Electrochemistry

Electrochemistry is the branch of physical chemistry that studies the various aspects of interconversion of chemical into electrical energy and electrical energy into chemical energy.

Electrolysis:

The process of decomposition of an electrolyte by the passage of electric current through it is called electrolysis.

The process is carried out in an electrolytic cell that consists of positive and negative electrodes held apart and dipped into a solution containing positive and negative charged ions. The electrode connected with the positive end of the battery is called positive electrode or anode whereas the electrode connected to the negative end of the battery is called negative electrode or cathode.

The electrically charged atoms or radicals that move towards the respective electrodes are called ions. Ions moving towards the cathode are known as cations and the ions travelling towards anode are called anions.

Quantitative Aspects of Faraday's Law of Electrolysis:

Faraday's first law of Electrolysis:

The law states that, "The amount of any substance deposited or dissolved at a particular electrode is proportional

to the quantity of the electricity passed i.e. $\omega \propto Q$.

or $\omega \propto I \times t$.

$\Rightarrow \omega = zIt$.

where ω is the mass of substance deposited in gram. Q is the amount of charge passed in coulombs, I is current strength in amperes, t is the time for which current flows through the cell in seconds and z is the electrochemical equivalent.

<u>Electrochemical equivalent:</u>

It is the mass of substance deposited in grams either by passing one coulomb of charge or by passing one ampere of current for one second.

<u>One faraday:</u>

One faraday is the quantity of charge carried by one mole of electrons.

$$1F = 1.6 \times 10^{-19} \times 6.022 \times 10^{23} \text{ Coulombs.}$$

$$= 96500 \text{ C.}$$

<u>Faraday's Second Law of Electrolysis:</u>

The law states that, "When same quantity of electricity is passed through different electrolytes, the amount of

products obtained are proportional to their chemical equivalents or equivalent weights.

From the first law, $w = ZIt$.

$$\Rightarrow w = \frac{EIt}{96500} \qquad \left[\because Z = \frac{E}{96500}\right]$$

$$\Rightarrow \frac{w}{E} = \frac{It}{96500}$$

$$\Rightarrow \frac{w}{E} = \frac{Q}{96500} = \text{no. of equivalents}$$

$$\therefore \frac{w}{E} = \text{constant}.$$

i.e. If the quantity of charge passed through cells connected in series is same, the amount of substance deposited at various electrodes in terms of equivalents would be same.

Chemical Cells:

A chemical cell converts chemical ~~cell~~ energy into electrical energy.

Electrochemical Cells:

A system consisting of two electrodes dipping into solutions of different electrolytes or of same electrolyte having different concentrations and is in electric communication is termed as an electrochemical cell.

Types of Electrochemical Cells:

① **Electrolytic Cells:** Electrolytic cells are those electrochemical cells in which non-spontaneous chemical reactions are made to occur by continuous supply of electrical energy. i.e. In

electrolytic cells, electrical energy is converted into chemical energy.

