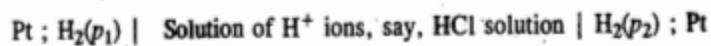## CONCENTRATION CELLS

In the case of galvanic cells discussed earlier, the electrical energy arises from the chemical reactions which take place in the cells. There is, however, another category of cells in which the EMF arises not due to any chemical reaction but due to transfer of matter from one half-cell to the other because of a difference in the concentrations of the species involved. These are called **concentration cells.**
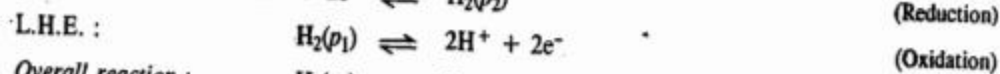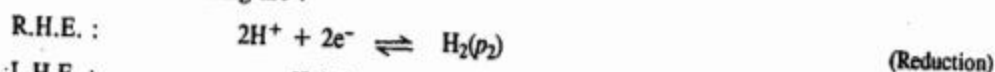
Cocentration cells are of two types, *viz.,*

1. Electrode-Concentration Cells   and   2. Electrolyte-Concentration Cells.

1. Electrode-Concentration Cells. In these cells, two like electrodes at different concentrations are dipping in the same solution. Two hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute an electrode-concentration cell. This may be represented as follows :

$$Pt \; ; H_2(p_1) \; | \quad Solution \; of \; H^+ \; ions, \; say, \; HCl \; solution \; | \; H_2(p_2) \; ; Pt$$

The reactions occurring are :

R.H.E. : $2H^+ + 2e^- \rightleftharpoons H_2(p_2)$ (Reduction)

L.H.E. : $H_2(p_1) \rightleftharpoons 2H^+ + 2e^-$ (Oxidation)

Overall reaction : $H_2(p_1) \rightleftharpoons H_2(p_2)$

This reaction is evidently independent of the concentration of the electrolyte.

At moderate pressures, H_2 can be considered to be an ideal gas so that the ratio of the activities can be considered to be equal to the ratio of the gas pressures. Hence, the Nernst equation may be written as
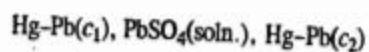
$$E = E° - \frac{0·0591}{2} \log (p_2/p_1) \quad \text{at } 25°C$$
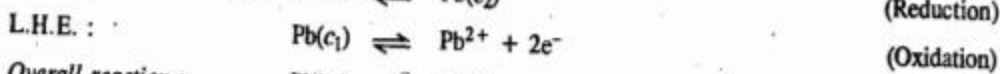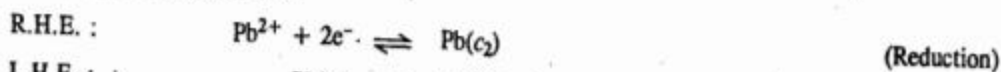
Since, by definition, $E°=0$, we have

$$E = -0·02955 \log (p_2/p_1) = 0·02955 \log (p_1/p_2)$$

When $p_2 < p_1$, the EMF is positive so that the whole process is spontaneous, being equivalent to the expansion of H_2 gas.

Another example of the electrode-concentration cell is that of an amalgam with *two different concentrations* of the same metal :

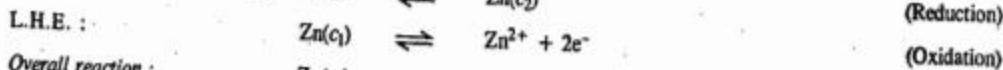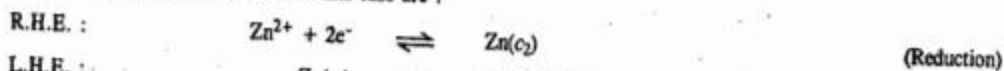$$\text{Hg-Pb}(c_1), \text{PbSO}_4(\text{soln.}), \text{Hg-Pb}(c_2)$$

The electrode reactions are :

R.H.E. : $Pb^{2+} + 2e^- \rightleftharpoons Pb(c_2)$ (Reduction)

L.H.E. : $Pb(c_1) \rightleftharpoons Pb^{2+} + 2e^-$ (Oxidation)

Overall reaction : $Pb(c_1) \rightleftharpoons Pb(c_2)$

The EMF of the cell is given by

$$E = E_R - E_L = \left(E_{Pb}° - \frac{0·0591}{2}\log c_2\right) - \left(E_{Pb}° - \frac{0·0591}{2}\log c_1\right)$$

$$= \frac{0·0591}{2} \log \frac{c_1}{c_2} = 0·02955 \log \frac{c_1}{c_2}$$

Here, too, if $c_2 < c_1$, the EMF is positive so that the whole process is spontaneous, *i.e.*, lead will go spontaneously from the higher concentration amalgam to the lower concentration amalgam.

Example 18. Calculate the EMF of the electrode-concentration cell Hg-Zn(c_1), $Zn^{2+}(aq)$; Hg-Zn(c_2) at 25°C, if the concentrations of the zinc amalgam are : $c_1=2$ g of zinc per 100 g of mercury and $c_2=1$ g of zinc per 100 g of mercury.

Solution : The half-cell reactions in this case are :

R.H.E. : $Zn^{2+} + 2e^- \rightleftharpoons Zn(c_2)$ (Reduction)

L.H.E. : $Zn(c_1) \rightleftharpoons Zn^{2+} + 2e^-$ (Oxidation)

Overall reaction : $Zn(c_1) \rightleftharpoons Zn(c_2)$

$$\therefore \quad E = \frac{0·0591}{2} \log \frac{c_2}{c_1} = -0·02955 \log \left(\frac{1}{2}\right) = 8·8\times10^{-3} \text{ V}$$

Example 19. Calculate the EMF of the electrode-concentration cell : Pt ; $H_2(p_1)$, HCl, $H_2(p_2)$; Pt at 25°C if $p_1 = 600$ torr and $p_2 = 400$ torr.

Solution : The cell reactions in this case are :

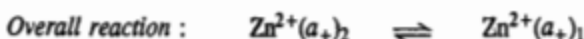| R.H.E. : | $2H^+ + 2e^-$ | $\rightleftharpoons$ | $H_2(p_2)$ | (Reduction) |
| L.H.E. : | $H_2(p_1)$ | $\rightleftharpoons$ | $2H^+ + 2e^-$ | (Oxidation) |
| Overall reaction : | $H_2(p_1)$ | $\rightleftharpoons$ | $H_2(p_2)$ | |

$$\therefore \quad E = -\frac{0.0591}{2} \log \frac{400 \text{ torr}}{600 \text{ torr}} = -0.02955 \log \frac{2}{3} = 5.19 \times 10^{-3} \text{ V}$$

2. Electrolyte-Concentration Cells. In these cells, the two electrodes of the same metal are dipping in solutions of metal ions of different concentrations and hence of different activities. One such cell is represented below :

$$\text{Zn, Zn}^{2+}(a_+)_1 \parallel \text{Zn}^{2+}(a_+)_2, \text{Zn}$$

In this case, both the electrodes are of the same metal (Zn) and these are in contact with solutions of the same ions (Zn^{2+}). The concentrations and hence activities of the ions are, however, different. Let $(a_+)_1$ and $(a_+)_2$ be the activities of zinc ions in the two electrolytes surrounding the electrodes. The two electrolytes, which are generally $ZnSO_4$ solutions, are separated from each other by a *salt bridge*. This is represented by the double line put in between the two half-cells.

The reactions occurring are :

R.H.E. :	$Zn^{2+}(a_+)_2 + 2e^-$	$\rightleftharpoons$	$Zn(s)$	(Reduction)
L.H.E. :	$Zn(s)$	$\rightleftharpoons$	$Zn(a_+)_1 + 2e^-$	(Oxidation)
Overall reaction :	$Zn^{2+}(a_+)_2$	$\rightleftharpoons$	$Zn^{2+}(a_+)_1$	

The net process thus involves the transfer of 1 mole of Zn^{2+} ions from the solution in which the activity is $(a_+)_2$ to the solution in which the activity is $(a_+)_1$.

According to Nernst equation, the reduction potentials of R.H.E. and L.H.E. are given by

$$E_R = E_{el}^\circ - \frac{RT}{nF} \ln \frac{1}{(a_+)_2} = E_{el}^\circ + \frac{RT}{nF} \ln (a_+)_2 \qquad \ldots(45)$$

and

$$E_L = E_{el}^\circ - \frac{RT}{nF} \ln \frac{1}{(a_+)_1} = E_{el}^\circ + \frac{RT}{nF} \ln (a_+)_1 \qquad \ldots(46)$$

$$\therefore \quad E_{cell} \equiv E = E_R - E_L = \frac{RT}{nF} \ln \frac{(a_+)_2}{(a_+)_1} \qquad \ldots(47)$$

For the process to be feasible, EMF should be positive. Hence, $(a_+)_2 > (a_+)_1$.

Substituting activities $(a_+)_1$ and $(a_+)_2$ by molalities m_1 and m_2 (vide Eq. 38), in Eq. 47, we have

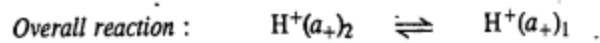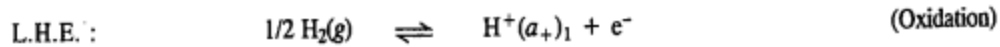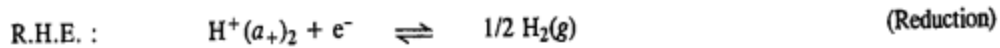$$E_{cell} \equiv E = \frac{RT}{2F} \ln \frac{\gamma_2 m_2}{\gamma_1 m_1} \qquad \ldots(48)$$

where γ_1 and γ_2 are activity coefficients of the electrolytes in the two solutions.

