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.
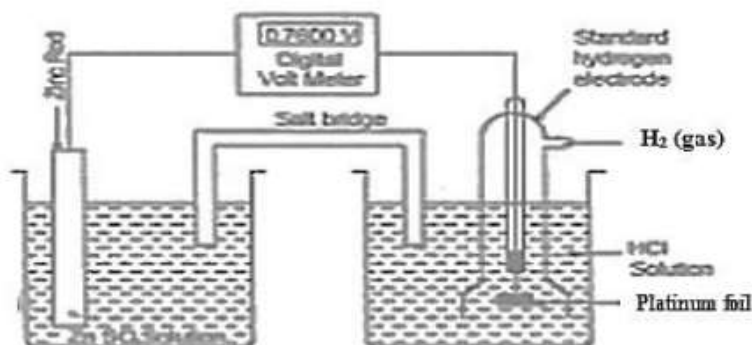
The resultant cell can be represented in the following manner,

$$\text{Zn/Zn}^{2+}//\text{H+}_{(1M)}/\text{H2}_{(1atm)}/\text{Pt}$$
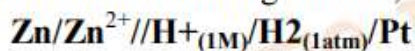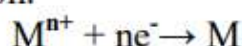
$$E^0 \text{ Cell} = E^0_{cathode} - E^0_{anode}$$

$$= E^0_{SHE} - E^0_{Zn/Zn2+}$$

$$0.76 \text{ V} = 0 - E^0_{Zn/Zn2+}$$

$$(E^0_{Zn/Zn2+} = -0.76V)$$

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.

$$M^{n+} + ne^- \rightarrow M$$

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

$$\Delta G = \Delta G^0 + RT \ln K \qquad (1)$$

Where ΔG is the free energy change, ΔG^0 is the standard free energy change, R is the universal gas constant, K is the equilibrium constant and T is the temperature in Kelvin.

$$K = \frac{[M]}{[M+]}$$

According to Gibbs-Helmholtz suggestion,

$$\Delta G = -nFE \ \& \ \Delta G^0 = -nFE^0 \qquad\qquad (2)$$

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 $R = 8.314 J/K$, $T = 298K$ & $F = 96500C$, 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,

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

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 $E^0_{(cell)}$ 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_0cell= 1.1V.

$$\text{Log K} = \frac{n E_{ocell}}{0.0591} = \frac{2 \times 1.1}{0.0591} = 37.22$$
$$K = 1.68 \times 10^{37}$$

➢ Calculate the standard emf of $H_2 - O_2$ fuel cell. (E^0values for hydrogen and oxygen half cells are -0.40V & 0.83V respectively.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode} = E^0_{O2} - E^0_{H2} = 0.83 - (-0.40) = 1.23V$$

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

$$\text{Log K} = \frac{n E_{ocell}}{0.0591} = \frac{2 \times 0.295}{0.0591} = 10$$
$$K = 10^{10}$$

➢ What is the concentration of Ni^{2+} in the cell at 25^0C, if the emf is 0.601V? Given that E_0 Ni(s)/Ni^{2+} is -0.25V & E_0 Cu(s)/Cu^{2+} is 0.34V. Ni(s)/Ni^{2+} $_{(a=?)}$//Cu^{2+} $_{(0.75M)}$/Cu(s).

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu2+]}{[Ni2+]}$$

Where $E^0_{cell} = 0.34$ (-0.25) = 0.59, E_{cell}= 0.601V

$$0.601 = 0.59 + 0.0295 \log \frac{0.75}{[Ni2+]}$$

$$\frac{0.011}{0.0295} = \log \frac{0.75}{[Ni2+]}$$

$$\frac{0.75}{[Ni2+]} = 2.356.$$

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

➤ Calculate the emf of the cell Zn/Zn^{2+} (0.01M)//Cu^{2+} (0.1M)/Cu. Write its half-cell reactions isE^0_{Zn} is -0.76V and E^0_{Cu} is +0.34V.

