UNIT-I: ELECTROCHEMISTRY (9)

Reference books:

- 1. Engineering chemistry by PC Jain & M Jain
- 2. Engineering chemistry by Sashi Chawla
- 3. Engineering chemistry by OG Palanna

Introduction, conductance, types of conductance- specific, equivalent, molar conductance and their interrelationship- numericals. Principle and applications of conductometric titrations- strong acid *vs* strong base, weak acid *vs* strong base and mixture of acids *vs* strong base.

Concept of electrode potential, Helmholtz electrical double layer theory, electro motive force (EMF). Electrochemical series – applications. Nernst equation-derivation, applications and numericals. Concentration cells- numericals.

Types of electrodes- construction and working of calomel electrode (CE), quinhydrone electrode and glass electrode (GE). Determination of pH using glass electrode and quinhydrone electrode. Applications of potentiometry- acid base and redox titration (Fe(II) Vs KMnO₄).

Electro chemistry.

Electrochemistry is a branch of physical chemistry which mainly deals with the relation between electrical energy and chemical energy or vice versa.

Based on the conductance property substances can be classified as

1. Conductors 2. Insulators 3. Semiconductors 4. Superconductors.

Types of conductors:

Conductors can be further classified in to two types based on physical state and charge carriers they are

Electronic conductors	Electrolytic conductors
1. These are solids	1. These are liquids or solutions
2. charge carriers are valance electrons	2. Charge carriers are mobile ions
3. There is no chemical change	3. There is chemical change
4. As the temperature increases conductance decreases	4. As the temperature increases conductance increases and viscosity decreases

Types of conductance:

Specific conductance:

Definition: Conductance offered by 1 c.c of an electrolyte solution.

Units: Siemen per centimeter (S / c.m.)

Resistance R, is proportional to the distance between the electrodes l, and is inversely proportional to the cross-sectional area of the electrodes A

Concept of electrode potential, Helmholtz electrical double layer theory, electro motive force (EMF).

Electrochemical series – applications.

Nernst equation-derivation, applications and numericals.

Concentration cells- numericals.

Types of cells:

Cell is a device which converts either chemical energy to electrical energy or vice-versa cells are **three types**. They are:-

- 1. Electrolytic cells
- 2. Galvanic or electrochemical voltaic cell
- 3.Fuel cells

Galvanic cell

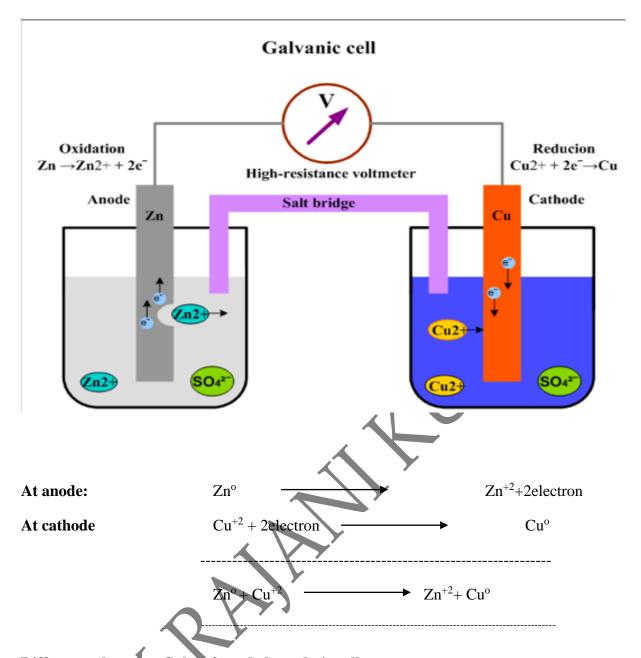
Cell consists of two electrodes namely anode and cathode i.e. each electrode can be considered as one half cell. Each electrode can be constructed by placing metal rod into its own solution or some other electrolyte solution. Connect both the half cells by open circuit through voltmeter which indicates the direction of flow of electrons when both the half cells are connected together, electrons can flow from anode (high electron density) to cathode (lower electron density) after few minutes, flow of electrons will stop Due to accumulation positive and negative charges respectively at anode & cathode compartments. To make the flow of current continuous, place salt bride between two half cells which completes internal circuit.

