

## **ELECTROCHEMISTRY**

Introduction, Single electrode potential, Origin of single electrode potential theory, Nernst equation to calculate the electrode potential, Numerical problems. Electrochemical cells - galvanic cell and electrolytic cell, representation of galvanic cell, Construction and working of galvanic cell, Liquid junction potential, Functions of salt bridge, EMF of cell, Determination of EMF of cell by Poggendorff's method using Standard cell, Construction, working, application and limitations of calomel electrode, Numerical problems. Construction, working, applications, advantages and limitations of glass electrode, Numerical problems. Classification of Batteries – Introduction, primary and secondary with examples; construction, working and applications of lead acid battery. Construction, working and applications of Ni-Cd and Li-ion batteries, advantages and disadvantages. Fuel Cells – Introduction, construction and working of AFC & PEMFC, advantages and disadvantages. Metal finishing – Electroplating – polarization, over voltage, decomposition potential including determination of decomposition potential. Characteristics of good deposit, Factors influencing the nature of the deposit, Methods of cleaning the metal surface. Electroplating of Cu & Cr & electroless plating of Cu.

### **1 INTRODUCTION**

Electrochemistry deals with the behavior of electrolytes in solution and interconversion of chemical and electrical energies; that is, the study of chemical changes due to the flow of an electric current and production of electric current due to chemical reaction. Electrolysis, electrometallurgy and electroplating use electrical energy to drive chemical reactions, while chemical energy is transformed into electricity in galvanic cells, batteries and fuel cells. Substances such as metals and alloys conduct electricity under the influence of an applied electric potential through a flow of electrons and hence are known as electronic conductors. The flow of electricity in electronic conductors does not cause any physical or chemical change in the conductor. On the other hand electrolyte solutions and molten salts conduct electricity through the migration of ions and are known as electrolytic conductors or electrolytes. When direct current is passed through an electrolyte solution, decomposition and changes occur in the composition of the electrolyte. The practical importance of electrochemistry includes electroplating, electroextraction of metals, electrorefining of metals, and electro-production of certain compounds.

## 1.1 ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes or metallic conductors, in contact with an electrolyte, an ionic conductor. An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a tube containing a concentrated electrolyte solution in agar jelly that completes the electrical circuits and enables the cell to function. So an electrochemical cell can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells can be classified into two types:

- *Galvanic Cells*
- *Electrolytic Cells*

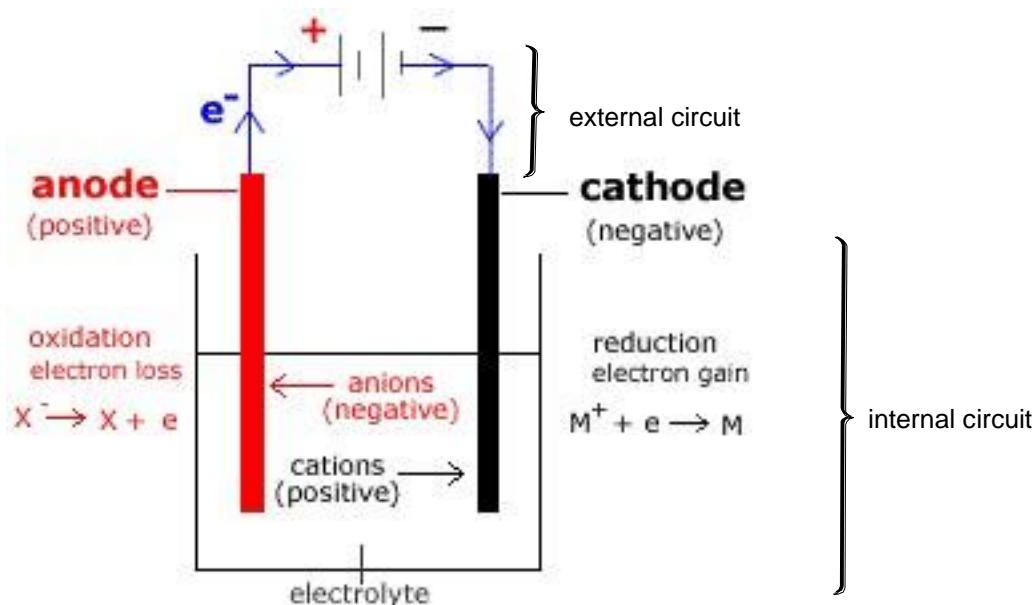


Fig.1.1. A schematic diagram of Electrochemical Cell

### 1.1.1 Galvanic Cells

A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous redox reaction occurring inside it. Galvanic cell generally consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or connected through a salt bridge. It is a single arrangement of two electrodes in one or two electrolytes which converts stored up chemical energy in the form of electroactive materials (anode & cathode active

materials) directly into electrical energy. The negatively charged electrons flow from anode to cathode and are attracted to the positive cathode through the external circuit.

### **Anode vs. Cathode:**

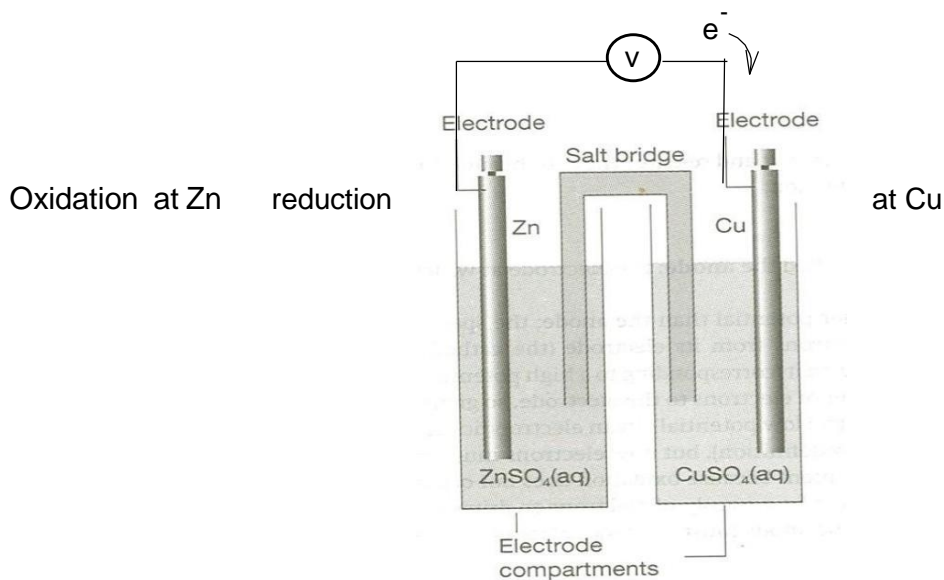
#### **Anode ;**

- the electrode at which oxidation occurs
- is where electrons are produced
- is what anions migrate towards
- has a -ve sign.