The cell reaction is

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

Nernst equation for this cell reaction is

$$E\ cell = E0\ cell + \frac{0.0591}{2} \log \frac{[Cu2+]}{[Zn2+]}$$

But $E^0_{cell} = E^0_R - E^0_L = 0.34 + 0.76 = 1.1V$

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

➤ Calculate the equilibrium constant of the reaction, $Cu + 2Ag^* \rightarrow Cu^{2+} + 2Ag$
(E_0 Ag(s)/Ag^* is 0.80V & E_0 Cu^{2+}/Cu(s) is 0.34V.)

Eocell= E_0 Ag(s)/Ag^* - E_0 Cu^{2+}/Cu(s) = 0.80 – 0.34 = 0.46

$$Log\ K = \frac{nEocell}{0.0591} = \frac{2 \times 0.46}{0.0591} = 15.57$$

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

➤ Calculate the emf of the following cell at 25^0C,
Zn|Zn^{2+} (a – 0.0004) || Cd^{2+}(a – 0.2) |Cd; ($E^0_{Cd2+/Cd}$ = -0.403V & $E^0_{Zn2+/Zn}$ = -0.76V)
$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Cd2+/Cd} - E^0_{Zn2+/Zn} = -0.403 + 0.76$
= 0.357V
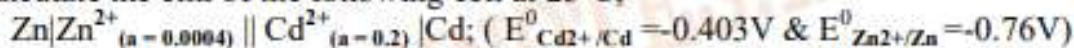
$$E\ cell = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cd2+]}{Zn2+} = 0.357 + \frac{0.0591}{2} \log \frac{[0.2]}{0.0004}$$
= 0.4367V

➤ Find the single electrode potential for copper metal in contact with0.1M Cu^{2+} solution at 298K. $E^0_{Cu2+/Cu}$ = 0.34V

$$E_{Cu} = E^0_{Cu} + \frac{0.0591}{2} \log [Cu^{2+}] = 0.34 + \frac{0.0591}{2} \log [0.1]$$
= 0.31045V

➤ Determine the standard emf of the cell and standard free energy change of the cell reaction. Zn, Zn^{2+} || Ni^{2+}, 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^0_{cell} = E cathode - E anode = - 0.25 - (- 0.76) = + 0.51 V

E^0_{cell} is + ve and ΔG^0 should be - ve.

ΔG^0 = - n FE^0_{cell}

ΔG^0 = - (2X 96500 X 0.51) = - 98430 Joules

➤ Calculate the amount of electrical energy available from dry cell of EMF 1.5 V which consumes 10g Zn.(At wt. of Zn = 65.5g)

ΔG = -nFE = -2X96500X1.5 = 289500J

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

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
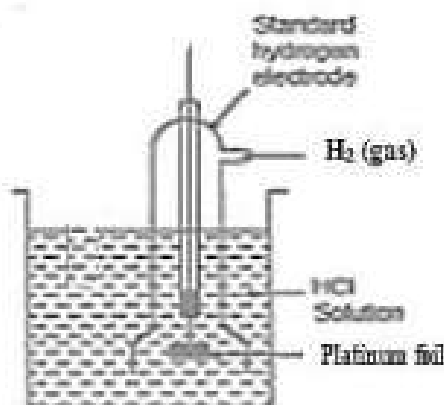
Characteristics of SHE

