3. Preparation of 0.05 (N) Mohr solution in 2 (N) H_2SO_4 (100 ml)

Relative equivalent mass of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O = 392.16$

Initial mass (g)	Final mass (g)	Mass of Mohr salt transferred (g)	Mass of Mohr salt to be taken (g)	Strength of Mohr solution
...	...	...	1.96	...(N)

[Dissolve the required amount of Mohr salt in 100 ml 2 (N) H_2SO_4 which is prepared by diluting 5.6 ml concentrated H_2SO_4 (36 N) to 100 ml carefully and then cooling.]

4. Titration and recording of e.m.f.: Volume of Mohr solution taken = 25 ml

No. of observations	No. of drops of $K_2Cr_2O_7$ (n) added	Observed e.m.f. (E_{cell}) volt or mV
1	0	
2	2	
3	4	
⋮	⋮	
⋮	⋮	
⋮	⋮	

5. Calibration of 1 cc of $K_2Cr_2O_7$ solution to number of drops : 1 cc = ... n' (drops say)

6. Graph plotting and Calculations

n	E_{cell} (volts)	ΔE_{cell} (volts)	Δn	$\Delta E_{cell}/\Delta n$ volt/drop
0 (n_1)	E_1	—	—	—
2 (n_2)	E_2	$E_2 - E_1$	$n_2 - n_1$	⋮
4 (n_3)	E_3	$E_3 - E_2$	$n_3 - n_2$	⋮
⋮	⋮	⋮	⋮	⋮

7. Calculation of strength of Mohr solution and formal potential of Fe (III)-Fe(II)—system

i. From the plot of E_{cell} vs. n, $E^{o}_{Fe^{3+}/Fe^{2+}} = E_{cal} + \left(E_{cell}\right)_{1/2} = \cdots$ volt.

Expected value of $E^{o}_{Fe^{3+}/Fe^{2+}} = +0.68$ volt in (M) H_2SO_4 medium

ii. From the plot of $\Delta E/\Delta n$ vs. n, number of drops of $K_2Cr_2O_7$ solution required = ... = ... ml

Hence strength of Mohr solution = ... (N).

Experiment 10

Potentiometic titration of Zn(II) *solution by potassium ferrocyanide solution and also determination of the composition of* Zn(II)-*ferrocyanide complex.*

Theory: The electrode potential for the redox system

$$\left[Fe(CN)_6\right]^{3-} + e \rightleftharpoons \left[Fe(CN)_6\right]^{4-}$$ is given by Nernst equation as

$$E = E^{\circ} + \frac{RT}{F} \ln \frac{C_{[Fe(CN)_6]^{3-}}}{C_{[Fe(CN)_6]^{4-}}}$$

where E° is the standard reduction potential of $\left[Fe(CN)_6\right]^{3-} - \left[Fe(CN)_6\right]^{4-}$ system.

If a clean platinum electrode is inserted into the solution of a mixture of $K_4\left[Fe(CN)_6\right]$ and $K_3\left[Fe(CN)_6\right]$, it will serve as an electrode. If we couple this electrode with a standard calomel (saturated) electrode, then the cell which is constructed for the experiment is

$$\underset{(L)}{\overset{(-)}{\text{Saturated calomel electrode}}} \parallel \underset{\substack{\text{(Mixture of solution)}\\ (R)}}{\left[Fe(CN)_6\right]^{4-} - \left[Fe(CN)_6\right]^{3-}} \overset{(+)}{/\,Pt}$$

Pictorially it is represented as below:

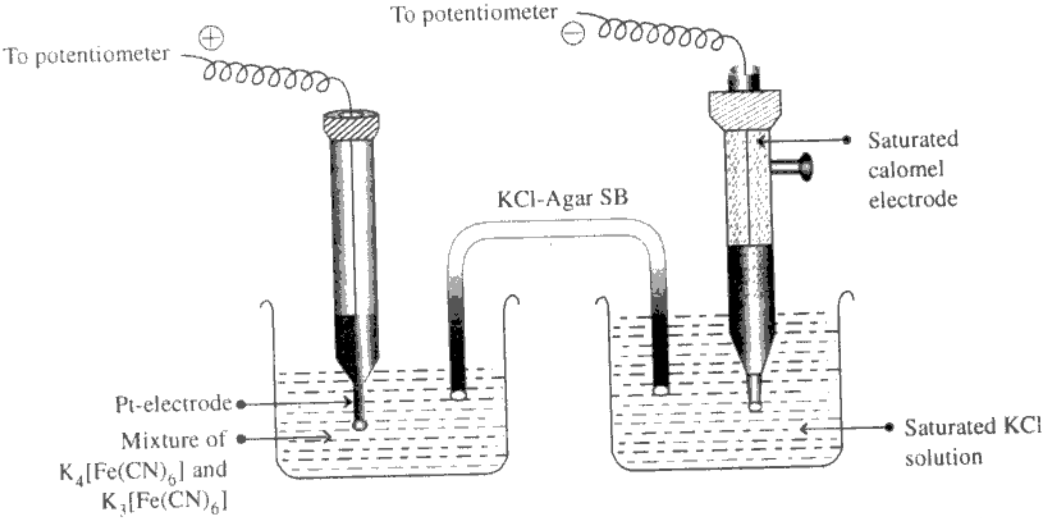

Fig. 6.25: Cell constructed for potentiometric titration of Zn(II) solution with $K_4Fe(CN)_6$ solution

The observed e.m.f. of the cell is given by

$$E = E_R - E_L$$

$$= E^{\circ} + \frac{RT}{F} \ln \frac{C_{[Fe(CN)_6]^{3-}}}{C_{[Fe(CN)_6]^{4-}}} - E_{cal} = E^{\circ} - E_{cal} + \frac{RT}{F} \ln \frac{C_{[Fe(CN)_6]^{3-}}}{C_{[Fe(CN)_6]^{4-}}}$$

$$= E^{\circ} - E_{cal} + 0.0591 \log \frac{C_{[Fe(CN)_6]^{3-}}}{C_{[Fe(CN)_6]^{4-}}} \text{ [at 25 °C].} \quad (1)$$

Here E_{cal} is the reduction potential of saturated calomel electrode.

When Zn(II) solution is added to the system, $\left[Fe(CN)_6\right]^{4-}$ is removed and the proportions of $\left[Fe(CN)_6\right]^{3-}$ increases. From equation (1) it is evident that with the progressive addition of Zn(II), the observed e.m.f. will gradually increase. At the equivalence point, there will be a sharp increase in e.m.f. due to sudden removal of all $\left[Fe(CN)_6\right]^{4-}$.

If we plot $\Delta E/\Delta n$ vs. n (n is the number of drops of $ZnSO_4$ added) the nature of curve will be of the following type (Fig. 6.26).

From the equivalence point, corresponding to the peak, volume of $ZnSO_4$ required can be known. Volume of $K_4[Fe(CN)_6]$ taken for estimation is also known. Therefore, strength of $K_4[Fe(CN)_6]$ can be calculated as strength of $ZnSO_4$ is known (prepared).

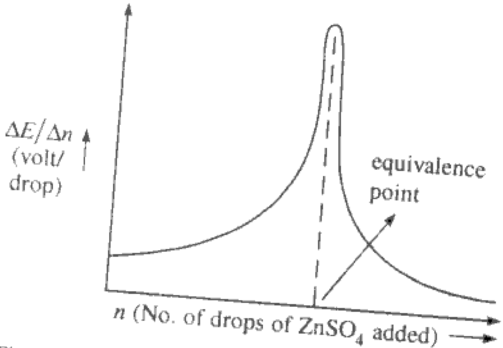

Fig. 6.26: Plot of $\Delta E/\Delta n$ vs. n (no. of drops of $ZnSO_4$ solution added for the titration of $K_4Fe(CN)_6$ solution with $ZnSO_4$ solution.

