

MODULE-1

ELECTROCHEMISTRY AND ANALYTICAL TECHNIQUES **CONTENTS**

Introduction, electrochemical cells – Definition, Types of electrochemical cells, Construction, working & representation of galvanic cell. Modern sign conventions, single electrode potential, standard electrode potential. E.M.F of a cell, derivation of Nernst Equation.

Concentration cell- Definition with example, derivation of emf of concentration cell. Types of electrodes. Secondary reference electrodes –calomel electrode, ion selective electrodes- glass electrode. Determination of pH of a solution using glass electrode. Potentiometric estimation of FAS using $K_2Cr_2O_7$ solution. Numerical problems on E , E^0 , E_{cell} , E^0_{cell} and concentration cells.

Analytical techniques: Introduction, principle and instrumentation: Colorimetric sensors–estimation of copper, Potentiometric sensors – estimation of iron and Conductometric sensors –estimation of weak acid.

10 hours

ELECTROCHEMISTRY

Electro-chemistry is a branch of science, which deals with conversion of chemical energy into electrical energy and vice-versa.

Electro chemical cell

An electro chemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy.

Classification: Electrochemical cells can be classified into 2 types. They are-

- (1). Galvanic cells or voltaic cells (converts chemical energy into electrical energy).
- (2). Electrolytic cells (Converts electrical energy into chemical energy).

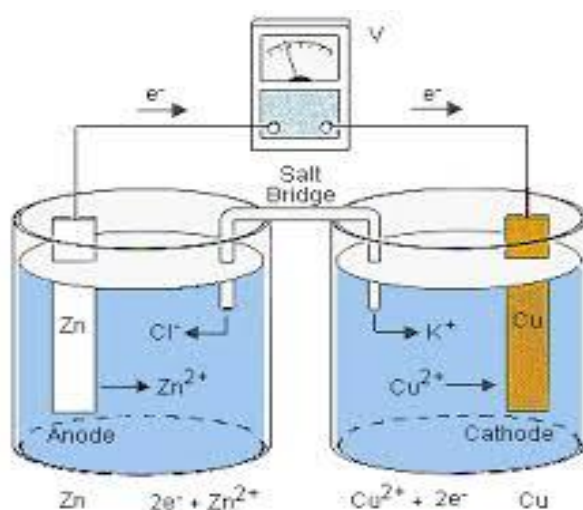
A galvanic cell is a device which converts chemical energy into electrical energy.

Electrolytic cell is a device which converts electrical energy into chemical energy.

Galvanic cells or Voltaic cells

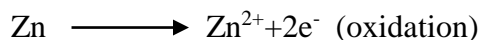
Galvanic cell generally consists of two electrodes dipped in two electrolyte solution which are connected through a salt bridge.

Example: Daniel cell

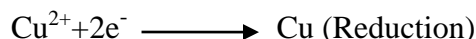


Daniel cell consists of Zn electrode dipped in ZnSO_4 solution and Cu electrode dipped in CuSO_4 solution. The two solutions are connected by a salt bridge. The salt bridge is a U-tube filled with saturated solution of KCl or NH_4NO_3 and it provides a passage of ions from one half cell to another without mixing of two solutions. When Zn and Cu electrodes are connected externally through an ammeter by using a wire, the following reactions are observed.

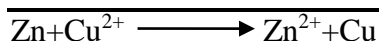
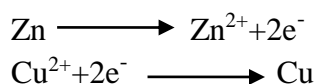
At anode zinc passes into the solution (dissolution) as Zn^{2+} ion and liberating 2 electrons.



At cathode Cu^{2+} ions gain electron and reduce to metallic copper (deposition), which is deposited at the copper electrode.



The overall chemical reaction may thus be represented by,



Representation of galvanic cell



In the construction of galvanic cell the electrode with high reduction potential acts as cathode ($\text{Cu} = +0.34\text{V}$) and electrode with low reduction potential acts as anode ($\text{Zn} = -0.76\text{V}$).

