MODULE I -ELECTROCHEMISTRY

Introduction

Electrochemistry is the branch of chemistry which deals with the relation between chemical energy and electrical energy.It includes two types of cells.

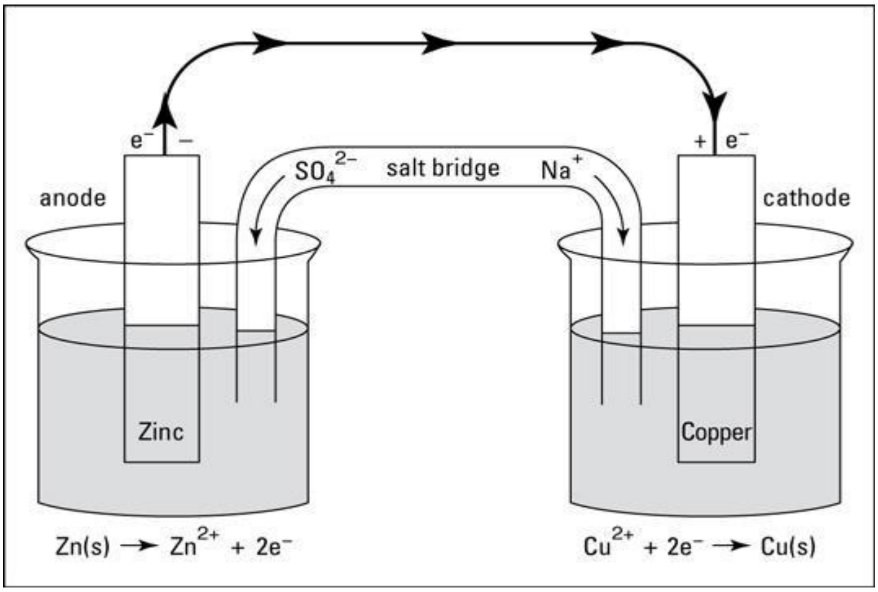
They are:-

1. Electrolytic cell- it is used to convert electrical energy in to chemical energy.
2. Electrochemical cell- it is used to convert chemical energy in to electrical energy.it is also called galvanic cell or voltaic cell.

Differences between electrolytic and electrochemical cells

Electrolytic cell	Electrochemical cells
Conversion of electrical energy into chemical energy	Chemical energy into electrical energy
The anode is positive plate and cathode is negative plate	The anode is negative plate and cathode is positive plate
Electrons are supplied to the cell from the external power supply	Electrons are drawn from the cell.
Not a spontaneous reaction	Spontaneous reaction.
Eg: Electroplating	Eg: Corrosion
The extent of chemical reaction occurring at the electrode is governed by Faraday's law of electrolysis.	The e.m.f of the cell depends on the concentration of the electrolyte and chemical nature of the electrode (Nernst Equation)

Daniel cell: It consist of Zn electrode immersed in $ZnSO_4$ solution in abeaker and a Cu electrode immersed in $CuSO_4$ solution in abeaker and they are connected by means of salt bridge.The cell is represented as, $Zn/Zn^{2+}// Cu^{2+}/Cu$



Cell reaction

The Zn metal at the anode losses electrons and get dissolved and metal at the cathode gains electrons and grows.

The flow of electrons in the cell is from Zn – electrode to the Cu- electrode.

At the anode, $Zn \rightarrow Zn^{2+} + 2e$ (Oxidation)

At the cathode, $Cu^{2+} + 2e^{-} \rightarrow Cu$ (Reduction)

Net reaction is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (Cell reaction)

Redox Reactions

Oxidation is a process, which involves loss of electrons by a substance, while reduction is a process, which involves gain of electrons by a substance. Any substance that loses electrons is said to be oxidized and the one which gains electrons is said to be reduced. However, in a chemical reaction, substance can lose electrons only if there is another substance which can gain electrons. This means that oxidation can occur only if reduction also occurs at the same time or vice-versa. These Reactions in which oxidation and reduction take place simultaneously are called redox Reactions

Representation of a cell

Anode half cell is written on the left and cathode half cell on the right. For anode ,the electrodes written first and then electrolyte. For cathode, the electrolyte is written first and then electrode. The two half cells are separated by a double vertical line(salt bridge)

Eg.A cell constructed by coupling Zn electrode dipped in 0.5M $ZnSo_4$ and Ni electrode dipped in 0.05M $NiSO_4$ can be represented by

$Zn/ZnSO_{4\,(0.5m)}//NiSO_{4(0.05m)}$

Salt Bridge

It is a U shaped glass tube filled with jelly like substance agar-agar and gelatine mixed with an electrolyte like KCl, KNO_3,K_2SO_4, NH_4NO_3 etc. The speciality of this electrolyte is that the cation and anion of electrolyte migrate at the same rate.

Functions of Salt Bridge

1. Provides the continuity of electrical circuit. i.e.the flow of ions between the components.
2. To allow the movement of ions from one solution to the other without mixing of the twoSolutions.
3. It prevents the diffusion of interfering ions from one compartment to another.
4. Salts like KCl, NH_4NO_3 are used for making salt bridge. Ions like K^+ and Cl^- has equal mobility and get drifted to cathode and anode compartments respectively under the potential difference.

