Reversible and Irreversible cells :

(A) A cell is said to work reversibly in the thermodynamic sense when it is generating infinitesimally small current so that the cell reaction always remains virtually in a state of equilibrium.

A cell is said to be reversible if it satisfies the following three conditions.

(a) If the opposing EMF equal to that of the cell is applied to the cell, no current should flow in the circuit and no chemical reaction should take place.

(b) If the opposing EMF infinitesimally smaller than that of the cell is applied, an infinitesimally small current should flow from the cell and an infinitesimally small reaction should take place.

(c) If an opposing EMF infinitesimally greater than that of the cell is applied an infinitesimally small current should flow in the opposite direction and an infinitesimally small reaction in the opposite direction should occur.

e.g. of Reversible cells are Daniel cell, Weston cell, lead storage battery.

(B) An irreversible cell is the one in which the cell reaction can't be reversed. Such electrochemical cells can't be recharged. e.g. Dry cell, Mercury cells. These are called primary cells. When fully used up, they become dead.

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EMF of a cell:

The difference between electrode potentials of the two electrodes constituting an electrochemical cell is called electromotive force (EMF) of a cell, which causes the

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current to flow from cathode to anode of the cell in the external circuit. It is measured in volts and can be expressed as,

$$EMF = E_R - E_L.$$

$$\Rightarrow EMF = E_{cell} = E_{cathode} - E_{anode}.$$

where, E_R and E_L represents the electrode potential of the electrode on right hand side and on left hand side respectively.

If all the reactants and products giving rise to the cell reaction, are in their standard state, i.e. when the concentration of the ions in solution is 1.0 M and temperature is at 298 K, the corresponding EMF generated is called as Standard EMF.

Significance of EMF:

(a) If $E_{cell} = 0$, the reaction is in equilibrium.

(b) If $E_{cell} = +ve$, the reaction is spontaneous.

(c) If $E_{cell} = -ve$, the reaction is spontaneous in opposite direction.

Measurement of EMF:

The EMF of the cell can be measured by using:

(a) A voltmeter

(b) A potentiometer

(c) A direct reading potentiometer.

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(b) Potentiometric Method :

Potentiometric method based on Poggendorff compensation principle is used for accurate measurement of EMF. In this method, the unknown EMF of the cell is opposed by another continuously changing EMF until the two exactly balance each other and no current flows through the circuit.

Let, AB is a stretched wire of uniform thickness. S is a cell whose EMF is constant and exactly known. Let it be V, and connected to the ends ~~of the wire~~ A and B of the wire. Let X be the cell whose EMF is to be determined. One end of this cell is connected to A end of the wire while the other end of the cell is connected to a sliding contact (jockey) Y through the galvanometer G. The two potentials S and X are made to oppose each other. The jockey is moved along the wire AB till at a particular point on it, say C, there is no deflection in the galvanometer.

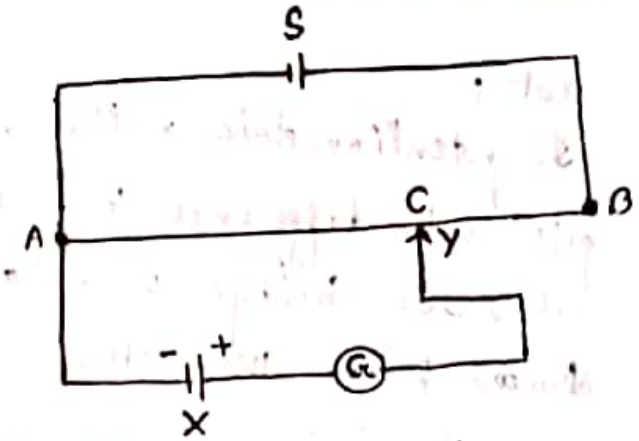

Fig: Potentiometric method.

$\because E_S \propto$ length AB.

$E_X \propto$ length AC.

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$$\frac{E_s}{E_x} = \frac{AB}{AC}.$$

$$\Rightarrow E_x = \frac{AC}{AB} \cdot E_s.$$

Thus, knowing AC, AB and E_s, E_x can be calculated.

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Electrode Potential:

In an electrochemical cell, oxidation occurs at one electrode and reduction at the other. In other words, one electrode has the tendency to loose electrons while the other has the tendency to gain electrons. The tendency of an electrode to lose or gain electrons is called electrode potential.

The electrode potential is further called oxidation potential if oxidation takes place at the electrode. It is termed as reduction potential if reduction takes place at the electrode.

If in the half cell, the metal rod is suspended in a solution of 1 M concentration and the temperature is kept at 298 K, the electrode potential is termed as standard electrode potential (E^o).