#### **Cathode ;**

- the electrode at which reduction occurs
- is where electrons are consumed
- is what cations migrate towards
- has a +ve sign

A typical galvanic cell can be illustrated by Daniel cell (Fig. 1.1.1)

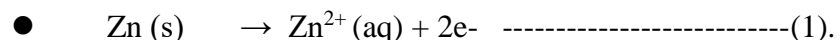


Half cell I (Anode compartment)

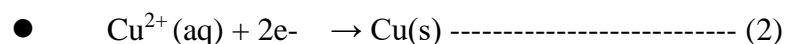
Half cell II (Cathode compartment)

Fig.1.1.1. A schematic diagram of Daniel cell

A Daniel cell consists of two compartments, one of which contains zinc rod dipped in zinc sulphate solution and the other with a copper rod dipped in a copper sulphate solution. The two electrolytes are connected by a salt bridge. When the zinc and copper rod electrodes are connected externally through a voltmeter by using a wire, the following oxidation-reduction reactions taking place at the electrodes. At the zinc electrode, zinc goes into the solution as  $\text{Zn}^{2+}$  ions, liberating two electrons. In the process zinc undergoes oxidation liberating two electrons. The positive ion flows from the salt bridge to the cathode and the zinc electrode becomes lighter.



At the copper electrode reduction of  $\text{Cu}^{2+}$  ions takes place with the deposition of metallic copper on the copper rod, by consuming two electrons. The negative ions flow from salt bridge to anode and copper electrode becomes heavier. The ionic conduction in the solution is coupled to the electronic conduction in the electrodes.



Each of these reactions is known as half cell reaction. The reaction (1) in which loss of electrons takes place is called oxidation half reaction; while the reaction 2, in which gain of electrons takes place, is called reduction half reaction. The net reaction is obtained by adding reactions 1 and 2. i.e.  $\text{Zn(s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu(s)}$  is called redox or oxidation – reduction reaction. When the circuit is closed, the electrons flow from zinc to copper through the external wire to feed the  $\text{Cu}^{2+}$  ions in the process of discharging copper and thus electrical energy or current is produced which may be used for the purpose of external work.

As in the case of Daniel cell, by the combination of any two different electrodes materials one can construct a galvanic cell. The electrode with a greater tendency to go into the solution by liberating electrons acts as an anode, & the other one with more tendency to undergo reduction acts as a cathode. In a galvanic cell anode is negative and the cathode is positive. The reason to this nomenclature is that oxidation is accompanied by the liberation of electrons which are given up to that electrode which thereby acquires a negative charge. Reduction on the other hand, is accompanied by absorption of electrons by reactant in solution from the electrode, which thereby acquires a positive charge. Hence the flow of electrons is from the negative electrode to positive electrode and the direction of flow of positive electricity, which is known as conventional current, is from the cathode to anode.

### 1.1.2 Electrolytic cells

An electrolytic cell is an electro –chemical cell in which a non- spontaneous reaction is driven by an external source of current although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation is positive.

The electrolytic cell (Fig.1.1.2) find wide applications in the purification of metals & also in electro deposition of a metal on to the surface of another metal, alloy or any conductor in general, by the process of electrolysis.

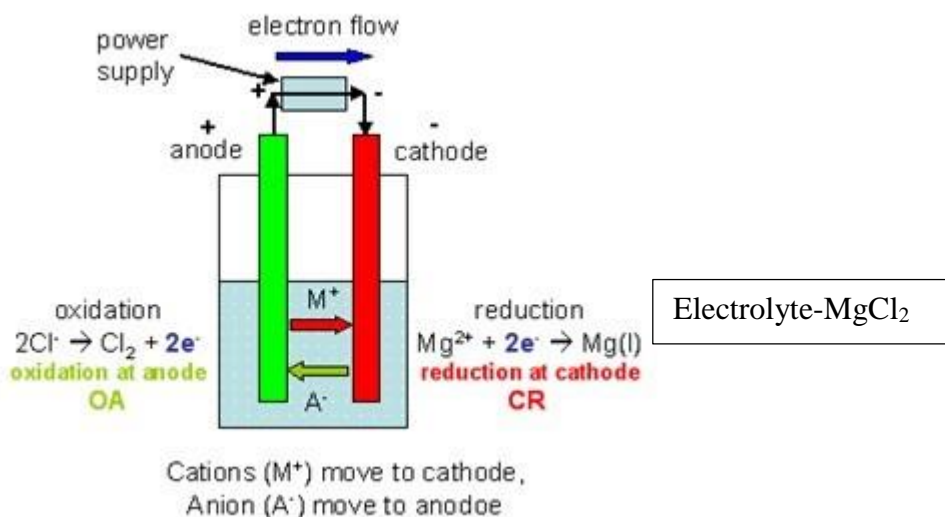


Fig.1.1.2 Schematic diagram of an electrolytic cell

Electrolysis involves the conversion of electrical energy into chemical energy i.e. chemical changes are brought about by the expense of electrical energy. Since electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change, & this is equal but opposite in sign to the free energy decrease accompanying the reverse spontaneous process. This is true when electrolysis is carried out reversibly. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell.

### 1.1.3 Representation of a galvanic cell

According to the present convention, a galvanic cell is represented by keeping in view the following points:

1. The anode is written on the left hand side and the cathode is written on the right hand side of cell representation.

- The anode is written by writing the metal (or solid phase) first and then the electrolyte along with the concentration in the bracket. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species.

Anode representation

Metal/ Metal ion (concentration) i.e.  $M/M^{n+}(c)$

$Zn | Zn^{2+}$  or  $Zn; Zn^{2+}$  or  $Zn | ZnSO_4(1M)$  or  $Zn; ZnSO_4(1M)$

- The cathode of the cell is represented by metal ion first and then the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon.

Cathode representation:

$M^{n+}(c) / M$  i.e. Metal ion (concentration) / Metal

e.g.  $Cu^{2+} | Cu$  or  $Cu^{2+}; Cu$  or  $Cu^{2+}(1M); Cu$  or  $CuSO_4(1M)/Cu$

- A salt bridge is indicated by two vertical lines, separating the two half-cells. Thus the

Daniel cell, may be represented as:

$Zn | ZnSO_4(1M) || CuSO_4(1M)/Cu$

$Cu(s) / Cu^{2+}(aq) || Ag^+(aq) / Ag(s)$

### Comparisons of Galvanic and Electrolytic cells

Galvanic Cell	Electrolytic Cell
Cell reaction is spontaneous	Cell reaction is non-spontaneous
Converts chemical energy to electrical energy	Converts electrical energy into chemical energy
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Usually have two electrodes and two electrolytes	Single electrolyte and two electrodes
Used as a potable source of electrical energy in cars, flashlights and calculators	Used for electrolysis apparatus like electroplating and electrorefining
Example. Daniel cell	Example. Electroplating of nickel