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

$$Pt, H_{2 \text{ (g) 1atm}} / H^+_{\text{ (1M)}}$$

Cell reaction:

$$\frac{1}{2} H_2 \rightarrow H^+ + 1e^-$$

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

$$H^+_{\text{ (1M)}} / H_{2 \text{ (g) 1atm}}, Pt$$

Cell reaction:

$$H^+ + 1e^- \rightarrow \frac{1}{2} H_2$$
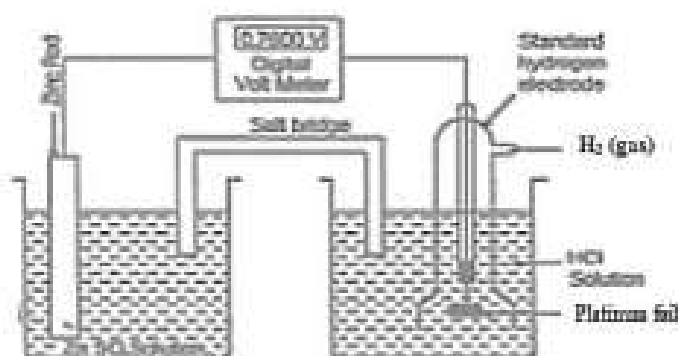
Uses:

It is used for determining unknown potential of an electrode.

Working of SHE (Determination of E° using SHE)

Consider a Zinc rod dipped in ZnSO4 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.

$$Zn_{(S)} / Zn^{2+} (1M) // H^+(1M) / Pt, H_2 (g) \text{ 1atm}$$

$$E^0 Cell = E^0_{cathode} - E^0_{anode}$$
$$= E^0_{SHE} - E^0_{Zn/Zn2+}$$
$$0.76 \text{ V} = 0 - E^0_{Zn/Zn2+}$$

$E^0_{Zn/Zn2+} = -0.76V$

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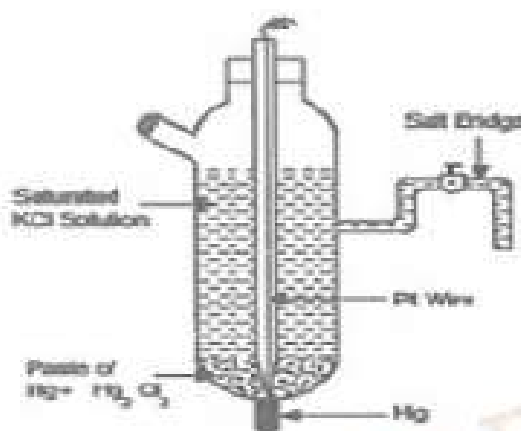
Calomel electrode consists of a glass having side tube on both sides. Mercury covered with a paste of Hg_2Cl_2 is taken at the bottom the glass tube. Inside the glass tube 0.1N or 1N or saturated KCl solution is taken. A Pt wire is dipped into the glass tube containing Hg, which helps for electrical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

Calomel electrode can be represented as, **$Pt,Hg_{(l)}|Hg_2Cl_{2(s)}|KCl(sat)$**

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

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

Oxidation

$2Hg_{(l)} \rightarrow 2Hg^+ + 2e^-$

$2Hg^+ + 2Cl^- \rightarrow Hg_2Cl_2$

Overall oxidation reaction

$2Hg_{(l)} + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

Reduction

$Hg_2Cl_2 \rightarrow 2Hg^+ + 2Cl^-$

$2Hg^+ + 2e^- \rightarrow 2Hg$

Overall reduction reaction

$Hg_2Cl_2 + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-$

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.

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$
$$Zn \rightarrow Zn^{2+} + 2e^-$$
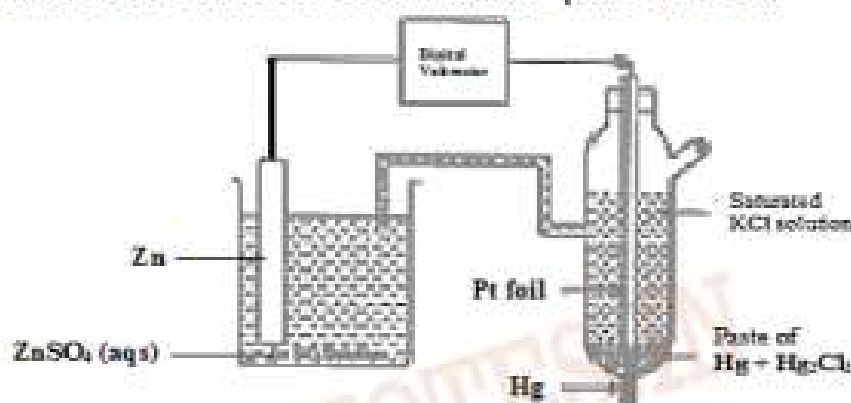
The resultant cell can be represented as