Single electrode potential:

The contribution of each electrode to the cell potential is called single electrode potential. It is not possible to determine experimentally the potential of a single electrode (of a half cell). It is the difference of potential between two electrodes and can

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be measured by combining them to give a complete cell. By arbitarily fixing potential of one electrode as zero, it is possible to assign numerical values to potential of the various other electrodes. By convention, potential of a standard (normal) hydrogen electrode (NHE or SHE) is taken as the standard reference electrode.

Standard Hydrogen Electrode (SHE):

~~The~~ standard electrode potential has been taken to be zero. The SHE consists of a Pt. foil coated with finely divided

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Platinum, called Platinum black, dipping into a solution of an acid (1M), generating hydrogen ions. Hydrogen gas at a pressure of one atmosphere is continuously bubbled into the solution and the temperature is maintained at 298 K.

The following reactions occur at the surface of the Platinum foil:

$$H_2(g) \rightarrow 2H^+_{(aq)} + 2e^-$$

$$2H^+_{(aq)} + 2e^- \rightarrow H_2(g)$$

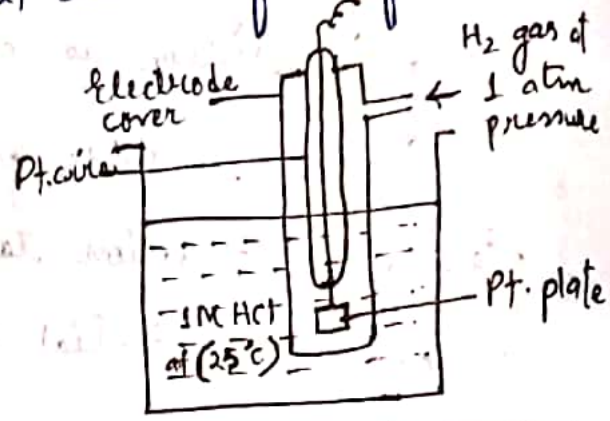

Fig: Standard Hydrogen electrode.

Depending upon the type of the reaction, the hydrogen electrode can act as an anode or cathode in an electrochemical cell.

However it is not convenient to use standard H_2 electrode as reference electrode. This is because, it is difficult to maintain the activity of the H^+ ion in the sol^n and to keep the pressure of the gas uniformly at 1 atm.

Therefore, instead of SHE, calomel electrode is extensively used as reference electrode.

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Types of Reversible Electrodes:

① Metal - Metal ion electrode:

This type of electrode consists of metal in contact with the solutions of its own ions.

$$M_{(s)} \rightleftharpoons M^{+}_{(aq)} + e^{-}$$

e.g. Zn metal rod in contact with its own ions,

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^{-}.$$

② Gas electrodes: Such electrodes consist of gases which are continuously passed through the solutions of their own ions at one atm pressure. e.g. Pt, Au, Graphite etc. are dipped into the solution containing the ions of the gas. ~~and~~ ~~will~~ When the gas is bubbled through the solution, the metal adsorbs the gas and an equilibrium is at once established between the gas and its ions.

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e.g. (i) Hydrogen electrode: It consists of platinised Pt. strip exposed to a current of hydrogen gas partially dipped in an acid solution. Hydrogen gas is adsorbed on platinum black, and the half cell reaction is represented as:

$$H_2(g) \rightleftharpoons 2H$$

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

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

(ii) Oxygen electrode: Here, oxygen gas is ~~bub~~ bubbled through a solution containing hydroxyl ions at one atm pressure and ~~Pt at~~ platinised Pt. strip is exposed to the current of oxygen.

$$\frac{1}{2}O_2(g) + H_2O + 2e^- \rightleftharpoons 2OH^-(aq).$$

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③ Metal-metal insoluble salt ion electrodes:

It consists of a metal in contact with one of its sparingly soluble salt and a solution of a soluble salt having common anion with the sparingly soluble salt. An important electrode consists of mercury, its sparingly soluble salt, viz. mercurous chloride and a solution of KCl having a common ion (i.e. Cl^- ion) with the sparingly soluble salt. The half cell is represented as:

$$Hg : Hg_2Cl_{2(s)}, KCl_{(soln)}.$$

④ Inert metal oxidation-reduction (Redox) electrode:

It consists of an inert electrode, viz. Pt or Au immersed in a mixture solution containing both the oxidised and the reduced forms of a molecule or ion. The inert metal acts as an electron reservoir. The electrons from the reservoir can be used up if some of the oxidised form changes into the reduced form. e.g. Mixed solution of ferrous and ferric ions.

$$Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + e^-.$$

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Table 4.1 Standard Electrode (Reduction) Potentials at 298 K.