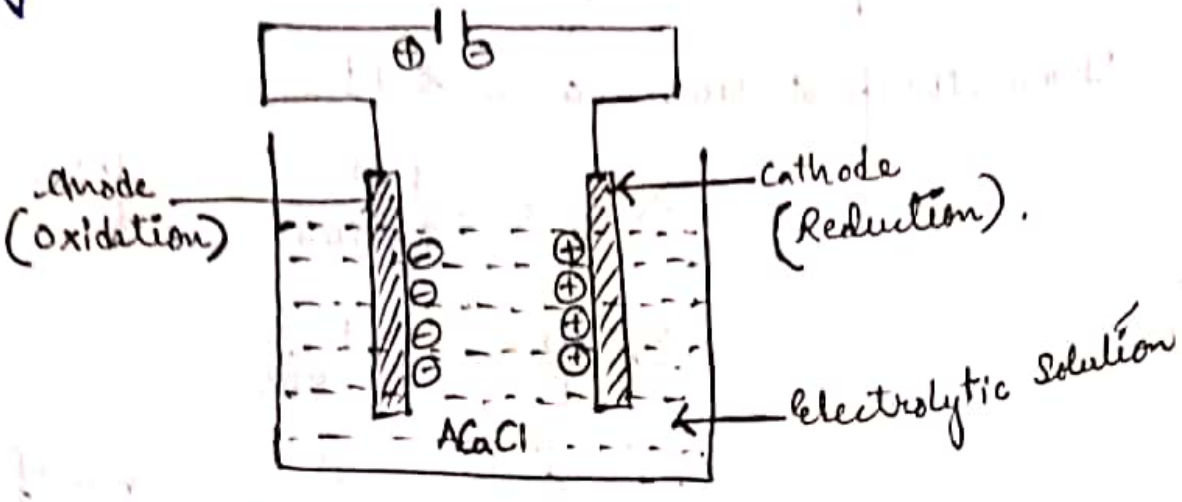

Fig: Electrolytic cell.

One of the simplest electrolytic cell is that, in which two copper strips are dipped in an aqueous solution of NaCl. A DC voltage, when applied to the electrodes, Na^+ ions discharge at the cathode and the following reaction takes place.

$$Na^+ + e^- \longrightarrow Na$$

i.e. Na metal is deposited at the cathode. At the anode, ~~copper is converted to Cu^{2+} ions by~~ Cl^- ions lose electrons and thus undergo oxidation as follows –

$$Cl^- \longrightarrow Cl + e^-$$

Overall reaction may be written as –

$$Na^+ + Cl^- \longrightarrow Na + \frac{1}{2}Cl_2$$

(2) Galvanic cells:

A galvanic cell is a device in which the free energy of a physical or chemical process is converted into electrical energy.

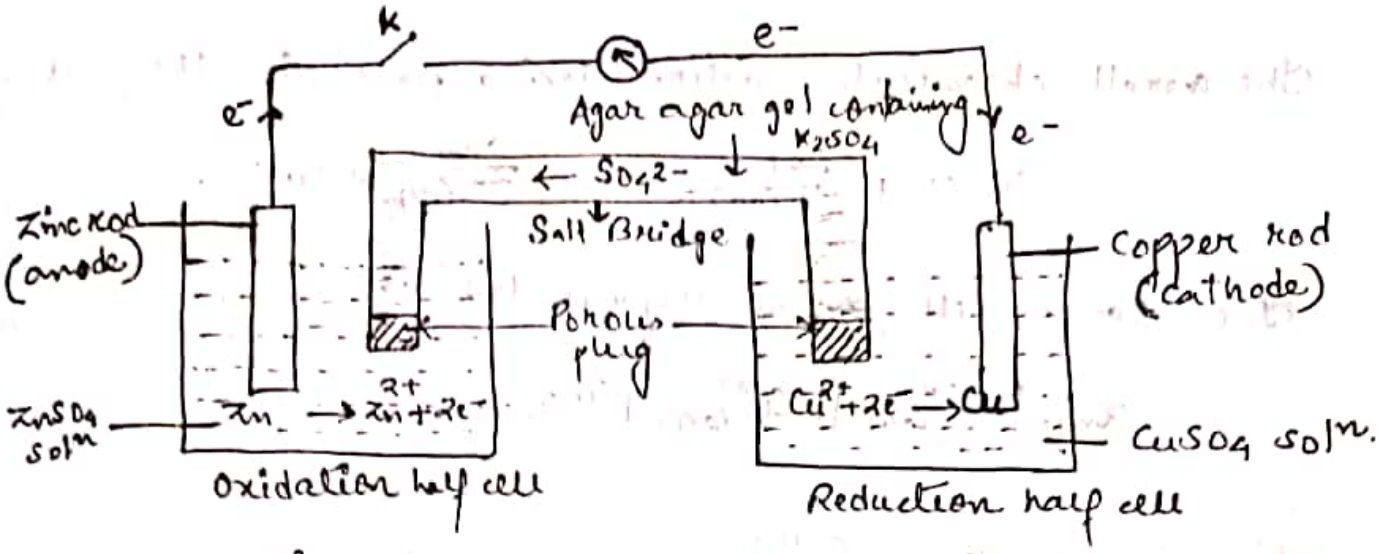

Fig: Galvanic cell (Daniel cell)