Types of Electrodes

Electrode is parts of an electrochemical setup were an element is in contact with its own ions at which oxidation or reduction takes place.

1. Metal/Metal ion electrode (M/M^{n+})

When a metal is immersed in its own salt solution such type of electrode is called metal/metal ion electrode is formed. Eg: Zn/Zn^{2+}, Cu/Cu^{2+}

In general M/M^{n+}

The electrode reaction is $M^{n+} + ne^{-} \rightarrow M$

Electrode potential depends on the logarithmic concentration of metal ion.

2. Gas Electrode

The gas is bubbled around an inert metal like platinum which is immersed in a solution containing ions of the same gas. Eg: Hydrogen electrode or SHE, chlorine electrode.

Electrode potential depends on the logarithmic concentration of the ion and the pressure at which the gas is bubbled.

3. Metal insoluble metal salt/ common ion electrode

The metal (M) is covered with an insoluble metal salt (MX) is in contact with a solution containing an anions of the insoluble metal salt(X). Eg: Calomel electrode ($Hg/Hg_2Cl_2/Cl^-$), silver-silver chloride electrode ($Ag/AgCl_2/Cl^-$)

Electrode potential is the logarithmic concentration of the common ion (Cl^-)

4. Redox electrode

In this electrode, an inert metal is immersed in a solution containing ions of the same metal having two different oxidation states. Eg: $Pt/Fe^{2+}/Fe^{3+}$

Reaction: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Electrode potential is the Ratio of logarithmic concentration of all ionic species involved in the redox reaction.

5. Ion selective electrode

In this type, the sensing part of the electrode is usually made of an ion-specific membrane. The membrane can be glass membrane, crystalline membrane and ion-exchange resin membrane. Eg: Glass electrode.

Helmholtz Electrical Double Layer

When a metal electrode is in contact with its own salt solution .The following reaction can occur,

At the anode, $M \rightarrow M^{n+} + ne$ (oxidation) → (1)

At the cathode, $M^{n+} + ne^{-} \rightarrow M$ (Reduction) → (2)

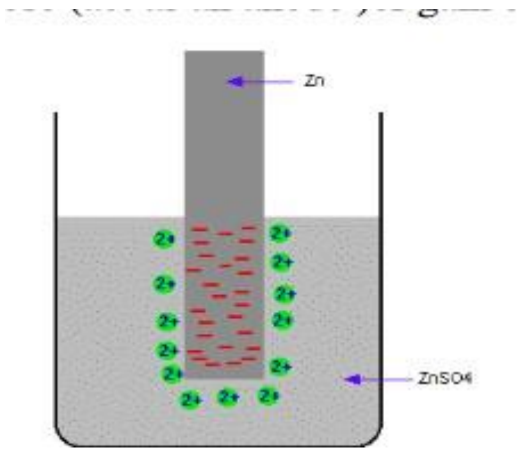
Eg: Zn metal dipped in $ZnSO_4$ solution

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

Zn atom liberates its electrons.

- Zn^{2+} ions enter in to the electrolyte solution leaving behind the electrons on the electrode.
- The electrode gets negative charge and solution side gets positive charge due to excess Zn^{2+} ions.

- Thus positive and negative ions remain close to the metal surface forming a double layer. This is called Helmholtz electrical double layer.



The tendency of the electrode to lose electrons is called oxidation potential and the tendency of the electrode to gain electrons is called reduction potential. This potential difference becomes a constant at equilibrium.

The constant potential difference developed when a metal is in contact with its own salt solution is called **single electrode potential**.

The constant potential difference developed when a metal is in contact with its own salt solution of concentration 1M at 25°C is called the standard electrode potential of themetal.

Factors affecting electrode potential

1.Concentration of metal irons in the solution

2.Temperature of the solution

3.Nature of the metal

Reference Electrodes

A reference electrode is an electrode which has a stable electrode potential. These electrodes are used to find out the potential of other electrode.

Reference electrodes are of two types. Primary reference electrode and secondary reference electrode. Primary → SHE

Secondary → Calomel electrode, glass electrode, quinhydrone electrode

1. Standard Hydrogen Electrode (SHE)

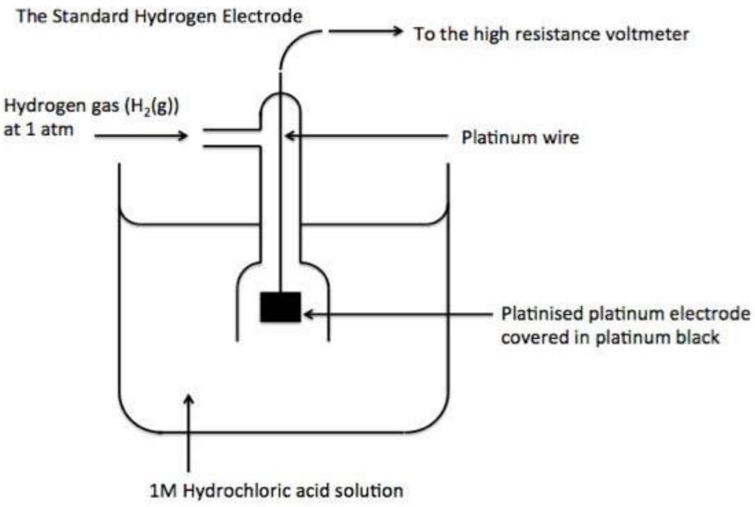
The standard hydrogen electrode is a gas electrode, used as primary reference electrode. The electrode can be represented as