Electrode		Half-Cell. Reaction (Oxidised form + ne^- → Reduced form)		E° (Volts)
$F_2 \mid F^-$	STRONGEST OXIDIZING AGENT	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	WEAKEST REDUCING AGENT	2.87
$Co^{3+} \mid Co^{2+}$		$Co^{3+} + e^- \rightarrow CO^{2+}$		1.81
$H_2O_2 \mid H_2O$		$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$		1.78
$MnO_2, H^+ \mid Mn^{2+}$		$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$		1.61
$Au^{3+} \mid Au$		$Au^{3+} + 3e^- \rightarrow Au(s)$		1.50
$MnO_4^- \mid Mn^{2+}$		$MnO_4^- + 8H^+ \rightarrow 5e^- + Mn^{2+} + 4H_2O$		1.49
$Cl_2 + Cl^-$		$Cl_2(g) + 2e^- \rightarrow 2Cl^-$		1.36
$Cr_2O_7^{2-}, H^+ \mid Cr^{3+}$		$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$		1.33
$O_2, H^+ \mid H_2O$		$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$		1.23
$Br_2 \mid Br^-$		$Br_2(l) + 2e^- \rightarrow 2Br^-$		1.09
$NO_3^-, H^+ \mid NO$		$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$		0.97
$Hg^{2+} \mid Hg_2^{2+}$		$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$		0.92
$Hg^{2+} \mid Hg$		$Hg^{2+} + 2e^- \rightarrow Hg$		0.85
$Ag^+ + \mid Ag$		$Ag^+ + e^- \rightarrow Ag$		0.80
$Hg_2^{2+} + \mid Hg$		$Hg_2^{2+} + 2e^- \rightarrow 2Hg$		0.79
$Fe^{3+} + \mid Fe^{2+}$		$Fe^{3+} + e^- \rightarrow Fe^{2+}$		0.77
$MnO_4^- \mid MnO_4^{2-}$		$MnO_4^- + e^- \rightarrow MnO_4^{2-}$		0.56
$I_2 \mid I^-$		$I_2 + 2e^- \rightarrow 2I^-$		0.54
$Cu^+ + Cu$		$Cu^+ + e^- \rightarrow Cu$		0.52
$Cu^{2+} + \mid Cu$		$Cu^{2+} + 2e^- \rightarrow Cu$		0.34
$AgCl \mid Ag$		$AgCl + e^- \rightarrow Ag + Cl^-$		0.22
$Cu^{2+} \mid Cu^+$		$Cu^{2+} + e^- \rightarrow Cu^+$		0.15
$AgBr \mid Ag$		$AgBr + e^- \rightarrow Ag + Br^-$		0.10
$H^+ \mid H_2$		$2H^+ + 2e^- \rightarrow H_2(g)$		0.0
$Fe^{3+} \mid Fe$		$Fe^{3+} + 3e^- \rightarrow Fe$		−0.04
$Pb^{2+} \mid Pb$		$Pb^{2+} + 2e^- \rightarrow Pb$		−0.13
$Sn^{2+} \mid Sn$		$Sn^{2+} + 2e^- \rightarrow Sn$		−0.16
$Ni^{2+} \mid Ni$		$Ni^{2+} + 2e^- \rightarrow Ni$		−0.25
$Fe^{2+} \mid Fe$		$Fe^{2+} + 2e^- \rightarrow Fe$		−0.44
$Cr^{3+} \mid Cr$		$Cr^{3+} + 3e^- \rightarrow Cr$		−0.74
$Zn^{2+} \mid Zn$		$Zn^{2+} + 2e^- \rightarrow Zn$		−0.76
$Al^{3+} \mid Al$		$Al^{3+} + 3e^- \rightarrow Al$		−1.66
$Mg^{2+} \mid Mg$		$Mg^{2+} + 2e^- \rightarrow Mg$		−2.36
$Ce^{3+} \mid Ce$		$Ce^{3+} + 3e^- \rightarrow Ce$		−2.48
$Na^+ \mid Na$		$Na^+ + e^- \rightarrow Na$		−2.71
$Ca^{2+} \mid Ca$		$Ca^{2+} + 2e^- \rightarrow Ca$		−2.87
$Ba^{2+} \mid Ba$		$Ba^{2+} + 2e^- \rightarrow Ba$		−2.91
$Cs^+ \mid Cs$		$Cs^+ + e^- \rightarrow Cs$		−2.92
$K^+ \mid K$		$K^+ + e^- \rightarrow K$		−2.93
$Li^+ \mid Li$	WEAKEST OXIDIZING AGENT	$Li^+ + e^- \rightarrow Li$	STRONGEST REDUCING AGENT	−3.05

INCREASING STRENGTH OF OXIDIZING AGENT

INCREASING STRENGTH OF REDUCING AGENT

*The unit of electrode potential is volt.