### 1.1.4 LIQUID JUNCTION POTENTIAL

The potential set up at the junction of the two electrolytes because of the difference in the speeds of the cations in one direction and anions in the other i.e. potential at the junction of the two electrolytes because of unequal migration of ions across the boundary between the two solutions is called the liquid junction potential,  $E_j$ . In a Daniel cell, if the concentrations of  $\text{ZnSO}_4(\text{aq})$  and  $\text{CuSO}_4(\text{aq})$  are equal  $\text{SO}_4^{2-}$  ions do not diffuse across the junction and the charge cannot flow around the circuit. But  $\text{Cu}^{2+}$  ions diffuse into  $\text{ZnSO}_4(\text{aq})$  and  $\text{Zn}^{2+}$  ions diffuse into  $\text{CuSO}_4(\text{aq})$  because  $\text{Cu}^{2+}$  ions are slightly more mobile than  $\text{Zn}^{2+}$  ions. This produces a small excess positive charge on the  $\text{ZnSO}_4(\text{aq})$  side of the junction and equal negative charge on the  $\text{CuSO}_4(\text{aq})$  side. The liquid junction potential is the difference between the electric potential developed in the two solutions across their interface

i.e.  $E_j = \phi_{\text{soln, R}} - \phi_{\text{soln, L}}$  where  $\phi_{\text{soln, R}}$  is the electric potential of the electrolyte solution on the right hand side half cell in the cell scheme.  $\phi_{\text{soln, L}}$  is the electric potential of the electrolyte solution on the left hand side half cell. Generally, LJPs are of the order of a few millivolts.

### 1.1.5 SALT BRIDGE

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge containing salts such as  $\text{KCl}$ ,  $\text{KNO}_3$ , and  $\text{NH}_4\text{NO}_3$  whose ions have the same migration velocities. Then the ions move with equal speed to anode and cathode compartments minimizing the junctions potentials almost zero. A salt bridge is used to connect electrolytically, the two electrolyte solutions of a galvanic cell, as shown in the Fig. 1.1.5.

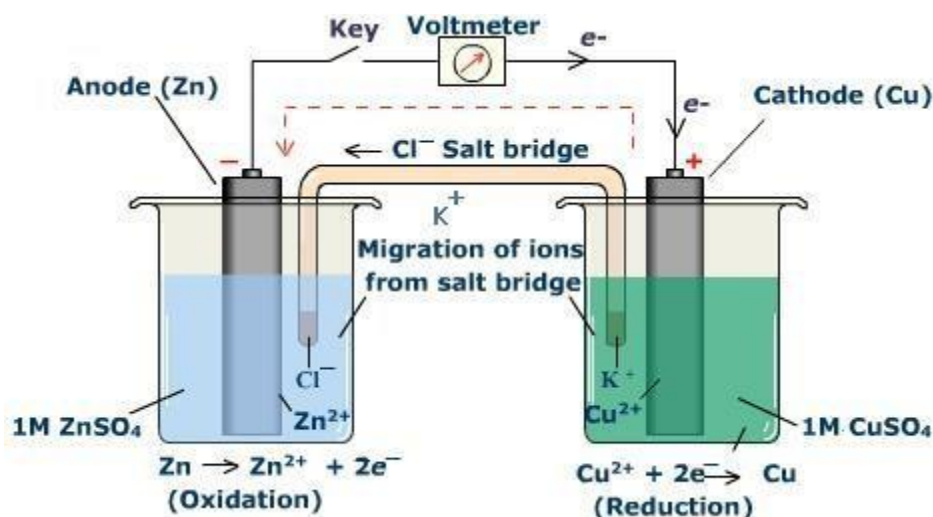


Fig.1.1.5 Daniel Cell indicating the function of a salt bridge

The salt bridge consists of a saturated solution of a salt such as KCl or  $\text{NH}_4\text{NO}_3$ , whose ions have almost same migration velocities. The positive and negative ions of the salt in the salt bridge migrate with equal speed into cathode and anode compartments respectively, thereby minimizing liquid junction potential.

The salt bridge is prepared by dissolving 5g agar in 100 mL aqueous solution of KCl containing 35 g of KCl and filling in a U-tube. On cooling, the agar forms a jelly with KCl solution in it. A salt bridge has the following functions:-

1. It provides electrical contact between the two electrolyte solutions of a cell i.e., it physically separates the two electrolytes but completes the electrical circuit by altering ions causing charge to move from half cell to the other.
2. It minimizes liquid junction potential in galvanic cells containing two electrolyte solutions in contact. i.e., it reduces the LJP to a minimum by nearly equal diffusion rates of cations and anions.
3. It maintains the electrical neutrality of the two half cells i.e., it prevents any net charge accumulates in the two electrolytes.

### 1.1.6 ELECTROMOTIVE FORCE OF THE CELL

Electricity cannot flow from one electrode to another unless there is a potential difference between the two points. The difference of potential, which causes a current to flow from the electrode at higher potential to an electrode at lower potential is called the “electromotive



force”(e.m.f.) of the cell “or the “cell potential” and is expressed in volts V. The emf of a cell is denoted by  $E_{\text{cell}}$ . Mathematically,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The driving force that pushes the negatively charged electrons away from the anode and pulls them towards the cathode is known as emf. The  $E_{\text{cell}}$  depends on the nature of the electrodes composition, (combination of electrodes, strong tendency to lose or gain electrons produces large cell potential) temperature ( $E \propto T$ ) and concentration of the electrolyte solutions. To facilitate comparison of different galvanic cells, their standard emf, denoted by  $E^0_{\text{cell}}$  is used. Standard emf of a cell is defined as the emf of a cell when the reactants & products of the cell reaction are at a unit concentration or unit activity, at 298 K and at 1 atmospheric pressure including pure solids and liquids.

The emf of a cell represents the driving force of a cell reaction. As represented by the thermodynamic relation,

$$\Delta G = -nFE$$

Where  $\Delta G$  is the free energy change accompanying a cell reaction,  $n$  is the number of electron transfer during the cell reaction, and  $F$  is the Faraday constant,  $F = eN_A$ , the magnitude of the charge per mole of electrons. Hence the above equation is the key connection between the electrical measurements on the one hand and thermodynamic properties on the other.

The cell reaction is spontaneous or feasible when  $\Delta G$  is negative.  $\Delta G$  can be negative only if the emf of the cell is positive, because, the other two factors,  $n$  &  $F$  are always positive. Thus emf of a galvanic cell is always positive. The positive emf value indicates the spontaneity of cell reaction in the given direction. When the cell potential is large, a given number of electrons traveling between the electrodes can do a large amount of electrical work. When the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

### 1.1.7 Measurement of emf of a cell

The emf cannot be measured accurately by connecting directly a voltmeter between the two electrodes, because during such a measurement, a part of the cell current is drawn to deflect the needle as part of the emf is used to overcome the internal resistance of the cell. Consequently, such a measurement would indicate a potential difference less than the actual emf of the cell. For precise

emf measurements potentiometers are used, which require extremely small current at the balance point.