A Daniel cell is an example of Galvanic cell. Daniel cell is also called Zinc-Copper cell. It consists of a copper rod dipping in a solution of copper sulphate and a zinc rod dipping in a solution of zinc sulphate. The two metal rods are connected

through an ammeter and the two solutions are connected through a salt bridge, i.e. an inverted U-shaped glass tube filled with a solution of an electrolyte like $KCl / K_2SO_4 / KNO_3$ held in a gel made from agar agar. The salt bridge is used for making electrical contact between the two electrolytic solutions. It allows the movement of ions from one solution to the other without mixing of the two solutions. As soon as the circuit is closed by pressing the key (K), current starts flowing which is indicated by deflection in the ammeter and the following reactions take place :-

At anode,

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-.$$

At cathode,

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s).$$

The overall chemical reaction taking place in the cell is

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

The Daniel cell can be represented as,

$$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}.$$

The Copper - Silver Cell:

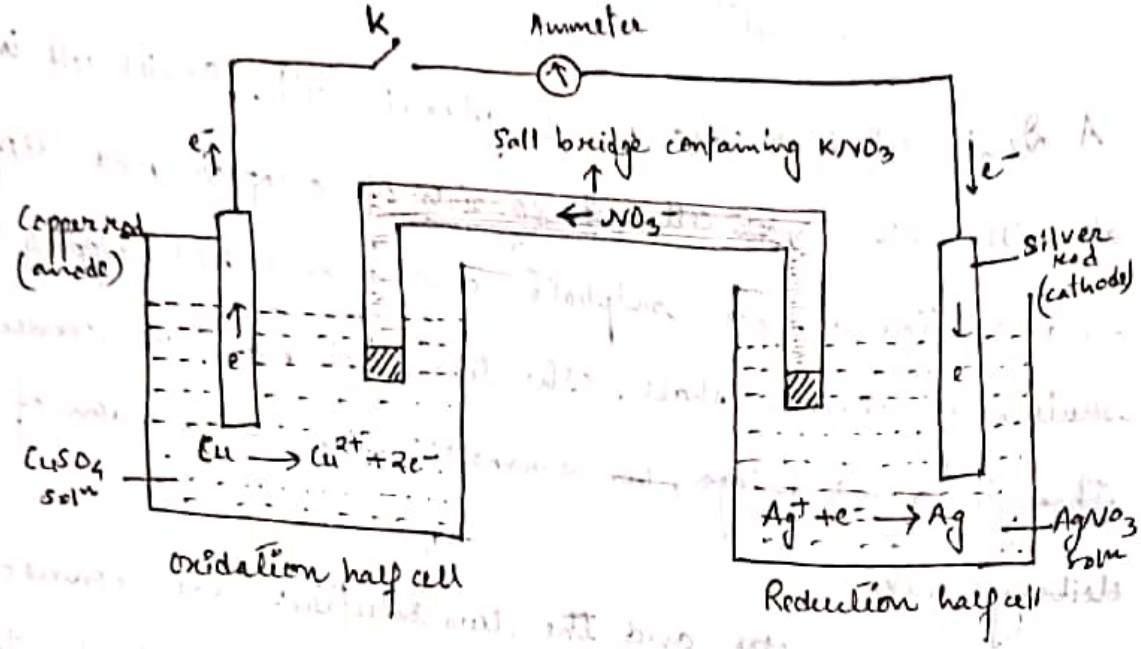

Fig: Copper - Silver Cell

The Copper-Silver cell consists of a copper rod dipped into a solution of $CuSO_4$ and silver rod dipped into a solⁿ of $AgNO_3$. The two rods are connected by wire through a voltmeter and two solutions are connected by a salt bridge containing KNO_3. Following reactions take place in the cell:

At anode: $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ (O.H.R.).

At cathode: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$ (R.H.R.)

The overall reaction is,

$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}.$$

Rules of oxidation/reduction of ions:

① Predicting anode and cathode of a spontaneous cell:

An electrode with higher standard electrode reduction potential will act as cathode and is given a positive sign while the electrode with lower E° value will act as anode of spontaneous cell and is given a negative sign. e.g. E° for Cu^{2+}/Cu (+0.34) is higher than E° for Zn^{2+}/Zn (−0.763).

