



സഹായി

SFI GEC PALAKKAD

MODULE I

ELECTROCHEMISTRY AND CORROSION

The branch of chemistry which deals with two forms of energy such as electrical energy and chemical energy and the inter-conversion of one form to another is called electrochemistry. Thus there are two types of electro chemical changes. On the basis of electrochemical changes, cells are of two types.

1. Electrolytic cell
2. Galvanic cell (Voltaic cell) (Electro chemical cell)

Differences between electrolytic cell & galvanic cell

Electrolytic cell	Electro chemical cell
<ul style="list-style-type: none">• It is used for the conversion of electrical energy to chemical energy.• It requires EMF.• Anode is +ve and cathode is -ve.• Discharges of ions occur at both the electrodes.• Non-spontaneous reaction occurs.• These are irreversible.	<ul style="list-style-type: none">• It is used for the conversion of chemical energy to electrical energy.• It produces EMF.• Anode is -ve and cathode is +ve.• Discharges of ions occur only at cathode.• Spontaneous reaction occurs.• These may be reversible.

Comparison of electrolytic cell & galvanic cell

Electrolytic cell	Electro chemical cell
<ul style="list-style-type: none">• Oxidation takes place at the anode and reduction at the cathode.• Flow of electrons from anode to cathode.• Electrons leave the cell at anode and enter the cell at cathode.	<ul style="list-style-type: none">• Oxidation takes place at the anode and reduction at the cathode.• Flow of electrons from anode to cathode.• Electrons leave the cell at anode and enter the cell at cathode.

Electrode potential and its origin

When a metal rod is immersed in a solution of its own ion, it will either undergo oxidation or reduction. As a result metal rod attains positive or negative charge. If the metal rod attains the positive charge, then it can attract the negatively charged free ions from the solution & if the metal rod attains negative charge, then it can attract the positively charged free ions from the solution. As a result a layer of both positive and negative charge is produced on the metal rod. This will lead to the development of a potential and is called electrode potential.

Electrode potential (E) is defined as the tendency of an electrode to lose or gain electrons when it is immersed in a solution of its own ions. Electrode potential is of two types. They are

1. Oxidation potential
2. Reduction potential

Oxidation potential

It is defined as the tendency of an electrode to lose electrons when it is immersed in a solution of its own ions.

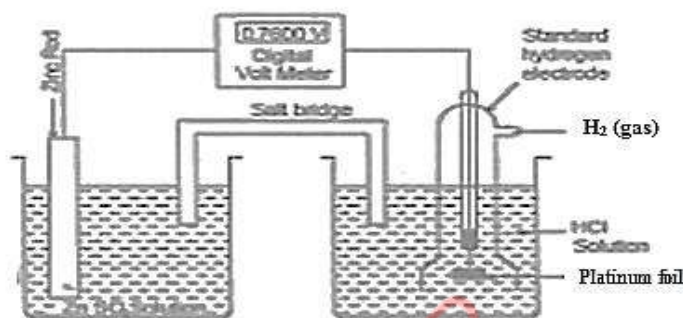
Reduction potential

It is defined as the tendency of an electrode to gain electrons when it is immersed in a solution of its own ions.

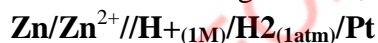
Electrode potential becomes constant at equilibrium then it is called standard electrode potential (E^0). It is defined as the tendency of an electrode to lose or gain electrons when it is immersed in a solution of its own ions of 1M concentration, 1atm pressure and 298K or 25°C.

It is not possible to find out the absolute value of electrode potential, since neither oxidation nor reduction takes place independently both occur simultaneously. Hence we can find out the relative value of electrode potential by coupling it with universally accepted reference electrode such as SHE or NHE. Its potential is arbitrarily fixed as zero. It can function as an anode or cathode depending on the nature of the other electrode to which it is connected.

In order to measure the standard electrode potential of Zn rod, (Zn rod dipped in 1M $ZnSO_4$ solution) Zn electrode is coupled with SHE internally using salt bridge and externally using volt meter. Zn has greater tendency for oxidation than SHE. So Zn can function as anode and SHE can function as the cathode. The resultant cell potential can be read directly from the volt meter.



The resultant cell can be represented in the following manner,



$$E^0_{Cell} = E^0_{cathode} - E^0_{anode}$$

$$= E^0_{SHE} - E^0_{Zn/Zn^{2+}}$$

$$0.76 V = 0 - E^0_{Zn/Zn^{2+}}$$

$$(E^0_{Zn/Zn^{2+}} = -0.76V)$$

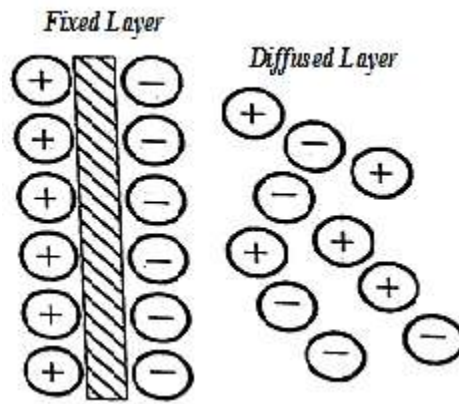
Helmholtz electrical double layer

When an electrode is immersed in a solution of its own ions an electrical double layer is produced. It is the double layer of both positive and negative charges. Electrical double layer corresponds to an electrical capacitor. Electrical properties can be explained qualitatively by using the concept of electrical double layer at the solid liquid interphase. This concept was proposed by the scientist, Helmholtz. He considered that electrical double layer is produced at the surface of separation between the two phases, i.e. the solid electrode and liquid electrolyte. Electrical double layer consists of two parts.

1). Fixed part 2) Diffused part

Fixed part: It is fixed to the solid electrode. It contains either positive or negative ions.

Diffused part: It extends some distance into the solution. It contains both positive and negative ions. The existence of charges of opposite signs on the diffused to the fixed part of the electrical double layer develops a potential between the two layers. This potential is called electro kinetic potential or zeta potential.



According to electrostatic theory, the potential difference between the two layers (Φ) is given by

$$\Phi = \frac{\sigma a}{\epsilon_0 \epsilon}$$

Where ' σ ' is the charge density, i.e. $\text{Charge} / \text{Unit area}$

' a ' is the distance between the layers of positive and negative charges.

' ϵ ' is the dielectric constant of the medium and ϵ_0 that of free space.

Electrochemical series

An electrochemical series is a series in which the electrodes are arranged in the increasing order of reduction potential or decreasing order of oxidation potential. On moving down the series, reduction potential increases and oxidation potential decreases. Thus this series gives the increased tendency of electrodes to get reduced or decreases tendency of electrodes to get oxidised. The electrodes present at the top of the series can function as anode and those present at the bottom of the series can function as cathode. This series is also called activity series, since the electrodes at the top of the series is more reactive than those present at the bottom.

Anodic (Active)

Potassium (K)
 Calcium (Ca)
 Sodium (Na)
 Magnesium (Mg)
 Aluminium (Al)
 Zinc (Zn)
 Iron (Fe)
 Nickel (Ni)
 Tin (Sn)
 Leads (Pb)
 Hydrogen (H)
 Copper (Cu)
 Mercury (Hg)
 Silver (Ag)
 Platinum (Pt)
 Gold (Au)
 Fluorine (F)

Cathodic (Noble)

Hydrogen has zero reduction potential. Above hydrogen, all the electrodes have negative reduction potential and below hydrogen, all the electrodes have positive reduction potential.

Applications of electrochemical series

1. To know the relative ease of oxidation and reduction:

Greater the reduction potential, more easily the substance undergoes reduction and is a better oxidising agent. (Eg. Fluorine). Similarly greater the oxidation potential, more easily the substance undergoes oxidation and is a better reducing agent. (Eg. Pottasium).