$$Zn/Zn^{2+}//KCl_{(satt)}/Hg_2Cl_{2(s)}/Hg_{(l)}/Pt$$
$$E_{cell} = E_R - E_L = E_{cal} - E_{Zn/Zn2+} = 0.2422 - E_{Zn/Zn2+}$$
$$E_{Zn/Zn2+} = 0.2422 - E_{cell}$$

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 015glass 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.

Ag,AgCl(s)/HCl(0.1N)/Glass//
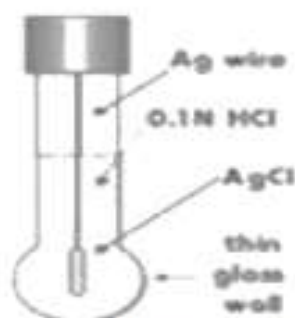
Glass electrode works on the principle that potential difference between the surface of the glass membrane and a solution is a linear function of P^H. Here the glass membrane acts as an ion selective membrane sensitive to $[H^+]$. So an ion exchange reaction occurs between singly charged cations of glass (Na^+) & H^+ ions of solution. Finally an equilibrium is established between (Na^+) ions of glass & H^+ ions of solution.

$$H^+_{(solution)} + Na^+Gl^- \rightarrow Na^+_{(solution)} + H^+Gl^-$$
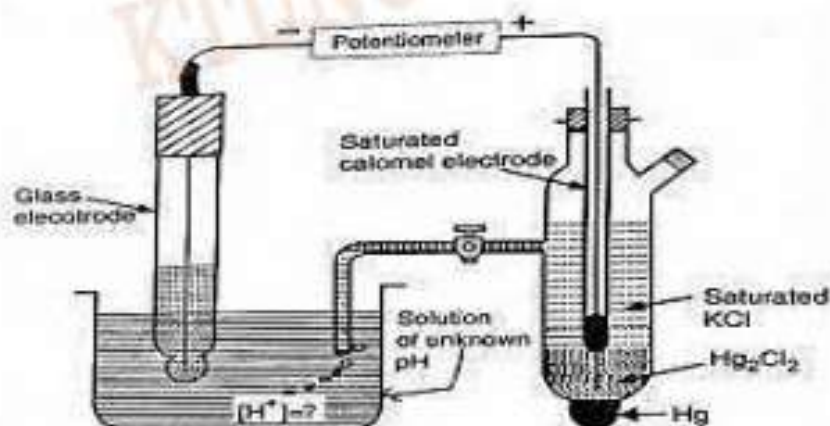$$E_G = E^0_G + 0.0591 \log [H^+] = E^0_G - 0.0591\ P^H$$
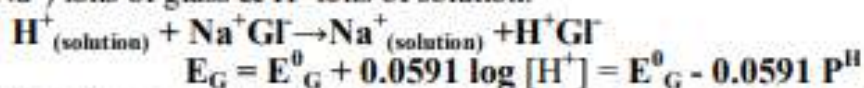
The potential of glass electrode varies with concentration of H^+ ions. E^0_G is constant and it depends on the nature of the glass and also the P^H of the solution taken inside the glass bulb.
$E^0_G = 0.6990$ V

