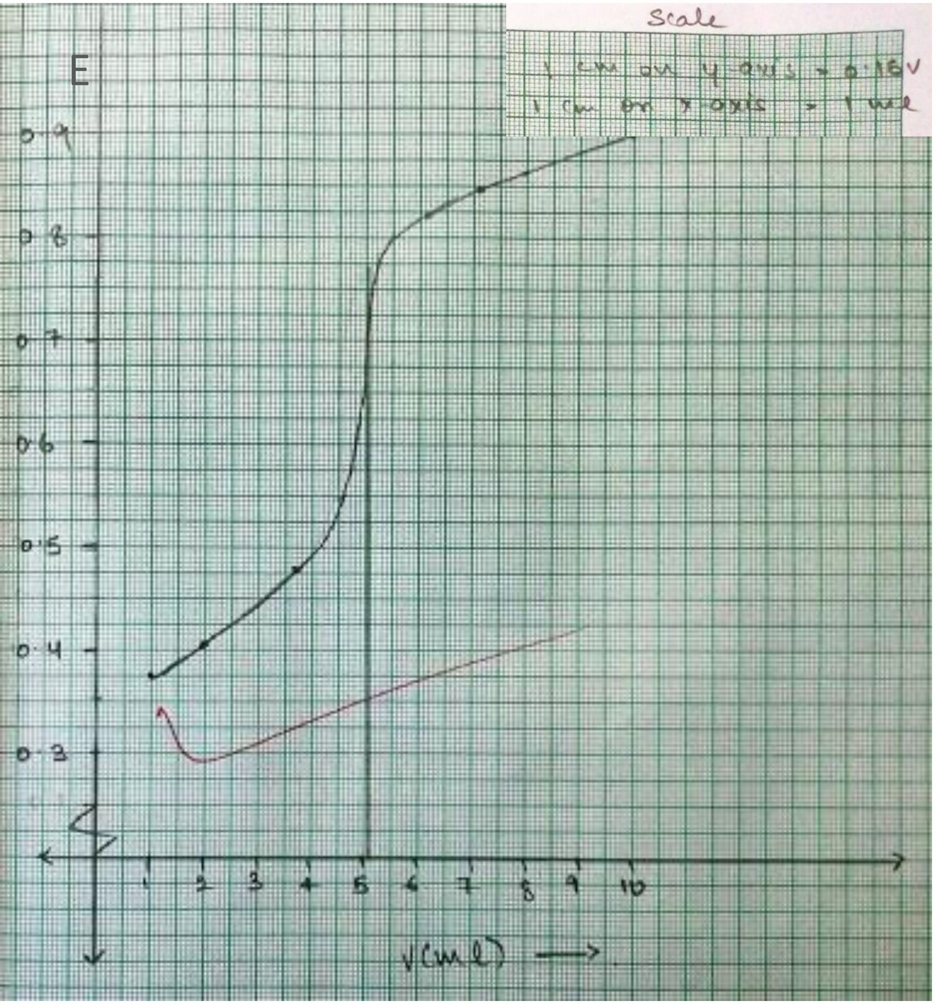
OBSERVATION TABLE :

Pilot Reading :