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Nernst equation:

Nernst found that the value of electrode (reduction) potential depends upon the concentration of the electrolyte. The Nernst equation telling the concentration dependence of electrode, the reduction potential for the reaction,

$$M^{n+}_{(aq)} + ne \longrightarrow M_{(s)}$$ is given by..

$$E_{M^{n+}} = E^{\circ}_{M^{n+}/M} + \frac{2.303\,RT}{nF} \log\left[M^{n+}(aq)\right].$$

$$= E^{\circ}_{M^{n+}/M} + \frac{2.303 \times 8.314\,JK^{-1}mol^{-1} \times 298\,K}{n \times 96500\,C\,mol^{-1}} \log\left[M^{n+}(aq)\right]$$

$$= E^{\circ}_{M^{n+}/M} + \frac{0.0591\,JK^{-1}}{n} \cdot \log\left[M^{n+}(aq)\right].$$

$$= E^{\circ}_{M^{n+}/M} + \frac{0.0591\,V}{n} \log\left[M^{n+}(aq)\right].$$

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Applications of EMF measurements:

① Determining the free energy, enthalpy and entropy of a cell reaction:

We know that the decrease in free energy of the system at constant pressure is given by the Gibb's Helmholtz equation.

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \longrightarrow (I)$$

Since, for a reversible cell,

$$\boxed{\Delta G = -nFE_{cell}} \longrightarrow (II)$$

$$\therefore -nFE_{cell} = \Delta H + T\left[\frac{\partial(-nFE_{cell})}{\partial T}\right]_p$$

$$\Rightarrow nFE_{cell} = -\Delta H + nFT\left[\frac{\partial E_{cell}}{\partial T}\right]_p \longrightarrow (III)$$

$$\Rightarrow E_{cell} = -\Delta H/nF + T\left[\frac{\partial E_{cell}}{\partial T}\right]_p \longrightarrow (IV)$$

where n and F are constants.

Evidently whether the electrical energy, viz. nFE, is equal to or greater ~~the~~ or less than the enthalpy of the cell reaction (ΔH), it depends upon the sign of $\left(\frac{\partial E}{\partial T}\right)_p$ i.e. upon the sign of the temperature coefficient of EMF of the cell.

Thus,

ⓐ If temp^r coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ is zero, as in the case of Daniel cell, i.e. $\left(\frac{\partial E}{\partial T}\right)_p = 0$, then $nFE = -\Delta H$.

Then, the electrical energy produced will be equal to the enthalpy of the cell reaction.

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(b) If $\left(\frac{\partial E}{\partial T}\right)_p$ is +ve, i.e. $\left(\frac{\partial E}{\partial T}\right)_p > 0$ then $nFE > -\Delta H$

Then, the electrical energy produced will be greater than the enthalpy of the cell reaction. The additional energy required will be supplied to the cell by the surroundings and if that is not possible, the temperature of the cell will fall during its working.

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(c) If $\left(\frac{\partial E}{\partial T}\right)_p$ is negative i.e. $\left(\frac{\partial E}{\partial T}\right)_p < 0$, then $nFE < -\Delta H$

The electrical energy produced will be smaller than the enthalpy of the cell reaction. The difference between the two values will be given out as heat to the surroundings and if that is not possible the temp. of the cell will rise during its operation.

Eqn (iii) $\Rightarrow \Delta H = -nFE_{cell} + nFT\left(\frac{\partial E_{cell}}{\partial T}\right)_p$.

$$\Rightarrow \boxed{\Delta H = -nF\left[E_{cell} - T\left(\frac{\partial E_{cell}}{\partial T}\right)\right]_p} \longrightarrow (v).$$

$$\cancel{\Rightarrow \Delta H = -nF}\Big[$$

$$\because \boxed{\Delta G = \Delta H - T\Delta S} \longrightarrow (vi)$$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \longrightarrow (vii)$$

Putting the expressions for ΔG and ΔH,

$$\Delta S = \frac{1}{T}\left[\left[-nFE_{cell} + nFT\left(\frac{\partial E_{cell}}{\partial T}\right)_p\right] - \left(-nFE_{cell}\right)\right]$$

$$\Rightarrow \boxed{\Delta S = nF\left(\frac{\partial E_{cell}}{\partial T}\right)_p}. \longrightarrow (viii)$$