② Predicting relative strength of oxidising or reducing agent:

The greater the standard electrode potential of an electrode, the more is the tendency of the element or ion of the cathode to get reduced and hence, the stronger the oxidising agent it is. While an electrode with lesser value of E° will have more tendency of its element to get oxidised and hence, the stronger the reducing agent it will be.

(b) Calculating the standard EMF of the cell:

Knowing the values of the standard electrode potentials of the two electrodes of the cell as represented, we can find E°_{cell} by using the relation,

$$E^\circ_{cell} = E^\circ_R - E^\circ_L .$$

$$\text{or } E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} .$$

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

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 of 298 K, the corresponding EMF generated is called as Standard EMF.

<u>Significance of EMF:</u>

(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.

(a) By the use of a voltmeter:

The easiest way to measure the EMF of a cell is to connect its two electrodes to a voltmeter. The potential difference can be read directly from the voltmeter. However, this process

has some disadvantages as —

① The voltmeter draws some current from the cell, thereby changing the EMF of the cell.

② Since at the time of measurement of EMF, a current is flowing through the circuit, therefore a part of EMF will be utilized to overcome the internal resistance of the cell.

ⓑ 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

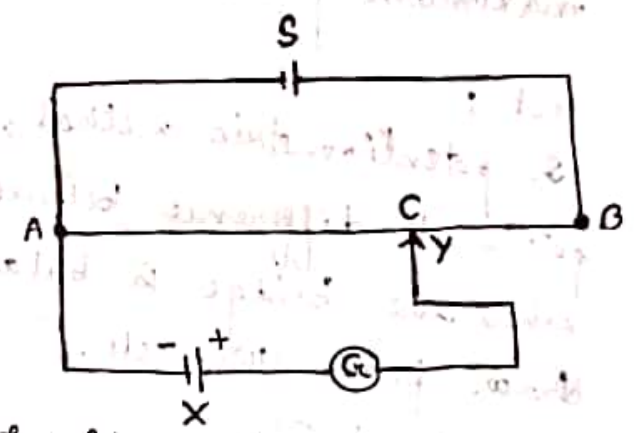

Fig: Potentiometric method.

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.

$\because E_S \propto$ length AB.

$E_X \propto$ length AC.

$$\frac{E_S}{E_X} = \frac{AB}{AC}$$

$$\Rightarrow E_X = \frac{AC}{AB} \cdot E_S$$

Thus, knowing AC, AB and E_S, E_X can be calculated.

© <u>Direct Reading Potentiometer :</u>

In this method, since at the time of measurement of potential (EMF) no current is flowing through the circuit, so no potential is used in overcoming any internal resistance of the cell. Consequently, there is no change in the EMF of the cell. So, this is the actual EMF of the cell, i.e. The maximum potential that can be drawn from the cell.

<u>Note</u> :

In potentiometric method, measured EMF is the maximum potential difference between the Two electrodes of The cell as when the bridge is balanced, there is no current being drawn from the cell.

Standard Cell :

A standard cell is a cell which should fulfil the following requirements.

(i) It should have a constant and reproducible cell potential i.e. EMF.

(ii) Its EMF should not undergo any change with the passage of time.

(iii) The temperature coefficient of EMF should be very low.

The cell which meets the above requirements to the maximum extent is Weston standard cell.