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, Ag,AgCl$_{(S)}$/0.1N HCl/Glass/Solution of Unknown P^H// KCl$_{(sat)}$/Hg$_2$Cl$_{2(s)}$/Hg$_{(l)}$/Pt

$$E_{cell} = E_R - E_L = E_{SCE} - E_G$$
$$= 0.2422 - (E^0_G - 0.0591\ P^H)$$
$$= 0.2422 - E^0_G + 0.0591\ P^H$$

E^0_G of glass electrode can be determined by using a solution of known P^H.
$$0.0591\ P^H = E_{cell} + E^0_G - 0.2422$$
$$P^H = \frac{E_{Cell} + E^0G - 0.2422}{0.0591}$$

Advantages of glass electrode

1. It is very simple to operate.

2. It can be use 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 has 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 25^0C. Given that $E_{SCE} = 0.2422V$.

$$E_{cell} = E_{cal} - E_{H2} = 0.2422 + 0.0591\ P^H = 0.523V$$
$$P^H = \frac{0523 - 0.2422}{0.0591} = 4.75$$

➤ Potential of H_2 electrode set up in acid solution of unknown strength is 0.295 volts at 25^0C when coupled with SHE. Find the P^H of the solution.

$$E_{H2} = E^0_{H2} + 0.0591\ \log\ [H+] = -0.0591 P^H$$
$$E_{Cell} = E_{Cathode} - E_{Anode} = E_{SHE} - E_{H2} = 0 + 0.0591\ P^H = 0.0591 P^H$$
$$P^H = \frac{E_{H_2}}{0.0591} = \frac{0.295}{0.0591} = 4.99$$

➤ Find out the PH 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°C. Given that $E_{SCE} = 0.2422V$ and $E^0{}_{Glass} = 0.57V$.
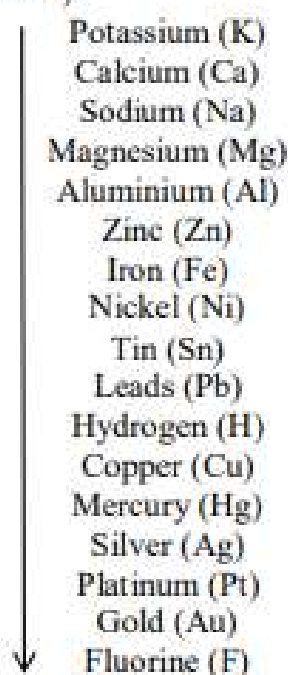
$$P^H = \frac{E_{Cell} + E^0 G - 0.2422}{0.0591} = \frac{0.205 + 0.57 - 0.2422}{0.0591} = 9.02$$

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:

$$E^o{}_{Cell} = E^o{}_{Cathode} - E^o{}_{Anode}$$

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. $\Delta G = -nFE_{cell}$ Hence, Ecell should be positive for spontaneous reaction. Ecell of the cell can be calculated from the redox potentials by using the relation Ecell= $E_{cathode} - E_{anode}$

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.

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.

Then electrical energy = nFE = - ΔG

$$\Delta G = -nFE$$

Criteria for spontaneity in terms of cell emf

Case 1: If $\Delta G < 0$ or ΔG is –ve, then Ecell > 0 or Ecell is +ve and the reaction will be spontaneous.

Case 2: If $\Delta G = 0$, then Ecell = 0 and the reaction will be in equilibrium.

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

Fundamentals for the measurement of conductivity

Ohm's law:

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

$$I \infty V$$
$$V = IR$$

Resistance:

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

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

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

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 $Scm^{-1}mol^{-1}$.

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

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 $Scm^{-1}equi^{-1}$.