The potentiometric measurement of emf of a cell works based on Poggendorff's compensation method. In this method, emf of a test cell is opposed by the impressed emf from an external source of emf, and the measurement is made when there is no net flow of current in the circuit. The basic principle is that the emf of the cell to be measured is exactly balanced by an equal and opposite known emf so that no current flows in the circuit (null point). A schematic diagram of the potentiometer is shown in Fig.1.1.7

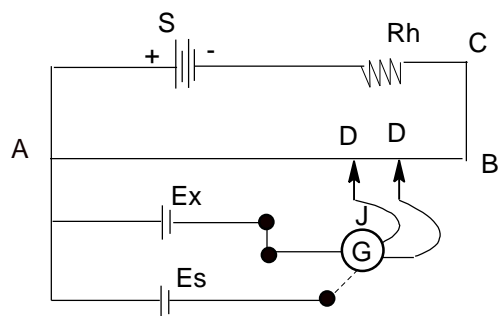


Fig.1.1.7. Potentiometric arrangement for the measurement of EMF of a galvanic cell.1.1.5

AB- Potentiometric wire

S- Storage battery

Es- Standard cell

Ex- unknown cell

G- Galvanometer

J- Sliding contact.

Rh – adjustable resistance

The two terminals of a storage battery(S) which has a constant and higher emf than the test cell, is connected to two ends of a long uniform wire AB of high resistance. The positive terminal of the test cell is connected to the end A, to which the positive terminal of S is connected & the negative terminal is connected to a sliding contact J through a galvanometer (G). The sliding contact is moved along the wire AB until the null point is reached, which is indicated by no current flow in the galvanometer. The position of a null point is noted & the distance AD is measured. The emf of the unknown cell  $E_x$  is proportional to the length AD.

- $E_x \propto AD$

Then the test cell  $E_x$  is replaced by a standard cell  $E_s$ , whose emf, is known the position of the sliding contact is readjusted by moving it over AB, as before, till null point  $D^1$  is reached. The length  $AD^1$  is measured. The emf of the standard cell  $E_s$  is proportional to the length  $AD^1$ .

- $E_s \propto AD^1$
- $\frac{E_x}{E_s} = \frac{AD}{AD^1}$
- $E_x = \frac{AD}{AD^1} \times E_s$

Thus the emf of the test cell is calculated by substituting the emf of the standard cell in the above equation.

### 1.1.8 Standard cell requirements:

1. Its emf should remain constant for a longer period of time.
2. It should be capable of providing highly reproducible emf.
3. The temperature coefficient of emf should be negligibility small i.e.  $(\delta E / \delta T) = 0$
4. The cell reaction should be reversible.
5. It should not be subjected to permanent damage due to the passage of current.
6. A standard cell is one which has a constant and reproducible known emf with a negligible variation of emf with temperature e.g. Weston standard cell or Weston cadmium cell.

## 1.2 Energetic of cell reactions:

### 1.2.1 The relation between $E$ and $\Delta G$ :

A cell in which the overall reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given number of electrons can accomplish depends on the cell potential.

The maximum electrical work as per thermodynamics, chemical reaction can do is given by the value  $\Delta G$  for the reaction.

$$W_{e, \max} = \Delta G \text{-----} 1$$

Where,  $W_e$  is electrical work. It follows that, to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly. Only then it is producing maximum work and only then we can relate electrical work to  $\Delta G$ . Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly

opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows.

The net electrical energy and the emf of the cell produced in a cell is the product of the quantity of electricity that passes through the cell and the emf of the cell.

$$W_e = QE \text{ Joules.} \text{-----}(2)$$

Q is the quantity of electrical charge in coulombs produced by the reaction and E is the emf of the cell in volts.

Charge on 1 mol ( $6.02 \times 10^{23}$ ) electrons is F coulombs, where F is Faraday constant. When n electrons take part in the cell reaction, n mols of electrons are involved per mol of a reactant of the reaction. Hence charge on n mol of electrons = nF coulombs. This is the charge, Q in coulombs produced by the reaction. For 1 mole of electrons transferred in the cell reactions, the quantity of electricity = 1F

If n moles of electrons are transferred in the cell reactions, the quantity of electricity = n F

$$\text{Therefore electrical energy} = nFE, \text{-----}(3)$$

In a large number of reactions, electrical energy produced is not equal to chemical energy.

$$\text{Electrical energy produced} = \text{decrease in free energy for cell reaction i.e. } -\Delta G = nFE \quad \text{or } \Delta G = -nFE \text{ Joules-----}(4)$$

If we know emf E,  $\Delta G$  can be calculated. The larger the value of cell potential the further the reaction is equilibrium.

### 1.2.2 Relation between E and $\Delta H$

$$\text{Enthalpy Change } \Delta H = nF[T(\delta E/\delta T)_P - E] \text{-----}(5)$$

If we know emf and temperature coefficient of emf,  $\Delta H$  can be calculated..

### 1.2.3 Relation between E and $\Delta S$ :

$$\Delta S = nF(\delta E/\delta T)_P \text{-----}(6)$$

### 1.2.4 Numerical Problems

1. Emf of Weston Cadmium cell is 1.0183 V at 293 K and 1.0181 V at 298 K. Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of the cell reaction at 298 K.

**Solution:-**  $\Delta G$ :  $\Delta G = -nFE$   $n = 2$  for the cell reaction;

$$F = 96,500 \text{ C} \quad E = 1.0181 \text{ V at 298 K}$$

$$\Delta G = -2 \times 96,500 \times 1.0181 \text{ J} = -196.5 \text{ KJ}$$

$$\Delta H: \Delta H = nF [ T (\delta E / \delta T)_P - E]$$

$$(\delta E / \delta T)_P = 1.0181 - 1.0183 / 298-293 = -0.0002 / 5 \\ = -0.00004 \text{VK}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta H = 2 \times 96,500 \{ [298 \times (-0.00004)] - 1.0181 \} \\ = -198.8 \text{ KJ}$$

$$\Delta S: \Delta S = nF(\delta E / \delta T)_P$$

$$= 2 \times 96,500 \times (-0.00004) = -7.72 \text{JK}^{-1}$$

2. The emf of the cell  $\text{Cd}|\text{CdCl}_2, 2.5 \text{ H}_2\text{O (saturated)}||\text{AgCl(s)}|\text{Ag}$  is 0.6753V and 0.6915 V at 298 K and 273 K respectively. Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of the cell reaction at 298 K.