Determination of composion of the complex formed

Let 10 ml $K_4[Fe(CN)_6]$ is taken for titration.

Let the number of moles of $K_4\left[Fe(CN)_6\right]$ present in 10 ml solution = a.

If at the equivalence point V ml $ZnSO_4$ solution is required, then V ml of $ZnSO_4$ solution combines with 10 ml $K_4\left[Fe(CN)_6\right]$ solution.

Let the number of moles of $ZnSO_4$ present in V ml solution = b.

Then find the ratio, $\dfrac{\text{No. of moles of } ZnSO_4}{\text{No. of moles of } K_4\left[Fe(CN)_6\right]} = \dfrac{b}{a}$.

From this ratio we can conclude about the composition of the complex formed.

Materials

i. 100 ml $\frac{M}{6}$ $ZnSO_4$ solution

ii. 100 ml $\frac{M}{100}$ $K_4\left[Fe(CN)_6\right]$ solution

iii. 100 ml ≈ $\frac{M}{100}$ $K_3\left[Fe(CN)_6\right]$ solution

iv. Pt-electrode and saturated calomel electrode

v. KCl-Agar salt bridge

vi. Potentiomter, (vii) Microburrette, 100 ml beaker, pipette (10 ml), etc.

Procedure

i. Prepare 100 ml $\frac{M}{6}$ $ZnSO_4$ solution, 100 ml $\frac{M}{100}$ $K_4\left[Fe(CN)_6\right]$ solution and 100 ml $\frac{M}{100}$ $K_3\left[Fe(CN)_6\right]$ solution.

ii. Take 10 ml $K_4\left[Fe(CN)_6\right]$ solution and 10 ml $K_3\left[Fe(CN)_6\right]$ solution (of order ~ 0.01 M) in a clean 100 ml beaker (use pipette) and insert the clean and dry Pt-electrode into the solution. Connect the saturated calomel electrode through KCl-Agar salt bridge as shown inFig. 6.25. Then connect the cell to the terminals indicated in the potentiometer.

iii. Add one drop of $ZnSO_4$ solution from a microburette into the solution in the beaker—a white precipitate will be formed. Shake well and note the meter reading. Continue the titration adding 1 drop of $ZnSO_4$ solution at each time. Take 5 to 6 more readings after sharp change (equivalence point).

iv. Calculate $\Delta E/\Delta n$ and plot it against n. Detect the equivalence point in the graph and note the number of drops of $ZnSO_4$ required.

v. Calibrate 20 drops of $ZnSO_4$ solution into volume (ml).

vi. Calculate the strength of $K_4[Fe(CN)_6]$ solution. Also calculate the number of moles of $ZnSO_4$ and $K_4[Fe(CN)_6]$. Then find ratio $\frac{b}{a}$ and conclude about the composition of Zn(II) ferrocyanide complex that is formed.

Results and Calculations

1. Recording of laboratory temperature

	Before experiment	After experiment	Mean
Temperature →	··· °C	··· °C	··· °C

2. Preparation of 100 ml $\frac{M}{6}$ $ZnSO_4$ solution: Relative molar mass of $ZnSO_4 \cdot 7H_2O = 287.35$

Initial mass (g)	Final mass (g)	Mass of $ZnSO_4$ transferred (g)	Mass of $ZnSO_4$ to be taken (g)	Strength of $ZnSO_4$ solution
...	...	...	4.789	··· (M)

3. Preparation of100 ml 0.01 (M) $K_4[Fe(CN)_6]$ solution: Relative molar mass of $K_4[Fe(CN)_6] \cdot 3H_2O = 422.26$.

Initial mass (g)	Final mass (g)	Mass of $K_4[Fe(CN)_6]$ transferred (g)	Mass of $K_4[Fe(CN)_6]$ to be taken (g)	Strength of $K_4[Fe(CN)_6)]$ solution
...	...	...	0.4222	··· (M)