2. To predict whether the metal will react with acid to give hydrogen gas:

Metals present above hydrogen in the electrochemical series can react with acids to give hydrogen gas. This is because these metals have greater tendency to undergo oxidation with respect to hydrogen, since they have negative reduction potential.

3. To calculate the standard emf of the cell:

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

If we know the position of electrodes in the electrochemical series, we can easily predict which electrode can function as anode and which one can function as cathode.

4. Displacement reactions

A metal with lower reduction potential can displace a metal with higher reduction potential from its salt solution. Zn can displace Cu from CuSO_4 solution.

5. To predict the spontaneity of any redox reaction

For any spontaneous reaction, free energy change (ΔG) should be negative. $\Delta G = -nFE_{\text{cell}}$
Hence, E_{cell} should be positive for spontaneous reaction. E_{cell} of the cell can be calculated from the redox potentials by using the relation $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Relationship between electrical energy and free energy

The electrical energy produced by the working of the cell is the product of quantity of electricity passed through the cell and emf of the cell. If in a particular cell reaction, 'n' is the number of electrons get transferred, then the quantity of electricity passed through the cell is 'nF' and E is the emf of the cell.

$$\text{Then electrical energy} = nFE$$

But Gibbs and Helmholtz suggested that electrical energy produced due to the working of the cell is always accompanied with decrease in free energy.

$$\text{Then electrical energy} = nFE = -\Delta G$$

$$\Delta G = -nFE$$

Criteria for spontaneity in terms of cell emf

Case 1: If $\Delta G < 0$ or ΔG is -ve, then $E_{\text{cell}} > 0$ or E_{cell} is +ve and the reaction will be spontaneous.

Case 2: If $\Delta G = 0$, then $E_{\text{cell}} = 0$ and the reaction will be in equilibrium.

Case 3: If $\Delta G > 0$ or ΔG is +ve, then $E_{\text{cell}} < 0$ or E_{cell} is -ve and the reaction will be non-spontaneous.

Nernst equation

Nernst equation is the fundamental equation that gives the relationship between electrode potential and concentration of electrolyte. To derive Nernst equation, consider a general reversible reaction.



For a reversible reaction, free energy change (ΔG) is related to the equilibrium constant (K) by an expression.

$$\Delta G = \Delta G^{\circ} + RT \ln K \quad (1)$$

Where ΔG is the free energy change, ΔG° is the standard free energy change, R is the universal gas constant, K is the equilibrium constant and T is the temperature in Kelvin.

$$K = \frac{[\text{M}]}{[\text{M}^{n+}]}$$

According to Gibbs-Helmholtz suggestion,

$$\Delta G = -nFE \text{ \& } \Delta G^0 = -nFE^0 \quad (2)$$

Substituting equation (2) in equation (1)

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

Dividing above equation by $-nF$, on both sides and convert natural log into base 10, we get

$$E = E^0 - 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^+]}$$

Since $[M] = 1$, then the equation becomes;

$$E = E^0 - 2.303 \frac{RT}{nF} \log \frac{1}{[M^+]}$$

$$E = E^0 + 2.303 \frac{RT}{nF} \log [M^{n+}]$$

On substituting $R = 8.314 \text{ J/K}$, $T = 298 \text{ K}$ & $F = 96500 \text{ C}$, we get simplified form of Nernst equation;

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

Where E is the electrode potential, E^0 is the standard electrode potential.

For a reaction of the type $aA + bB \rightleftharpoons cC + dD$, Nernst equation becomes,

$$E = E^0 + \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

From the above equation, it can be concluded that

- (1) When $[M^{n+}]$ increases E increases
- (2) The electrode potential E decreases as the increase in temperature.
- (3) The electrode potential normally refers to the reduction reaction at an electrode.

Applications of Nernst equation

1. Nernst equation can be used to study the effect of electrolyte concentration on electrode potential.
 2. It can be used for the calculation of the potential of a cell under nonstandard conditions
 3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, if $E^0_{\text{(cell)}}$ and concentration of the other ionic species are known
 4. The P^H of a solution can be calculated from the measurement of electrode potential
- Nernst equation can be used for finding the valency of an ion or the number of electrons involved in the electrochemical reaction.

- Calculate the equilibrium constant for Daniel cell at 25^0C . $E^0_{\text{cell}} = 1.1 \text{ V}$.

$$\log K = \frac{nE^0_{\text{cell}}}{0.0591} = \frac{2 \times 1.1}{0.0591} = 37.22$$

$$K = 1.68 \times 10^{37}$$

- Calculate the standard emf of $\text{H}_2 - \text{O}_2$ fuel cell. (E^0 values for hydrogen and oxygen half cells are -0.40 V & 0.83 V respectively).

$$E^0_{\text{cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}} = E^0_{\text{O}_2} - E^0_{\text{H}_2} = 0.83 - (-0.40) = 1.23 \text{ V}$$

- At 25^0C the standard emf of a cell having reaction involving two electron charge is found to be 0.295 V . Calculate the equilibrium constant of the reaction.

$$\log K = \frac{nE^0_{\text{cell}}}{0.0591} = \frac{2 \times 0.295}{0.0591} = 10$$

$$K = 10^{10}$$

- What is the concentration of Ni^{2+} in the cell at 25^0C , if the emf is 0.601 V ? Given that $E^0_{\text{Ni(s)}/\text{Ni}^{2+}}$ is -0.25 V & $E^0_{\text{Cu(s)}/\text{Cu}^{2+}}$ is 0.34 V . $\text{Ni(s)}/\text{Ni}^{2+} \text{ (a=?)} // \text{Cu}^{2+} \text{ (0.75M)}/\text{Cu(s)}$.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ni}^{2+}]}$$

Where $E^{\circ}_{\text{cell}} = 0.34 - (-0.25) = 0.59$, $E_{\text{cell}} = 0.601 \text{ V}$

$$0.601 = 0.59 + 0.0295 \log \frac{0.75}{[\text{Ni}^{2+}]}$$

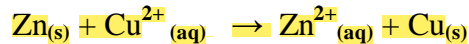
$$\frac{0.011}{0.0295} = \log \frac{0.75}{[\text{Ni}^{2+}]}$$

$$\frac{0.75}{[\text{Ni}^{2+}]} = 2.356$$

Therefore $[\text{Ni}^{2+}] = 0.3183 \text{ M}$

- Calculate the emf of the cell $\text{Zn}/\text{Zn}^{2+} (0.01 \text{ M}) // \text{Cu}^{2+} (0.1 \text{ M})/\text{Cu}$. Write its half-cell reactions is E°_{Zn} is -0.76 V and E°_{Cu} is $+0.34 \text{ V}$.

The cell reaction is



Nernst equation for this cell reaction is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\text{But } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = 0.34 + 0.76 = 1.1 \text{ V}$$

$$\text{Therefore } E_{\text{cell}} = 1.1 + \frac{0.0591}{2} \log \frac{[0.1]}{[0.01]} = 1.1295 \text{ V}$$

- Calculate the equilibrium constant of the reaction, $\text{Cu} + 2\text{Ag}^{+} \rightarrow \text{Cu}^{2+} + 2\text{Ag}$ ($E^{\circ}_{\text{Ag(s)}/\text{Ag}^{+}}$ is 0.80 V & $E^{\circ}_{\text{Cu}^{2+}/\text{Cu(s)}}$ is 0.34 V .)

$$E_{\text{cell}} = E^{\circ}_{\text{Ag(s)}/\text{Ag}^{+}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu(s)}} = 0.80 - 0.34 = 0.46$$

$$\log K = \frac{nE_{\text{cell}}}{0.0591} = \frac{2 \times 0.46}{0.0591} = 15.57$$

$$K = 3.775 \times 10^{15}$$

- Calculate the emf of the following cell at 25°C ,



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.403 + 0.76 = 0.357 \text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cd}^{2+}]}{[\text{Zn}^{2+}]} = 0.357 + \frac{0.0591}{2} \log \frac{[0.2]}{0.0004} = 0.4367 \text{ V}$$

- Find the single electrode potential for copper metal in contact with 0.1 M Cu^{2+} solution at 298 K . $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$

$$E_{\text{Cu}} = E^{\circ}_{\text{Cu}} + \frac{0.0591}{2} \log [\text{Cu}^{2+}] = 0.34 + \frac{0.0591}{2} \log [0.1] = 0.31045 \text{ V}$$

- Determine the standard emf of the cell and standard free energy change of the cell reaction. $\text{Zn}, \text{Zn}^{2+} || \text{Ni}^{2+}, \text{Ni}$. The standard reduction potentials of Zn^{2+}/Zn and Ni^{2+}/Ni half cells are -0.76 V and -0.25 V respectively.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.25 - (-0.76) = +0.51 \text{ V}$$

E°_{cell} is +ve and ΔG° should be -ve.