Differentiating eqn (ii) partially w.r.t. 'T' at constant 'P',

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -nF\left(\frac{\partial E_{cell}}{\partial T}\right)_p. \longrightarrow (ix)$$

From eqns (viii) and (ix),

$$\boxed{\Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_p}. \longrightarrow (x)$$

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(2) Determining equilibrium constant of a cell reaction:

Let us consider a following reaction occuring in a reversible cell:

$$aA + bB \rightleftharpoons cC + dD.$$

As per the thermodynamic equation, the decrease in energy of the reaction is given by:

$$-\Delta G = -\Delta G^{\circ} - RT \ln Q \longrightarrow (I).$$

where, ΔG° = Decrease in energy of the above reaction when all the reactants and the products are in their standard states of unit activity.

Q = Reaction quotients of the activities of reactants and products at any given stage of the reaction.

Thus, ~~$Q = (aC)^c \, a_D$~~

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}.$$

$\because -\Delta G = nFE \longrightarrow (II)$, where E = EMF of the cell in volts

n = no. of Faradays involved

$\therefore$ (I) and (II)

$$\Rightarrow nFE = -\Delta G^{\circ} - RT \ln Q. \longrightarrow (III)$$

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again, $-\Delta G^\circ = RT\ln K$. (IV) (van't Hoff reaction isotherm).

where K is equilibrium constant of the reaction.

$\therefore$ (III) and (IV) $\Rightarrow nFE = RT\ln K - RT\ln Q$.

$$\Rightarrow nFE = RT\ln K - RT\ln \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}.$$

$$\Rightarrow E = \frac{2.303RT}{nF}\log K - \frac{2.303RT}{nF}\log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At 298 K, $$E = \frac{0.0591}{n}\log K - \frac{0.0591}{n}\log \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

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Thus, knowing the E.M.F. of the cell and the molar concentrations of the reactants and the products, the equilibrium constant of the reaction can be calculated.

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Concentration cells:

To form a galvanic cell, we bring two half cells together. If the electrochemical ~~cells~~ reactions in the half cells differ, the overall cell reaction is a chemical reaction and we call it a electrochemical cell. e.g. Daniel cell.

If the electrochemical reactions in the two half cells are the same but one species is at a different concentration in each half cells, the cell will have a non-zero emf and its overall reaction will account to transfer of electrolyte from one concentration to another. Such cell is called a concentration cell.

e.g. $Pt.H_{2(g)} \mid HCl_{(m_1)} \mid HCl_{(m_2)} \mid H_{2(g)}.Pt.$

<u>LHE</u>: $H^+_{(m_1)} + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$

<u>RHE</u>: $H^+_{(m_2)} + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$.

$(RHE - LHE) \Rightarrow H^+_{(m_2)} \rightleftharpoons H^+_{(m_1)}$

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Concentration cell with transference:

To discuss the working procedure, let us consider the following single cell of this type as follows.

$$Pt, H_2(g, 1\ atm) | HCl_{(a_1)} | HCl_{(a_2)} | H_2(g, 1\ atm), Pt.$$

Let, 1 Faraday of electricity flows through the cell. Then

Left hand electrode :—

$$\frac{1}{2}H_2 \rightleftharpoons H^+_{(a_+)_1} + e^-$$

Right hand electrode :—

$$H^+_{(a_+)_2} + e^- \rightleftharpoons \frac{1}{2}H_2(g)$$

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i.e. H^+ ions are generated at the LHE and consumed in the RHE as the current flows. As the anion move in the direction opposite to that of cation, Cl^- ions migrate from right to left. Let, t_+ and t_- are the transport of H^+ and Cl^- respectively. Thus, t_- equivalent of Cl^- ions will be ~~transformed~~ transferred from the solⁿ of activity a_2 to that of activity a_1.

$$t_- Cl^-_{(a_-)_2} \longrightarrow t_- Cl^-_{(a_-)_1}.$$

Simultaneously,

$$t_+ H^+_{(a_+)_1} \longrightarrow t_+ H^+_{(a_+)_2}$$

Thus, the net result of flow of 1 Faraday of electricity may be summed up as follows,

<u>LHE</u>: Gain of 1 gram equivalent of H^+ ions. Step (I)

Loss of t_+ gram equivalent of H^+ ions. Step (II)

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

$= t_-$ gram equivalent.

Net gain of Cl^- ion $= t_-$ gram equivalent.

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R.H.E: Loss of 1 gram equivalent of H^+ ions.