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

Construction

- It is a primary reference electrode.
- A small Pt plate coated with Pt black is connected to a Pt wire which sealed in a glass jacket.
- Glass jacket having an inlet for Hydrogen gas at the top and a number of small holes at the bottom for the escape of Hydrogen gas.

- It is dipped in 1M HCl solution at 298K.



Working

- SHE is a reversible electrode which can act as cathode or anode, depending on the potential of electrode to which it is coupled.
- The electrode potential of hydrogen electrode fixed as zero volt.
- At the cathode, $2H^+ + 2e^- \rightarrow H_{2(g)}$ (reduction)

If the potential of coupled electrode is less than zero (Eg: Zn, Mg)

- At the anode, $H_{2(g)} \rightarrow 2H^+ + 2e^-$ (oxidation)

If the potential of coupled electrode is greater than zero (Eg: CU, Ag)

Limitations

- It is readily affected by compounds of Hg, As and S and it cannot be used in solution Containing these ions.
- It cannot be used in presence of strong oxidizing and reducing agents.
- It is expensive due to Pt.
- The Pt surface must be specially prepared and maintained or it is difficult to maintain Pt surface.

Applications

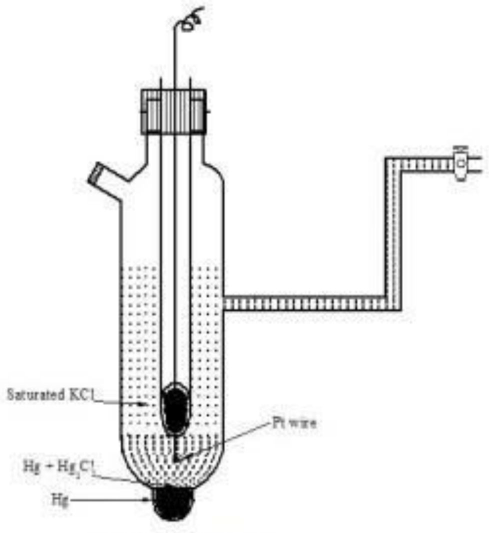
- Used as a reference electrode for increasing the electrode potential of other electrodes.
- Used in the determination of p^H.

2. Calomel Electrode

Saturated calomel electrode is a secondary reference electrode. This is an example of metal-metal insoluble metal salt electrode and solution of its common ion.

Construction and Working

- It consists of a glass tube in the bottom of which is a layer of Hg.
- Over the Hg layer, there is a layer of solid mercurous chloride. (Hg_2Cl_2)
- The remaining portion is filled with normal, desinormal or saturated KCl
- A Pt wire is dipped in to the Hg- layer is used for making electrical contact.
- The side tube is used for making contact with a salt bridge.



Standard Calomel Electrode

Working

It can act as an anode or cathode depending on the electrode potential of the coupled electrode.

- If it can act as anode,

  $2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^-$

  Here the electrode potential of the coupled electrode is greater than calomel electrode.

- If it can act as cathode, $Hg_2Cl_2 + 2e^{-} \rightarrow 2Hg + 2Cl^{-}$

  Here the electrode potential of the coupled electrode is less than that of calomel electrode.

- Depending up on the concentration of the KCl solution used, various values of electrode potential are reported.

Saturated - 0.2422V (SCE)
1 N - 0.2810V (NCE)
0.1 N - 0.3335(DCE)