**Solution.** Here  $n = 2$ ,  $E = 0.6753 \text{ V}$  at 298 K and 0.6915 at 273 K.

$$\therefore (\delta E / \delta T)_P = (0.6753-0.6915) \text{ V} / (298-273) \text{ K} = -0.00065 \text{ V/K}$$

$$\text{Now at 298 K, } \Delta H = nF [ T (\delta E / \delta T)_P - E]$$

$$= 2 \text{ mol} \times 96,500 \text{ C mol}^{-1} \{ [298 \text{ K} \times (-0.00065 \text{ V/K})] - 0.6753 \text{ V} \} \\ = -167.7 \text{ KJ}$$

$$\Delta G \text{ at 298 K ; } \Delta G = -nFE = -2 \times 96,500 \times 0.6753 = -130.33 \text{ KJ}$$

$$\Delta S = nF(\delta E / \delta T)_P$$

$$= 2 \times 96,500 \times (-0.00065) = -125.45 \text{ J.K}^{-1}$$

### 1.3 SINGLE ELECTRODE POTENTIAL

The potential of the single electrode is the difference of potential between a metal and the solution of its salt. i.e the tendency of an electrode to lose or gain electrons when in contact with its own ions in the solution. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and acts as an anode. The electrode with higher electrode potential has a higher tendency to undergo reduction and acts as a cathode.

Example: In case of Zn in  $\text{ZnSO}_4$  solution acquires a negative charge (Fig. 1.3a).

$\text{M(s)} \rightarrow \text{M}^{n+} + n\text{e}^-(\text{aq})$  (1) Dissolution reaction and conversely, the metal shows the tendency to go into the solution as metal ion by losing electrons (Fig. 1.3b).

$\text{M}^{n+}(\text{aq}) + n\text{e}^-(\text{aq}) \rightarrow \text{M(s)}$  (2) Deposition reaction

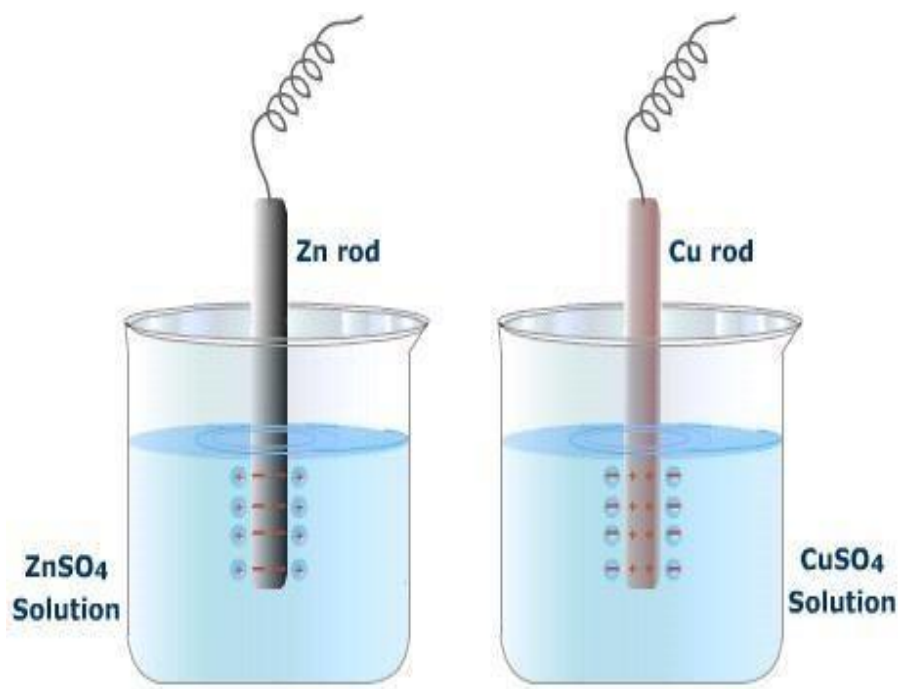


Fig.1.3a. Zinc ions move into solution leaving behind electrons making it electron rich

Fig.1.3b. Copper ions get deposited as copper leaving behind free negatively charged sulfate ions in solution makes the electrode electron poor

The rate of this reaction depends on,

- (i) The nature of the metal
- (ii) The temperature
- (iii) The concentration of metal ions in solution.

When a metal is placed in the solution of its own salt, the chemical reaction (1) or (2), takes place depending on whether the dissolution reactions are faster than deposition or vice versa.

A dynamic equilibrium is established, because negative or positive charge developed on the metal attracts the positively or negatively charged free ions in the solution. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a short layer of positive ions or negative ions as in the figure is formed at the junction of the electrode and the solution. This layer is called a Helmholtz electrical double layer. A difference of potential is consequently, set up

between the metal and the solution. This potential difference will persist as long as the charge is allowed to remain on the metal and this will prevent any further passing of the positive ions from or to the metal. At equilibrium the potential difference between the metal & solution becomes a constant value. The equilibrium potential difference so established is called the “electrode potential” of the metal. Thus, the electrode potential of a metal is the measure of the tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 298K. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized & this tendency, is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as reduction potential. By convention, electrode potential refers to reduction potential.

### 1.3.1 Measurement of electrode potential

It is impossible to determine the absolute half cell potential. We can only measure the difference in potential between two electrodes potentiometrically, by combining them to form a complete cell. All voltage measuring devices determine differences in potential. If one knob of voltmeter is connected to a test electrode, another one will make contact with the solution in the electrode compartment via another conductor. This second contact involves solid/ solution interface and acts as a second half cell. The redox reaction must take place if the charge is to flow and potential is to be measured. A potential is associated with this second reaction and absolute half cell potential is not obtained. What we measure ultimately is the difference between the half cell potential of test electrode and a half cell made up of the second contact and the solution. Therefore, absolute electrode potentials cannot be measured. We can only determine the relative value of electrode potential, if we can fix arbitrarily the potential of any one electrode. For this purpose, the potential of a standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) (i.e., a platinum electrode in contact with 1 M  $\text{H}^+$  ion concentration and hydrogen gas at 1 atmospheric pressure is constantly bubbled through it) has been arbitrarily fixed as zero and the numerical values of electrode potentials of different electrodes are relative values w.r.t SHE. Therefore, single electrode potentials of electrodes are referred to as potentials on the hydrogen scale.

**Sign of electrode potential:** When an electrode is coupled with a SHE, if reduction occurs then EP is given a +ve sign e.g Copper electrode + SHE

- $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$  reduction at copper electrode (cathode)
- $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+ + 2\text{e}^-$  oxidation at hydrogen electrode (anode)  $\rightarrow E^0 = 0.34 \text{ volt}$

A +ve sign on the EP value indicates that the half cell acts as cathode and accepts electrons from the hydrogen electrode.

Similarly, when an electrode is coupled with SHE, if oxidation occurs then EP is given a -ve sign

e.g . Zinc electrode + SHE

- $\text{Zn (s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$  (oxidation at Zinc electrode)
- $2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$  (reduction at Hydrogen electrode)  $\rightarrow E^0 = - 0.76 \text{ volt}$

A –ve sign on the electrode potential value indicates that the half cell acts as an anode by releasing electrons to the hydrogen electrode.

### 1.3.2 Standard electrode potential:

Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration at 298 K involving pure solids and liquids. If the electrode involves a gas, then the gas is at 1 atmospheric pressure. It is denoted by  $E^0$ . When elements are arranged in increasing order (downwards) of their standard electrode potential, a series called electrochemical series is obtained. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and it acts as anode similarly electrode with higher electrode potential has higher tendency to undergo reduction and acts as cathode.