4. Preparation of 100 ml 0.01 (M) $K_3[Fe(CN)_6]$ solution: Relative molar mass of $K_3[Fe(CN)_6]$ = 329.16

Initial mass (g)	Final mass (g)	Mass of $K_3[Fe(CN)_6]$ transferred (g)	Mass of $K_3[Fe(CN)_6]$ to be taken (g)	Strength of $K_3[Fe(CN)_6]$ solution
...	...	...	0.3291	··· (M)

5. Titration and recording of e.m.f.'s

$\left.\begin{array}{l}\text{Volume of } K_4[Fe(CN)_6] \text{ solution taken} = 10 \text{ ml} \\ \text{Volume of } K_3[Fe(CN)_6] \text{ solution taken} = 10 \text{ ml}\end{array}\right\}$ in a 100 ml beaker

Observation number	No. of drops of $ZnSO_4$ solution added	Observed e.m.f. (in V or mV)
1	1	...
2	2	...
3	3	...
4	4	...
⋮	⋮	...

6. Calibration of number of drops of $ZnSO_4$ solution to volume (ml)

Observation No.	No. of drops of $ZnSO_4$ solution (from microburette)	Volume of 20 drops of $ZnSO_4$ solution (ml)	Mean volume of of 20 drops (ml) $ZnSO_4$ solution	No. of drops for 1 ml solution
1	20	...	V ml (say)	$\frac{20}{V} = n'$ (say)
2	20	...		
3	20	...		

7. Graph plotting and calculation of strength of $K_4[Fe(CN)_6]$ solution

No. of drops of $ZnSO_4$ solution added	Observed e.m.f. E (volt)	ΔE(volt)	Δn	$\frac{\Delta E}{\Delta n}$ volt/drop
1 (n_1)	E_1	—	—	—
2 (n_2)	E_2	E_2-E_1	n_2-n_1	⋮
3 (n_3)	E_3	E_3-E_2	n_3-n_2	⋮
⋮ ⋮	⋮	⋮	⋮	⋮
⋮ ⋮	⋮	⋮	⋮	⋮

From the graph, obtained by plotting $\Delta E/\Delta n$ vs. n, it is found that the number of drops of $ZnSO_4$ solution, at equivalence point (corresponding to the peak) $= n''$ (say). So, the volume of $ZnSO_4$ required for 10 ml $K_4[Fe(CN)_6]$ solution $= \frac{n''}{n'}$ ml $= x$ ml (say).

Therefore, the strength of $K_4[Fe(CN)_6]$ solution

$= \frac{x \times S}{10}(M) = y(M)$ (say), where S is the strength of $ZnSO_4$ solution in molarity.

Compare this stength, obtained potentiometrically, with the strength of $K_4[Fe(CN)]$ solution you have prepared by accurate weighing.

Determination of Composition of Zn(II) – $Fe(CN)_6^{4-}$ complex

Number of moles of $ZnSO_4 = \frac{x \times \text{molar concentration of } ZnSO_4 \text{ solution}}{1000} = b$

Again, number of moles of $K_4[Fe(CN)_6]$ that combine with $ZnSO_4$

$$= \frac{10 \times \text{molar concentron of } K_4[Fe(CN)}{1000} = \frac{y}{100} = a.$$

Thus, the ratio $= \frac{\text{No. of moles of } ZnSO_4}{\text{No. of moles of } K_4[Fe(CN)_6]} = \frac{b}{a}$.

Expected value of the ratio is $\frac{3}{2}$.

Hence, the precipitation reaction that takes place in neutral medium according to the following equation.

$$3ZnSO_4 + 2K_4[Fe(CN)_6] = K_2Zn_3[Fe(CN)_6]_2 \downarrow + 3K_2SO_4$$

[N.B.: $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ must be fresthly prepared. Otherwise their concentrations will change in presence of air and the result will be inaccurate].