Application

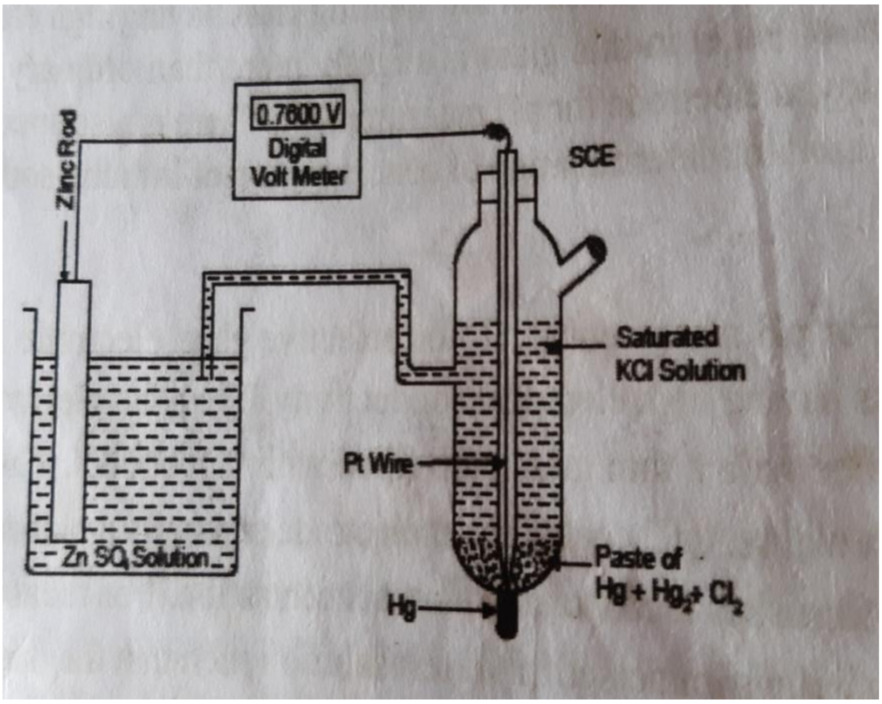
1. Used for determination of electrode potential.
2. Used to find out p^H of an unknown solution.

Limitations

1. Toxic nature of mercury
2. Cannot be used above 50^0c because the mercurous chloride breakdowns yielding an unstablereadings.

Determination of E^0 using Calomel electrode

To measure, the standard electrode potential of Zn electrode, the Zn electrode is couple with saturated Calomel electrode through a salt bridge. The digital voltmeter reading directly gives the cell emf.



The electrode having higher reduction potential undergoes reduction and is the cathode and the electrode having lower reduction potential undergoes oxidation and is the anode.The reduction potential of SCE is 0.2422V is higher than the standard reduction potential of $Zn^{2+}/Zn= {}^{-}0.76$ v . i.e., reduction takes place at SCE and the Zn electrode undergo oxidation.

Cathode:

$Hg_2Cl_2 + 2e^{-} \rightarrow 2Hg + 2Cl^{-}$

Anode:

$Zn \rightarrow Zn^{2+} + 2e$

The cell may represented as $Zn/Zn^{2+}// Cl^{-}/Hg_2Cl_2/Hg$

$E_{cell} = E_{R} - E_{L}$

$E_{cell} = E_{sce} - E_{Zn^{2+}/Zn}$

When concentration of $[Zn^{2+}] = 1$ M

$E_{cell} = 0.2422\ V - E^{0}_{Zn2+/Zn}$

By measuring cell emf $E^{0}_{Zn2+/Zn}$can be calculated.

Cu-electrode: To measure, the standard electrode potential of Cu electrode, the Cu electrode is couple with saturated Calomel electrode through a salt bridge. The digital voltmeter reading directly gives the cell emf.

The electrode having higher reduction potential undergoes reduction and is the cathode and the electrode having lower reduction potential undergoes oxidation and is the anode. The reduction potential of SCE is 0.2422V is lower than the standard reduction potential of $Cu^{2+}/Cu = +0.34$ v. i.e., oxidation takes place at SCE and the Cu electrode undergo reduction.

Anode:

$2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$

Cathode:

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

The cell may represented as $Hg /Hg_2Cl_2/Cl^{-}// Cu/Cu^{2+}$

$E_{cell} = E_{R} - E_{L}$

$E_{cell} = E_{Cu^{2+}/Cu} - E_{sce}$

When concentration of $[Cu^{2+}] = 1$ M

$E_{cell} = E^{0}_{Cu^{2+}/Cu} - 0.2422\ V$

By measuring cell emf $E^{0}_{Cu^{2+}/Cu}$can be calculated.

3.Glass Electrode

Glass electrode is a secondary reference electrode which produces a constant and reproducible electrode potential. It is ion selective electrodes and used for the p^H measurements.

Construction and Working

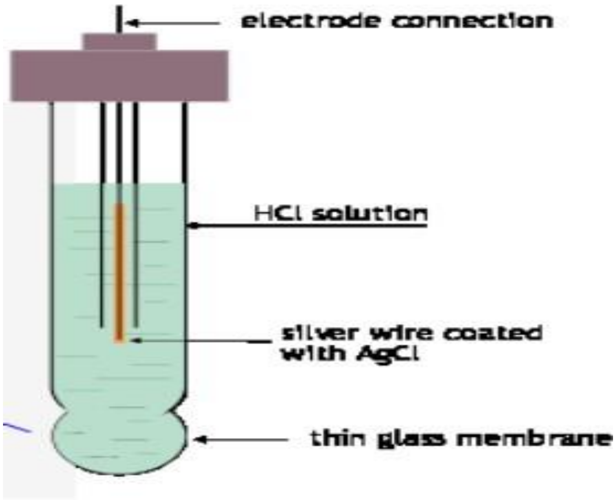
- It is made up of a special type of glass relatively low melting point and high electrical conductivity.
- Long glass tube with a thin glass bulb filled with 0.1M HCl.
- A Pt wire or silver wire coated with a layer of AgCl is inserted into it to make electrical contact.