Again, it gains t_+ gram equivalent

$\therefore$ Net loss of H^+ ions $= (1 - t_+)$ gram equivalent of H^+ ions.
$= t_-$ " " " " "

At the same time, net loss of Cl^- ions $= t_-$ gram equivalent.

Thus,

$$t_-(H^+)(a_+)_2 \longrightarrow t_-(H^+)(a_+)_1 .$$

$$t_- Cl^-(a_-)_2 \longrightarrow t_- Cl^-(a_-)_1 .$$

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∴ EMF of the cell with transference,

$$E_{cell} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_- \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1}$$

$$\Rightarrow \boxed{E_{cell} = t_- \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2}}$$

where $a_\pm$ is the mean ionic activity and by definition, $(a_\pm)^2 = (a_+)(a_-)$.

For 1:1 electrolyte,

$$a = (a_\pm)^2$$

$$\therefore \boxed{E_{cell} = t_- \cdot \frac{RT}{F} \ln \frac{a_2}{a_1}}$$

Concentration cell without transference:

Let us consider the example,

Pt. $H_2(g)$, $HCl(a_1)$ | $AgCl(s)$, Ag

Let, the activity of H^+ ions, in the solution is a_1 and that of the Cl^- ion is a_2.

Reduction half cell reacⁿ –

$$AgCl_{(s)} + e^- \rightleftharpoons Cl^-_{(a_-)_1} + Ag_{(s)} \longrightarrow (1)$$

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Oxidation half cell reactⁿ –

$$\frac{1}{2} H_2(g) \rightleftharpoons H^+_{(a+)_1} + e^- \longrightarrow \text{(II)}$$

The net reaction is taking place by adding (I) and (II).

$$\text{(I)} + \text{(II)} \Rightarrow \frac{1}{2} H_2(g) + AgCl_{(s)} \rightleftharpoons H^+_{(a+)_1} + Cl^-_{(a-)_1} + Ag_{(s)} \longrightarrow \text{(III)}$$

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

$$Pt.\ H_2(g),\ HCl\ (a_2) \mid HCl_{(s)},\ Ag.$$

The net cell reaction for passing 1 Faraday electricity will now be

as follows –

$$\frac{1}{2}H_2(g) + AgCl_{(s)} \rightleftharpoons H^+_{(a+)_2} + Cl^-_{(a-)_2} + Ag_{(s)} \longrightarrow (iv)$$

Finally consider the situation in which the two cells are connected to each other in such a way that the current pass in opposite direction. Thus,

$$Pt.\ H_2(g) \mid HCl_{(a_1)} \mid AgCl_{(s)} \mid Ag \mid AgCl_{(s)} \mid HCl_{(a_2)} \mid H_2(g),\ Pt.$$

The overall reaction for passage of 1 F of electricity,

$$H^+_{(a+)_2} + Cl^-_{(a-)_2} \rightleftharpoons H^+_{(a+)_1} + Cl^-_{(a-)_1}$$

Thus for flow of 1 F of electricity, the overall reaction is the transfer of 1 mol of each of H^+ and Cl^-.

$$E_{cell} = \frac{RT}{F} \ln \frac{(a+)_2}{(a+)_1} + \frac{RT}{F} \ln \frac{(a-)_2}{(a-)_1}$$

$$\Rightarrow \boxed{E_{cell} = \frac{RT}{F} \ln \frac{(a\pm)_2^2}{(a\pm)_1^2}}$$

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Liquid Junction Potential (L.J.P):

In a cell when two electrolyte solutions of different concentrations are kept in direct contact with each other, a potential develops at the junction (boundary) of the two solutions due to difference in the rates of diffusion of the two ions. This potential is called liquid junction potential.

If a cell acquires a liquid junction potential, then the emf of the cell is given by,

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$$E_{cell} = E_1 + E_2 + E_{LJP}$$

where E_1 and E_2 are the oxidation and reduction potential of the cell.

Calculation of Liquid Junction Potential:

As know,

$$E_{cell} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (I)$$

$$E_{c.o.l} = \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (II)$$

Eqn (I) includes the potential at the junction of the two solutions & can also be written as,

$$E_{cell} = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \longrightarrow (III)$$

Eqn (II) does not include the potential at the junction of the two solutions or the liquid junction potential. and can also be written as,

$$E_{c.o.l} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

∴ The liquid junction potential is given by,

$$E_{L.J.P} = E_{cell} - E_{c.o.l}$$

$$= 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} - \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= \left[2t_- - 1\right] \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= \left[2t_- - (t_+ + t_-)\right] \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$\Rightarrow E_{L.J.P} = (t_- - t_+) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \longrightarrow (IV)$$

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from eqn (IV) it is clear that the magnitude as well as sign of $E_{L.J.P}$ depends upon the transference numbers of cations and anions.