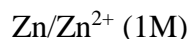
Cell notation and conventions

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

- 1) Anode is written on left hand side, while cathode is written on the right-hand side.
- 2) The anode is written by writing the metal first (or solid phase) and then the electrolyte. The two are separated by vertical line. The electrolyte may be represented by the formula of the whole compound or by the ionic species and concentration may also be mentioned in bracket.

Example: $\text{Zn}_{(\text{s})}/\text{ZnSO}_{4(\text{solution})} \text{ 1M}$

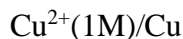
OR



- 3) The cathode of the cell is written on the right-hand side. In this case the electrolyte is represented first and the metal (or solid phase) thereafter. The two are separated by a vertical line.

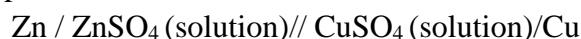
Example: $\text{CuSO}_{4(\text{solution})} 1\text{M}/\text{Cu}(\text{s})$

Or



- 4) A salt bridge is indicated by two vertical lines separating the two half cells.

Example: Daniel cell is represented as,



OR



- 5) EMF of the cell is calculated using the equation

$$E_{\text{cell}} = E_{\text{RHSE}} - E_{\text{LHSE}}$$

$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

Or

$$\text{Standard emf} = E^0_{\text{Cell}} = E^0_{(\text{cathode})} - E^0_{(\text{anode})}$$

Problems:

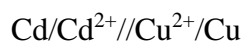
- 1) Give the representation of a standard cadmium copper cell, write the electrode and cell reactions and calculate standard emf of the cell. If standard electrode potentials of cadmium and copper are -0.4 and +0.34 V respectively.

$$\text{Ans: } E^0_{\text{cd}} = -0.4\text{V}$$

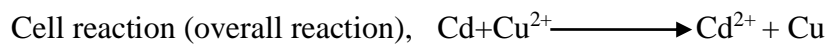
$$E^0_{\text{cu}} = 0.34$$

$E^0_{\text{cd}} < E^0_{\text{cu}}$. Therefore cadmium acts as anode and copper acts as cathode.

Cell representation:-



Electrode reactions:



Standard emf of cell,

$$E^0_{\text{Cell}} = E^0_{\text{cathode}} - E^0_{\text{Anode}}$$

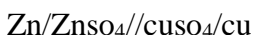
$$= E^0_{\text{cu}} - E^0_{\text{cd}}$$

$$= 0.34 - (-0.4)$$

$$= 0.34 + 0.4$$

$$E^0_{\text{Cell}} = 0.74 \text{ V}$$

- 2) Calculate the standard emf of the following cell at 25°C, writing its half cell reaction and net cell reaction.



Standard potential of copper and zinc electrodes are +0.34 and -0.76 volts respectively.

Answer: 1.1v

Single electrode potential (E): The tendency of a electrode to **lose or gain** electrons when it is in contact with its own ions is called electrode potential or single electrode potential and it is denoted by 'E'.

Standard electrode potential (E⁰): Standard electrode potential is the electrode potential when it is in contact with a solution of **unit concentration at 298 K (25°C) and 1atms.pressure**. It is denoted by E⁰.

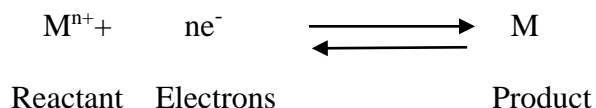
Electromotive force (EMF) of a cell (E_{cell}): The difference of potential, which causes a current to flow from the electrode of higher potential to another of lower potential is called the electromotive force (emf) of the cell and is expressed in volts. It is denoted by E_{cell}.

Standard emf (E⁰_{cell}): Standard emf of a cell is defined as the emf of a cell obtained when it is in contact with unit concentration at 298 K and at 1 atmospheric pressure and is denoted by E⁰_{cell}.

Nernst Equation

Derivation of Nernst equation:

Consider an electrode metal M dipped in its own ions Mⁿ⁺, the reversible redox electrode reaction is



The change in free energy of the electrode reaction is related to the electrode potential as follows

$$\Delta G = nFE$$

$$\text{Or } \Delta G = -nFE$$

In its standard state,

$$\Delta G^\circ = -nFE^\circ$$

Where ΔG° is known as the standard free energy change, E° is the standard electrode potential, F is the faraday constant and n is the no. of electrons involved in the electrode reaction.