Consider another similar concentration cell represented by

$$\text{Pt, H}_2(g), \text{H}^+(a_+)_1 \parallel \text{H}^+(a_+)_2, \text{H}_2(g), \text{Pt}$$
$$\quad \quad 1 \text{ atm} \qquad \qquad \qquad 1 \text{ atm}$$

In this case, both the electrodes are hydrogen gas electrodes which are in contact with hydrogen ions of different activities. The two solutions which are generally solutions of hydrochloric acid, are separated by a salt bridge, as before.

The following processes take place at the two electrodes :

R.H.E. : $\qquad H^+(a_+)_2 + e^- \rightleftharpoons 1/2\ H_2(g)$ $\qquad\qquad$ (Reduction)

L.H.E. : $\qquad 1/2\ H_2(g) \rightleftharpoons H^+(a_+)_1 + e^-$ $\qquad\qquad$ (Oxidation)

Overall reaction : $\qquad H^+(a_+)_2 \rightleftharpoons H^+(a_+)_1$
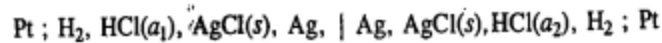
The EMF of the cell will be given, as before, by reduction potential of right hand electrode minus reduction potential of left hand electrode. The reduction potentials of the two electrodes and the EMF of the cell are given as follows :
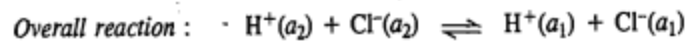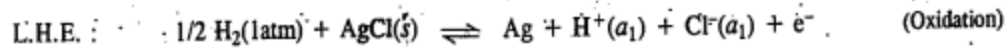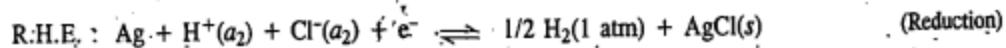
$$E = E_R - E_L = \left(E_{el}^\circ - \frac{RT}{F} \ln \frac{1}{(a_+)_2} \right) - \left(E_{el}^\circ - \frac{RT}{F} \ln \frac{1}{(a_+)_1} \right)$$

$$= \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} \qquad\qquad\qquad\qquad ...(49)$$

For E to be positive, $(a_+)_2$ should be greater than $(a_+)_1$.

We shall now consider a cell consisting of two cells connected back to back through silver electrodes :

$$Pt\ ;\ H_2,\ HCl(a_1),\ AgCl(s),\ Ag,\ |\ Ag,\ AgCl(s), HCl(a_2),\ H_2\ ;\ Pt$$

The electrode reactions are :

R.H.E. : $Ag + H^+(a_2) + Cl^-(a_2) + e^- \rightleftharpoons 1/2\ H_2(1\ atm) + AgCl(s)$ $\qquad$ (Reduction)

L.H.E. : $\qquad 1/2\ H_2(1atm) + AgCl(s) \rightleftharpoons Ag + H^+(a_1) + Cl^-(a_1) + e^-$ $\qquad$ (Oxidation)

Overall reaction : $\quad H^+(a_2) + Cl^-(a_2) \rightleftharpoons H^+(a_1) + Cl^-(a_1)$

Thus, the overall reaction involves no chemical change. It consists only of the transfer of HCl from solution of activity a_2 to solution of activity a_1.

The EMF of the cell is given by

$$E_{cell} = E = E_R - E_L$$

$$= E_{el}^\circ - \frac{RT}{F} \ln \frac{1}{(a_{H^+})_2 (a_{Cl^-})_2} - \left(E_{el}^\circ - \frac{RT}{F} \ln \frac{1}{(a_{H^+})_1 (a_{Cl^-})_1} \right)$$

$$= \frac{RT}{F} \ln \frac{(a_{H^+})_2 (a_{Cl^-})_2}{(a_{H^+})_1 (a_{Cl^-})_1} = \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2}$$

$$= \frac{2RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = 0\cdot 1182 \log \frac{(a_\pm)_2}{(a_\pm)_1} \quad \text{at } 25^\circ C$$

where $(a_\pm)_1$ and $(a_\pm)_2$ are the mean ionic activities of the HCl solutions in the two cells.

Here, too, we see that when $a_2 > a_1$, E is positive so that the process is spontaneous from right to left and consists in the dilution of HCl from activity a_2 to activity a_1 even though the two solutions are not in contact with each other.

Example 20. Calculate the EMF of the concentration cell consisting of zinc electrodes, one immersed in a solution of 0·01 molality (number of moles dissolved per kg of the solvent) and the other in a solution of 0·1 molality at 25°C. The two solutions are separated by a salt bridge. The mean activity coefficient of the electrolyte may be assumed to be unity.
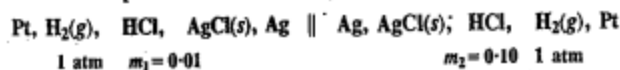
Soluton. The cell may be represented as

$$\text{Zn, Zn}^{2+}(m_1=0\cdot01) \parallel \text{Zn}^{2+}(m_2=0\cdot1), \text{Zn}$$

The EMF of the cell, E, is given by

$$E = \frac{RT}{nF} \ln \frac{(a_+)_2}{(a_+)_1} = \frac{2\cdot303\,RT}{2F} \log \frac{\gamma_2 m_2}{\gamma_1 m_1} \qquad \text{(Eq. 48)}$$

$$= \frac{0\cdot0591}{2} \log \frac{0\cdot10}{0\cdot01} \text{ at } 25°C \qquad (\because \ \gamma_1 = \gamma_2 = 1)$$

$$= 0\cdot0295 \text{ V}$$

Example 21. Find the pontential difference between the hydrogen electrodes in the cell

$$\text{Pt, H}_2(g), \quad \text{HCl}, \quad \text{AgCl}(s), \text{Ag} \parallel \text{Ag, AgCl}(s); \quad \text{HCl}, \quad \text{H}_2(g), \text{Pt}$$
$$\text{1 atm} \quad m_1 = 0\cdot01 \qquad\qquad\qquad m_2 = 0\cdot10 \quad \text{1 atm}$$

at 25°C. The activity coefficients of 0·01 m and 0·10 m solutions are 0·95 and 0·85, respectively.

Solution : The potential difference (E) between the two hydrogen electrodes is given by Eq. 49, viz.,

$$E = \frac{RT}{nF} \ln \frac{(a_+)_2}{(a_+)_1} = \frac{2\cdot303\,RT}{nF} \log \frac{\gamma_2 m_2}{\gamma_1 m_1}$$

$$= \frac{0\cdot0591}{1} \log \frac{0\cdot10 \times 85}{0\cdot01 \times 95} \quad \text{at } 25°C = 0\cdot056 \text{ V}$$

Types of Electrolyte–Concentration Cells

Electrolyte–concentration cells in which solutions of the same electrolyte of different concentrations are used are of two types. In one of the types, the two electrolytic solutions are not in direct contact with each other and the transference of ions from one solution to the other does not take place directly. These are called **concentration cells without transference.** The two solutions are separated from each other by means of a salt bridge or by some other means to be considered shortly. In the second type, the two solutions are in direct contact with each other. The transference of ions from one solution to the other takes place directly. Such cells are called **concentration cells with transference.** We shall consider here both the types of concentration cells.

Concentration Cells Without Transference. The two concentration cells discussed above in which the two solutions are separated from each other through a salt bridge fall in this category. But, more often some other means are employed to keep the solutions apart and bring about the transference of ions indirectly.

In order to understand the setting up of such a cell, consider a simple electrochemical cell such as

$$\text{Pt, H}_2(g), \text{HCl }(a_1) \mid \text{AgCl}(s), \text{Ag}$$
$$\text{1 atm}$$
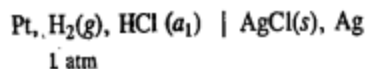
Let the activity of H^+ ions in the solution be $(a_+)_1$ and that of Cl^- ions be $(a_-)_1$. Since reduction takes place at the right hand electrode and oxidation at the left hand electrode, the two half-cell

reactions will be as follows :
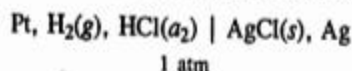
Reduction half-cell reaction :

$$AgCl(s) + e^- \rightleftharpoons Cl^-(a_-)_1 + Ag(s) \qquad \text{...(i)}$$

Oxidation half-cell reaction :

$$1/2\ H_2(g) \rightleftharpoons H^+(a_+)_1 + e^- \qquad \text{...(ii)}$$
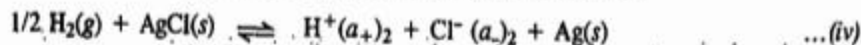
The *net reaction* taking place in the cell for one faraday of electricity is obtained by adding equations *(i)* and *(ii)*. Thus,
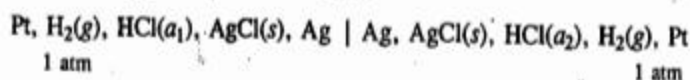
$$1/2\ H_2(g) + AgCl(s) \rightleftharpoons H^+(a_+)_1 + Cl^-(a_-)_1 + Ag(s) \qquad \text{...(iii)}$$

Now consider the same cell with the difference that the activity of HCl solution is now a_2.

$$Pt, H_2(g), HCl(a_2)\ |\ AgCl(s), Ag$$
$$\text{1 atm}$$

The net *cell reaction* for one faraday of electricity will now be as follows :

$$1/2\ H_2(g) + AgCl(s) \rightleftharpoons H^+(a_+)_2 + Cl^-(a_-)_2 + Ag(s) \qquad \text{...(iv)}$$

Finally, consider the situation when the two cells are connected to each other in such a way that they send current in *opposite direction*. Thus,

$$Pt, H_2(g), HCl(a_1), AgCl(s), Ag\ |\ Ag, AgCl(s), HCl(a_2), H_2(g), Pt$$
$$\text{1 atm} \qquad\qquad\qquad\qquad\qquad\qquad \text{1 atm}$$

The overall reaction of the combined cell for the passage of one faraday of electricity will, evidently, be obtained by subtracting equation *(iv)* from equation *(iii)*, i.e.,

$$H^+(a_+)_2 + Cl^-(a_-)_2 \rightleftharpoons H^+(a_+)_1 + Cl^-(a_-)_1 \qquad \text{...(51)}$$
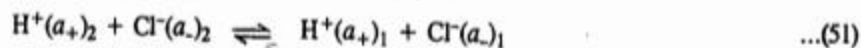
Thus, for the flow of one faraday of electricity, the overall reaction is the transfer of one mole of each of H^+ and Cl^- ions or one mole of HCl, from a solution of activity a_2 to that of activity a_1.