Anode is a place where oxidation takes places. Due to the oxidation at anode, electron density is more than that of at cathode. Hence –ve sign is given to anode and +ve sign for cathode. Salt bridge is a U shaped thin glass tube, which contains agar- agar medium in which either KCl/KNO₃/NH₄NO₃ is placed.

The selection of electrolyte depends on transport number of both +ve and -ve ions.

Salt bridge makes the flow of current continuous by allowing the ions from one compartment to another or by supplying its ions to cathode and anode compartments to maintain electrical neutrality.

Ex.: Daniel cell



Differences between Galvanic and electrolytic cell.

Galvanic cell	Electrolytic cell
1. It converts chemical energy to	1. It converts electrical energy to
electrical energy	chemical energy
2. Cell itself acts as a source of current	2. Source of current is required
3. Anode and cathode are represented	3. Anode and cathode are indicated by
by –ve and +ve sign respectively.	+ve and –ve sign.
4. Spontaneous Redox reaction takes	4. Non- Spontaneous Redox reaction
places	takes places (electrolysis)
5. Salt bridge is required	5. Salt bridge is not required

Cell notation:

To represent Galvanic cell in a simple way, IUPAC given certain rules they are:-

1. Anode half-cell always should be written on left hand side where cathode cell has to be written on right hand side.

- 2. Anode half-cell should be written by writing its solid phase followed by liquid phase whereas cathode half-cell should be written by writing liquid phase followed by solid phase. Vertical lines between two phases indicate phase separation (boundary).
- 3. Two vertical lines between anode and cathode which indicates salt bridge.
- 4. If concentration of electrolyte is known, electrolyte concentration has to be written subscript.

Ex: 1.
$$Zn/Zn^{+2}$$
 // Cu^{+2}/Cu for Daniel cell. (1M) (1M)

Zn $\longrightarrow Zn^{+2} + 2$ electron at **anode**

$$Cu^{+2} + 2$$
 electron $\longrightarrow Cu$ at **cathode**

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$
 cell reaction

2. $Mg/Mg^{+2}//Zn^{+2}/Zn$
 $Mg \longrightarrow Mg^{+2} + 2$ electron at **anode**

$$Zn^{+2} + 2$$
 electron $\longrightarrow Zn$ at **cathode**

$$Mg + Zn^{+2} \longrightarrow Zn + Mg^{+2}$$
 cell reaction

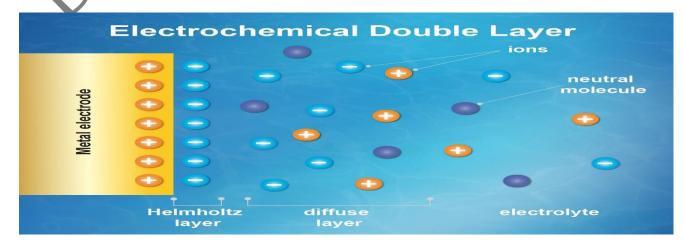
Electrode potential: when a metal rod placed in its own solution or its electrolyte it undergoes either dissolution or deposition. It is due to difference in concentration of metal ions between solid and liquid phases.

Dissolution or deposition depends on nature of metal, concentration of solution, temperature and pressure. For a metal the other 3 factors i.e. concentration, temperature and pressure will decide the electrode potential.

Electrode potential is defined as measure of the tendency of a metal rod to undergo oxidation or reduction when it contacts with solution.

Development of electrode potential:

When metal rod contacts with a solution, if it undergoes oxidation the formed electrons retained by metal rod, as a result metal rod gets –ve charge. The +ve ions present in the solution form as a layer around the metal rod, which gives a double layer known as "Helmholtz double layer formation".



Dissolution or deposition takes places till equilibrium attained.

At equilibrium, rate of dissolution = rate of deposition (Oxidation potential) = (Reduction potential)

Hence, oxidation and reduction potentials are same for a metal rod but signs are reverse.

Standard electrode potential (E^O): it's a measure Tendency of a metal rod to loose or gain of electrons when it contacts with a solution of 1M concentration at 25°C temperature and 1 atm pressure is called standard electrode potential.