For a spontaneous reaction (reversible reaction), the change in free energy, ΔG and its equilibrium constant K, are interrelated as,

$$\Delta G = \Delta G^\circ + RT \ln K_c$$

Where R= gas constant and T= absolute temperature

$$\text{Since } K_c = \frac{[product]}{[reactant]}$$

Therefore,

$$\Delta G = \Delta G^\circ + RT \ln \frac{[product]}{[reactant]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

Substitute -nFE for ΔG and - nFE° for ΔG°

$$\therefore -nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nFE^\circ + RT \ln [M] - RT \ln [M^{n+}]$$

$$-nFE = -nFE^\circ + RT \{ \ln [M] - \ln [M^{n+}] \}$$

Since, the concentration of the metal is unity under standard conditions i.e. [M] = 1

$$-nFE = -nFE^\circ + RT \{ 0 - \ln [M^{n+}] \}$$

$$-nFE = -nFE^\circ - RT \ln [M^{n+}]$$

Divide through by -nF

$$-\frac{nFE}{-nF} = -\frac{nFE^\circ}{-nF} - \frac{RT}{-nF} \ln [M^{n+}]$$

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

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

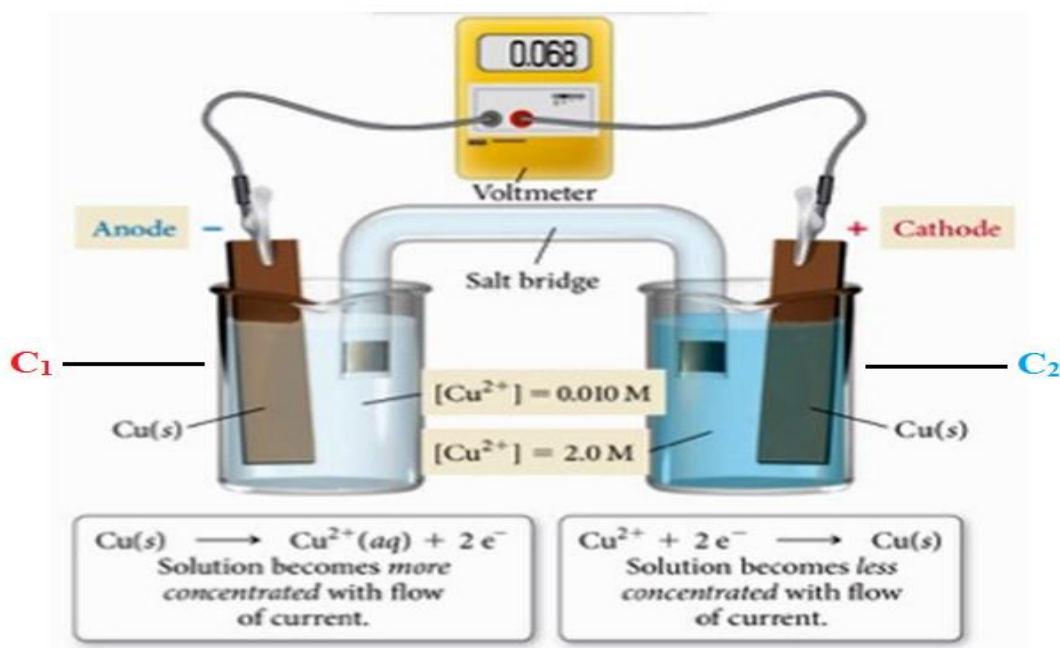
$$E = E^\circ + \frac{0.0591 \log [M^{n+}]}{n}$$

This equation is known as the Nernst equation for electrode potential.

Concentration cells: Cell consists of two electrodes made of same metal dipped in same ionic solutions of the metal of different concentrations.