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

$$\Delta G^{\circ} = -(2 \times 96500 \times 0.51) = -98430 \text{ Joules}$$

- Calculate the amount of electrical energy available from dry cell of EMF 1.5 V which consumes 10 g Zn . (At wt. of $\text{Zn} = 65.5 \text{ g}$)

$$\Delta G = -nFE = -2 \times 96500 \times 1.5 = -289500 \text{ J}$$

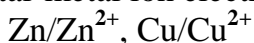
$$\text{Therefore electric energy available for } 10 \text{ g Zn} = \frac{289500 \times 10}{65.5} = 44198 \text{ J}$$

Types of electrodes

- 1) Metal-metal ion electrode
- 2) Gas electrode
- 3) Metal-metal insoluble salt electrode
- 4) Redox electrode
- 5) Ion selective electrode

1. Metal-metal ion electrode

A metal is immersed in its own ionic solution, resultant electrode is called metal-metal ion electrode.



$$E_{\text{cell}} = E^0_{\text{cell}} + 0.0591 \log [\text{Zn}^{2+}]$$

Here the electrode potential depends on the $[\text{M}^{n+}]$

2. Gas electrode

In gas electrode, gas is passed through an inert electrode like platinum which is immersed in a solution containing its own ion.



Here the electrode potential depends on the [ion] and the pressure at which gas is bubbled.

3. Metal-metal insoluble salt electrode

In metal-metal insoluble salt electrode, metal is covered with a paste of its insoluble metal salt which is in contact with a solution containing a common ion with the insoluble salt.

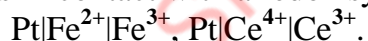


$$E_{\text{cal}} = E^0_{\text{cal}} - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 = E^0_{\text{cal}} - \frac{2.303RT}{F} \log [\text{Cl}^-]$$

Here the electrode potential depends on the [common ion]

4. Redox electrode

An electrode is in contact with a redox system is called redox electrode.



$$E_{\text{cell}} = E^0_{\text{cell}} + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

In these electrodes the electrode potential depends on the ratio of concentration of all ionic species involved in the redox reaction.

5. Ion selective electrode

In this electrode, the sensing part of the electrode is made up of an ion selective membrane.

Eg. Glass electrode consists of an ion selective membrane sensitive to H^+ ions.

Reference electrode

It is not possible to find out the absolute value of electrode potential, since neither oxidation nor reduction takes place independently both occur simultaneously. Hence we can find out the relative value of electrode potential by coupling it with universally accepted reference electrode.

An ideal reference electrode is one whose potential is accurately known, constant and is completely sensitive to the concentration of analyte solution.

Types of reference electrodes

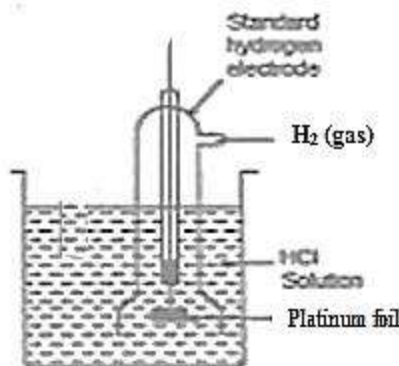
Reference electrodes are of two types. They are

1. Primary reference electrode (SHE)

2. Secondary reference electrode (Calomel electrode and glass electrode)

Standard Hydrogen Electrode (SHE)

It consists of platinum foil coated with Pt black which is immersed in a solution of 1M HCl. Hydrogen gas at 1atm pressure is bubbled over the electrode



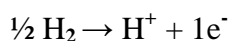
Characteristics of SHE

1. Its potential is arbitrarily fixed as zero.
2. It is reversible electrode, i.e. it can function as an anode or cathode depending on the nature of the other electrode to which it is connected.

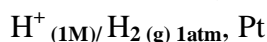
If it functions as an anode, it can be represented as



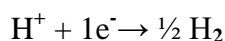
Cell reaction:



If it functions as a cathode, it can be represented as



Cell reaction:

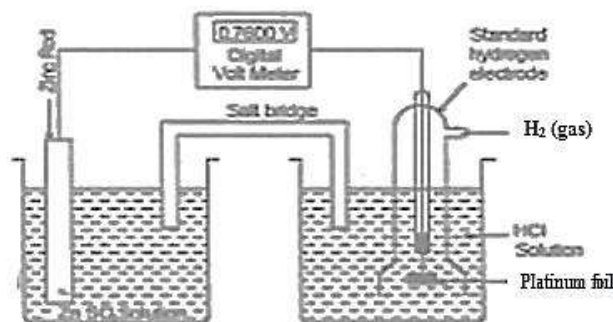
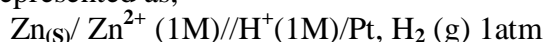


Uses:

It is used for determining unknown potential of an electrode.

Working of SHE (Determination of E° using SHE)

Consider a Zinc rod dipped in ZnSO_4 solution of 1M concentration which is coupled with SHE externally using voltmeter and internally through salt bridge. Now, the resultant cell can be represented as,



$$\begin{aligned} E^\circ_{\text{Cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{SHE}} - E^\circ_{\text{Zn/Zn}^{2+}} \\ 0.76 \text{ V} &= 0 - E^\circ_{\text{Zn/Zn}^{2+}} \end{aligned}$$

$$E^0_{\text{Zn/Zn}^{2+}} = -0.76\text{V}$$

E^0 Cell can be directly read out from the voltmeter and E^0 Cathode is zero. Hence we can find out E^0_{Anode} (E^0_{Zn}).

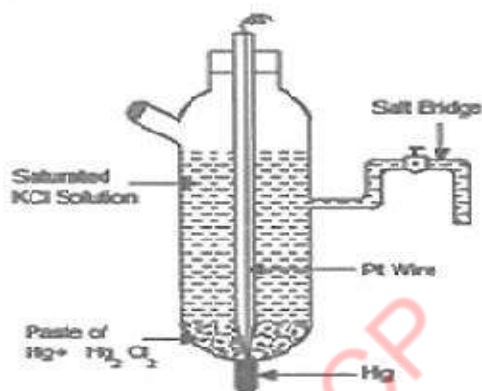
Draw backs of SHE

1. It is very difficult to set up.
2. It cannot be used as a reference electrode if the solution contains reducible substances such as copper, silver etc.
3. It causes poisoning of the Pt foil.

Secondary Reference Electrode

Secondary Reference Electrode is a reference electrode with known constant potential and can be coupled with other electrodes to determine the unknown potential.

Calomel Electrode



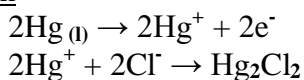
Calomel electrode consists of a glass having side tube on both sides. Mercury covered with a paste of Hg_2Cl_2 is taken at the bottom the glass tube. Inside the glass tube 0.1N or 1N or saturated KCl solution is taken. A Pt wire is dipped into the glass tube containing Hg, which helps for electrical contact. Potential of calomel electrode depends on the concentration of KCl solution taken in the glass tube.