Hence, EMF of such a cell would be given by

$$E_{\text{w.o.t.}} = \frac{RT}{F}\ln\frac{(a_+)_2}{(a_+)_1} + \frac{RT}{F}\ln\frac{(a_-)_2}{(a_-)_1} \qquad \text{...(52)}$$

$$= \frac{RT}{F}\ln\frac{(a_\pm)_2^2}{(a_\pm)_1^2} \qquad \text{(vide Eq. 37)} \qquad \text{...(53)}$$

where $(a_\pm)_1$ and $(a_\pm)_2$ are the mean ionic activities of the electrolyte in the two solutions and the subscript w.o.t. stands for 'without transference'. Applying Eq. 43, we have

$$E_{\text{w.o.t.}} = (RT/F)\ln(a_2/a_1) \qquad \text{...(54)}$$

where a_1 and a_2 are the activities of hydrochloric acid in the two solutions.

It will be observed that the cell reaction does not involve transfer of electrolyte from one solution to the other directly. It takes place indirectly. The cell is, therefore, a **concentration cell without transference**.

If the middle electrode, viz., Ag, AgCl(s), is withdrawn, the two solutions of HCl will be in direct contact with each other. The cell will then become a concentration cell with transference. A little reflection shows that a concentration cell with transference in which the two electrodes are

reversible with respect to cations (H^+ ions in the present case) can be converted into a concentration cell without transference by interposing in between another electrode which is reversible with respect to anions (Cl^- ions in the present case).

Another example of a concentration cell without transference, in which the electrodes are reversible with respect to a cation, is given below :

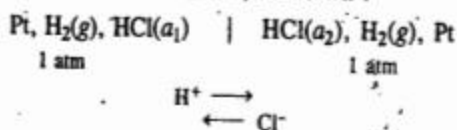$$Zn, ZnSO_4(a_1), PbSO_4(s), Pb, PbSO_4(s), ZnSO_4(a_2), Zn$$
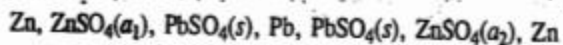
Concentration cells without transference in which the end electrodes are reversible with respect to an anion and in which an electrode reversible with respect to a cation is inserted in between, are also known. One such cell is as represented below :

$$Ag, AgCl(s), HCl(a_1), H_2(g), HCl(a_2), AgCl(s), Ag$$

The end electrodes are reversible with respect to Cl^- ions while the intermediate electrode is reversible with respect to H^+ ions.

Concentration Cells with Transference. Now consider a concentration cell formed by combining two hydrogen gas electrodes in contact with HCl solutions of different concentrations. The two solutions are in direct contact with each other, as shown :

$$Pt, H_2(g), HCl(a_1) \quad | \quad HCl(a_2), H_2(g), Pt$$
$$\text{1 atm} \qquad\qquad\qquad \text{1 atm}$$
$$H^+ \longrightarrow$$
$$\longleftarrow Cl^-$$

The reaction on the left involves oxidation and that on the right involves reduction, as usual.

The following changes are involved for the flow of one faraday of electricity :

Left Hand Electrode :

$$\tfrac{1}{2}H_2(g) \rightleftharpoons H^+(a_+)_1 + e^- \qquad\qquad ...(i)$$

Right Hand Electrode :

$$H^+(a_+)_2 + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad\qquad ...(ii)$$

Thus, H^+ ions are generated at the left hand electrode and consumed at the right hand electrode as the current follows. Since the solutions *are in direct contact* with each other, *the ions are free to move from one solution to the other* when current flows through the cell. In the present case, evidently, H^+ ions move from the solution on the left hand side to that on the right hand side. Since anions move in direction opposite to that in which cations move, Cl^- ions migrate from right to left, as shown in the cell above.

Let t_- be the transport number of Cl^- ion and t_+ ($= 1 - t_-$) that of H^+ ion in HCl. Then, for one faraday of electricity passing through, t_- faraday will be carried by Cl^- ions and t_+ faraday by H^+ ions. According to Faraday's second law, t_- equivalent of Cl^- ions will be transferred from the solution of activity a_2 to the solution of activity a_1. This may be represented as

$$t_- Cl^-(a_-)_2 \rightleftharpoons t_- Cl^-(a_-)_1 \qquad\qquad ...(iii)$$

At the same time, t_+ equivalent of H^+ ions will be transferred from the solution of activity a_1 to that of activity a_2 which may be represented as

$$t_+ H^+(a_+)_1 \rightleftharpoons t_+ H^+(a_+)_2 \qquad\qquad ...(iv)$$
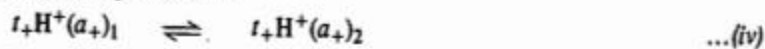
The net result for the flow of one faraday of electricity is summed up below :

Left Hand Electrode. The following operations occur at this electrode :

    Gain of 1 gram equivalent of H^+ ions by process (i)

    Loss of t_+ gram equivalent of H^+ ions by process (iv)

∴   Net gain of H^+ ions $= (1 - t_+)$ gram equivalent $= t_-$ gram equivalent

At the same time,

    net gain of Cl^- ions $= t_-$ gram equivalent by process *(iii)*

Right Hand Electrode. The following operations occur at this electrode :

    Loss of 1 gram equivalent of H^+ ions by process *(ii)*

    Gain of t_+ gram equivalent of H^+ ions by process *(iv)*

∴   Net loss of H^+ ions $= (1 - t_+)$ gram equivalent $= t_-$ gram equivalent

At the same time,

    net loss of Cl^- ions $= t_-$ gram equivalent by process *(iii)*

Thus, for every one faraday of electricity, there is net transfer of t_- gram equivalent of H^+ ions and t_- gram equivalent of Cl^- ions from right to left, *i.e.*, from the solution in which activity of HCl is a_2 to that in which activity of HCl is a_1.

These changes are represented as

$$t_- \, H^+(a_+)_2 \; \rightleftharpoons \; t_- \, H^+(a_+)_1$$

$$t_- \, Cl^-(a_-)_2 \; \rightleftharpoons \; t_- \, Cl^-(a_-)_1$$

The EMF of concentration cell with transport, on analogy with Eq. 52, therefore, is given by

$$E_{w.t.} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_- \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} \qquad \text{...(55)}$$

If $(a_+)_1$ and $(a_+)_2$ are the mean ionic activities of the two hydrochloric acid solutions, it follows by the definition given in Eq. 33 that

$$(a_\pm)_1^2 = (a_+)_1(a_-)_1 \text{ and } (a_\pm)_2^2 = (a_+)_2(a_-)_2$$

Eq. 55, therefore, may be put as

$$E_{w.t.} = t_- \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2} \qquad \text{...(56)}$$

Knowing that the activity of a uni–univalent electrolyte is given by $a = (a_\pm)^2$, Eq. 56 may also be written as

$$E_{w.t} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad \text{...(57)}$$

where a_2 and a_1, as already stated, are activities of HCl solutions of the right and the left hand electrode, respectively.

Eq. 57 is used for calculating activity of an electrolyte at a given concentration from the experimental value of $E_{w.t.}$ One of the solutions used should be of known activity.

Liquid Junction Potential (L.J.P.)

Eq. 57 derived above for the EMF of a concentration cell with transference *includes the potential at the junction of the two solutions* of HCl as well. Eq. 53 for EMF derived earlier when the two

solutions are not in direct contact with each other *does not include the liquid junction potential.* Eqs. 57 and 53 may be reproduced as

$$E_{w.t.} = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \qquad ...(58)$$

$$E_{w.o.t.} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \qquad ...(59)$$

Hence, liquid junction potential E_l is given by

$$E_l = E_{w.t.} - E_{w.o.t.} = (2t_- - 1)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= (t_- + (1 - t_+) - 1] \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= (t_- - t_+) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \qquad ...(60)$$

It is evident from Eq. 60 that the sign as well as the magnitude of L.J.P. depends on *the transference numbers of the anion and cation.* If the transference numbers of the anion and cation of an electrolyte are the same or nearly the same, *i.e.,* $t_- = t_+$, then L.J.P. = 0 or negligibly small. If the transference number of cation is greater than that of anion, *i.e.,* $t_+ > t_-$, then L.J.P. will be negative and if reverse is the case, *i.e.,* $t_- > t_+$, then L.J.P. will be positive and will add to the EMF of the cell.