Standard oxidation potential (SOP): it's a measure Tendency of a metal rod to undergo oxidation or to lose electrons when it contacts with a solution of 1M concentration at 25°C and 1atm pressure is called SOP.

Standard Reduction potential (SRP): it's a measure Tendency of a metal rod to undergo reduction or to gain electron when it contacts with the solution of 1M concentration at 25°C and 1 atm pressure is called SRP.

Nernst Equation: - Nernst derived an equation to calculate electrode potential at a given concentration, temperature from its standard electrode potential and standard temperature 25°C.

He derived an equation based on concept of free energy. Free energy is defined as the amount of energy required to do some work i.e. work is obtained by the expense of free energy.

-
$$\Delta G=W_{max}$$

In a galvanic cell, electrical work is produced by the expense of chemical energy. This work is a product of **nFE** i.e. W=nFE

Where n=no. of moles of electrons transferred

F=charge of 1 mole of electron

E=Potential

$$\Delta G = n F E$$
 and $-\Delta G^{O} = n F E^{O}$

According to vanthoff Isotherm equation this gives the relation between change in free energy and reaction coefficient.

$$\Delta G = \Delta G^0 + RT \ln Q$$

If the reaction is at equilibrium Q can be substituted by K where k is equilibrium constant.

$$\Delta G = \Delta G^0 + RT \ln k$$

On substitution -nFE= -nFE⁰+RTlnK

On dividing the above equation By (-nF)

$$E=E^0-RT/nF lnK$$

$$E=E^0-RT/nF ln [P]/[R]$$

On substitution R=8.314Joule Kelvin/MOL, T=298k, F=96500 coulombs.

$$E=E^0-0.0591/n log [P]/[R]$$

For a given reaction $Zn^{+2} + 2$ electron

The Nernst equation is $E_{z_{n+2}/z_n} = E_{z_{n+2}/z_n} - 0.0591/2 \log [Z_n]/[Z_n^{-2}]$

The above Nernst equation is useful to calculate Reduction potential of a given system.

Applications:

- 1. To calculate Electrode potential of an electrode at given concentration
- 2. To calculate cell EMF At a given concentration.
- 3. To calculate equilibrium constant.
- 4. To calculate change in free energy.

CELL EMF

EMF- it is the driving force to drive the electrons from low reduction potential to high reduction potential i.e., cell EMF depends on both oxidation tendency of anode and reduction tendency of cathode i.e.; $E_{cell} = E_{oxidation of anode} + E_{reduction of cathode}$

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

Where E_R = reduction potential of cathode half cell.

E_L =Reduction potential of anode half cell.

$$Zn+Cu^{+2}$$
 $Zn^{+2}+Cu$

Cu⁺²+2electron → Cu (Reduction)

Zn
$$\xrightarrow{}$$
 Zn⁺²+2 electron (Oxidation)

$$E=E^0-0.0591/2 log [Zn^{+2}]/[Cu^{+2}]$$

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

$$= [E^0{}_{Cu+2/Cu} \text{ -} 0.0591/2 \text{ log 1/ } Cu^{+2}] \text{-} [\ E^0{}_{Zn+2/Zn} \text{ -} 0.0591/2 \text{ log 1/ } Zn^{+2}]$$

1. Calculate the single electrode potential of the following Zn electrode. $E_{Zn^{+2}(0.01M)}/Zn$ at 25^0 $E^0_{Zn^{+2}/Zn}$ =-0.76V.

Sol:
$$E=-0.76-0.0591/2 \log 1/[Zn^{+2}]$$

$$E = -0.761 - 0.02955 \log 1/10^{-2}$$

$$=-0.8201 \text{ V}$$

2. A silver rod (bar) is placed in a solution of Feso4 will a reaction takes places or not? Explain. $E^0_{Ag+/Ag} = +0.80 \quad E^0_{Fe+2/Fe} + -0.44V$

Sol: No there is no Reaction between Ag bar and ferrous sulphate because SRP values indicating that Ag reaction potential is more than iron potential. Ag prefers to undergo reduction more than iron. But Ag is already in reduced form, Hence there is no reaction.