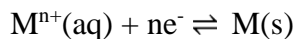
Reducing agents	Stable ions	Electrode half reaction $E^0$ volts
Lithium	$\text{Li}^+$	-3.03
Potassium	$\text{K}^+$	-2.92
Aluminium	$\text{Al}^{3+}$	-1.66
Zinc	$\text{Zn}^{2+}$	-0.76
Iron	$\text{Fe}^{3+}$	-0.44
Lead	$\text{Pb}^{2+}$	-0.13
$\text{H}_2$	$2\text{H}^+$	0
Copper	$\text{Cu}^{2+}$	0.34
Silver	$\text{Ag}^+$	0.80
Gold	$\text{Au}^{3+}$	1.52



Fig. 1.3.2. Selected standard electrode potentials

### 1.3.3 Nernst equation

Nernst equation is an expression of a quantitative relationship between electrode potential/cell potential and concentration of the electrolyte species in an electro-chemical reaction. i.e. mathematical expression that relates the potential of an electrode to the concentrations of those species in solution that are responsible for the potential. Consider a general redox reaction:



$$E = E^{\circ} + 2.303RT/nF \log [M^{n+}]$$

E= Electrode potential at some moment in time

$E^{\circ}$ = Standard electrode potential

R= Universal gas constant (joules per mol per K)

T= Temperature in Kelvin scale F= Faraday constant (96,500 Coulombs)

n = Number of electrons transferred in the half reaction/ cell reactions

$[M^{n+}]$ = Concentration of metal ion at that moment in time (moles per litre).

At 298 K, when the values of R.T and F are substituted, the equation reduces to,

$$E = E^{\circ} + (0.0592/n) \log [M^{n+}]$$

This expression is known as the Nernst equation for electrode potential at 298 K. From these equations, it is clear that,

- i) If the concentration of the solution ( $M^{n+}$ ) is increased, the electrode potential increases and vice versa.
- ii) If the temperature is increased, the electrode potential increases and vice versa.

The Nernst equation can also be applied for the calculation of emf of a cell. Consider the cell reaction  $aA + bB \rightleftharpoons cC + dD$

The Nernst equation for the emf of the cell is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - 2.303RT/nF \log [C]^c [D]^d / [A]^a [B]^b$$

At 298 K,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n) \log [C]^c [D]^d / [A]^a [B]^b$$

Where n is the number of electrons transferred during the cell reaction and  $E^\circ_{\text{cell}}$  is the standard emf of the cell.

### 1.3.3.1 Significance of the Nernst equation

1. It can be used to calculate the potential of a cell that operates under non-standard conditions. The Nernst equation tells us that a half cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in one-electron oxidation or reduction. For two electron processes, the variation will be 28 millivolts per ten fold concentration change. Thus for the dissolution of metallic copper



the potential  $E = (-0.337) - .0295 \log [\text{Cu}^{2+}]$  becomes more positive (the reaction has a greater tendency to take place) as the cupric ion concentration decreases.

2. It can be used to measure the equilibrium constant for a reaction. At equilibrium the overall cell potential for the reaction is zero. i.e.  $E=0$

Nernst equation,

$$0 = E^\circ - \frac{RT}{nF} \ln K_c$$

$$K_c = e^{nFE^\circ / RT}$$

## 1.4 Calomel electrode

The calomel electrode (Fig.1.4.1), a mercury mercurous chloride electrode develops + 0.242 V at 289 K when the KCl solution is saturated. It has been found that the potential of the calomel electrode, on the hydrogen scale varies with the concentration of the potassium chloride solution used. The concentration of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode respectively.

### 1.4.1 Construction & Working:

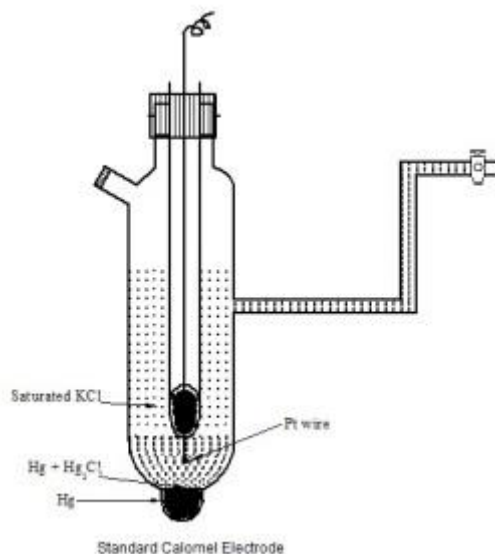
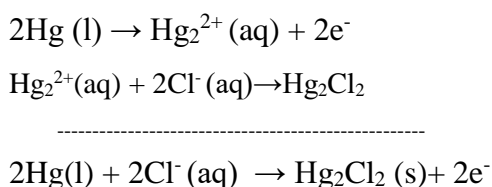


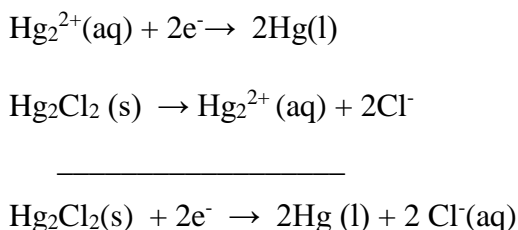
Fig.1.4.1 Schematic diagram of calomel electrode.

It consists of a tube, in the bottom of which is a layer of mercury, over which is placed a paste of mercury and mercury chloride. The remaining portion of the cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire sealed at its end fixed into the main tube dipping into the mercury layer is used for making electrical contact. The electrode can be represented as  $\text{Hg(l)}/\text{Hg}_2\text{Cl}_2(\text{sat'd})/\text{KCl}^-(\text{sat'd}/x\text{M})$

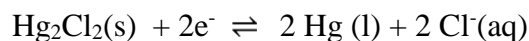
The calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell. When it acts anode, the electrode reaction is



When it acts as cathode, the electrode reaction is,



The net reversible electrode reaction is,



Electrode potential is given by

$$E = E^\circ - \frac{2.303 RT}{2F} \log [\text{Cl}^-]^2$$

$$= E^\circ - 0.0591 \log [\text{Cl}^-] \text{ at } 298 \text{ K}$$

#### 1.4.2 Uses:

Since the electrode potential is a constant it can be used as a secondary reference electrode to replace the inconvenient SHE for potential measurements.

i) To determine the electrode potential of the unknown electrode

**For example:** The test electrode,  $\text{Zn}_{(\text{s})} / \text{Zn}^{2+}_{(\text{aq})}$  is coupled with a saturated calomel electrode.



The emf of the so formed cell is determined experimentally by potentiometric method.