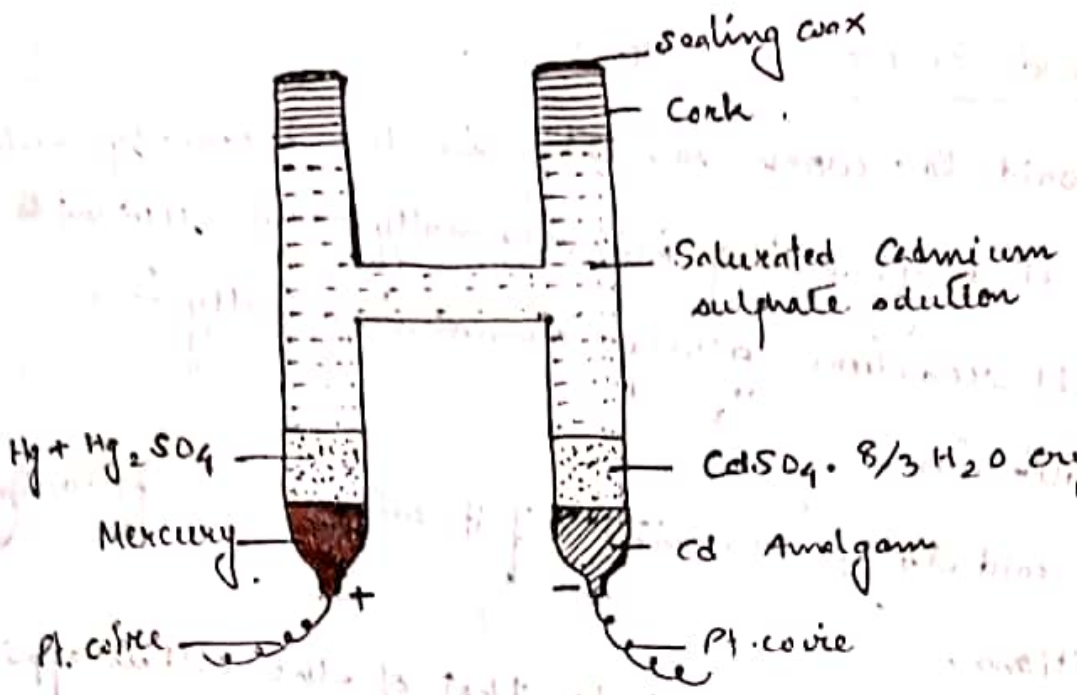

Fig: Weston Standard Cell

Weston standard cell consists of an H-shaped glass vessel. ~~The~~ ~~left~~ One of the limbs contains mercury covered with a paste of mercurous sulphate and mercury. This limb acts as cathode. The other limb acting as anode contains cadmium amalgam covered with crystals of solid $CdSO_4 \cdot 8/3\ H_2O$ and the saturated solution of $CdSO_4$. Small platinum wires are sealed at the lower ends of the two limbs for electrical connections. The limbs are closed with cork and sealing wax at the top. Following reactions take place in the cell:

At anode: $Cd \longrightarrow Cd^{2+} + 2e^-$

At cathode: $Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$

The overall reaction is:

$$Cd + Hg_2SO_4 \longrightarrow 2Hg + Cd^{2+} + SO_4^{2-}$$

The EMF of this cell is 1.0185 V at 288 K and 1.0181 V at 298 K. This is a reversible cell and undergoes the following reversible cell reaction.

$$Cd(s) + Hg_2SO_4(aq) \rightleftharpoons CdSO_4 \cdot \frac{8}{3}H_2O(s) + 2Hg(l)$$

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.

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 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

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:

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

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

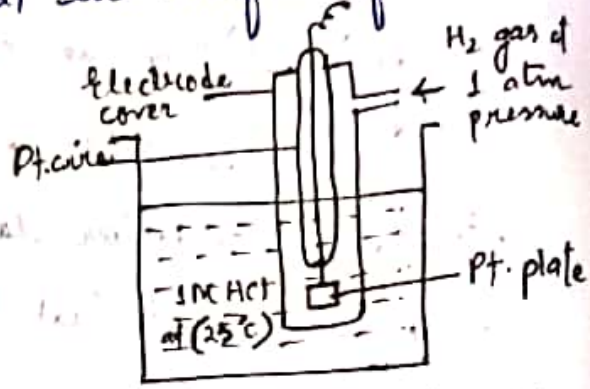

Fig: Standard Hydrogen electrode.

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.

Saturated Calomel Electrode:

Calomel electrode consists of Hg, solid mercurous chloride (calomel) and a solⁿ of KCl. The electrode is represented as —

$$Hg \mid Hg_2Cl_2(solid) \mid KCl(sol^n)$$

In this electrode, mercury of high great purity is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of Hg_2Cl_2.