3. Calculate cell EMF for the given galvanic cell. Zn/Zn⁺² $(0.1M)//Fe^{+2}$ (0.01M)//Fe, E^0 _{Zn+2/Zn} = -0.76V and E^0 _{Fe+2/Fe}=-0.44V

Sol:
$$Zn \longrightarrow Zn^{+2} + 2e$$
lectron \longrightarrow Fe $Zn + Fe^{+2} + 2e$ lectron \longrightarrow Fe $Zn + Fe^{+2} \longrightarrow$ Fe $+ Zn^{+2}$

$$E^{0}_{cell} = E^{0}_{R} + E^{0}_{L}$$

$$= -0.44 - (-0.76)$$

$$= -0.44 + 0.76 = 0.32 \text{V.}$$

$$E^{0}_{cell} = E^{0}_{cell} -0.0591/n \log [P]/[R]$$

$$= 0.32 - 0.0591/2 \log [Zn^{+2}]/Fe^{+2}]$$

$$= 0.32 - 0.02955 \log 10^{-1}/10^{-2}$$

*Galvanic cells can be classified into 2 types based on Chemical reactions involving in galvanic cell they are

1. Reversible cell

=0.290V.

2. Irreversible cell

Reversible cell: - The cell which satisfies the following 3 conditions is known as reversible cell. They are

- 1. If external EMF= galvanic cell EMF, no current flows either from galvanic to external source or vice-versa.
- 2. If the external EMF infinitesimally less than the actual EMF of the cell is applied to it, the current will flow from the cell, which is proportional to the chemical change occurring in the cell. i.e; current can be produced continuously.

$$Zn+Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Ex: for reversible cells UPS battery, car batteries, Ni-Cd battery etc.

3. If the external EMF infinitesimally greater than the actual EMF of the cell is applied to it, the current will start flow in opposite direction and cell gets reversed.

Irreversible cell:- The cell which cannot satisfy the above 3 conditions is known as irreversible cell. Ex; dry cell.

Single electrode potential cannot be determined individually. To determine the electrode potential of a given system, that should be coupled with another half cell whose potential known, to make complete electrochemical cell through potentiometer

The electrode whose potential is known is called as standard or reference electrode.

Electro Chemical Series (ECS):-

Single electrode potentials cannot be determined individually

Reference electrodes are 2 types. They are

- 1. Primary reference electrode (PRE)
- 2. Secondary reference electrode (SRE)

PRE is one based on its electrode potential value other systems E.P. can be determined. SHE or normal hydrogen electrode is used as PRE, whose potential is tentatively fixed as zero volts to use as reference electrode.

In common laboratory, H₂electrode cannot be constructed. Hence in the place of H₂ electrode other electrodes are used as reference electrodes whose electrode potential is determined by connecting it to SHE. These electrodes are known as SRE.

The electrode potentials values of all the electrodes are arranged in the increasing or decreasing order of their SRP values, this series is known as electro chemical series.

Generally, electrodes arranged in the increasing order of their SRP values. The resultant series is known as electrochemical series (ECS). ECS is the arrangement of the increasing order of their SRP values.

Ex
$$Li^{+1}/Li = -3.27 \text{ V}$$
 $Mg^{+2}/Mg = -2.14 \text{ V}$
 $ZN^{+2}/Zn = -0.76 \text{ V}$
 $Fe^{+2}/Fe = -0.44 \text{ V}$
 $H^{+}/H_{2} = 0.00 \text{ V}$
 $Cu^{+2}/Cu = 0.34 \text{ V}$
 $Fe^{+3}/Fe^{+2} = 0.72 \text{ V}$
 $Ag^{+}/Ag = 0.80 \text{ V etc.}$

Applications of E.C.S:-

1. Oxidizing and reducing power can be explained

Reducing power increases as -ve potentials are increased. Whereas, oxidizing powers increases as +ve potentials are increased.

In the above series, Ag⁺/Ag is best oxidizing agent and Li⁺/Li is the best reducing agent.

2. Liberation of H₂ gas.

All electrodes above hydrogen electrode in ECS can liberate H₂ gas from acid solution.

3. Displacement of metal:

Upper metal is the series can displaces lower metal from its solution

Ex. Zn can be displaced from iron solution where as Iron cannot displaces Zn solution.