Potassium chloride and ammonium nitrate are amongst the electrolytes in which transference numbers of cations and anions are nearly the same. The solutions of these electrolytes are, therefore, frequently used as salt bridge because the liquid junction potential is then reduced to a minimum.

Example 22. Calculate the liquid junction potential at 25°C between two solutions of HCl having mean ionic activities of 0·01 and 0·001, respectively. The transference number of H^+ ion (t_+) in HCl may be taken as 0·83.
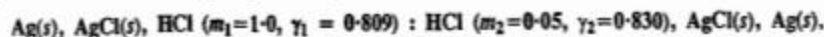
Solution : In this case, $t_+ = 0.83$ so that $t_- = 1 - t_+ = 0.17$

$$(a_\pm)_1 = 0.01 ; \quad (a_\pm)_2 = 0.001$$

$$E_l = (t_- - t_+)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad \qquad \text{(Eq. 60)}$$

$$= (0.17 - 0.83) 0.0591 \log \frac{0.001}{0.01} = 0.0039 \text{ V} \quad \text{(at 25°C)}$$

Example 23. Calculate the liquid junction potential associated with the following cell :

$$\text{Ag}(s), \text{AgCl}(s), \text{HCl } (m_1=1.0, \gamma_1 = 0.809) : \text{HCl } (m_2=0.05, \gamma_2=0.830), \text{AgCl}(s), \text{Ag}(s).$$

if the transference number of H^+ is 0·83.

Solution : $t_+ = 0.83$ so that $t_- = 1 - 0.83 = 0.17$. Hence, from Eq. 60,

$$E_l = (t_- - t_+)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = (t_- - t_+)\frac{RT}{F} \ln \frac{\gamma_2 m_2}{\gamma_1 m_1}$$

$$= (0.17 - 0.83) \times 0.0591 \log \frac{0.83 \times 0.05}{0.809 \times 1.0} \quad \text{at 25°C}$$

$$= 0.050 \text{ volt} = 50 \text{ mV}$$

Applications of EMF Measurements

The EMF measurements find a number of useful applications. Some of these are given below.

1.. **Determination of Activity Coefficients of Electrolytes.** Suppose we want to determine the activity coefficient of hydrochloric acid. Consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, the H^+ ion) and the other is reversible with respect to the anion (*i.e.*, the Cl^- ion). Evidently, the first electrode is the hydrogen electrode and the other can be the silver–silver chloride electrode. Accordingly, the cell arrangement is as follows :

$$\text{Pt ; } H_2(g) \text{ (1 atm) } | \text{ HCl } (m) | \text{ AgCl}(s), \text{ Ag}(s)$$

where m is the molality of HCl solution.

The cell reaction is

$$1/2\ H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(m) + Cl^-(m)$$

According to Eq. 20, the EMF of the cell at 25°C is given by

$$E = E^\circ - 0.0591 \log \frac{a_{H^+} a_{Cl^-}}{\left(a_{H_2}\right)^{1/2}} \qquad \text{...(61)}$$

$$= E^\circ - 0.0591 \log a_{H^+} a_{Cl^-} \qquad \text{...(62)}$$

because activity of each of Ag(s), AgCl(s) and $H_2(g)$ at 1 atm pressure is taken as unity.

As already discussed,

$$a_{H^+} a_{Cl^-} = (a_\pm)^2 = (\gamma_\pm m)^2 = \gamma_\pm^2 m^2 \qquad \text{(Eqs. 43 and 44)}$$

where $\gamma_\pm$ and m are the mean ionic activity coefficient and the molality of HCl, respectively. Substituting in Eq. 62, we get

$$E = E^\circ - 0.0591 \log \gamma_\pm^2 m^2 \qquad \text{...(63)}$$

$$= E^\circ - 0.1182 \log \gamma_\pm - 0.1182 \log m \qquad \text{...(64)}$$

Rearranging,

$$E + 0.1182 \log m = E^\circ - 0.1182 \log \gamma_\pm \qquad \text{...(65)}$$

The two unknowns E° and $\gamma_\pm$ in Eq. 65 can be determined by measuring the EMFs of the cell over various concentrations of HCl, including dilute concentrations. At infinite dilution, $m=0$ and $\gamma_\pm=1$ so that $\log \gamma_\pm=0$. Thus, a plot of $E+0.1182 \log m$ versus m, extrapolated to $m=0$ gives E° as the y–intercept. Knowing the value of E°, the mean ionic activity coefficient $\gamma_\pm$ of HCl at any other concentration can be determined from the EMF data of the cell at that concentration.

Alternatively, we can use the Debye–Hückel limiting law (DHLL) equation, *viz.*,

$$\log \gamma_\pm = -0.509 \, |z_+ z_-| \, I^{1/2} \qquad \text{...(66)}$$

to substitute for the $\log \gamma_\pm$ term in Eq. 65, giving

$$E + 0.1182 \log m = E^\circ + 0.0602 \, I^{1/2} \qquad \text{...(67)}$$

Thus, a plot of $E + 0.1182 \log m$ versus $I^{1/2}$ will give a straight line at low concentrations where the limiting law is valid. The extrapolation of this plot to $I^{1/2}=0$ gives E° as the y–intercept of the line.

In practice, however, an extension of the DHLL is needed to make a satisfactory linear extrapolation. For a uni–univalent electrolyte in dilute aqueous solution at 25°C, an empirical extension of Eq. 66 is

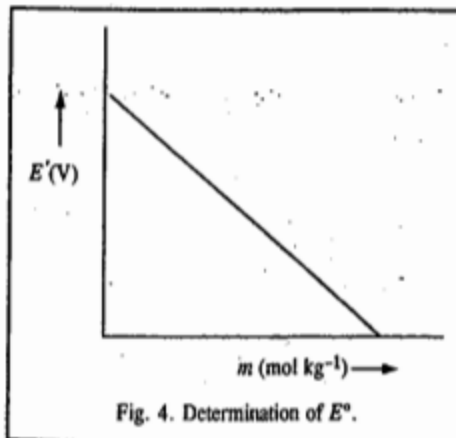$$\log \gamma_\pm = -0.509 \, m^{1/2} + bm \qquad \text{...(68)}$$

where b is an empirical constant.

Substituting this equation in Eq. 65 and rearranging the terms, we obtain

$$E + 0.1182 \log m - 0.0602\, m^{1/2} = E' = E° - (0.1182\, b)\, m \qquad \qquad ...(69)$$

This equation shows that the left hand side (which we have designated as E'), when plotted against m, will give a straight line whose intercept at $m=0$, is $E°$ (Fig. 4).

Example 25. Consider the following cell :

Ag(s), Ag$^+$($a=0.001$ m) || Ag$^+$($c=0.1$ m, a unknown), Ag(s)
Its EMF at 25°C is $+ 1.11$V. (a) Write the cell reaction and (b) Calculate the activity coefficient of the Ag$^+$ ion in 0.1 m solution.

Solution : (a) The cell reaction is

Ag$^+$ ($c=0.1$ m, $a=$say, x) $\rightleftharpoons$ Ag$^+$($a=0.001$ m)

It is a concentration cell with *no net reaction*. Hence,

Fig. 4. Determination of $E°$.

$$E = -0.0591 \log (0.001/x)$$

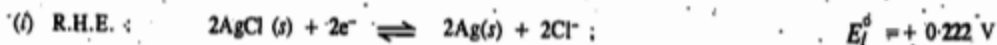$$\log \frac{0.001}{x} = -\frac{1.11\,V}{0.0591\,V} = -1.878$$

$$\log x = \log 0.001 + 1.878 = -1.122 = \bar{2}.878$$

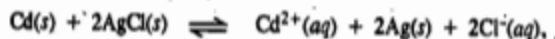Taking antilogs, $x=0.076$. Thus, $a = 0.076$. Hence, the activity coefficient

$$\gamma = a/c = 0.076/0.1 = 0.76$$

Example 26. EMF of the cell Cd(s), CdCl$_2$($m=0.02$) | AgCl(s), Ag(s) is found to be 0.780 V at 25°C. Using the standard potentials, viz., $E°_{Cd^{2+},Cd} = -0.403$ V and $E°_{AgCl,Cl^-} = + 0.222$ V, calculate the mean ionic activity coefficient of CdCl$_2$ at this temperature.

Solution : The half–cell reactions are :

(i) R.H.E. :   2AgCl (s) + 2e$^-$ $\rightleftharpoons$ 2Ag(s) + 2Cl$^-$; $E°_l = + 0.222$ V

(ii) L.H.E. :   2Cd(s) $\rightleftharpoons$ Cd^{2+}(aq) + 2e$^-$; $E°_l = - 0.403$ V .