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

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

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 R2, R3 and R4

Alternating Current is used. When current passes through the circuit, the resistors R2, R3 and R4 are so adjusted that a null point is obtained in the detector.
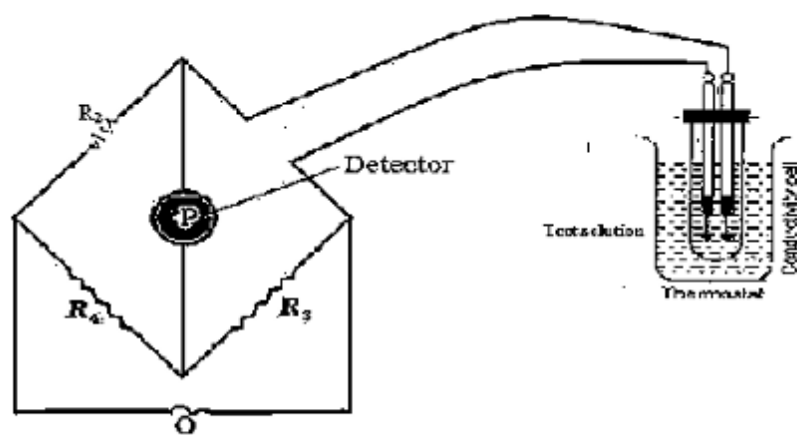
At the null point,

$$\frac{\text{Rsolution}}{R2} = \frac{R3}{R4}$$

$$\text{R solution} = \frac{R2R3}{R4}$$

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.

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

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

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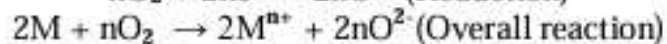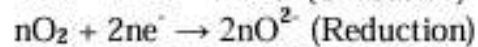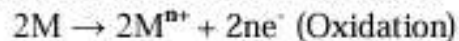
1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

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.

$$2M \rightarrow 2M^{n+} + 2ne^- \text{ (Oxidation)}$$
$$nO_2 + 2ne^- \rightarrow 2nO^{2-} \text{ (Reduction)}$$
$$2M + nO_2 \rightarrow 2M^{n+} + 2nO^{2-} \text{ (Overall reaction)}$$

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 volatalises 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. Extend 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.

$$M \rightarrow M^{n+} + 2ne^- \text{ (Oxidation)}$$
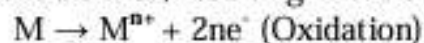
The M^{n+} ions so formed dissolves in the solution.

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.

$$2H^+ + 2e^- \rightarrow H_2 \text{ (g)}$$
$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
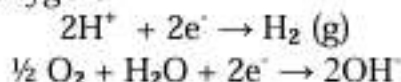
Corrosion with evolution of H_2 occurs, when the anodic area is very large and cathodic area is small and it usually occurs in acidic environments. Absorption of O_2 occurs in neutral or slightly alkaline medium.

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.

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Oxidation)}$$
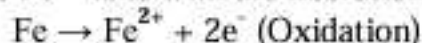
The electrons thus released from the anode move to the cathodic area through the metal. These electrons are then taken up oxygen molecule to form OH^- ions.

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
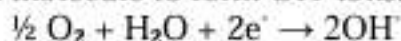
The Fe^{2+} ions formed at the anodic area and the OH^- ions formed at the cathodic area combine to form $Fe(OH)_2$ precipitate.

In the presence of excess of oxygen, $Fe(OH)_2$ precipitate easily oxidises to get yellow rust having the formula, $Fe_2O_3.2H_2O$

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$$
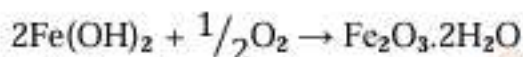
If the amount of oxygen is limited, then the corrosion product is black rust (Hydrated magnetite)

$$3Fe(OH)_2 + \tfrac{1}{2}O_2 \rightarrow Fe_3O_4.3H_2O$$
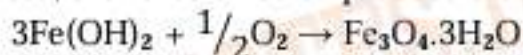
Galvanic series

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
• E^o is measured only for metals and non-metals.	• E^o is measured only for metals and alloys.
• E^o is measured by dipping pure metals in their 1M salt solution.	• E^o is measured by dipping metals and alloys in unpolluted sea water.
• SHE is used as the reference electrode.	• Calomel electrode is used as the reference electrode.
• Position of the metals is fixed.	• Position of the metal and alloys may change.
• It predicts the relative displacement tendencies.	• 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. Iconel
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.