<u>Case I</u>: If $t_- = t_+$, then $E_{L.J.P} = 0$

~~eg.~~ Examples of this type are provided by the electrolytes KCl and NH_4NO_3.

<u>Case II</u>: If $t_+ > t_-$, then $E_{L.J.P} = -ve$

<u>Case III</u>: If $t_- > t_+$, then $E_{L.J.P} = +ve$.

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Qualitative Discussion of Potentiometric titrations:

The potential of an electrode depends upon the concentration of the ion with which it is reversible. In a titration, there is continuous change in ionic concentration of the electrolyte solution (analyte) in the cell after each addition of small volume of the titrant, which can be followed by measuring the potential of the cell formed by the electrolyte sampled with a suitable electrode. The potentiometric titrations are thus, those titrations which involves the measurement of electrode potentials with the addition of the titrant. Therefore, the equivalence point can be found by plotting a graph between measured potentials of solution versus volume of titrant added.

The potentiometric titrations generally fall into the following three categories:

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(a) Acid - Base titrations

(b) Oxidation - Reduction (Redox) Titrations

(c) Precipitation Titrations.

(a) Acid - Base titrations :

In case of acid-alkali titrations. e.g. HCl vs NaOH, the emf of the solution is measured by immersing in the given volume of acid solution an electrode reversible to hydrogen ions. This electrode is coupled with a suitable reference electrode to form a complete cell. Generally, the acid solution is kept in contact with the quinhydrone or glass electrode. This forms one half cell which is connected to the calomel electrode to give a complete cell. The whole assembly is connected to the potentiometer and the variation of emf with changes in pH of the solution on each addition of alkali is recorded. The pH varies as, $E = E^{\circ} + 0.0591\ pH$ at 25°C.

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If a plot of E versus the volume of alkali added is made, the following graph is obtained.