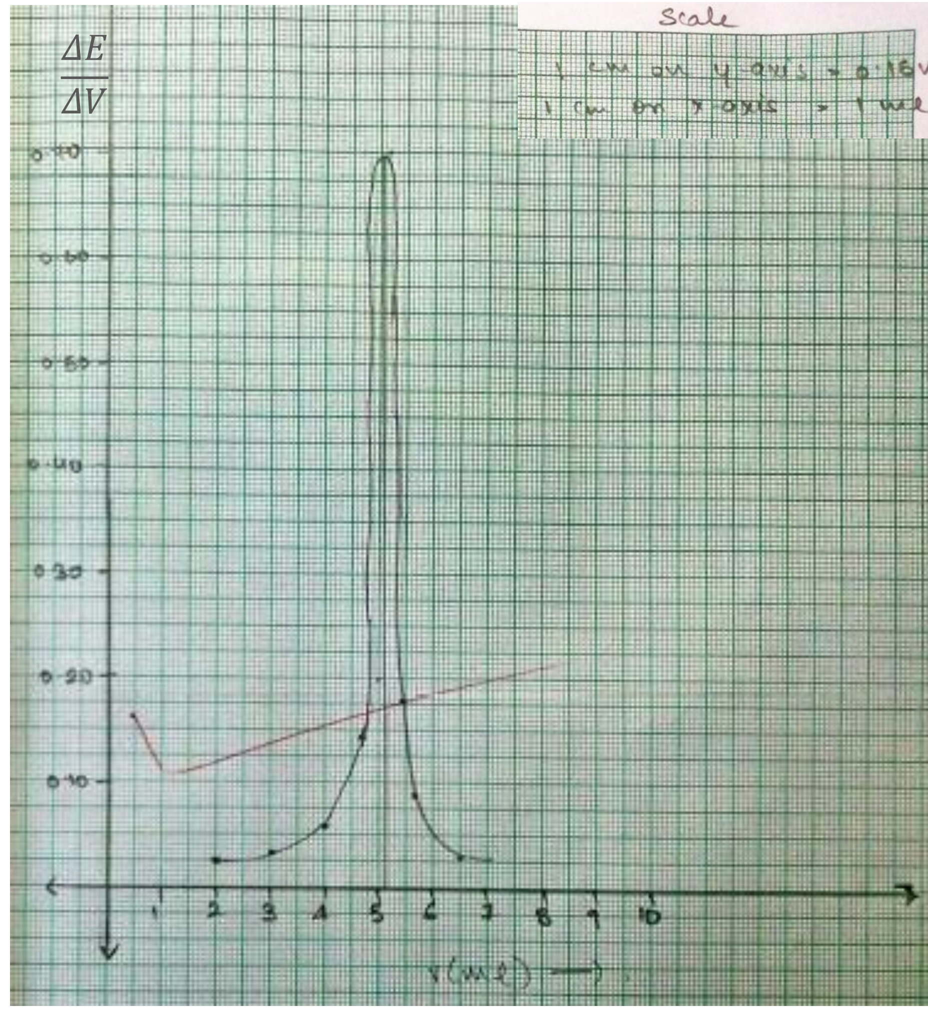
No.	Volume of Cerric Soln. (V mL)	E.M.F (E) in Volt	Δ E in volt	Δ V E in mL	Δ F/Δ V
1	1	0.375	—	—	—
2	2	0.412	0.037	1	0.037
3	3	0.433	0.021	1	0.021
4	4	0.462	0.029	1	0.029
5	5	0.680	0.218	1	0.218
6	6	0.806	0.126	1	0.126
7	7	0.832	0.026	1	0.026
8	8	0.845	0.013	1	0.013
9	9	0.855	0.01	1	0.01
10	10	0.860	0.005	1	0.005
11					
12					

Actual Reading :

No.	Volume of Cerric Soln. (V mL)	E.M.F (E) in Volt	Δ E in volt	Δ V E in mL	Δ F/Δ V
1	1	0.394	—	—	—
2	2	0.416	0.022	1	0.022
3	3	0.435	0.019	1	0.019
4	4	0.463	0.028	1	0.028
5	5	0.664	0.201	1	0.201
6	5.1	0.734	0.070	0.1	0.70
7	5.2	0.744	0.010	0.1	0.10
8	5.3	0.763	0.019	0.1	0.19
9	5.4	0.78	0.017	0.1	0.17
10	5.6	0.789	0.002	0.1	0.02
11	5.7	0.800	0.011	0.1	0.11
12	5.8	0.812	0.006	0.1	0.06
13	5.9	0.814	0.002	0.1	0.02
14	6.0	0.819	0.005	0.1	0.05
15	6.1	0.827	0.008	0.1	0.08
16	6.2	0.834	0.007	0.1	0.07
17					
18					
19					



Scale
1 cm on y axis = 0.1 V
1 cm on x axis = 1 ml
E
0.9
0.8
0.7
0.6
0.5
0.4
0.3
1
2
3
4
5
6
7
8
9
10
V(ml) ⟶



Scale
1 cm on y axis = 0.1 V
1 cm on x axis = 1 ml
$\frac{\Delta E}{\Delta V}$
0.70
0.60
0.50
0.40
0.30
0.20
0.10
1
2
3
4
5
6
7
8
9
10
V(ml) ⟶

CALCULATION:

From the graph:

The volume at equivalent point = ...5.1.... mL.

Volume of $FeSO_4(NH_4)_2SO_4$ = $N_1V_1 = N_2V_2$

$\therefore$ $N_2 = N_1V_1 / V_2$ = ..0.051... N

N_1 = Normality of $Ce(SO_4)_2$ = 0.25N

N_2 = Normality of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = 0.051 N

V_1 = Volume of $Ce(SO_4)_2$ = ...5.1..... mL (from the graph)

V_2 = Volume of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = 25 mL.

Amt. of $Fe(SO_4)_2(NH_4)_2SO_4\ 6H_2O$ = Normality x Eq. Wt. [M.W. = Eq. Wt. for FAS]

= Normality x M.W. = 0.051 x 392

= ..19.992.. g/L.