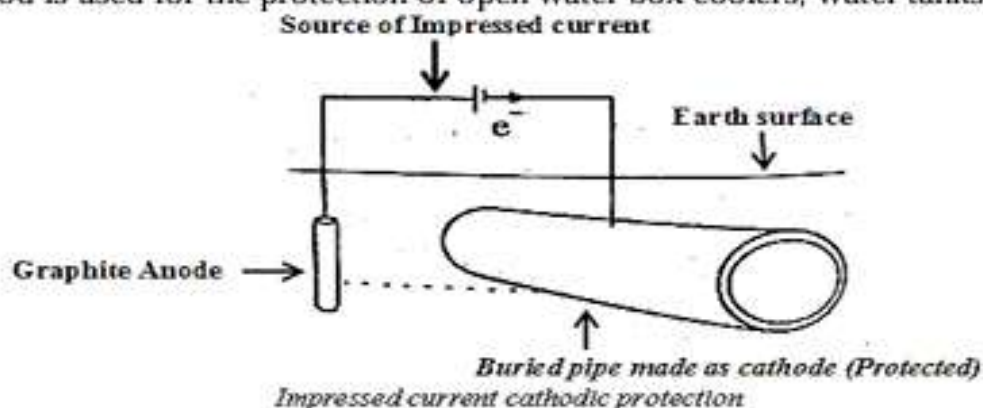*Sacrificial anodic protection*
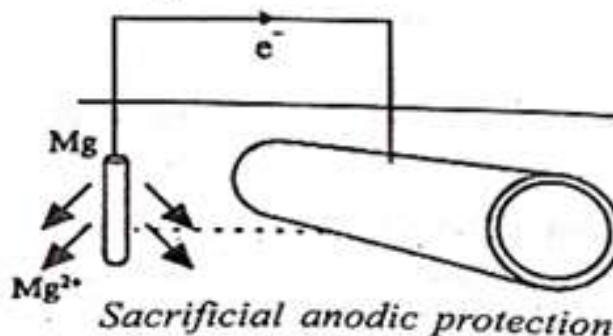
Here the more active anodic metal sacrifices for the protection of cathodic metal and is called sacrificial anode. Metals commonly used for this purpose re Mg, Zn, Al and their alloys.

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.

Impressed current cathodic protection

Comparison of sacrificial anode protection and impressed current cathodic protection

Sacrificial anode protection	Impressed current cathodic protection
• No external power supply is required.	• External power supply is required.
• Economical for short term protection.	• More suitable for long term protection.
• Investment is less.	• High investment is required.
• Requires periodical replacement of anodic material.	• Anodes are relatively stable and do not corrode.
• Suitable when current requirements and resistivity of the electrolyte are relatively low.	• 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.
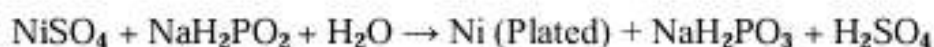
Electroless Nickel plating

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 (P^H maintenance). Air is then applied and heated. Electroless plating of Ni takes place as follows.

$$NiSO_4 + NaH_2PO_2 + H_2O \rightarrow Ni\ (Plated) + NaH_2PO_3 + H_2SO_4$$

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.
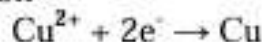- These deposits are more compact and highly adherent.

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.
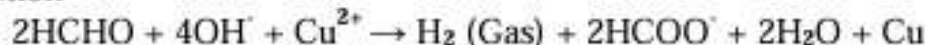
Oxidation

$$2HCHO + 4OH^- \rightarrow H_2\ (Gas) + 2HCOO^- + 2H_2O + 2e^-$$

Reduction

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Net reaction

$$2HCHO + 4OH^- + Cu^{2+} \rightarrow H_2\ (Gas) + 2HCOO^- + 2H_2O + Cu$$

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.