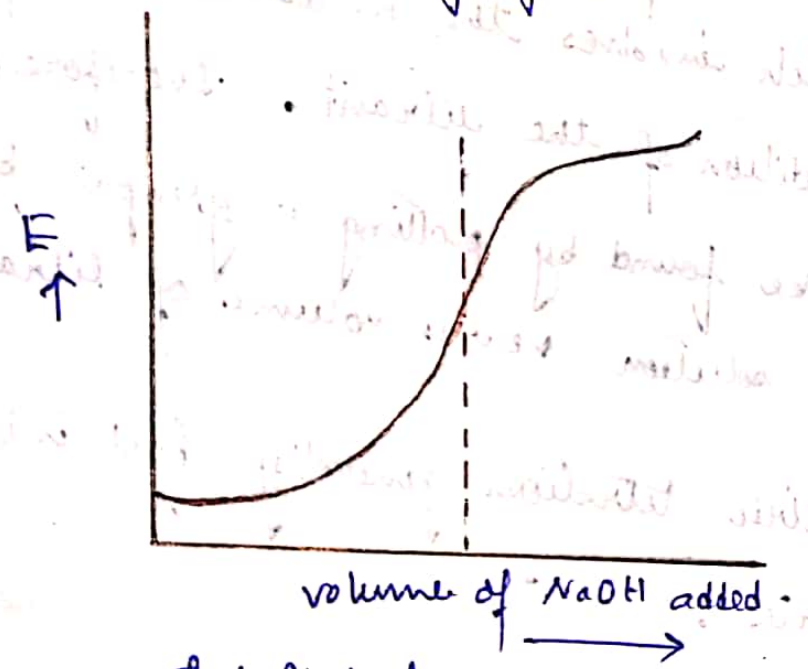

Fig: Plot of E vs volume of alkali added

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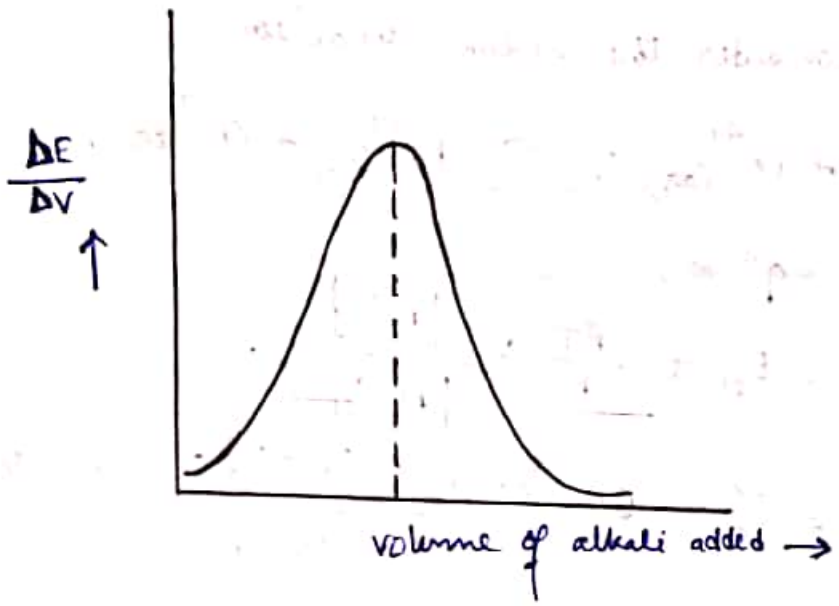
If a plot of $\frac{\Delta E}{\Delta V}$ is placed instead of emf of the cell versus the volume of alkali added, a maximum is observed at the end point as shown below:



~~(b) Oxidation~~

If a plot of $\frac{\Delta^2 E}{\Delta V^2}$ is placed versus the volume of alkali added, the following graph is obtained.

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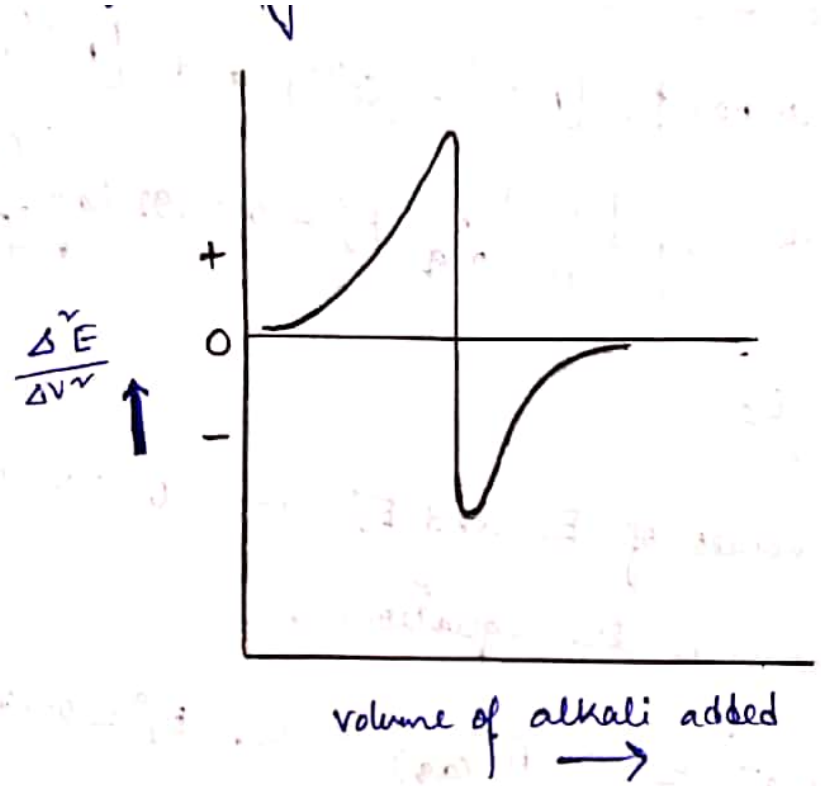

(b) <u>Oxidation - Reduction (Redox) Titrations :</u>

The redox titrations are also carried out potentiometrically. Here, the electrode reversible with respect to H^+ ions is replaced by an inert metal, such as platinum wire,

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immersed in a solution of containing both the oxidised and reduced forms of the same species. The electrode acts as an oxidation - reduction electrode.

Let us consider the redox reaction

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

The Nernst eqn is,

$$E_{el} = E^{\circ}_{el} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}.$$

$$= E^{\circ}_{el} + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{at } 25^{\circ}C.$$

If the ratio $\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.01$,

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

$$= E^{\circ}_{el} - 0.1182.$$

At the equivalence point, $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$.

$$\therefore E_{eq} = E^{\circ}_1 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}, \quad E_{eq} = E^{\circ}_2 + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}.$$

$$\therefore E_{eq} = \frac{E^{\circ}_1 + E^{\circ}_2}{2}.$$

The numerical values of E°_1 and E°_2 are 0.77 V and 1.61 V respectively, according to the equations :

$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}, \quad E^{\circ}_1 = 0.77\,V$$

$$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}, \quad E^{\circ}_2 = 1.61\,V.$$

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