4. Spontaneity of a reaction:

If E_{cell}=+ve, that is a spontaneous reaction

If E_{cell}=-ve, non spontaneous reaction

If E_{cell}=0, equilibrium.

ightharpoonup Calculate E_{cell} and explain spontaneity for given galvanic cells.

$$E^0_{Ni+2/Ni} = -0.21, E^0_{Cu+2/Cu} + 0.34$$

Sol: 1.
$$E^0_{cell} = E^0_R + E^0_L$$

$$E^{0}_{cell} = 0.34 \cdot (-0.21) = 0.55V$$

 E_{cell} is +ve hence, this reaction is a spontaneous reaction.

2.
$$Ag/Ag^{+}(1M)//Zn^{+2}(1M)/Zn$$

$$E^{+}{}_{Ag+\!/Ag}=\!\!0.80~V,~E^{0}{}_{Zn+2\!/Zn}\!\!=\!\!-0.76~V$$

Sol 2.
$$E^{0}_{cell} = -0.76 - (0.80) = -1.56V$$

E_{cell} is -ve hence, this reaction is a non-spontaneous.

Types of electrodes:

Based on composition electrodes can be classified into

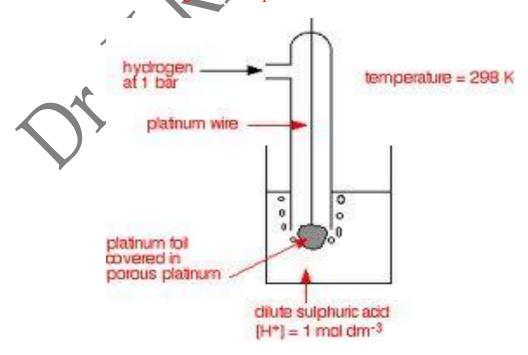
- 1. Gas –ion electrode ex: H₂ electrode, O₂ electrode, Cl₂ electrode etc.
- 2. Metal-metal ion electrode ex: Cu/Cu⁺², Zn/Zn⁺² etc.
- 3. **Metal-metal insoluble salt electrode** ex: calomel, Ag-Agcl electrode.
- 4. **Redox electrode** ex: Quinhydron electrode, Fe⁺³/Fe⁺² electrode.
- 5. **Ions selective electrode** ex: glass electrode.
- 1. Gas –ion electrode: SHE or HE (hydrogen electrode) hydrogen electrode 1101–111 syllabus

It can be constructed by placing a pt wire in given HCl or (H_2SQ_4) (either 1M or some concentration) Cover the Pt wire with glass hood, which prevents contamination of H_2 gas with environment. Glass hood provided with inlet through which allow the pure H_2 (g) over Pt wire through HCl solution at 1atm and 25° C.

A potential is developed on the surface of Pt where H_2 (g) and Hcl or (H₂SO₄) solution contacting together. This potential is fixed as zero to determine electrode potentials of other systems. If the concentration Of HCl is 1M that electrode is known as SHE. The role of Pt wire is to provide electrical contact and helps in getting equilibrium between H^+ and H_2 .

Limitation:

- 1. If any impurities present in H_2 (g) that deactivate Pt surface. Hence, pure H_2 (g) is required.
- 2. Maintenance 1atm throughout the experiment is difficult.



Notation:-If it acts as Anode Pt, $H_2(g)/H^+(1M)$

Electrode Reaction:- $2H^++2$ electron \longrightarrow H_2

Nernst equation:- $E_{H+/H2} = E^0_{H+/H2} - 0.0591/2 \log [H_2]/[H^+]^2$ $= 0 - 0.0591/2(-2) \log [H^+]$

 $=+0.0591 \log [H^+]$

 $E_{H+/H2} = -0.0591PH$

HYDROGEN ELECTRODE NOT IN SYLLABUS

2. Metal-Metal insoluble salt electrode:

This electrode can be constructed by taking pure metal, its insoluble salt and a solution having anion of insoluble salt.

Electrode potential depends on the concentration of solution having anion of insoluble salt.

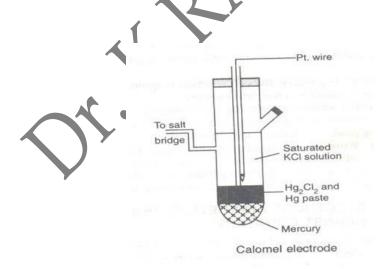
Ex: calomel electrode, Ag-AgCl electrode.