Then

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.2444 - E_{\text{Zn}}$$

$$E_{\text{Zn}} = 0.2444 - E_{\text{cell}}$$

ii) To determine the pH of a solution cell:  $\text{Hg}(\text{l}) / \text{Hg}_2\text{Cl}_2 (\text{s}) // \text{H}^+ / \text{pt}, \text{H}_2 (\text{g})$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 0.242 - (-0.0592 \text{ pH})$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.242}{0.0592}$$

#### 1.4.3 Advantages

- It is very simple to construct.
- It can be used for a long time without much attention.
- Electrode potential is stable over a long period (reproducibly).
- It has the low temperature coefficient of emf.
- It is less prone to contamination because the mercury/ mercurous chloride interface is protected inside a tube not in direct contact with the electrolyte.

#### 1.4.4 Disadvantages

- Calomel electrodes should not be used above 50°C because the mercurous chloride breaks down, yielding unstable readings. This is important if substantial temperature changes occur during measurement.
- Calomel electrode should be used with proper precaution as mercury compounds are toxic.

### 1.5 Ion Selective Electrode.

The electrode which is sensitive to a specific ion present in an electrolyte whose potential depends upon the activity of a specific ion in the electrolyte is called an ion selective electrode. The magnitude of the potential of this electrode is an indicator of the activity of the specific ion in the electrolyte. Example for this type of electrode is glass electrode.

#### 1.5.1 Glass electrode: Construction

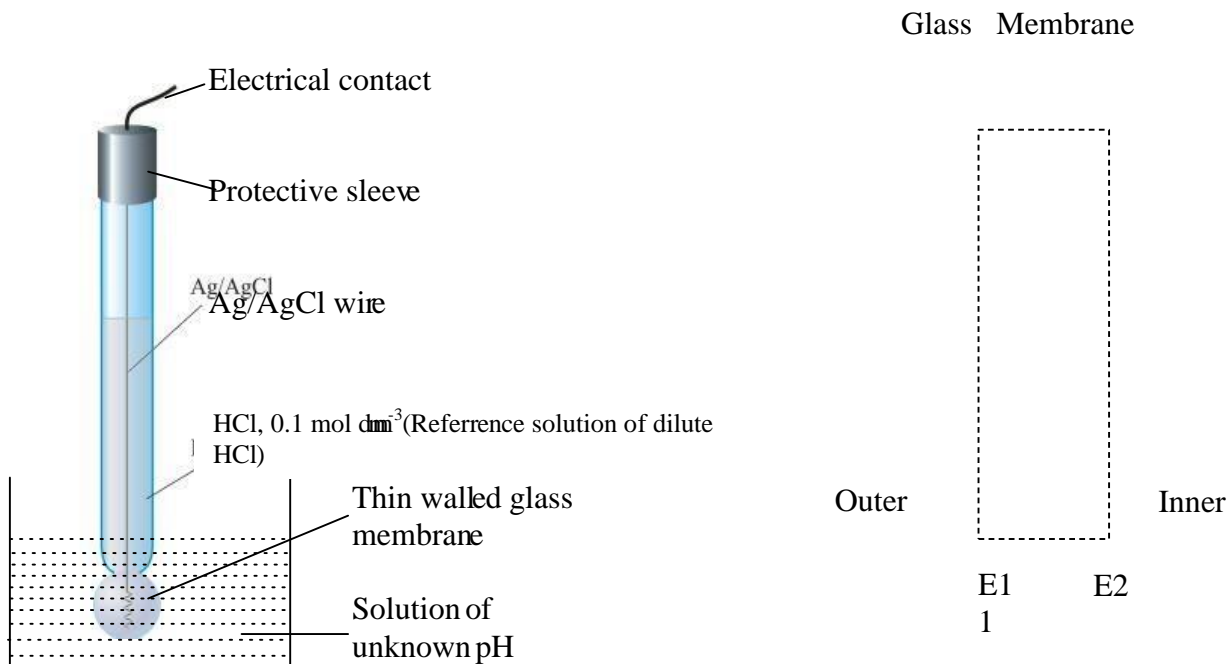


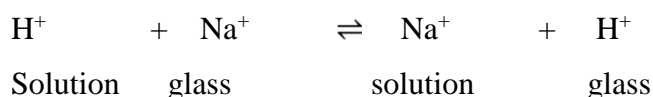
Fig.1.5.1a. Schematic diagram of the Glass electrode

Fig. 1.5.1b. Line sketch of a glass membrane showing outer analyte solution and internal reference solution.

The electrode consists of a thin glass membrane, typically about 0.03 to 0.1 mm thick, sealed onto one end of a heavy-walled glass tube. A special variety of glass (corning 015 glass with

approximate composition 20 % Na<sub>2</sub>O, 6 % CaO & 72 % SiO<sub>2</sub>) is used which has a low melting point and high electrical resistance. The glass bulb is filled with a solution of constant pH (0.1 M HCl). A small volume of saturated silver chloride is contained in the tube. A silver wire in this solution forms a silver/silver chloride reference electrode which is connected to one of the terminals of a potential measuring device. The internal reference electrode is a part of the glass electrode and it is not the pH sensing element. Only the potential that occurs between the outer surface of the glass bulb and the test solution responds to pH changes.

**1.5.2 Working:** A silicate glass used for membranes consists of an infinite 3D- network of SiO<sub>4</sub><sup>4-</sup> groups in which each silicon is bonded to four oxygen and each oxygen is shared by two silicons. There are sufficient cations to balance the negative charge of the silicate groups within the interstices of this structure. Singly charged cations such as sodium and lithium are mobile in the lattice and are responsible for electrical conduction within the membrane. The glass is a partially hydrated aluminosilicate containing sodium or calcium ions. The hydration of a pH sensitive glass membrane involves an ion-exchange reaction between singly charged cations in the interstices of the glass lattice and protons from the solution. The process involves univalent cations exclusively because divalent cations are too strongly held within the silicate structure to exchange with ions in the solution and hence immobile. The ion-exchange reaction can be written as



The Na<sup>+</sup> ions on the glass membrane are exchanged for H<sup>+</sup> ions in the solution. The potential of the electrode is controlled by the difference between the hydrogen ion concentration inside and outside the thin glass membrane. Since the H<sup>+</sup> ion concentration inside the electrode is constant, the electrode's potential varies only with the concentration of H<sup>+</sup> in the solution outside. Thus the potential arises from the difference in positions of ion-exchange equilibrium on each of the two surfaces. The surface exposed to the solution having the higher H<sup>+</sup> concentration becomes positive with respect to the other surface. This charge difference or potential serves as the analytical parameter when the pH of the solution on one side of the membrane is held constant. Evidently the selectivity of glass electrodes is related both to the ability of the various monovalent cations to penetrate into the glass membrane and to the degree of attraction of the cations to the negative sites within the glass.