These are the cells, which consists of two electrodes made of same metal dipped in same ionic solutions of the metal of different concentrations. The two solutions are in contact through a salt bridge. Because of difference in concentration of two solutions, a potential is developed.

Ex: Two Cu electrodes are dipped in CuSO₄ solution of different concentrations 0.01 M (C₁) and 2M (C₂).



High concentration act as a **cathode** and **lower** concentration act as **anode**

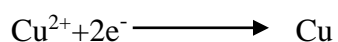
The cell is represented as,

$\text{Cu}/\text{Cu}^{2+}_{(C_1)}//\text{Cu}^{2+}_{(C_2)}/\text{Cu}$ [where c_1 and c_2 are the concentrations of metal ions (Mn^+) in contact with two electrode and $c_2 > c_1$]

At anode Cu gets converted into Cu^{2+} ions and goes in to the solution liberating 2 electrons (oxidation taken place).



At cathode Cu^{2+} ions deposited as copper metal.



The emf of the cell is given by,

$$E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}} \quad (\text{Or}) \quad (E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}).$$

$$E_{\text{Cathode}} = E^{\circ}_{\text{Zn}} + \frac{2.303RT \log[C_2]}{nF}$$

$$E_{\text{Anode}} = E^{\circ}_{\text{Zn}} + \frac{2.303RT \log[C_1]}{nF}$$

$$E_{\text{Cell}} = (E^{\circ}_{\text{Zn}} + \frac{2.303RT \log[C_2]}{nF}) - (E^{\circ}_{\text{Zn}} + \frac{2.303RT \log[C_1]}{nF})$$

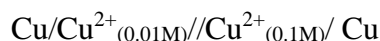
$$E_{\text{Cell}} = \frac{2.303RT}{nF} (\log [C_2] - \log [C_1])$$

$$E_{\text{Cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

PROBLEMS

(1). Two copper rods are placed in CuSO_4 solution of concentration 0.1M & 0.01M separately in the form of a cell. Write the scheme of the cell and calculate its emf at 298⁰K.

Answer: Cell representation,



$$E_{\text{Cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \quad [(c_2 > c_1)]$$

$$= \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

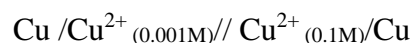
$$= 0.02955 \log 10$$

$$= 0.02955 \times 1$$

$$E_{\text{Cell}} = \mathbf{0.02955V}$$

(2). A concentration cell is constructed by dipping Cu rod in 0.001M & 0.1M CuSO_4 solution. Calculate the emf of the cell at 298⁰K.

Answer: Cell representation,



$$E_{\text{Cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

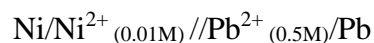
$$= \frac{0.0591}{2} \log \frac{0.1}{0.001}$$

$$= \frac{0.0591}{2} \log 100$$

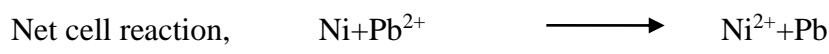
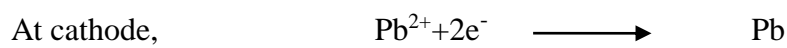
$$\mathbf{E_{Cell} = 0.0591V}$$

(3). A cell is formed by dipping Nickel rod in 0.01M Ni²⁺ solution and lead rod in 0.5M Pb²⁺ solution. The standard electrode potentials of Ni & Pb are -0.24V & -0.13V respectively. Write the cell representation, cell reaction & calculate the emf of the cell.

Answer: Cell representation,



Cell reaction,



$$E^0_{\text{Cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}}$$

$$= E^0_{\text{Pb}^{2+}/\text{Pb}} - E^0_{\text{Ni}/\text{Ni}^{2+}}$$

$$= -0.13 - (-0.24)$$

$$\mathbf{E^0_{Cell} = 0.11V}$$

$$E^0_{\text{Cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{concentration at cathode}]}{[\text{concentration at anode}]}$$