Electrode representation is, Pt/0.1MHCl,glass/Test H^+solution

The electrode potential of glass electrode is $E_G = E^0_G + 0.0591 \log[H^+]$

$E_G = E^0_G - 0.0591[pH]$

E^0_G is a constant depending upon the nature of the glass and p^H of the solution taken inside the glass tube.



Determination of p^H by using glass electrode

Principle:

The H^+ ion concentration inside the electrode is constant. When this electrode is dipped in to a solution of unknown H^+, it becomes sensitive to the outside concentration in the solution.

The potential difference is developed across the membrane. By measuring that potential difference, we can find out p^H.

Procedure

- Unknown solution is taken in beaker,
- Glass electrode is dipped in it.
- It is connected to a saturated calomel electrode.
- emf of the cell is measured.

$E_{cell} = E_C - E_\alpha$

$E_{cell} = E_{calomel} - E_{glass}$

$$E_{cell}=0.2422-[E^0_G-0.0591pH]$$

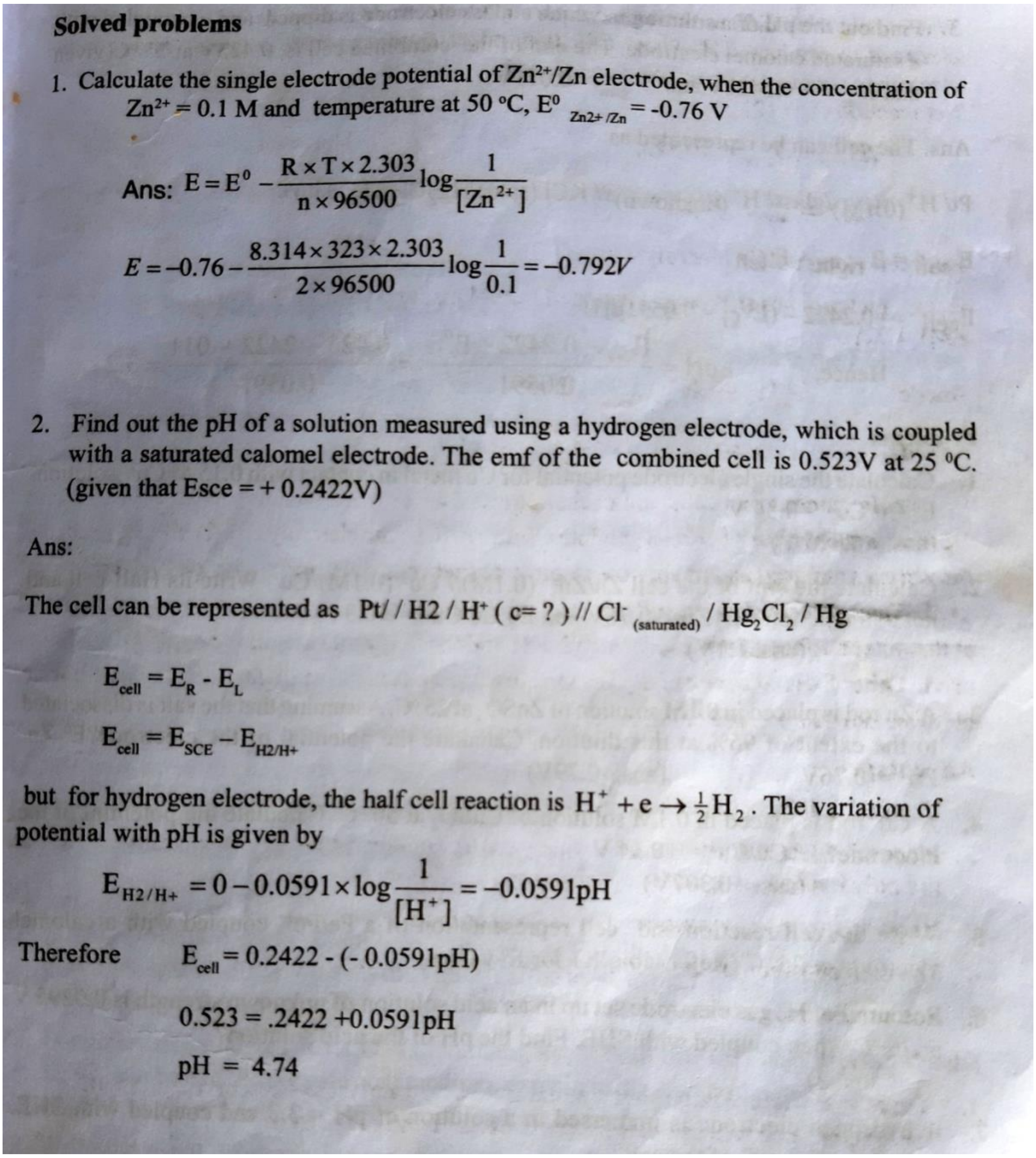
$$pH=\frac{E_{cell}+E^0_G-0.2422}{0.0591}$$

Advantage

1. It is simple and easily be used.
2. Used in p^H range 0 -12.
3. The results are accurate.
4. Can be used in presence of strong oxidising and reducing agents.