Hence, adding Eqs. (i) and (ii), we get

Cd(s) + 2AgCl(s) $\rightleftharpoons$ Cd^{2+}(aq) + 2Ag(s) + 2Cl$^-$(aq).

$$E° = E°_R - E°_L = 0.222 - (- 0.403) = 0.625 \text{ V}$$

CdCl$_2$ ionises in solution as CdCl$_2$(aq) $\rightleftharpoons$ Cd^{2+}(aq) + 2Cl$^-$(aq)

Thus, the number of ions produced on ionization of CdCl$_2$ = 3 with $x=1$ and $y=2$. Hence,

$$a_{CdCl_2} = (a_\pm)^{x+y} = (a_+)^x (a_-)^y \; ; \; a_+ = \gamma_+ m_+ = \gamma_+ mx = \gamma_+ m \qquad (\because x = 1)$$

$$a_- = \gamma_- m_- = \gamma_- my = 2\gamma_- m \qquad \qquad (\because y = 2)$$

$$a_{CdCl_2} = (a_\pm)^3 = (\gamma_+ m)(2\gamma_- m)^2 = 4(\gamma_+ \gamma_-^2) m^3 = 4(\gamma_\pm)^3 m^3$$

The EMF of the cell is given by $E = E° - \dfrac{0.0591}{2} \log a_+ a_-^2 = E° - \dfrac{0.0591}{2} \log (a_\pm)^3$ at 25°C
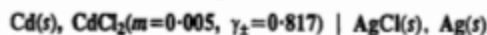
or $\qquad$ $0.780 \not{=} 0.625 - 0.0295 \log [4(\gamma_\pm)^3 m^3]$

$$\log 4(\gamma_\pm)^3 m^3 = -\frac{0.780 - 0.625}{0.0295} = -5.2546 = \overline{6}.754$$

Taking antilogs, $\qquad$ $4(\gamma_\pm)^3 m^3 = 5.57 \times 10^{-6}$

$$\therefore \quad \gamma_\pm = \left(\frac{5.57 \times 10^{-6}}{4m^3}\right)^{1/3} = \left(\frac{5.57 \times 10^{-6}}{4(0.02)^3}\right)^{1/3} = 0.558$$

Example 27. Calculate the EMF of the following cell at 25°C :

$$Cd(s), CdCl_2(m=0.005, \gamma_\pm=0.817) \mid AgCl(s), Ag(s)$$

using the data given in the last example.

Solution : As shown in the last example, $E^\circ = 0.625$ V

Also, $\qquad$ $a_{CdCl_2} = (a_\pm)^3 = 4(\gamma_\pm)^3 m^3$

The EMF of the cell is given by

$$E = E^\circ - \frac{0.0591}{2} \log(a_+ a_-^2) = E^\circ - \frac{0.0591}{2} \log(a_\pm)^3$$

$$= E^\circ - 0.0295 \log [4\gamma_\pm)^3 m^3]$$

$$= 0.625 - 0.0295 \log [4(0.817)^3(0.005)^3] = 0.819 \text{ V}$$

2. Determination of Transport Numbers. As has been shown earlier, the EMF of a concentration cell *with transference*, represented by $E_{w.t.}$, in which the end electrodes are reversible with respect to cation, is given by Eq. 57, viz.,

$$E_{w.t.} = t_-(RT/F) \ln (a_2/a_1) \qquad \qquad ...(i)$$

The EMF of the same cell with the same solutions but *without transference*, denoted by $E_{w.o.t.}$, is given by Eq. 54, viz.,

$$E_{w.o.t.} = (RT/F) \ln (a_2/a_1) \qquad \qquad ...(ii)$$

Dividing (i) by (ii), we have

$$t_- = E_{w.t.}/E_{w.o.t.} \qquad \qquad ...(61)$$

Thus, the ratio of the EMFs of the two concentration cells, one with transference and the other without transference, gives the *transference number of the anion*, if the end electrodes are reversible with respect to the *cation*.

If the end electrodes are reversible with respect to the *anion*, then the ratio of the two EMFs will give the transference number of the *cation* of the electrolyte.

3. Determination of Valency of Ions in Doubtful Cases. The valency of mercurous ion was in doubt for a considerable time. It was finally established by determining the EMF of a concentration cell of the type given below :

Mercury, Mercurous nitrate solution (c_1) || Mercurous nitrate solution (c_2), Mercury

The salt bridge represented by the two vertical lines connecting the two solutions contains saturated solution of ammonium nitrate.

The EMF of the cell, E, assuming the activity coefficients to be equal to unity, is given by the expression

$$E = (RT/nF) \ln (c_2/c_1)$$

where n is the valency of mercurous ion and c_2 is greater than c_1. Thus,

$$E = \frac{0.0591}{n} \log \frac{c_2}{c_1} \quad \text{(at 25°C)}$$

It was found that when c_2/c_1 was 10, the EMF was 0.0295 volt. Therefore, the valency of mercurous ion is 2 and it should be represented as Hg_2^{2+}.

5. Determination of pH. a. By using hydrogen electrode. The potential of a hydrogen electrode in contact with a solution of H^+ ions involving the reaction

$$H^+ + e^- \rightleftharpoons 1/2 \ H_2 \ (1 \ atm)$$

is given by Nernst equation, viz.,

$$E_{el} = E_{el}^\circ + 2 \cdot 303 (RT/F) \log [H^+] \qquad \qquad ...(70)$$

By convention, $= E_{(el)}^\circ$, i.e., the standard electrode potential of hydrogen electrode, is zero.

$$\therefore \qquad E_{el} = \frac{2 \cdot 303 \, RT}{F} \log [H^+] = - 0 \cdot 0591 \, pH \quad (at \ 25°C) \qquad ...(71)$$

Thus, the potential of a hydrogen electrode depends upon the pH of the solution with which it is in contact. This can be determined by combining the hydrogen electrode with a reference electrode, say, calomel electrode. The complete cell is represented as
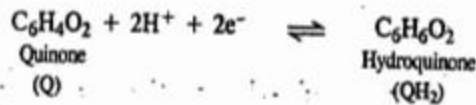
$$Pt, H_2 \ (1 \ atm), H^+(c = unknown) \ || \ KCl \ (sat. \ soln.), Hg_2Cl_2(s), Hg.$$
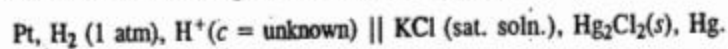
The EMF of the cell is determined potentiometrically. This is given by

$$E = E_R - E_L = 0 \cdot 2422 - (- 0 \cdot 0591 \, pH)$$

or

$$0 \cdot 0591 \, pH = E - 0 \cdot 2422$$

or

$$pH = \frac{E - 0 \cdot 2422}{0 \cdot 0591}$$

b. By using quinhydrone electrode. The quinone-hydroquinone system involves the following equilibrium :

$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_6O_2$$

Quinone
(Q)

Hydroquinone
(QH₂)

For the reduction reaction given above, the potential developed on a platinum electrode immersed in this system is given by the Nernst equation as

$$E_{el} = E_{el}^{\circ} - \frac{2 \cdot 303RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2} \qquad \ldots(73)$$

$$= E_{el}^{\circ} + \frac{2 \cdot 303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]} \qquad \ldots(74)$$

$$= E_{el}^{\circ} + \frac{2 \cdot 303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2 \cdot 303RT}{F} \log H^+ \qquad \ldots(75)$$

Instead of taking quinone and hydroquinone, a small amount of *quinhydrone*, which is an equilimolar compound of quinone (Q) and hydroquinone [QH]₂, is taken. Since hydroquinone (QH₂) is a weak acid, its ionisation is very small particularly if the pH of the solution is less than 7. Therefore, the concentration of hydroquinone [QH₂] is the same as that of quinone [Q], *i.e.*, the quantity $[Q]/[QH_2]$ is unity. The middle term in Eq. 75, therefore, reduces to zero. Hence,

$$E_{el} = E_{el}^{\circ} + \frac{2 \cdot 303RT}{2F} [H^+] = E_{el}^{\circ} + 0 \cdot 0591 \log [H^+] \text{ at } 25°C$$

$$= E_{el}^{\circ} - 0 \cdot 0591 \, pH \qquad \ldots(76)$$

The standard electrode potential of the quinhydrone electrode, $E_{el}^{\circ} = + 0 \cdot 06996$ V

$$\therefore \quad E_{el}^{\circ} = + 0 \cdot 6996 - 0 \cdot 0591 \, pH \qquad \ldots(77)$$

Thus, the potential of the quinhydrone electrode, just as that of the hydrogen electrode, depends upon the pH of the solution with which it is in contact, *i.e.*, the quinhydrone electrode behaves as a reversible hydrogen electrode. Consequently, this electrode can be used for measuring pH values of solutions.

This electrode is preferred to the hydrogen electrode as it can be set up easily by merely adding a pinch of quinhydrone to the solution under examination and inserting a clean platinum electrode for making electrical connection. The electrode gives accurate results even in the presence of oxidising ions which usually interfere with the working of the hydrogen electrode.

The quinhydrone electrode is combined with a saturated calomel electrode to form a cell. The combination may be represented as

Hg, Hg₂Cl₂ (s), KCl (sat. soln.) || H⁺(unknown conc.) Q, QH₂; Pt

The EMF of the above cell is given by

$$E = E_R - E_L = (0 \cdot 6996 - 0 \cdot 591 \, pH) - 0 \cdot 2422 \text{ at } 25°C$$

or

$$0 \cdot 0591 \, pH = 0 \cdot 6996 - 0 \cdot 2422 - E$$

$$\therefore \quad pH = \frac{0 \cdot 6996 - 0 \cdot 2422 - E}{0 \cdot 0591} \qquad \ldots(78)$$

Limitation of quinhydrone electrode. The quinhydrone electrode cannot be used for solutions of pH more than 8. In more alkaline solutions, hydroquinone ionises appreciably as an acid and also gets oxidised partly by atmospheric oxygen. This alters the normal equilibrium between quinone and hydroquinone which forms the basis of the above equation.