Calomel electrode can be represented as, $\text{Pt, Hg(l)} | \text{Hg}_2\text{Cl}_{2(s)} | \text{KCl(sat)}$

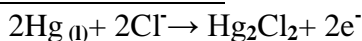
$$E_{\text{cal}} = E^0_{\text{cal}} - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 = E^0_{\text{cal}} - \frac{2.303RT}{F} \log [\text{Cl}^-] = E^0_{\text{cal}} - \frac{0.0591}{1} \log [\text{Cl}^-]$$

Saturated Calomel Electrode is generally used, since it is easy to set up and its emf will not change with chemical reaction.

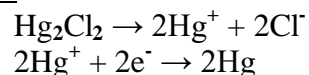
Oxidation



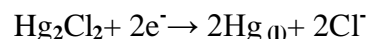
Overall oxidation reaction



Reduction



Overall reduction reaction



Overall reaction when oxidation takes place is just reverse of the overall reaction when reduction takes place. Hence calomel electrode is reversible with respect to chloride ions.

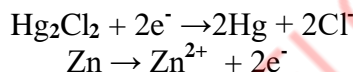
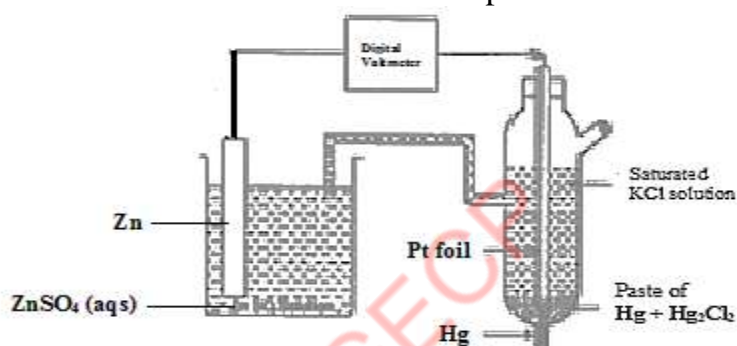
Potential of calomel electrode depends on the concentration of KCl solution.

Concentration	0.1N	1N	Saturated
E	0.3335 V	0.2810 V	0.2422 V

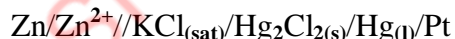
If the calomel electrode is filled with 0.1 N or 1 N KCl, then the calomel electrode is called Normal Calomel Electrode (NCE) and if it is filled with saturated KCl, then it is called Saturated Calomel Electrode (SCE)

Working of Calomel electrode (Determination of electrode potential using calomel electrode)

In order to measure the electrode potential of an electrode, (Zn electrode) it is coupled with SCE using a digital volt meter. The volt meter reading will give the cell emf. The reduction potential of SCE is 0.2422V is higher than the reduction potential of Zn^{2+}/Zn (-0.76V). Therefore reduction reaction takes place at SCE.



The resultant cell can be represented as



$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{\text{cal}} - E_{\text{Zn}/\text{Zn}^{2+}} = 0.2422 - E_{\text{Zn}/\text{Zn}^{2+}}$$

$$E_{\text{Zn}/\text{Zn}^{2+}} = 0.2422 - E_{\text{cell}}$$

E_{cell} can be read directly from volt meter.

Advantages of Calomel electrode

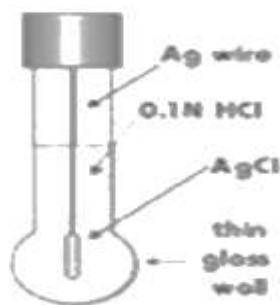
1. It is very easy to set up.
2. Its emf will not change with chemical reaction.

Glass electrode

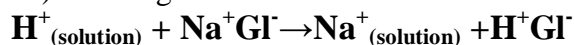
Glass electrode is a secondary reference electrode. Corning 015 glass has been used for making glass electrode. It is a special type of glass with low melting point and high electrical conductivity. It consists of 72% SiO_2 , 6% CaO & 22% Na_2O .

Construction;

It consists of a thin glass bulb in which Ag wire coated AgCl is used as an internal reference electrode. It is then filled with 0.1N HCl solution.



Glass electrode works on the principle that potential difference between the surface of the glass membrane and a solution is a linear function of P^H . Here the glass membrane acts as an ion selective membrane sensitive to $[H^+]$. So an ion exchange reaction occurs between singly charged cations of glass (Na^+) & H^+ ions of solution. Finally an equilibrium is established between (Na^+) ions of glass & H^+ ions of solution.



$$E_G = E_G^0 + 0.0591 \log [H^+] = E_G^0 - 0.0591 P^H$$

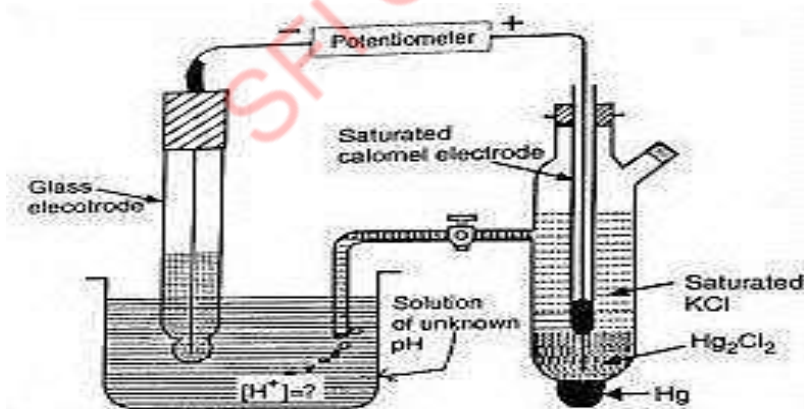
The potential of glass electrode varies with concentration of H^+ ions. E_G^0 is constant and it depends on the nature of the glass and also the P^H of the solution taken inside the glass bulb.

$$E_G^0 = 0.6990 \text{ V}$$

The concentration of H^+ ion inside the glass is constant, i.e. P^H is constant. But when it is dipped into a solution of unknown P^H , concentration of H^+ ion inside the glass bulb changes. As a result, P^H changes. This results in the development of a potential difference.

Determination of PH using glass electrode

Glass electrode is used as an internal reference electrode. In order to determine the unknown PH of a solution, glass electrode is coupled with SCE and the resultant cell can be represented like this, $\text{Ag, AgCl(s)/0.1N HCl/Glass/Solution of Unknown } P^H // \text{KCl}_{(sat)}/\text{Hg}_2\text{Cl}_2\text{(s)}/\text{Hg(l)}/\text{Pt}$



$$\begin{aligned} E_{\text{cell}} &= E_R - E_L = E_{\text{SCE}} - E_G \\ &= 0.2422 - (E_G^0 - 0.0591 P^H) \\ &= 0.2422 - E_G^0 + 0.0591 P^H \end{aligned}$$

E_G^0 of glass electrode can be determined by using a solution of known P^H .

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

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

Advantages of glass electrode

1. It is very simple to operate.

2. It can be used to find the P^H of oxidising, reducing and even coloured solutions.
3. Glass electrode works effectively in the P^H range of 1-9 and is unaffected by oxidising, reducing and poisoning agents.
4. Electrodes made of special glasses can be used upto a P^H of 12.

Draw backs of glass electrode

1. It cannot be used as a reference electrode for solutions having P^H greater than 12.
2. Glass membrane has very high resistance. So ordinary potentiometers cannot be used for determining potential of electrode instead special electronic potentiometers have to be used.