Limitations

1. As the glass electrode has very high electrical resistance, electronic potentiometer must be used to find EMF.
2. Due to highly absorptive nature a lot of working is required.



Solved problems

1. Calculate the single electrode potential of Zn^{2+}/Zn electrode, when the concentration of Zn^{2+} = 0.1 M and temperature at 50 °C, $E^0_{Zn2+/Zn} = -0.76$ V

Ans: $$E=E^0-\frac{R\times T\times 2.303}{n\times 96500}\log\frac{1}{[Zn^{2+}]}$$

$$E=-0.76-\frac{8.314\times 323\times 2.303}{2\times 96500}\log\frac{1}{0.1}=-0.792V$$

2. Find out the pH of a solution measured using a hydrogen electrode, which is coupled with a saturated calomel electrode. The emf of the combined cell is 0.523V at 25 °C. (given that Esce = + 0.2422V)

Ans:

The cell can be represented as $Pt // H2 / H^+ (c=?) // Cl^-_{(saturated)} / Hg_2Cl_2 / Hg$

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

$$E_{cell} = E_{SCE} - E_{H2/H+}$$

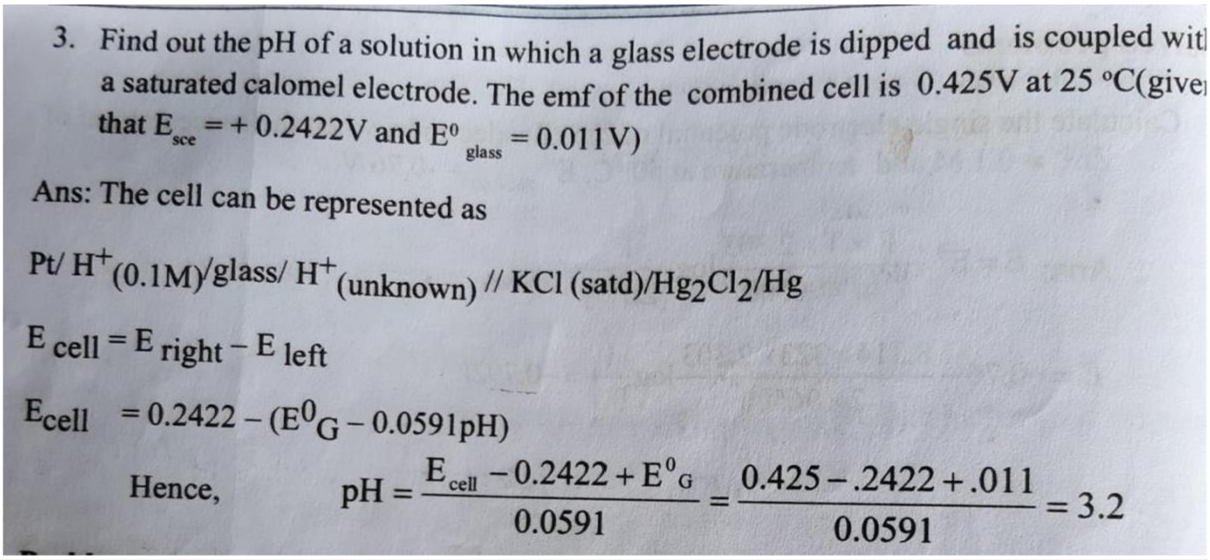
but for hydrogen electrode, the half cell reaction is $H^+ + e \rightarrow \frac{1}{2}H_2$. The variation of potential with pH is given by

$$E_{H2/H+} = 0-0.0591\times\log\frac{1}{[H^+]}=-0.0591pH$$

Therefore $E_{cell} = 0.2422 - (-0.0591pH)$

$0.523 = .2422 + 0.0591pH$

pH = 4.74



3. Find out the pH of a solution in which a glass electrode is dipped and is coupled wit a saturated calomel electrode. The emf of the combined cell is 0.425V at 25 °C(give that $E_{sce} = + 0.2422V$ and $E^0_{glass} = 0.011V$)

Ans: The cell can be represented as

$Pt/ H^+(0.1M)/glass/ H^+(unknown) // KCl (satd)/Hg_2Cl_2/Hg$

$E_{cell} = E_{right} - E_{left}$

$E_{cell} = 0.2422 - (E^0_G - 0.0591pH)$

Hence, $$pH = \frac{E_{cell} - 0.2422 + E^0_G}{0.0591} = \frac{0.425 - .2422 + .011}{0.0591} = 3.2$$

Electrochemical Series

A series which represents an arrangement of various metal electrodes in the increasing order of their standard reduction potentials or decreasing order of oxidation potential is called electrochemical series.