Example 30. While determining the pH of a solution, the quinhydrone electrode, H^+, Q, QH_2 was used in conjunction with a saturated calomel electrode, as represented below :

Hg, Hg_2Cl_2 (s) ; KCl (sat. soln.) $\|$ H^+(unknown); Q, QH_2, Pt
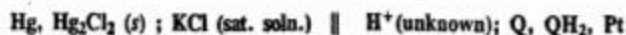
The EMF of the cell was found to be 0·26 volt at 25°C. Calculate the pH of the solution at this temperature. $E_{calomel}$ = + 0·24 volt at 25°C and $E^\circ_{(H^+,Q,QH_2)}$ = + 0·70 V.

Solution : The EMF of the cell is given by

$$E = E_R - E_L$$

$$0\cdot26 = 0\cdot70 - 0\cdot0591\ pH - 0\cdot24 \qquad\qquad \text{(at 25°C)}$$

$$pH = \frac{0\cdot70 - 0\cdot24 - 0\cdot26}{0\cdot0591} = 3\cdot37$$

c. By using glass electrode. It has been found by experiment that difference of potential exists at the interface between glass and a solution containing hydrogen ions. The magnitude of this difference of potential for a given variety of glass varies with the concentration of the hydrogen ions and, at 25°C, is given by the equation

$$E_G = E^\circ_G + 0\cdot0591 \log [H^+] \qquad\qquad\qquad ...(79)$$

$$= E^\circ_G - 0\cdot0591\ pH \qquad\qquad\qquad\qquad ...(80)$$

where E°_G is a constant for the given glass electrode. The electrode reaction is assumed to involve the reduction of H^+ ions. The glass electrode, thus, functions in the same manner as a reversible hydrogen electrode.

The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is blown in the form of a bulb which is then sealed to the bottom of a glass tube (Fig. 5). A solution of 0·1 molar hydrochloric acid, which furnishes a constant hydrogen ion concentration, is placed inside the bulb and a Ag,AgCl electrode or simply a platinum wire is inserted to make electrical contact as shown. The reference electrode employed is usually the calomel electrode. The schematic arrangement of the cell thus formed may be represented as

Pt, 0·1 M HCl | glass |Experimental soln.| KCl (salt. soln.) $Hg_2Cl_2(s)$, Hg.
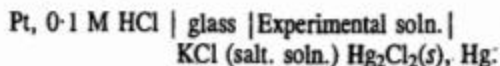
The EMF of such a cell can be determined conveniently by means of a potentiometer. Since the potential of the calomel electrode is known,

Fig. 5. Determination of pH by glass electrode

that of the glass electrode can be easily calculated and the pH of the experimental solution is evaluated. The value of E°_G is first obtained by working with solutions of known pH.
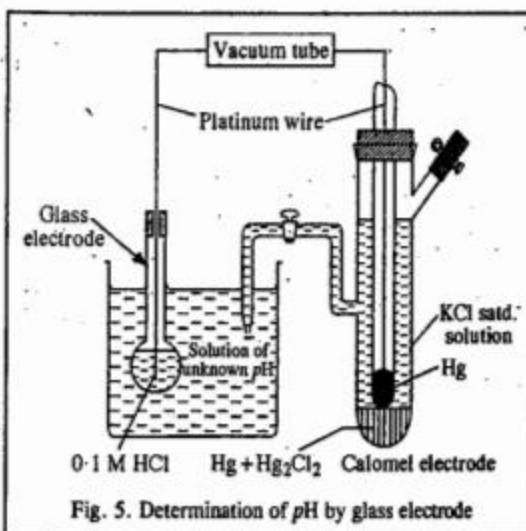
The pH of the solution is given by

$$pH = \frac{E_G^{\circ} - 0.2422 - E}{0.0591} \quad \text{at } 25°C \qquad ...(81)$$

The glass electrode has a number of advantages over other electrodes. It can be used even in strong oxidising solutions which interfere even with quinhydrone electrode. It can also be used in the presence of metallic ions, poisons, etc. It is simple to operate and is, therefore, extensively used in chemical, industrial, agricultural and biological laboratories.

Potentiometric Titrations. As discussed earlier, the potential of an electrode depends upon the concentration of the ion to which it is reversible in accordance with Nernst equation. In a titration, there is change in ionic concentration which can be followed by measuring the potential of a suitable electrode. The potentiometric titrations are, thus, those titrations which involve the measurement of electrode potentials with the addition of the titrant.

The potentiometric titrations generally fall into the following three categories :

1. Acid–Base Titrations
2. Oxidation–Reduction (Redox) Titrations
3. Precipitation Titrations

There are a number of advantages of potentiometric titrations over the ordinary titrations involving the use of indicators. Potentiometric titrations can be carried out in coloured solutions while indicators cannot be used in such cases. Also, in ordinary titrations, one must have a prior information about the relative strengths of acids and bases before a proper indicator is selected. However, no such information is required in the case of potentiometric titrations.

Acid–Base Titrations. Suppose we want to titrate a solution of HCl against NaOH. Any electrode whose potential depends upon H^+ ion concentration (e.g., hydrogen electrode, quinhydrone electrode, glass electrode) is placed in the HCl solution. It is connected to a reference electrode (e.g., calomel electrode, Ag,AgCl electrode) to form a galvanic cell. If hydrogen electrode is used as the H^+ indicating electrode and a saturated calomel electrode is used as the reference electrode, then the galvanic cell may by represented as

Pt, H_2(1 atm), H^+(c=unknown) || KCl sat. soln ; $Hg_2Cl_2(s)$, Hg

The EMF of the cell is measured potentiometrically. It is given by

$$E \equiv E = E_R - E_L = E_{calomel} - E_{hydrogen}$$
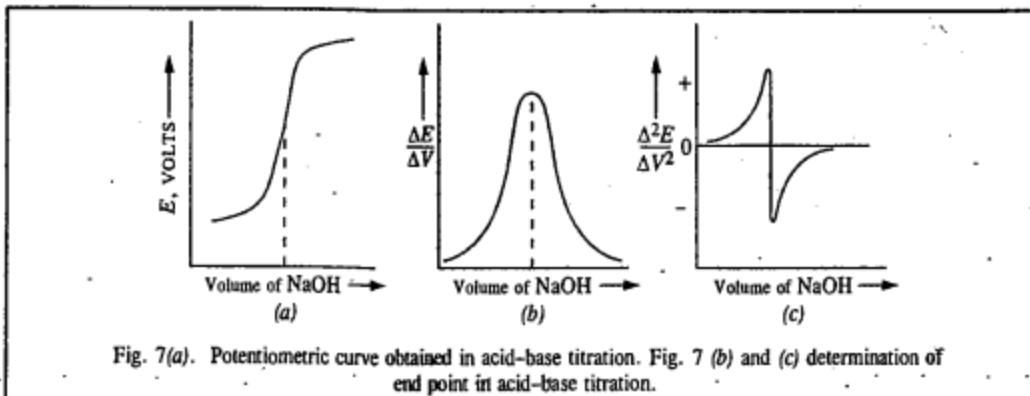$$= 0.2422 - 0.0591 \log H^+ = 0.2422 + 0.0591 \, pH \qquad ...(82)$$

Suppose 100 ml of 0.1 M HCl is to be titrated against 1 M NaOH (the titrant). The concentration of the titrant is usually 5 to 10 times higher than that of the solution to be titrated so that the volume change is as small as possible.

As the titration proceeds, the H^+ ion concentration goes on decreasing, i.e., pH of the solution goes on increasing, hence, according to Eq. 82, the EMF of the cell goes on increasing. It is evident that the EMF of the cell would increase by 0.0591 volt for every ten–fold decrease in the concentration of H^+ ions or one unit increase in the pH of the solution.

Assuming, for the sake of simplicity of calculations, that there is no change in volume during the titration, it is evident that the addition of first 9 ml of NaOH solution will give a change of 0.0591 volt. However, the addition of next 0.90 ml will produce the same change and the addition of next 0.09 ml will also produce the same change and so on. Thus, the EMF of the cell changes slowly at first but more and more rapidly as the end point approaches.

After the end point, further addition of NaOH produces very little change in the H^+ ion concentration and hence there is very little change in the EMF of the cell.

A plot of E against the volume of NaOH added is shown in Fig. 7(a). As can be seen, the EMF of the cell initially rises gradually and thereafter more rapidly near the equivalence point. Beyond the equilvalence point, the EMF of the cell again increases slightly on adding more of NaOH.

Fig. 7(a). Potentiometric curve obtained in acid–base titration. Fig. 7 (b) and (c) determination of end point in acid–base titration.

Once the titration curve is obtained, the analyst has to determine, by inspection, where the curve is steepest. He may draw a vertical line through the steep portion of the curve and find the intersection of this line with the volume axis. There occurs some uncertainty in this procedure and this will be reflected in the ultimate volume reading. For a reaction that goes to completion, the titration curve is so steep near the equilvalence point that the uncertainty is small. However, for a reaction with small equilibrium constant, the precision with which the equilvalence point may be determined becomes poorer.

Fig. 7(b) shows a plot of the slope of the titration curve, that is, the change in the EMF with change in volume ($\Delta E/\Delta V$) against the volume of the titrant. The resulting curve rises to a maximum at the equivalence point. The volume at the equivalence point is determined by drawing a vertical line from the peak to the volume axis. Of course, there is some uncertainty in locating exactly the peak. The more complete the reaction, the sharper the peak and hence the more accurate is the location of the equilvalence point.