$$= E^0_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Ni}^{2+}]}$$

$$= 0.11 + \frac{0.0591}{2} \log \frac{[0.5]}{[0.01]}$$

$$= 0.11 + 0.02955 \log 50$$

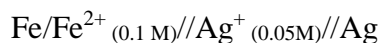
$$= 0.11 + 0.02955 \times 1.6989$$

$$= 0.11 + 0.0502$$

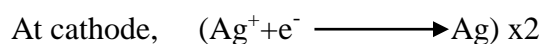
$$\mathbf{E_{Cell} = 0.1602V}$$

(4). An electro chemical cell consists of iron electrode dipped in 0.1 M FeSO₄ & silver electrode dipped in 0.05 M AgNO₃. Write the cell representation, cell reaction & calculate emf of the cell at 298K. Given that the standard reduction potential of iron & silver electrodes are -0.44 & +0.80V respectively.

Answer: Cell representation,



Half-cell reaction,



$$E^0_{\text{Cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}}$$

$$= E^0_{\text{Ag}^+/\text{Ag}} - E^0_{\text{Fe}/\text{Fe}^{2+}}$$

$$= 0.80 - (-0.44)$$

$$E^0_{\text{Cell}} = 1.24 \text{ V}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} + \frac{0.0591}{n} \log \frac{[\text{concentration at cathode}]}{[\text{concentration at anode}]}$$

$$= 1.24 + \frac{0.0591}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]}$$

$$= 1.24 + 0.02955 \log \frac{[0.05]^2}{[0.1]}$$

$$= 1.24 + 0.02955 \log 0.025$$

$$= 1.24 - 0.0473$$

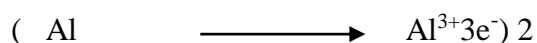
$$E_{\text{Cell}} = 1.1927 \text{ V}$$

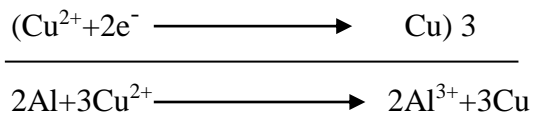
(5). Calculate the E_{Cell} , when Al & Cu electrodes are in contact with 0.02M Aluminium and 0.25M copper ions solutions respectively at 298 K. Write the cell representation & cell reactions. Given $E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ & $E^0_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$.

Cell representation



Reaction,





$$E_{\text{Cell}}^0 = E_{\text{Cu}}^0 - E_{\text{Al}}^0$$

$$= 0.34 - (-1.66)$$

$$= 2.0 \text{ V}$$

$$E_{\text{Cell}} = E_{\text{Cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{Al}^{3+}]^2}$$

$$= 2 + \frac{0.0591}{n} \log \frac{[0.25]^3}{[0.02]^2}$$

$$= \frac{0.0625}{0.0004} = 2.1938 = 0.00648$$

$$E_{\text{Cell}} = 2.0156 \text{ V}$$

Types of electrodes

Electrodes are mainly classified into four types, depending upon the purpose for which they are used.

- 1) Metal-Metal ion electrodes.
- 2) Metal-Metal salt ion electrode.
- 3) Gas electrode.
- 4) Ion selective electrode.

(1) **Metal-Metal ion electrode:** An electrode of this type consists of a metal dipped in a solution containing its own ions.

Example: Zn/Zn^{2+} , Cu/Cu^{2+} , Ag/Ag^+

(2) **Metal-Metal salt ion electrode:** These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution containing anion of the salt.

Example: Calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-$), Silver-Silver chloride electrode ($\text{Ag}/\text{AgCl}/\text{Cl}^-$)

(3) **Gas electrode:** These are the electrodes where gas will be in equilibrium with its ion present in an electrolyte.

Example: Hydrogen electrode ($\text{Pt}/\text{H}_2/\text{H}^+$), Chlorine electrode ($\text{Pt}/\text{Cl}_2/\text{Cl}^-$)

(4) **Ion selective electrode:** In an ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions.

Example: Glass electrode (exchange H^+ ions with the solution).

(These are the electrodes which are sensitive to particular ion species and will develop a potential, when a membrane is in contact with an ionic solution).