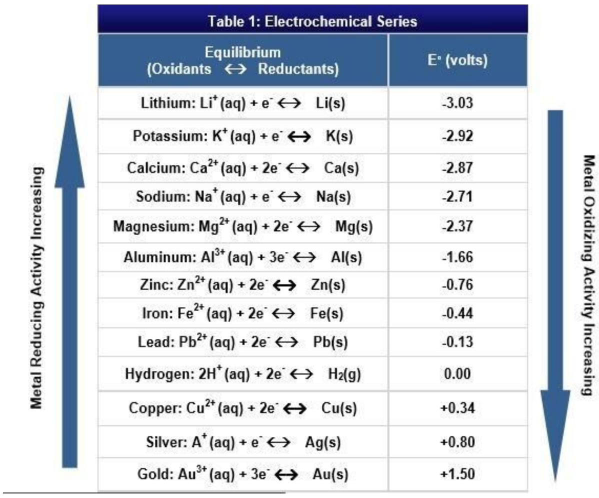


Table 1: Electrochemical Series

Equilibrium (Oxidants ↔ Reductants)	E° (volts)
Lithium: $Li^+(aq) + e^- \leftrightarrow Li(s)$	-3.03
Potassium: $K^+(aq) + e^- \leftrightarrow K(s)$	-2.92
Calcium: $Ca^{2+}(aq) + 2e^- \leftrightarrow Ca(s)$	-2.87
Sodium: $Na^+(aq) + e^- \leftrightarrow Na(s)$	-2.71
Magnesium: $Mg^{2+}(aq) + 2e^- \leftrightarrow Mg(s)$	-2.37
Aluminum: $Al^{3+}(aq) + 3e^- \leftrightarrow Al(s)$	-1.66
Zinc: $Zn^{2+}(aq) + 2e^- \leftrightarrow Zn(s)$	-0.76
Iron: $Fe^{2+}(aq) + 2e^- \leftrightarrow Fe(s)$	-0.44
Lead: $Pb^{2+}(aq) + 2e^- \leftrightarrow Pb(s)$	-0.13
Hydrogen: $2H^+(aq) + 2e^- \leftrightarrow H_2(g)$	0.00
Copper: $Cu^{2+}(aq) + 2e^- \leftrightarrow Cu(s)$	+0.34
Silver: $A^+(aq) + e^- \leftrightarrow Ag(s)$	+0.80
Gold: $Au^{3+}(aq) + 3e^- \leftrightarrow Au(s)$	+1.50

Applications of Electrochemical Series

1. **Reactivity of Metals:** Electrodes having negative values of standard electrode potential with respect to hydrogen have tendency to undergo oxidation where as electrodes having positive values have tendency to undergo reduction in aqueous solution.
2. **Displacement reaction:**

a)To predict whether a given metal will displace another from its saltsolution. Eg: Zn metal can displace Cu from $CuSO_4$

b) Metals having negative electrode potentials can displace hydrogen gas from acids.

eg: Metals like Fe,Zn,Al etc. Can liberate H_2 gas when react with acids.

3. **Spontaneity of a redox reaction:** The emf of the cell is positive, the cell reaction is spontaneous. If E_{cell} is negative, the reaction will not occur at all.
4. **Calculation of EMF of a cell:** EMF of the cell can be readily calculated from the relation $E_{cell} = E^0_R - E^0_L$

5. Predicting the anode and cathode: The electrode with higher reduction potential will act as cathode and the electrode having lower electrode potential will act as anode.

6. Prediction of relative oxidising and reducing tendency.

7.Corrosion: The metal higher in the series is anodic or more active and they are more prone to corrosion. The metals lower in the series are noble metals and they are less prone to corrosion.

NERNST EQUATION

The relation between the electrode potential and the concentration of the electrolyte solution is given by Nernst equation.

The potential of a single electrode or half cell varies with the concentration of ions in the cell. Walter Nernst derived a mathematical relationship which enables us to calculate the half cell potential e from the standard electrode potentialE^0 and the temperature of the cell.

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

$E=E^0+\frac{0.0591}{n}\log [M^{n+}]$ where, E^0=Standard electrode potential

R=gas constant; T=Kelvin temperature; n=number of electrons transferred in the half cell reaction; F=faraday of electricity; $[M^{n+}]$=concentration of electrolyte.

For a half cell, $E=E^0-\frac{0.0591}{n}\log 1/[M^{n+}]$

For a cell, $E=E^0-\frac{0.0591}{n}\log\frac{[product]}{[reactant]}$

Nernst Equation derivation

It gives us the effect of electrolyte concentration on electrode potential.

Consider a general reduction reaction, taking place at the electrode

$$M^{n+}_{(aq)} + ne \rightarrow M$$

The decrease in free energy, ΔGaccompanying this process is given by the well known thermodynamic equation (Vant Hoff's equation)

$\Delta G=\Delta G^0 + RT \ln Kc$ ....(1)

R = gas constant,Kc = Equilibrium constant

$Kc = \frac{[M]}{[M^{n+}]}$In a reversible cell, electrical energy is produced at the expense of decrease in free energy,and free energy is related with EMF of the cell as follows

$\Delta G=-nFE,\ \Delta G^0=-nFE^0$

Substitute in (1)

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

Dividing by –nF

$$E=E^0-\frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]} \quad ....(2)$$

Substituting the values of constants at the temperature T = 298 K,R= 8.314JK^{-1} mol^{-1}, F= 96500 C(Faraday)

$$E=E^0-\frac{8.314\times 298\times 2.303}{n\times 96500}\log\frac{[M]}{[M^{n+}]}$$

Pure solid [M] is taken as one

$$E = E^0 - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$,This equation is called Nernst equation.