- Find out the pH of a solution measured using Hydrogen electrode which is coupled with saturated calomel electrode. EMF of the combined cell is 0.523V at $25^\circ C$. Given that $E_{SCE} = 0.2422V$.

$$E_{cell} = E_{cal} - E_{H_2} = 0.2422 + 0.0591 P^H = 0.523V$$

$$P^H = \frac{0.523 - 0.2422}{0.0591} = 4.75$$

- Potential of H_2 electrode set up in acid solution of unknown strength is 0.295 volts at $25^\circ C$ when coupled with SHE. Find the P^H of the solution.

$$E_{H_2} = E^0_{H_2} + 0.0591 \log [H^+] = -0.0591 P^H$$

$$E_{Cell} = E_{Cathode} - E_{Anode} = E_{SHE} - E_{H_2} = 0 + 0.0591 P^H = 0.0591 P^H$$

$$P^H = \frac{E_{H_2}}{0.0591} = \frac{0.295}{0.0591} = 4.99$$

- Find out the P^H of a solution in which a glass electrode is dipped and is coupled with SCE. The EMF of the combined cell is 0.205V at $25^\circ C$. Given that $E_{SCE} = 0.2422V$ and $E^0_{Glass} = 0.57V$.

$$P^H = \frac{E_{Cell} + E^0_{G} - 0.2422}{0.0591} = \frac{0.205 + 0.57 - 0.2422}{0.0591} = 9.02$$

Primary and secondary cells

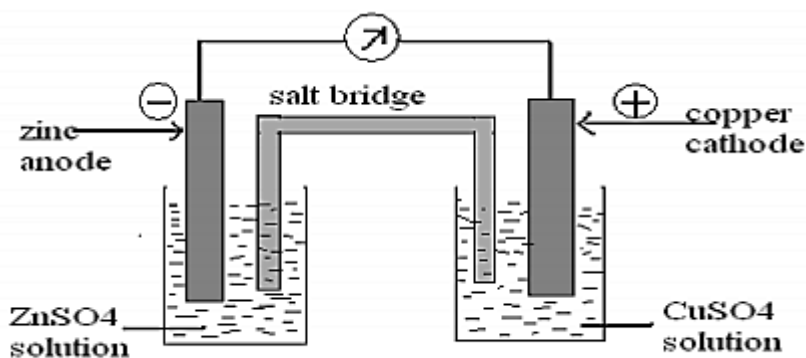
Cells which become dead over a period of time, because the chemical reaction occurs only once. After that the cell becomes exhausted or discharged. They cannot be recharged or reused again.

Eg. Dry cell, Daniel cell, mercury cell etc.

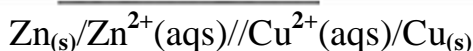
Daniel cell

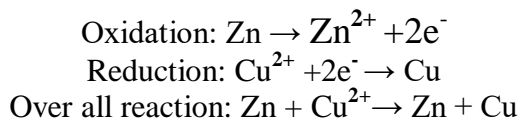
It is also called electrochemical cell or voltaic cell

It consists of Zn rod dipped in $ZnSO_4$ solution and Cu rod dipped in $CuSO_4$ solution. These two electrodes are connected externally using a volt meter and internally using salt bridge. The resultant cell can be represented like this.



DANIELL CELL





Temperature dependance of emf of a Daniel cell or effect of concentration on emf of a daniel cell.

Consider the Daniel cell reaction, $\text{Zn}_{(\text{s})} + \text{Cu}^{2+} \rightarrow \text{Cu}_{(\text{s})} + \text{Zn}^{2+}$,

Nernst equation is given as, $E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{2.303RT}{nF} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$

Case I, When $[\text{Cu}^{2+}] = [\text{Zn}^{2+}]$, logarithmic term becomes zero. Then $E_{\text{cell}} = E^{\circ}_{\text{cell}}$ & emf of the cell is independent of temperature.

Case II, When $[\text{Cu}^{2+}] < [\text{Zn}^{2+}]$, logarithmic term becomes negative. Then $E_{\text{cell}} < E^{\circ}_{\text{cell}}$ & emf of the cell decreases with rise in temperature.

Case III, When $[\text{Cu}^{2+}] > [\text{Zn}^{2+}]$, logarithmic term becomes positive. Then $E_{\text{cell}} > E^{\circ}_{\text{cell}}$ & emf of the cell increases with rise in temperature.

Salt Bridge

It is U-shaped tube containing semisolid paste prepared by adding agar-agar or gelatin to aqueous solution of strong electrolyte like KCl, KNO_3 , K_2SO_4 , NH_4NO_3 etc. Electrolyte should be inert.

Functions of the salt bridge

- It provides cations and anions to replace the ions lost or produced in the two half cells.
- It maintains electrical neutrality of the two solutions in the two half cells.
- It allows the flow of current by completing the electrical circuit.
- It prevents intermixing of solution as well as ions in the two half cells, which may lead to a precipitation reaction.

Variation of Emf of hydrogen electrode with P^{H} of the solution

For H_2 electrode, $E_{\text{H}_2} = E^{\circ}_{\text{H}_2} + 0.0591 \log [\text{H}^+] = -0.0591 P^{\text{H}}$

At $P^{\text{H}} = 0$, $E_{\text{H}_2} = -0.0591 P^{\text{H}} = 0.0591 \times 0 = 0 \text{ V}$

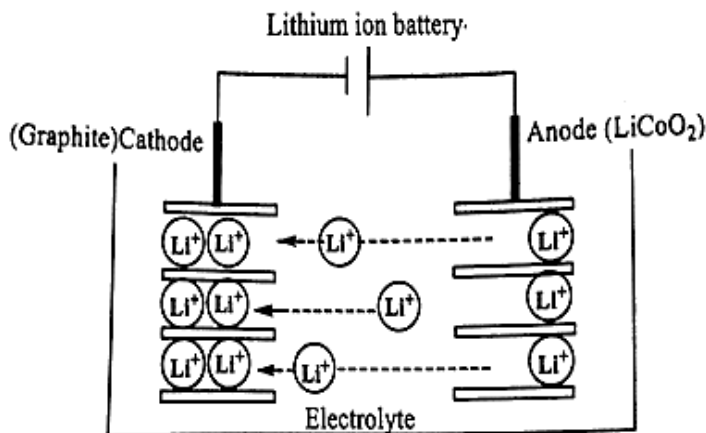
At $P^{\text{H}} = 7$, $E_{\text{H}_2} = -0.0591 P^{\text{H}} = 0.0591 \times 7 = 0.4137 \text{ V}$

At $P^{\text{H}} = 14$, $E_{\text{H}_2} = -0.0591 P^{\text{H}} = 0.0591 \times 14 = 0.8274 \text{ V}$

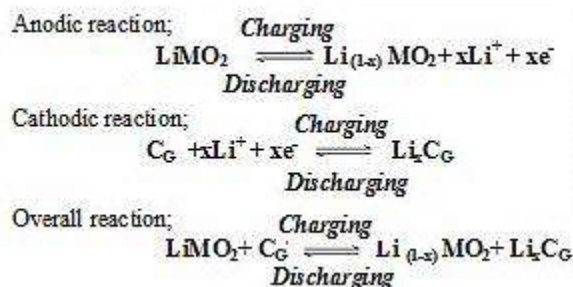
Secondary cell (Accumulators) (Storage cells)

Cells which can be recharged again and again by passing direct current through them. They can be reused. So they are called repeated action cells. They can store electrical energy in the form of chemical energy. Hence they are called storage cells (accumulators).

Lithium ion cell.



Lithium ion cell is a secondary cell in which lithium ions moves between cathode and anode during charging and recharging. In this cell, anode is LiMO_2 , cathode is graphite & electrolyte is an aprotic organic solution.



Thus there is the movement of lithium ions between the cathode and anode during charging and recharging. The main electrochemical reaction in lithium ion cell is the uptake of lithium ion at the cathode and their release during discharging

Cell representation; $\text{Li}_x\text{C}_G | \text{LiX in PC-EC} | \text{Li}_{(1-x)}\text{MO}_2$

Where LiX is lithium salt such as LiClO_4 , PC-EC is a mixed poly propylene carbonate and ethylene carbonate solvent & M is a transition metal such as Co, Mn or Ni.