Reference electrodes

Reference electrodes have a fixed electrode potential. Using these electrode potentials, the potential of any electrode can be measured. The best reference electrode used in standard hydrogen electrode, whose electrode potential at all temperatures is taken as zero.

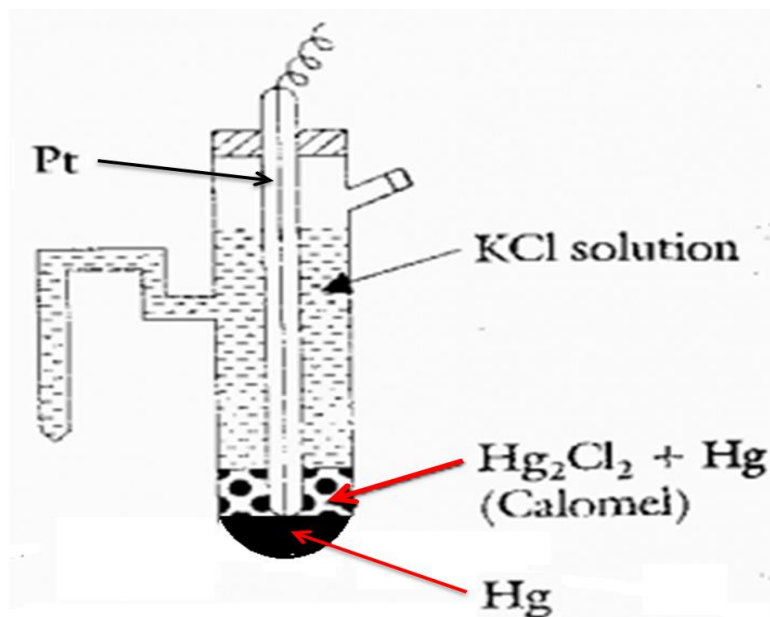
Classification of reference electrodes: Reference electrodes are classified into two types. They are,

- 1) Primary reference electrode Example: Hydrogen electrode.
(It is very difficult to set up because pure H_2 gas is required and production of pure H_2 gas is a problem, due to impurity it gets poisoned very quickly and also it is difficult to maintain H_2 gas uniformly at 1atmosphere).
- 1) Secondary reference electrode (Subsidiary reference electrode).
Example: Calomel electrode, Ag-AgCl etc.

Secondary reference electrode:

Because of the difficulties involved in the use of standard hydrogen electrode as reference electrode, some other electrodes of constant electrode potential are used they are called as secondary reference electrodes. The commonly used reference electrodes are calomel electrode and silver-silver chloride electrode.

Calomel electrode:



Mercury is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride with mercury and potassium chloride solution. A solution of KCl is introduced above the paste through the side tube. A platinum wire dipping into

the mercury layer and is used for making electrical contact. 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.

Calomel electrode can be represented as,

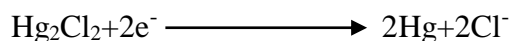


The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

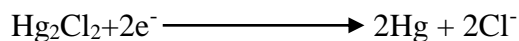
When it acts as anode, the electrode reaction is,



When it acts as cathode, the electrode reaction is,



Therefore, the net reversible electrode reaction is,



The electrode potential of calomel electrode depends upon the concentration of KCl solution used. The reduction potentials of various KCl concentrations at 25°C.

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

$$0.1\text{N KCl} = 0.334 \text{ V}$$

$$1\text{N KCl} = 0.281 \text{ V}$$

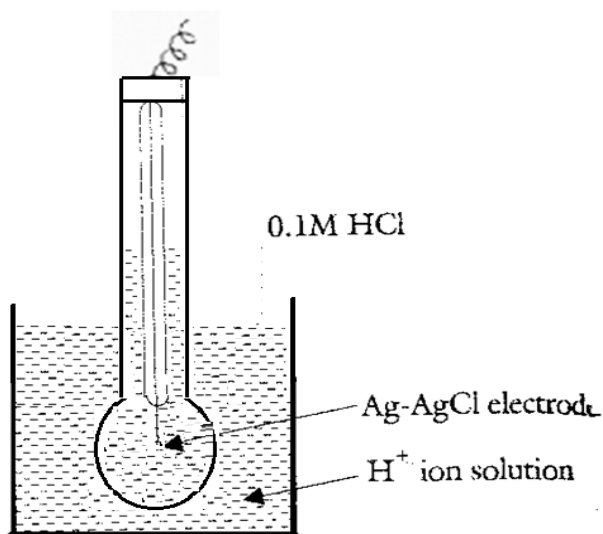
$$\text{Saturated KCl} = 0.2422 \text{ V}$$