A solⁿ of KCl is introduced above the paste through the side tube on right hand side.

The solution is either decinormal or normal or else the solution is fully saturated. The solution also fills the side tube ending in a jet on the left. A platinum wire shield in a glass tube make the electrical contact of the electrode with the circuit.

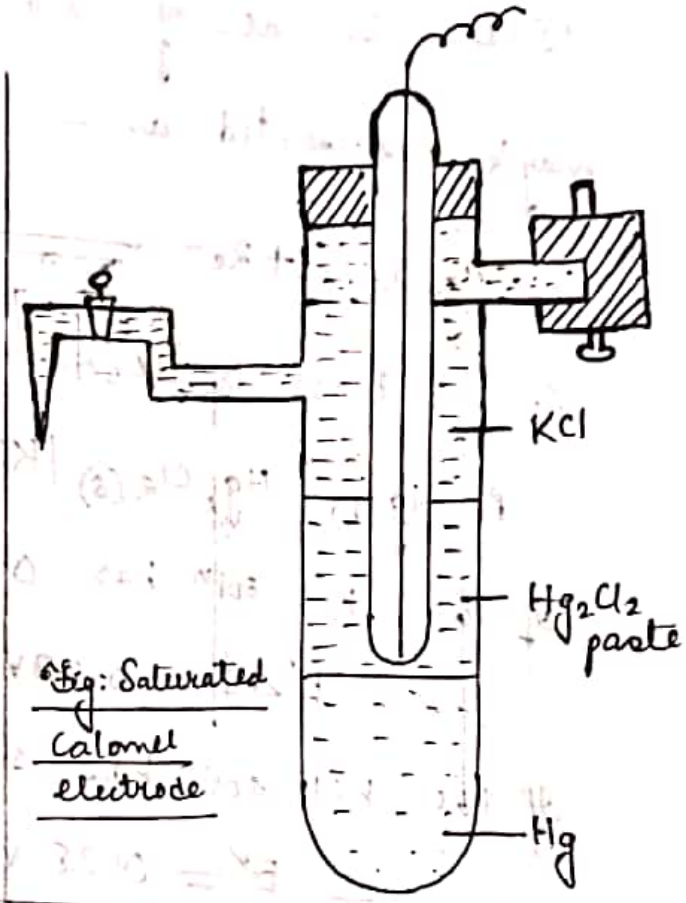

Fig: Saturated Calomel electrode

If the electrode reaction involves reduction, the Hg_2^{2+} ions furnished by the sparingly soluble Hg_2Cl_2 would be discharged in the electrode. Hence, more and more calomel would pass into the solⁿ. The result would increase in the concentration of chloride ions. The reacⁿ may be represented as —

$$Hg_2^{2+}{}_{(aq)} + 2e^- \rightleftharpoons 2Hg(l) ;$$

$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^- .$$

If on the other hand, electrode reaction involves oxidⁿ, the Hg_2^{2+} ion would combine with cations (furnished by KCl) forming Hg_2Cl_2. The result is the fall of Cl^- ion in the solⁿ. The reaction may be represented as —

$$2Hg(l) \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2e^- .$$

$$Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \rightleftharpoons Hg_2Cl_2\ (s) .$$

Thus, in case of calomel electrode, the electrode reaction may be represented as —

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons Hg_2^{2+}(l) + 2Cl^-(aq).$$

The electrode is denoted as,

$$Pt \cdot Hg(l) \mid Hg_2Cl_2(s) \mid KCl(agar)$$

If the KCl soln has 0.1 N strength, then

$$E^\circ = 0.33V.$$

If the KCl soln has 1 N strength, then

$$E^\circ = 0.28\ V.$$

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..

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

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

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

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

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.

(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.

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

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

$$\cancel{\Rightarrow \Delta H = -nF}\left[\right.$$

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

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

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),

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

(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.

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

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

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

n = no. of Faradays involved.

$\therefore$ (I) and (II)

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

Again, $-\Delta G^\circ = RT \ln K. \longrightarrow (IV)$ (Vant 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, $$E = \frac{0.0591}{n}\log K - \frac{0.0591}{n}\log \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

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.