Uses:

- It is used in lap tops.
- It is used in mobile phones.
- It is used in iPods.
- It is used in MP³ players.

Potentiometric titrations

Titrations which involve the measurement of potential of an indicator electrode with the addition of a titrant is called potentiometric titrations.

Merits of potentiometric titrations:

- No external indicator is required.
- Titrations of weak acids & bases can be carried out potentiometrically.

Principle:

The potential of an electrode dipping into the solution of an electrolyte depends upon the concentration of ions with which it is in equilibrium. Potentiometric titrations are based on the fact that potential of suitable indicator electrode is measured relative to that of a reference electrode and is related to the concentration changes in the solution being titrated. Near the end point, there is a sharp change in the potential of indicator electrode.

Types of potentiometric titrations

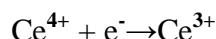
Three types of potentiometric titrations are

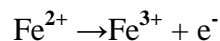
1. Acid – base titrations
2. Redox titrations
3. Precipitation titrations

Potentiometric redox titrations

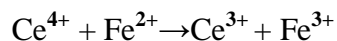
In order to explain the potentiometric titration, let us consider the oxidation of Fe^{2+} to Fe^{3+} by Ce^{4+} in acid medium.

The Ce^{4+} ions having greater reduction potential (1.60V) will undergo reduction & Fe^{2+} ions (0.77V) get oxidized to Fe^{3+} .





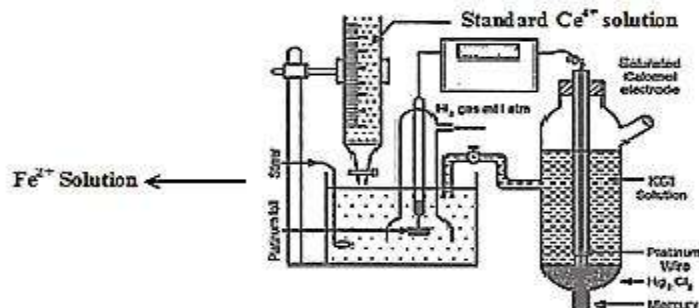
Over all reaction;



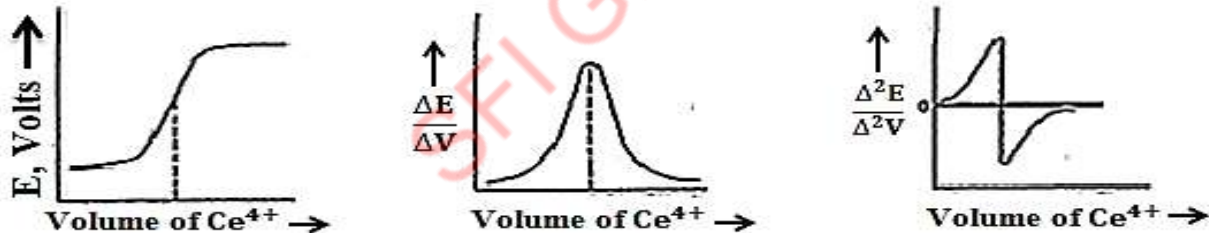
The potential of indicator electrode is

$$E = E_0 + \frac{0.0591}{n} \log \frac{[\text{oxidised state}]}{[\text{reduced state}]} = E_0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

20 ml ferrous sulphate solution is mixed with 20ml 4N H_2SO_4 in a beaker. A platinum electrode is then inserted into it. It is then coupled with SCE. The electrodes are then connected using a potentiometer. Then standard ceric ammonium sulphate solution is added from the burette. After each addition emf is noted. Emf is then plotted against volume of ceric solution. Emf initially increases with the addition of titrant due to the oxidation of Fe^{2+} . Near the end point potential changes sharply. After the end point emf changes very slowly.



Emf is then plotted against volume of Ce^{4+} solution, we get an 'S' shaped curve. More and most accurate results are obtained by plotting $\frac{\Delta E}{\Delta V}$ against volume of Ce^{4+} solution and $\frac{\Delta^2 E}{\Delta^2 V}$ against volume of Ce^{4+} solution, the following curves are obtained.



Uses of potentiometric titration

- There is no need of any external indicator.
- We can conduct the titration of coloured solutions.
- It is useful for the titration of very dilute solution with high degree of accuracy.
- It is useful for the titration of solution contains CN^- , Cl^- etc.

Fundamentals for the measurement of conductivity

Ohm's law:

It states that current passing through the conductor is directly proportional to the potential difference.

$$I \propto V$$

$$V = IR$$

Resistance:

It is the measure of obstruction to the flow of current. Its unit is Ω

$$R \propto l \text{ and } R \propto \frac{1}{A}$$

$$R = \rho \times \frac{l}{A}$$

Conductance:

It is the reciprocal of resistance.

$$C = \frac{1}{R}$$

Specific Resistance (Resistivity):

It is the resistance of a conductor of unit length and unit area of cross section. Or it is the resistance of unit volume of a conductor. Its unit is Ωcm

$$\rho = R \times \frac{A}{l}$$

Specific Conductance (Conductivity):

It is the reciprocal of resistivity. It is also defined as the conductance of unit length and unit area of cross section of a conductor. Its unit is Scm^{-1}

$$K = \frac{1}{R} \times \frac{l}{A} = C \times \frac{l}{A}$$

Molar conductance:

Molar conductance is the conductance of a solution containing 1mol of an electrolyte which is placed between two electrodes which are separated by unit distance. It is denoted by the letter λ_m . Its unit is $\text{Scm}^{-1}\text{mol}^{-1}$.

$$\lambda_m = \frac{1000K}{C}$$

Equivalent conductance:

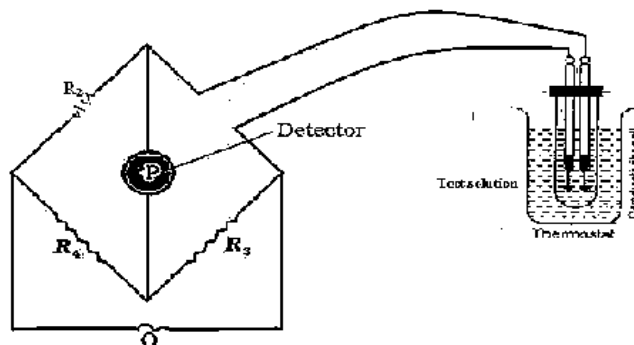
Equivalent conductance is the conductance of a solution containing 1gram equivalent of an electrolyte which is placed between two electrodes which are separated by unit distance. It is denoted by the letter λ . Its unit is $\text{Scm}^{-1}\text{equi}^{-1}$.

$$\lambda = \frac{1000K}{M}$$

The experimental arrangement and procedure for measuring conductance of an electrolytic solution

$$\text{Conductivity of the solution} = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A}$$

Thus for the measurement of conductivity of solution resistance of the solution is to be determined. Wheat stone bridge method is used for this purpose. In this method, a conductivity cell containing the solution is made one arm of the wheat stone bridge apparatus. The electrodes of the cell are made up of platinum coated with platinum black. Then the conductivity cell is placed in a thermostat to keep the temperature constant. In order to prevent electrolysis, an Alternating Current is used. When current passes through the circuit, the resistors R_2 , R_3 and R_4 are so adjusted that a null point is obtained in the detector.