Uses

1. Used as secondary reference electrode in the measurement of single electrode potential. It is commonly used as reference electrode in all potentiometric determinations.

Glass electrode

Glass electrode is a P^H sensitive electrode therefore it is widely used for P^H determination.



The glass electrode consists of a glass bulb made up a special type of glass with high electrical conductance. The glass bulb is filled with a solution of constant P^H (0.1 M HCl) and is inserted with Ag-AgCl electrode, which acts as internal reference electrode and also serves for the external electrical contact. The electrode is dipped in a solution containing H^+ ions (HCl in the bulb furnishes a constant H^+ ion concentration).

The glass electrode system can be represented as follows,

$Ag/AgCl_{(s)}/0.1M\ HCl/glass$

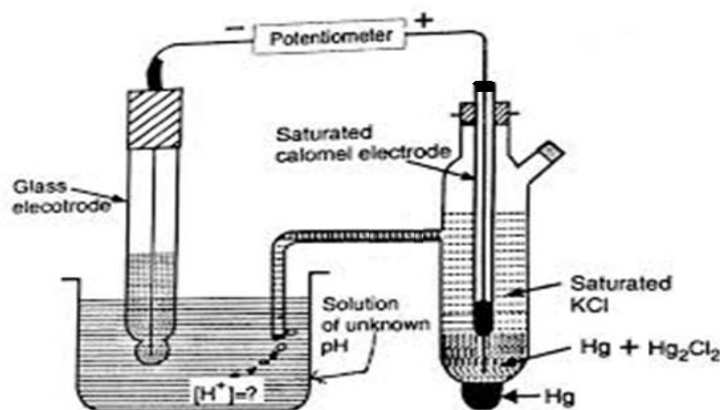
The potential of glass electrode depends upon the concentration of hydrogen ions present in the experimental solution. The expression which relates the glass electrode potential E_G with concentration of H^+ ions is,

$$E_G = E_G^0 + \frac{2.303RT}{F} \log [H^+] \quad (1)$$

Where E_G is standard glass electrode potential, The value of E_G^0 depends on the nature of glass used in the construction of the glass bulb.

The equation (1) can be written as, $E_G = E_G^0 + 0.0591 \log [H^+]$

$$E_G = E_G^0 - 0.0591 P^H$$

Determination of P^H of a solution using glass electrode**Glass electrode calomel electrode**

Cell representation

Glass electrode/solution of unknown pH // standard calomel electrode

Glass electrode is used as the working electrode for determining the P^H of solutions. Usually calomel electrode is used as the reference electrode. In order to determine the P^H of a solution, the glass electrode is placed in the experimental solution and this half-cell is coupling it with a saturated calomel electrode. The EMF of the cell is measured. Since the resistance is very high, so vacuum voltmeter is used to measure the EMF of the cell.

The emf of the cell is given by,

$$E_{\text{Cell}} = E_{\text{Calomel}} - E_{\text{Glass}}$$

$$= 0.2422 - [E_G^0 + \frac{2.303RT}{F} \log [H^+]] \quad [H^+ = 1]$$

$$= 0.2422 - [E_G^0 + 0.0591 \log [H^+]] \quad [n = 1]$$

$$= 0.2422 - [E_G^0 - 0.0591 P^H]$$

$$E_{\text{Cell}} = 0.2422 - E_G^0 + 0.0591 P^H$$

$$P^H = \frac{-0.2422 + E_{\text{Cell}} + E_G^0}{0.0591}$$

E_G^0 is the value of glass electrode can be determined by using a solution of unknown P^H.