Fig. 7(c) shows a plot of the change in the slope of a titration curve ($\Delta^2 E/\Delta V^2$) against the volume of the titrant. At the point where the slope $\Delta E/\Delta V$ is a maximum, the derivative of the slope is zero. The equivalence point is located by drawing a vertical line from the point at which $\Delta^2 E/\Delta V^2$ is zero on the volume axis. The steeper the portion of the curve joining the maximum and minimum value of $\Delta^2 E/\Delta V^2$, the more complete is the titration reaction.

Example 31. 25 ml of a solution of HCl (0·1 M) is being titrated potentiometrically against a standard (0·1 M) solution of NaOH using a hydrogen electrode as the indicator electrode and saturated calomel electrode (SCE) as the reference electrode. What would be the EMF of the cell initially and after the addition of 20, 24·9, 24·95, 25·00 25·05, 25·10 and 30·00 ml of NaOH solution ? Comment on the data obtained.

Solution : The galvanic cell formed in this case may be represented as follows :

$$Pt, H_2(1 \text{ atm}), H^+ (c=\text{unknown}) \;||\; KCl \text{ sat. soln.}, Hg_2Cl_2 (s), Hg$$
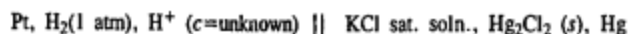
The EMF of the cell would be given

$$E = E_{SCE} - E_{hydrogen} = 0.2422 - 0.0591 \log H^+$$
$$= 0.2422 + 0.0591 \, pH \text{ at } 25°C \qquad\qquad (Eq. 82)$$

Initial pH of the titration solution, viz., 0·1 M HCl $= - \log [H^+] = - \log (0.1) = 1$ so that $E = 0.3013$ V.

Since the product of volume of the solution in ml and the concentration in mol dm^{-3} of a solute gives the amount of the solute in millimoles, hence

Amount of HCl initially present in the titration solution $= 25 \times 0.1 = 2.5$ millimoles

The amount of NaOH in 20 ml of 0·1 M solution added during titration $= 20 \times 0.1 = 2.0$ millimoles

$$\left.\begin{array}{l}\text{Amount of HCl left in the titration}\\\text{solution on adding 20 ml of NaOH}\end{array}\right\} = 2 \cdot 5 - 2 \cdot 0 = 0 \cdot 5 \text{ millimole}$$

Total volume of titration solution $= 25 + 20 = 45$ ml

$\therefore$ Concn. of HCl or of H^+ ions in the solution $= \dfrac{0 \cdot 5 \times 1000}{1000 \times 45}$ mol dm^{-3}

$\therefore$ pH of the titration solution $= - \log [H]^+ = - \log (0 \cdot 5/45) = 1 \cdot 95$

The corresponding value of E is $0 \cdot 2422 + 0 \cdot 0591 \times 1 \cdot 95 = 0 \cdot 3574$ V

Proceeding as above, the pH values of the titrand on the addition of 24·90 and 24·95 ml of NaOH solution come out to 3·70 and 4·00, respectively and the corresponding values of E are 0·4609 and 0·4786 V, respectively.

On the addition of 25 ml of NaOH, the acid is completely neutralised giving NaCl. The pH of the resulting solution is, therefore, 7 and $E = 0 \cdot 6560$ V

On adding 25·05 ml of NaOH, the excess volume of NaOH $= 0 \cdot 05$ ml

Amount of NaOH in 0·05 ml solution $= 0 \cdot 05 \times 0 \cdot 1 = 0 \cdot 005$ millimole

$\therefore$ Concn. of NaOH or OH$^-$ ions $= \dfrac{0 \cdot 005}{1000} \times \dfrac{1000}{50 \cdot 05}$ mol dm^{-3}

Since $\qquad [H^+] [OH^-] = 10^{-14}$ at 25°C,

$\therefore \qquad [H^+] = \dfrac{10^{-14} \times 50 \cdot 05}{0 \cdot 005}$ mol dm^{-3} and hence pH $= 10 \cdot 0$

The corresponding E value is 0·8332 V

Proceeding as above, the pH values of the titrand after the addition of 25·10 and 30·00 ml of NaOH solution would be 10·30 and 10·96, respectively and the corresponding E values are 0·8510 and 0·890 V, respectively.

The titration data obtained as above are summed up in Table 2.

TABLE 2
Potentiometric Titration of 0·1 M HCl Solution against 0·1 M NaOH Solution, at 25°C

Volume of NaOH solution added (ml)	EMF of the cell, E (volt)	Change in EMF (volt)
0·00	0·3013	
		0·0561
20·00	0·3574	
		0·1035
24·90	0·4609	
		0·0177
24·95	0·4786	
		0·1774
25·00	6560	
		0·1772
25·05	0·8332	
		0·0178
25·10	0·8510	
		0·0390
30·00	0·8900	

The EMF of the cell first increases only gradually and that too by small amounts at various steps of the titration. Thus, the EMF increases only from 0·3013 to 0·4786 V, i.e., by 0·1773 V, by the addition of as large a volume as 24·95 ml of NaOH. Around the end point, however, the same change in EMF is brought about by the addition of just a single drop of the titrant. As can be seen, the EMF around the end point increases sharply from 0·4786 to 0·8332 V by the addition of just two drops of NaOH. After the end point, there is again a small change in EMF.

If the above data are plotted graphically, the titration curve obtained would be exactly similar to the one shown earlier in Fig. 7(a).

2. Redox Titrations. Like acid–base titrations, the redox titrations are also carried out potentiometrically. In this case, the electrode reversible with respect to H^+ ions is replaced by an inert metal, such as platinum wire, immersed in a solution containing both the oxidised and the reduced forms of the same species. The electrode acts as an oxidation–reduction electrode.

Let us consider the redox reaction

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ce^{3+}(aq)$$

involving the oxidation of Fe^{2+} ions by Ce^{4+} ions being carried out potentiometrically. Prior to the addition of Ce^{4+} ions, the solution contains only the Fe^{2+} ions. On adding a small amount of Ce^{4+} ions to the solution, a small amount of Fe^{2+} ions is oxidised to Fe^{3+} ions. With the presence of both the Fe^{2+} and Fe^{3+} ions, the electrode behaves as an oxidation–reduction electrode whose potential, according to the Nernst equation, is given by

$$E_{el} = E_{el}^\circ + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad \text{(Eq. 28)}$$

$$= E_{el}^\circ + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}, \quad \text{at } 25°C \qquad \text{...(83)}$$

Evidently, the electrode potential is controlled by the ratio $[Fe^{3+}]/[Fe^{2+}]$. For instance, if the ratio is equal to 0.01, the electrode potential would be given by

$$E_{el} = E_{el}^\circ + 0.0591 \log (0.01) = E^\circ - 0.1182$$

With further addition of Ce^{4+} ions, the ratio $[Fe^{3+}]/[Fe^{2+}]$ changes, thereby changing the value of E_{el}. For every ten-fold change in the ratio of $[Fe^{3+}]/Fe^{2+}$, the potential of the electrode would change by 0.1182 V, evidently.

At the equivalence point, $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = Ce^{3+}]$ so that the electrode potential at the equilvalence point, E_{eq}, is given by

$$E_{eq} = E_1^\circ + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} = E_2^\circ + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]} \qquad \text{...(84)}$$

The above equations may be rewritten as

$$E_{eq} = E_1^\circ + 0.0591 \log [Fe^{3+}]/[Fe^{2+}] \qquad \text{...(85)}$$

and $\qquad E_{eq} = E_2^\circ + 0.0591 \log [Ce^{4+}]/[Ce^{3+}] \qquad \text{...(86)}$

Adding and simplifying, keeping in mind that at the equivalence point,

$$[Fe^{2+}] = [Ce^{4+}] \quad \text{and} \quad [Fe^{3+}] = [Ce^{3+}], \text{ we get}$$

$$E_{eq} = (E_1^\circ + E_2^\circ)/2 \qquad \text{...(87)}$$

The numerical values of E_1° and E_2° are 0.77 V and 1.61 V, respectively, according to the equations :

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) ; \qquad\qquad E_1^\circ = 0.77 \text{ V}$$

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq) ; \qquad\qquad E_2^\circ = 1.61 \text{ V}$$

Beyond the equivalence point, $[Fe^{3+}] \approx 0$ as a result of which the electrode potential thereafter is controlled only by the $[Ce^{4+}]/[Ce^{3+}]$ ratio.

For potentiometric measurements, the oxidation–reduction electrode (viz., Pt ; Fe^{3+}, Fe^{2+}) is combined with a reference electrode, e.g., a saturated calomel electrode, to form a galvanic cell which is represented as

$$Hg, Hg_2Cl_2 \ (s), \ KCl \ (sat. \ soln.) \ \| \ Fe^{2+}, Fe^{3+}; Pt$$
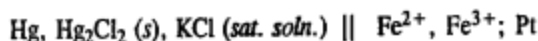
in accordance with the positions of these electrodes in the electrochemical series (Table 1).

Before the equilvalence point, the EMF of the cell would be given by

$$E = E_R - E_L = E_{el}^{\circ} = 0.0591 \log \{[Fe^{3+}]/[Fe^{2+}]\} - E_{calomel}$$

$$= 0.77 + 0.0591 \log \{[Fe^{3+}]/[Fe^{2+}]\} - 0.24 \qquad ... (88)$$

and *after the equilvalence point*, the EMF of the cell is given by

$$E = 1.61 + 0.0591 \log \{[Ce^{4+}]/[Ce^{3+}]\} - 0.24$$

At tne equivalence point, as already discussed, the EMF of the cell is given by

$$E = \frac{0.77 + 1.61}{2} - 0.24 \qquad ...(89)$$

The EMF of the cell is measured potentiometrically at each stage of titration and the EMF data thus obtained are processed for the equivalence point. The redox titration curve is exactly similar to the acid–base titration curve shown earlier in Fig. 7(a).