At the null point,

$$\frac{R_{\text{solution}}}{R_2} = \frac{R_3}{R_4}$$

$$R_{\text{solution}} = \frac{R_2 R_3}{R_4}$$

The reciprocal of this resistance will give the conductance of the solution. From the conductance we get the specific conductance of the solution. Since conductivity of the solution = $C \times \frac{l}{A}$, where 'l' is the distance between the electrodes and 'A' is the area of cross section of electrodes. For a particular conductivity cell, $\frac{l}{A}$ is constant and is called cell constant.

$$K = C \times \text{Cell constant}$$

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \frac{K}{C}$$

PROBLEMS

1. The specific conductivity of $N/50$ KCl solution at 25°C is $0.0002765\text{ohm}^{-1}\text{cm}^{-1}$. If the resistance of the cell containing this solution is 500Ω , what is its cell constant?

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A}$$

$$\text{Cell constant} = K \times R = 0.0002765 \times 500 = 0.13825\text{cm}^{-1}$$

2. The specific conductance of a decinormal solution of KCl at 18°C is $0.0112\Omega^{-1}\text{cm}^{-1}$. The resistance of the cell containing the solution at 18°C was found to be 55Ω . What is cell constant.

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{55} \times \text{cell constant} = 0.0112\Omega^{-1}\text{cm}^{-1}$$

$$\text{Cell constant} = K \times R = 0.0112 \times 55 = 0.616\text{cm}^{-1}$$

3. Find the specific conductance of a given solution at 298K . The resistance of the solution and 0.1M KCl solution are found to be $75\text{k}\Omega$ and $300\text{k}\Omega$ respectively at 298K in the same conductivity cell. Specific conductance of KCl is 0.012Scm^{-1} .

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{300} \times \text{cell constant} = 0.012\text{Scm}^{-1}$$

$$\text{Cell constant} = K \times R = 0.012 \times 300 = 3.6\text{cm}^{-1}$$

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \text{Cell constant} = \frac{1}{75} \times 3.6 = 0.048\text{Scm}^{-1}$$

4. The decinormal solution of an electrolyte in a conductivity cell whose electrodes are 2.1cm apart and 4.2cm^2 in area offered a resistance of 32Ω . Find the equivalent conductance of the solution.

$$\lambda_{\text{Eq}} = \frac{1000K}{C} = \frac{1000 \times l}{C \times R \times A} = \frac{1000 \times 2.1}{0.1 \times 32 \times 4.2} = 156.25\text{S cm}^{-1}\text{Eq}^{-1}$$

5. Calculate the conductivity of given NaCl solution at 298K , which shows a conductance of $560\mu\Omega^{-1}$ in the given cell at 298K . A standard solution of 0.1M KCl shows a conductance of $1200\mu\Omega^{-1}$ in that cell. Given that conductivity of 0.1M KCl at 298K is $0.01288\Omega^{-1}\text{cm}^{-1}$.

$$K_{\text{KCl}} = C_{\text{KCl}} \times \text{Cell constant}$$

$$\text{Cell constant} = \frac{K_{\text{KCl}}}{C_{\text{KCl}}} = \frac{0.01288}{1200 \times 10^{-6}} = 10.73\text{cm}^{-1}$$

$$K_{\text{NaCl}} = C_{\text{NaCl}} \times \text{Cell constant} = 560 \times 10^{-6} \times 10.73 = 6.01 \times 10^{-3}\Omega^{-1}\text{cm}^{-1}$$

Corrosion

Corrosion is the slow process of deterioration or destruction of the metal through the chemical or electrochemical changes taking place at its surface. Corrosion reactions are of two types. On the basis of this, theories of corrosion are of two types.

I. Dry corrosion (Chemical corrosion)

II. Wet corrosion (Electrochemical corrosion)

I. Dry corrosion:

Corrosion of this type gases occurs by the direct chemical attack of atmospheric gases on the metal in the absence of moisture. They are of three types.

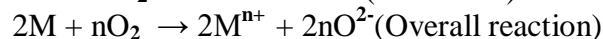
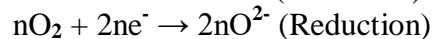
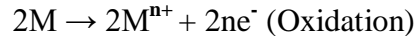
1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

1. Oxidation corrosion:

It occurs due to the direct action of oxygen on metals in the absence of moisture to form metal oxide. Alkali metals and alkaline earth metals undergo this type of corrosion even at low temperature, whereas noble metals like gold, silver and platinum undergo oxidative corrosion only at high temperature.

Mechanism:

Oxidation occurs at the surface of the metal to form the metal oxide. On oxidation, the metal atoms change to metal ions (M^{n+}) and oxygen changes to oxide ions (O^{2-}). These oppositely charged ions then combine together to form the metallic oxide.



Thus a thin layer of metal oxide is formed on the surface of the metal. The nature of the oxide film determines the further destruction of the metal. Films can be of different types.

a) Stable film:

Stable films can adhere tightly to the metal surface. This film can act as a protective coating to prevent further deterioration of the metal. Oxide films of Al, Sn, Cu, Pb etc. are included in this film.

b) Unstable films:

Unstable films readily decompose back to metal and oxygen. In this case metal will not undergo further deterioration. This type of film is obtained in the case of metals like gold, silver and platinum.

c) Volatile film:

This type of film volatilises off as soon as it is formed. Hence the underlying metal surface again becomes exposed for further attack of oxygen and this process continues. Here corrosion becomes a continuous process and the observed destruction will be maximum. Molybdenum can produce volatile oxide film.

d) Porous oxide film:

If the oxide film formed is porous, then the atmospheric oxygen can penetrate through the film to attack the underlying metal. Here also corrosion becomes a continuous process leading to the total destruction of the metal. Iron can produce this type of film.

2. Corrosion by other gases:

Similar to oxygen, some other gases also bring dry corrosion. They are SO_2 , CO_2 , Cl_2 , H_2S , F_2 , H_2 etc. Extent of corrosion is determined by its chemical affinity towards the metal. It also depends upon the nature of the film, whether the film is porous or protective.

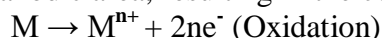
3. Liquid metal corrosion:

This type of corrosion is seen in nuclear power stations. It occurs due to the chemical action of flowing liquid metal on solid metal or alloys at high temperature. In such cases, solid metal may dissolve in the liquid metal or liquid metal may penetrate into the internals of solid metals.

II. Wet corrosion (Electrochemical corrosion)

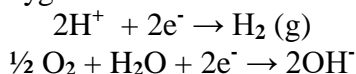
This type of corrosion can occur when a conducting liquid is in contact with a metal or when two dissimilar metals or alloys are partially immersed in a conducting solution.

Oxidation takes place at the anodic area, resulting in the corrosion of the metal.



The M^{n+} ions so formed dissolves in the solution.

Reduction occurs at the cathodic area. At the cathodic area, the dissolved constituents in the conducting medium accept electrons to form ions like OH^- , O^{2-} etc. The non-metallic ions so formed combine with the M^{n+} to form corrosion product. The electrons released at the anode flow through the metal and get consumed in the cathodic reaction, either for the evolution of hydrogen or for the absorption of oxygen.

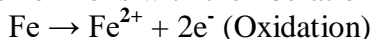


Corrosion with evolution of H_2 occurs, when the anodic area is very large and cathodic area is small and it usually occurs in acidic environments. Absorption of O_2 occurs in neutral or slightly alkaline medium.

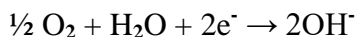
Rusting of iron

In this initially a thin film of iron oxide is formed on the surface of iron metal. Some cracks are developed on the iron oxide film. The surface of the metal acts as the anodic area, whereas the interior of the metal behaves as cathode.

At the anodic area, Fe dissolves as Fe^{2+} ions with the liberation of electrons.

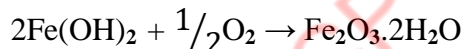


The electrons thus released from the anode move to the cathodic area through the metal. These electrons are then taken up oxygen molecule to form OH^- ions.

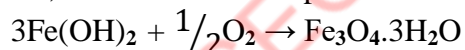


The Fe^{2+} ions formed at the anodic area and the OH^- ions formed at the cathodic area combine to form $\text{Fe}(\text{OH})_2$ precipitate.