### 1.5.3 Electrode Potential of GE

The overall potential of the glass electrode has three components- 1) The boundary potential  $E_b$ , which varies with the pH of the analyte solution. It is made up of two potentials,  $E_1$  &  $E_2$  which develop at the two surface of the glass membrane i.e. the potential developed at the inner glass surface & the potential developed at the outer glass surface.

$$E_b = E_1 - E_2 \quad (1)$$

Where  $E_b$  is the boundary potential

$E_1$  = potential developed at the interface between the exterior of the glass and the analyte solution

$E_2$  = Potential developed at the interface between the internal solution and the interior of the glass. The boundary potential is related to the concentration of hydrogen ion in each of the solution by the Nernst-like equation.

$$E_b = E_1 - E_2 = 0.0592 \log C_1 / C_2 \quad (2)$$

Where  $C_1$  = concentration of the analyte solution

$C_2$  = concentration of the internal solution

For a glass pH electrode the hydrogen ion concentration of the internal solution is held constant.

i) So eqn. (2) becomes

$$E_b = K + 0.0592 \log C_1 \quad (3) \quad (\text{Recall } \text{pH} = -\log [\text{H}^+])$$

$$E_b = K - 0.0592 \log \text{pH} \text{ where } K = -0.0592 \log C_2$$

The boundary potential is then a measure of

- 1) The hydrogen ion concentration of the external solution.
- 2) The potential of the internal Ag/AgCl reference electrode.  $E_{\text{Ag/AgCl}}$ .
- 3) A small unpredictable contribution called the asymmetry potential,  $E_{\text{asym}}$ .

The sources of the asymmetry potential include the following.

- i) Differing conditions of strain in the two glass surfaces during manufacture
- ii) Mechanical abrasion on the on the outer surface during use

iii) Chemical etching of the outer surface during use.

The asymmetry potential changes slowly with time. The glass electrode potential can be written in the equation form as

$$E_G = E_b + E_{\text{Ag/AgCl}} + E_{\text{asym}} \quad (4)$$

Substitution of eqn – (3) for  $E_b$ , gives

$$E_G = K + 0.0592 \log C_1 + E_{\text{Ag/AgCl}} + E_{\text{asym}}$$

$$= K - 0.0592 \log \text{pH} + E_{\text{Ag/AgCl}} + E_{\text{asym}} \quad (5)$$

$$E_G = E_G^\circ - 0.0592 \text{pH} \quad (6)$$

where  $E_G^\circ = K + E_{\text{Ag/AgCl}} + E_{\text{asym}}$ . a combination of three constant terms = constant. To measure the hydrogen ion concentration of the test solution, the glass electrode (indicator electrode) must be combined with an external reference electrode, which is required for all kinds of ion-selective electrode determinations.

#### 1.5.4 Applications: Determination of pH:

The glass electrode has an emf that changes with hydrogen ion concentration, i.e the glass electrode is the most important indicator electrode for hydrogen ion. It is used for the measurement of pH under many conditions and normally calomel electrode is used as reference electrode to complete the cell (Fig.1.4.4)

Cell: SCE / Test solution / GE

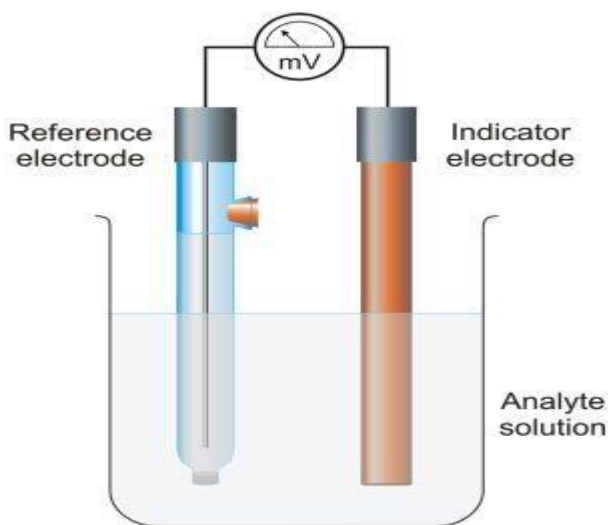


Fig.1.4.4. Set up of indicator electrode and reference electrode for the measurement of pH.



$E_{\text{cell}} = E_{\text{glass}} - E_{\text{calomel}}$  where  $E_{\text{glass}}$  = The E.P. of the glass electrode.

$E_{\text{calomel}}$  = the E.P. of the SCE

$$E_{\text{cell}} = E^{\circ}_{\text{G}} - 0.0592 \text{ pH} - 0.2444$$

The  $E^{\circ}_{\text{G}}$  value of a glass electrode can be determined by dipping the glass electrode in a solution of known pH. Typical fields are the clinical & food analysis, environmental monitoring (industrial waste acidity of rain) and process control (fermentation, boiler water, galvanization & precipitation)

#### 1.5.5 Advantages:

- It can be used without interference in solutions containing strong oxidants, strong reductants, proteins, viscous fluids and gases as the glass is chemically robust.
- The glass electrode gives accurate results in the pH range 2 – 10. With some special glass (by incorporation of  $\text{Al}_2\text{O}_3$  or  $\text{B}_2\text{O}_3$ ) measurements can be extended to pH values up to 12.
- It is immune to poisoning and is simple, robust and easy to operate.
- The equilibrium is reached quickly & the response is rapid.
- It can be used for very small quantities of the solutions. Small electrodes can be used for pH measurement in one drop of solution in a tooth cavity or in the sweat of the skin (micro determinations using microelectrodes)
- The glass electrode is much more convenient to handle than the inconvenient hydrogen gas electrode.
- Glass electrodes which are selective for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$  and  $\text{NH}_4^+$  ions are commercially available and these special electrodes are useful for measuring the above ions.

#### 1.5.6. Disadvantages:

- The bulb of this electrode is very fragile and has to be used with great care. The sensitive tip is easily scratched and ruined.
- The alkaline error arises when a glass electrode is employed to measure the pH of solutions having pH values in the 10-12 range or greater. In the presence of alkali ions, the glass

surface becomes responsive to both hydrogen and alkali ions. Hence the measured pH values are low and thus the glass pH electrode gives erroneous results in highly alkaline solutions.

- The acid error results in highly acidic solutions (pH less than zero) Measured pH values are high.
- Dehydration of the working surface may cause erratic electrode performance. It is crucial that the pH electrode be sufficiently hydrated before being used. When not in use, the electrode should be stored in an aqueous solution because once it is dehydrated, several hours are required to rehydrate it fully.
- As the glass membrane has a very high electrical resistance (50 to 500 M $\Omega$ ), the ordinary potentiometer cannot be used for measurement of the potential of the glass electrode. Thus special electronic potentiometers are used which require practically no current for their operation.
- Standardization has to be carried out frequently because asymmetry potential changes gradually with time. It is better to determine  $E^\circ_G$  for a glass electrode before use.
- The commercial version is moderately expensive.
- To some extent, the constant  $E^\circ_G$  is a function of the area of glass in contact with the acid analyte. For this reason, no two glass electrodes will have the same value of  $E^\circ_G$ . Note that  $E^\circ_G$  depends on a particular glass electrode used & it is not a universal constant.