Calomel electrode:

It can be constructed by placing pure mercury at the bottom of glass tube over which a mixture of mercury and mercurous chloride (Hg₂Cl₂). This mixture is commonly known calomel.

The remaining part of the glass tube filled with a solution Of KCl.

Insert a Pt rod or noble metal into Hg which provides electrical contact.



If calomel electrode acts as anode Pt, Hg, Hg₂Cl₂ (solid)/KCl (solution)

If calomel electrode acts as cathode KCl (solution)/Pt, Hg(l), Hg₂Cl₂ (solid)

Half cell (electrode) reaction

$$Hg_2Cl_2 + 2electron$$
 \longrightarrow $2Hg + 2Cl^-$

Nernst equation:

$$E_{cal} = E_{cal}^0 - 0.0591/2 \log [Hg]_2 [Cl^-]^2 / [Hg_2 Cl_2]$$

$$E_{cal} = E^{0}_{cal} - 0.0591 \log [Cl^{-}]$$

Concentration of [Hg] =concentration of [Hg₂Cl₂] i.e., activity=1.

The above equation Indicates electrode potential of calomel electrode depends on only concentration of Cl

If KCl solution is saturated calomel electrode.

$$E_{\text{sat.ce}}^{0} = 0.2421V$$

If KCl solution concentration is $1N E^0 = 0.28V$, If KCl concentration is $0.1N E^0 = 0.33V$

Limitation:

1. At higher temperature (more than 50^{0} C) $Hg_{2}Cl_{2}$ undergoes decomposition which changes its electrode potential.

Advantages:

- 1. Construction is simple
- 2. If concentration of KCl, temperature is constant, there is no change in electrode potential.

Determination of PH:

With the given acid construct in the form of hydrogen electrode and coupled with reference electrode saturated calomel electrode through potentiometer. PH can be calculated from $E_{\rm cell}$ as given below. The SRP values of hydrogen and saturated calomel electrodes indicates calomel electrode as cathode and hydrogen electrode acts as anode.

Hydrogen electrode is known as indicator electrode whereas standard calomel electrode (SCE) acts as reference electrode.

$$\begin{split} &E_{cell} {=} E_R {-} E_L \\ &= \! 0.2421 {-} (-0.0591PH) \\ &= \! 0.2421 {+} 0.0591PH \end{split}$$

$$\mathbf{P}^{\mathbf{H}} = (\text{Ecell} - 0.2421)/0.0591$$

3. REDOX-ELECTRODE

It can be constructed by placing a noble metal into a solution having both oxidized and reduced form of a reactant. Reactant may be molecular form or ionic form with different oxidation states.

Electrode potential depends on the concentration of oxidized and reduced form.

Ex: Fe⁺³-Fe⁺² electrodes

Quinhydrone electrode

Quinhydrone electrode:

It can be constructed by placing a noble metal like Pt in acid solution which contains oxidized and reduced form of Quinhydrone. Quinhydrone is a molecular compound having both Quinone and hydroquinone. These 2 molecules held together by weak attractions. When quinhydrone powder added to acid the following equilibrium is established.

$$Q+2H^++2$$
electron \longrightarrow QH_2

If this electrode acts as anode Pt,Q, QH₂/H⁺

If this electrode acts as cathode H⁺/ Pt, Q, QH₂

Nernst equation.

$$E_{Q,\,QH2}\!=\!\!E^0_{Q,\,QH2}\!-\!0.0591/2\,log\,[QH_2]/[Q][\,\text{N}^+]$$

$$E_{O,OH2} = E^{0}_{O,OH2} - 0.0591PH$$

Where $E^{0}_{Q,QH2}$ = standard electrode potential of Quinhydrone electrode.

$$E^{0}_{Q,QH2} = 0.6990V.$$

Determination of PH using Quinhydrone electrode & saturated Calomel electrode: -

With the given acid construct in the galvanic cell using quinhydrone electrode that should be coupled with saturated calomel electrode through potentiometer to determine P^H of a given solution.

Saturated calomel electrode acts as reference electrode and quinhydrone electrode acts as indicator or working electrode.