In the presence of excess of oxygen, $\text{Fe}(\text{OH})_2$ precipitate easily oxidises to get yellow rust having the formula, $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$



If the amount of oxygen is limited, then the corrosion product is black rust (Hydrated magnetite)



Galvanic series

Relative corrosion affinities of metals and alloys can be explained by using a series called galvanic series. This series can be prepared by studying the corrosion affinities of metals and alloys in unpolluted sea water without their oxide films. A metal high in this series is more anodic and undergoes corrosion faster than the metal below it. The position of a metal in the form of an alloy is different from that of the pure metal in this series.

Comparison of electrochemical series and galvanic series

Electrochemical Series	Galvanic series
<ul style="list-style-type: none"> • E^0 is measured only for metals and non-metals. • E^0 is measured by dipping pure metals in their 1M salt solution. • SHE is used as the reference electrode. • Position of the metals is fixed. • It predicts the relative displacement tendencies. 	<ul style="list-style-type: none"> • E^0 is measured only for metals and alloys. • E^0 is measured by dipping metals and alloys in unpolluted sea water. • Calomel electrode is used as the reference electrode. • Position of the metal and alloys may change. • It predicts the corrosion tendencies.

Galvanic series of metals and alloys

Active or Anodic

- ↑
1. Mg
 2. Mg Alloy
 3. Zn
 4. Al
 5. Cd
 6. Al Alloy
 7. Mild Steel
 8. Cast Iron
 9. High Ni Cast Iron
 10. Pb-Sn Solder
 11. Pb
 12. Sn
 13. Inconel
 14. Ni-Mo-Fe Alloys
 15. Brass
 16. Monel (30% Cu, 7% Ni and rest Fe)
 17. Ag Solder
 18. Cu
 19. Ni
 20. Cr Stainless steel
 21. 18-8 Stainless Steel
 22. 18-8 Mo Stainless Steel
 23. Ag
 24. Ti
 25. Graphite
 26. Au
 27. Pt

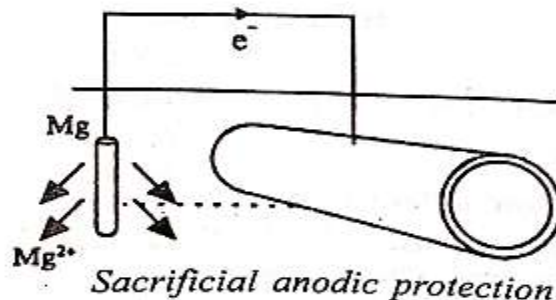
Noble or Cathodic

Cathodic Protection:

In this method, the metal to be protected is made as cathode so that corrosion will not occur. The following methods are employed for cathodic protection.

a) Sacrificial anodic protection:

In this method, the metal to be protected is connected by a wire to a more anodic or active metal. Then the more active metal will undergo corrosion and the cathode remains protected.

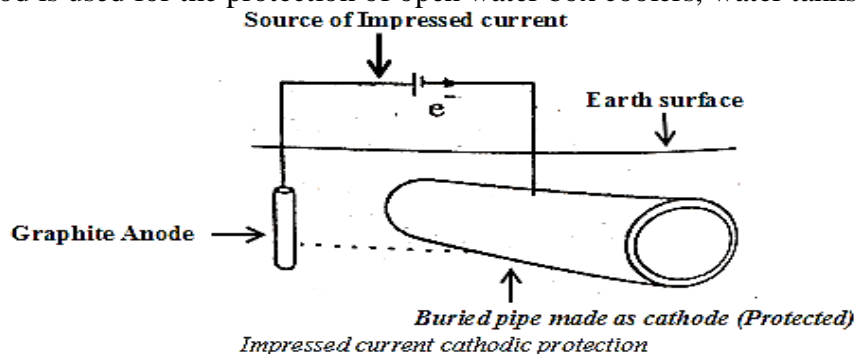


Here the more active anodic metal sacrifices for the protection of cathodic metal and is called sacrificial anode. Metals commonly used for this purpose are Mg, Zn, Al and their alloys.

b) Impressed current cathode protection:

In this method an impressed current is applied in opposite direction to nullify the corrosion current. As a result corroding metal is converted from anode to cathode. The impressed current

required can be obtained from a battery with an insoluble anode made of graphite or high silica iron. This method is used for the protection of open water box coolers, water tanks etc.



Comparison of sacrificial anode protection and impressed current cathodic protection

Sacrificial anode protection	Impressed current cathodic protection
<ul style="list-style-type: none"> • No external power supply is required. • Economical for short term protection. • Investment is less. • Requires periodical replacement of anodic material. • Suitable when current requirements and resistivity of the electrolyte are relatively low. 	<ul style="list-style-type: none"> • External power supply is required. • More suitable for long term protection. • High investment is required. • Anodes are relatively stable and do not corrode. • Suitable when current requirements and resistivity of the electrolyte are relatively high.

Electroless plating (Autocatalytic plating)

It is the method of depositing a metal from its salt solution on the catalytically active surface of the metal to be plated using a suitable reducing agent without using electrical energy.

In this process, metal piece to be plated is immersed in a mixture of reducing agent and a complex compound. The reducing agent reduces metal ion into metal which gets plated over the catalytically active surface of the metal to produce a thin uniform coating. This process is a controlled chemical reduction and is catalyzed by the metal or alloy being deposited. This method allows the easy preparation of films of low thickness using simple equipments. Most common electroless plating is electroless nickel plating.

Electroless Nickel plating

Pretreatment and activation of the surface

The surface to be plated is first degreased by using organic solvents or alkali. It is then followed by acid treatment. Surface of stainless steel is then activated by dipping in a hot solution of 50% dil. H_2SO_4 . Mg alloy surface can be activated by thin coating of Zn and Copper over it. Metals like Cu, Al and alloys like brass can be directly Ni plated without activation. Non-metallic articles like plastics, glasses are activated by dipping them in the solution of SnCl_2 and HCl followed by dipping in PdCl_2 solution. A thin layer of Pd will be formed on the surface upon drying.

Procedure

The pretreated object is immersed in the plating bath containing Nickel sulphate salt (Coating), hypophosphate reducing agent (Metal deposition), complexing agent like Sodium succinate (Quality improvement) and a buffer like Sodium Acetate (pH maintenance). Air is then applied and heated. Electroless plating of Ni takes place as follows.



Applications of electroless Ni plating

- It is extensively used in electronic applications.
- Electroless Ni plated polymers like ABS are used for decoration purpose.
- It is also used automotive fields.

Advantages

- No electricity is required.
- This can be carried out on insulators on insulators and semiconductor materials.
- This can be used to obtain uniform coating on irregular shaped objects.
- These deposits are more compact and highly adherent.

Electroless Copper plating

In this method, article to be plated is immersed in a plating bath containing CuSO_4 (As a source of Cu), formaldehyde (Reducing Agent), buffer solution of NaOH and Rochelle salt and a complexing reagent. Air is bubbled slowly through the medium to control the formation of cuprous oxide. Electroless plating of Cu takes place as follows.

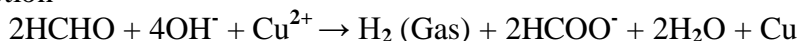
Oxidation



Reduction



Net reaction



Applications of electroless Cu plating

- Widely used for metalizing printed circuit boards.
- Used for plating on non-conductors.
- It is also used for making decorative plating on plastics.

Advantages

- This method produces even coatings.
- It does not use electrical power.
- This coating is having improved hardness, strength, ductility and resistance to corrosion.

Disadvantages

- The reducing agent, formaldehyde is a human health hazard.
- The instability of the electroless copper bath creates difficulties in process control.

Prepared by *Raji Sankar, Assistant Professor*

Dept. of mathematics & Basic sciences,

Sree Buddha College of Engineering, Pattoor