Example 32. Calculate the potential at 25°C of a cell consisting of saturated calomel electrode (SCE) and a platinum–wire indicator electrode dipping in a titration vessel that initially contains 25·00 ml of 0·01 M Fe^{2+}, after the addition of 5·00, 12·50, 20·00, 24·00, 25·00, 26·00 30·00 and 50·00 ml of 0·01 M Ce^{4+} solution. The SCE is attached to the negative terminal of the voltmeter.

Solution : The half-cell reactions in this case are :

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- ; \qquad\qquad E_{el}^{\circ} = 0.77 \text{ V}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} ; \qquad\qquad E_{el}^{\circ} = 1.61 \text{ V}$$

The overall reaction in the titration flask is the redox reaction

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

Before the equivalence point, the cell potential is controlled by the concentrations of Fe^{2+} and Fe^{3+} ions present in solution and after the equivalence point the cell potential is controlled by the concentrations of Ce^{3+} and Ce^{4+} ions.

Thus, before the equilvalence point, the cell potential is given by

$$E = E_1 - E_{SCE}, \quad \text{where } E_{SCE} = 0.24 \text{ V}$$

$$= E_1^{\circ} - 0.0591 \log \{[Fe^{2+}]/[Fe^{3+}]\} - E_{SCE}$$

$$= 0.77 - 0.0591 \log \{[Fe^{2+}]/[Fe^{3+}]\} - E_{SCE}$$

$$= 0.53 - 0.0591 \log \{[Fe^{2+}]/[Fe^{3+}]\}$$

During titration, the Fe^{2+} ions present in the titrand are oxidised to Fe^{3+} ions by the titrant. The concentrations of Fe^{3+} and Fe^{2+} ions which prevail after the addition of various of amounts of Ce^{4+} solution of known molarity and the resulting cell potentials can be calculated as shown below :

After the addition of 5·00 ml of Ce^{4+} solution, we have

$$[Fe^{3+}] = \frac{5.00 \text{ ml} \times 0.01 \text{ millimol/ml}}{(25.00 + 5.00) \text{ ml}} = 1.67 \times 10^{-3} \text{ M}$$

$$[Fe^{2+}] = \frac{(25.00 \text{ ml} \times 0.10 \text{ millimol / ml}^{-1}) - (5.00 \text{ ml} \times 0.01 \text{ millimol / ml}^{-1})}{(25.00 + 5.00) \text{ ml}}$$

$$= 6.67 \times 10^{-3} \text{ M}$$

Hence, using these values of $[Fe^{3+}]$ and $[Fe^{2+}]$, $E = 0.491$ V

Similarly, after the addition of 12·50, 20·00 and 24·00 ml of the titrant (Ce^{4+} solution), the concentrations and

the cell potentials would be as follows :

12·50 ml :
$$[Fe^{3+}] = \frac{12·50 \times 0·0100}{25·00 + 12·50} = 3·33 \times 10^{-3} M$$

$$[Fe^{2+}] = \frac{25·00 \times 0·010 - 12·50 \times 0·0100}{25·00 + 12·50} = 3·33 \times 10^{-3} M$$

$$E = 0·53 V \qquad (\because \text{ the logarithmic term} = 0)$$

20·00 ml : $[Fe^{3+}] = 4·44 \times 10^{-3} M$; $[Fe^{2+}] = 1·11 \times 10^{-3} M$; $\qquad E = 0·56 V$

24·00 ml : $[Fe^{3+}] = 4·90 \times 10^{-3} M$; $[Fe^{2+}] = 2·04 \times 10^{-3} M$; $\qquad E = 0·61 V$

The **equivalence point** of the titration is reached when 25·0 ml of the titrant is added. At the equivalence point we must use both half–cell reactions to calculate the potential :

$$E = 0·77 - 0·0591 \log \{[Fe^{2+}]/[Fe^{3+}]\}$$

and

$$E = 1·61 - 0·0591 \log \{[Ce^{3+}]/[Ce^{4+}]\}$$

Adding, we obtain,

$$2E = 2·38 - 0·0591 \log \{[Fe^{2+}]/[Ce^{3+}]/[Fe^{3+}] [Ce^{4+}]\}$$

At the equivalence point it is evident from the balanced chemical equation that

$$[Fe^{3+}] = [Ce^{3+}] \quad \text{and} \quad [Fe^{2+}] = [Ce^{4+}]$$

Using these substitutions, we obtain

$$2E = 2·38 V \qquad (\because \text{ the logarithmic term} = 0)$$

$$\therefore \qquad E_{eq} = 1·19 V \quad \text{and} \quad E = E_{eq} - E_{SCE} = 1·19 - 0·24 = 0·95 V$$

After the equivalence point, we use the following equation to calculate the cell potential :

$$E = E_2 - E_{SCE} = E_2^\circ - 0·0591 \log \{[Ce^{3+}]/[Ce^{4+}]\} - E_{SCE}$$

$$= 1·61 - 0·0591 \log \{[Ce^{3+}]/[Ce^{4+}]\} - E_{SCE}$$

$$= 1·37 - 0·0591 \log \{[Ce^{3+}]/[Ce^{4+}]\}$$

After the addition of 26·00, 30·00 and 50·00 ml of titrant, the concentrations and cell potentials are as follows :

26·00 ml : $[Ce^{4+}] = \frac{(26·00 - 25·00)(0·01)}{25·00 + 26·00} = 1·96 \times 10^{-4} M$

$[Ce^{3+}] = \frac{(25·00)(0·01)}{25·00 + 26·00} = 4·90 \times 10^{-3} M$

$E = 1·37 - 0·0591 \log$

$(4·90 \times 10^{-3})(1·96 \times 10^{-4}) = 1·29 V$

30·00 ml : $[Ce^{4+}] = 9·09 \times 10^{-4} M$;

$[Ce^{3+}] = 4·55 \times 10^{-3} M$

$E = 1·33 V$

50·00 ml : $[Ce^{4+}] = 3·33 \times 10^{-3} M$

$[Ce^{3+}] = 3·33 \times 10^{-3} M$

$E = 1·37 V \; (\because \text{ the logarithmic term} = 0)$

The results of the calculations are plotted as a titration curve shown in Fig. 8.

Note : The end point of a titration is usually considered to correspond to the inflection point. The equilvalence point in the curve corresponds to the inflection point only for titrations in which the molar quantities of *titrand* and *titrant* at the equilvalence point are equal (when the coefficients for titrand and titrant in the balanced chemical equations are identical) and for titrations in which the titrand is not significantly diluted by the addition of the titrant during the titration.
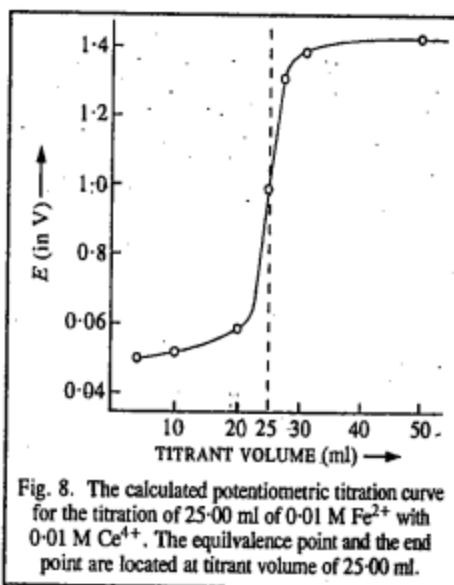

Fig. 8. The calculated potentiometric titration curve for the titration of 25·00 ml of 0·01 M Fe^{2+} with 0·01 M Ce^{4+}. The equilvalence point and the end point are located at titrant volume of 25·00 ml.

Precipitation Titrations. Suppose we want to standardise a solution of silver nitrate by titrating against a standard solution of potassium chloride. The silver electrode is used as the indicator electrode in this case.

The potential of the half-cell, Ag^+, Ag, is measured by connecting it with the calomel electrode, as usual. The solution is titrated against a standard solution of potassium chloride the strength of which is about 10 times higher. As the reaction proceeds, the Ag^+ ions get gradually precipitated as silver chloride.

$$Ag^+ + NO_3^- + (K^+ + Cl^-) \rightleftharpoons AgCl\downarrow + K^+ + NO_3^-$$
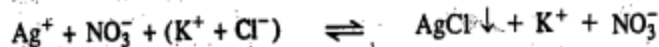
The concentration of Ag^+ ions goes on decreasing and hence the potential of the Ag^+, Ag

electrode, given by the Nernst equation, viz.,

$$E_{el} = E_{el}^{\circ} + 0.0591 \log [Ag^+] \qquad \text{(at 25°C)} \qquad ...(90)$$

goes on decreasing continuously on the progressive addition of KCl solution. The electrode potential will change slowly at first but more and more rapidly as the end point approaches. At the end point, the concentration of Ag^+ ions is very small as this is now only on account of slight solubility of AgCl. Hence, the change in electrode potential is maximum at the end point. If the addition of KCl is continued further, the concentration of Ag^+ ions remains almost unaffected except for very small decrease on account of the common ion effect. The addition of KCl beyond the end point, therefore, causes only a small change in the electrode potential.

The potentiometric titration curve obtained in this case is exactly similar to the one obtained in the case of acid–base titration described earlier.