The SRP value indicates that Quinhydrone electrode acts as cathode and SCE acts as anode.

Pt, Hg, Hg₂Cl₂,/Cl
$$^-$$
(saturated) // H $^+$ (x)/Pt, Q,QH2

$$E_{cell} = (E^0_Q - 0.0591PH) - (0.2421)$$

$$PH = E_{O}^{0} - E_{cell} - 0.2421/0.0591$$

Limitations:

1. Hydroquinone is weak acid which undergoes decomposition at higher PH (more than 8.5PH)

2. If any oxidizing impurities present in the solution which changes the concentration of quinine and hydroquinone as a result potential changes.

Advantages:

- 1. It is very simple to construction.
- 2. It is attaining equilibrium readily.
- 3. It is very useful in the titration of an acid by alkali.

4. Ion selective electrode:

A **glass electrode** is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion that is H⁺ ion. The most common application of ion-selective glass electrodes is for the measurement of pH. The pH electrode is an example of a glass electrode that is sensitive to hydrogen ions. Glass electrodes are important part of the instrumentation for chemical analysis and physico-chemical studies.

Glass electrode: -

Glass membrane is found to be sensitive to [H⁺] ions of acidic solution. The membrane undergoes ion exchange reactions, the Na⁺ ion of glass are exchanged with H⁺ ion.

$$[H^+] + Na^+Gl^- \longrightarrow Na^+ + Gl^-H^+$$
Membrane membrane

When a thin walled glass bulb containing N/10 acid HCl solution is immersed in an acidic solution different concentration a boundary potential E_b is developed across the glass membrane layer.

$$E_b = \frac{2.303 \, RT}{n \, F} \log \frac{c_A}{c_2}, \quad E_b = K - 0.091 \, P^H$$

$$E_b = E^\circ_G - 0.0591 \, \log r \qquad E_b = \frac{E^\circ}{G} - 0.0591 \, -\log[H^+]$$

$$E_b = E^\circ_G - 0.0591 \, P^H$$

When two solutions of different P^H values are separated by a this glass membrane, these develops a difference of potential between surfaces of the membrane. The P.D developed is \propto difference in P^H value.

Construction of Glass electrode: -

A glass membrane electrode is made up of a thin long glass tube with a thin walled glass membrane at the bottom end. A low melting point and high electrical conductance silicate glass, selected for this purpose to act as glass membrane.

Ag/AgCl electrode is dipped in a N/10 solution of HCl, while is taken the bulb at the electrode and is connected to the Pt wire or Ag-AgCl wire for external contact. The glass electrode is represented as

$$Ag \quad \left| \begin{array}{c|c} Agcl_{(5)} & N/10 \ Hcl \ Solution & Glass \ H^{+} \ ion \ solution \ (unknown \) \end{array} \right|$$

The glass electrode potential is given by

$$E_G = E_G^{\circ} - 0.0591 P^H$$

From the above expression the potential of a glass electrode E_G various with the ${\bf P}^{\bf H}$ of the acid solution.

Determination of P^{H} of a solution using glass electrode and saturated calomel electrode:

Glass or S.C.E electrodes

If
$$E_G^{\circ} > E_{SCE}^{\circ}$$

So E_{G}° acts as cathode & E_{SCE}° acts as anode

Cell notation:

S.C.E | G.E

Pt, Hg, Hg₂Cl₂
$$Cl_{[Sat]}^-$$
 | H⁺ N/10 HCl, Glassmembrane, Ag, AgCl, .

Anode reference Indicator

$$E_{cell} = E_{Cathode} - E_{anode}$$

$$E_{cell} = E_G - E_{SCE}$$

$$E_{cell} = [E_G - 0.0591 P^H] - 0.2422$$

$$E_{cell} + 0.2422 - E_{G}^{\circ} = -0.0591 P^{H}$$

$$-E_{cell} - 0.2422 + E^{\circ}_{G} = 0.0591 \, P^{H}$$

$$P^{H} = \frac{E_{G}^{\circ} - 0.2422 - E_{cell}}{0.0591}$$

Advantages:

- 1. Its simple and can easily be used
- 2. It is rapidly achieved
- 3. The results are acurate
- 4. It is not easily poisoned

Limitations:-

Works up to PH 12.0 – 12.5