It's clear that electrode potential is directly proportional to molar concentration of ions in the same solution and temperature.

Effect of temperature on EMF

Consider the Daniel cell reaction,

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

Nernst equation is given by $E_{cell} = E^0_{cell} - \frac{RT}{nF} ln \frac{[zn2+]}{[Cu2+]}$

Case 1

When $[Zn^{2+}] = [Cu^{2+}]$,the logarithmic term become zero,

i.e.$E_{cell} = E^0_{cell}$ and EMF of the cell will be independent of temperature.

Case 2

When $[Zn^{2+}] > [Cu^{2+}]$,the logarithmic term remains negative,

i.e.$E_{cell} < E^0_{cell}$and EMF decreases with rise of temperature.

Case 3

When $[Zn^{2+}] < [Cu^{2+}]$,the logarithmic term become positive,

i.e.$E_{cell} > E^0_{cell}$and EMF increases with rise of temperature.

Relationship between free energy and EMF the cell

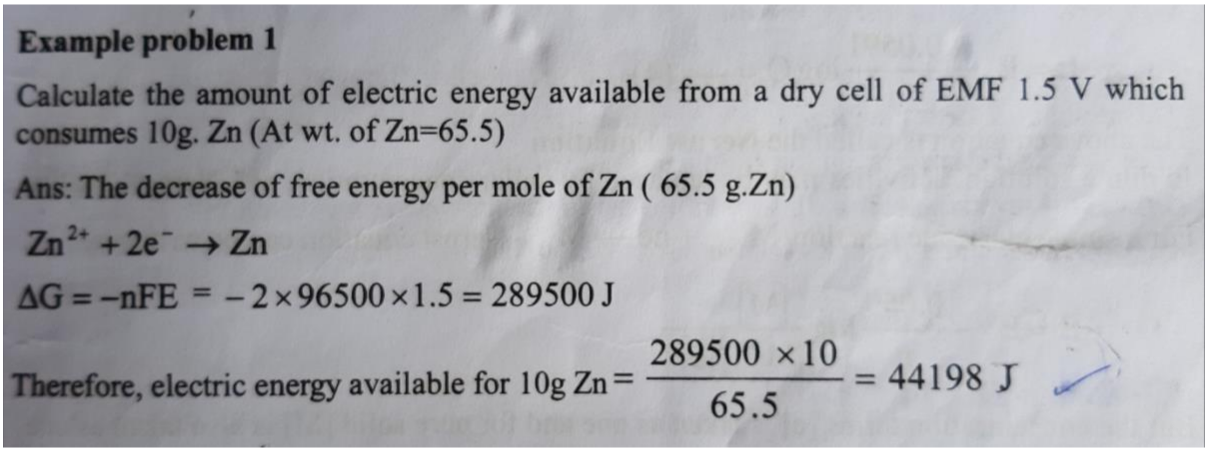
In a reversible cell, electrical energy is produced at the expense of decrease in free energyΔG,

Electrical energy produced per mol= nFE

ΔG=-nFE where F is called Faraday which is the charge of one mole of electrons.($F=6.023x10^{23}x1.6x10^{-19}=96500$ C); n is number of electrons; E is EMF

Applications of Nernst equation

1. To study the effect of electrolyte concentration on electrode potential.
2. Calculation of equilibrium constant of a reaction.
3. Determination of EMF.
4. Determination of unknown concentration.
5. Determination of a p^H of a solution.
6. Used for finding out valency of an ion.



Example problem 1

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

Ans: The decrease of free energy per mole of Zn (65.5 g.Zn)

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

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

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

Example Problem 2

Calculate the single electrode potential of Zn electrode at 25 °C, when the concentration of $[Zn^{2+}] = 0.01M$ ($E^0\ Zn^{2+}/Zn = -0.76V$)

Ans: The reduction reaction can be written as

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

The Nernst equation is given by $E = E^0 - \frac{0.059}{n}\log\frac{1}{[Zn^{2+}]}$ +

0.0295 × 2

$$E = -0.76 - \frac{0.059}{2}\log\frac{1}{0.01} = -0.76 - 0.059 = -0.819\,V$$

Example Problem 3

Calculate the EMF of a Daniel cell when the concentration $[Zn^{2+}] = 0.01M$ and Concentration of $[Cu^{2+}] = 0.1M$ given that $E^0\ Zn^{2+}/Zn = -0.76V$ and $E^0\ Cu^{2+}/Cu = +0.34V$.

L R

Ans: The cell representation is

$\overset{L}{Zn /Zn^{2+}}//\overset{R}{Cu^{2+}/ Cu}$

The cell reaction is

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

Nernst equation for this cell reaction is

$$E = E^0_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

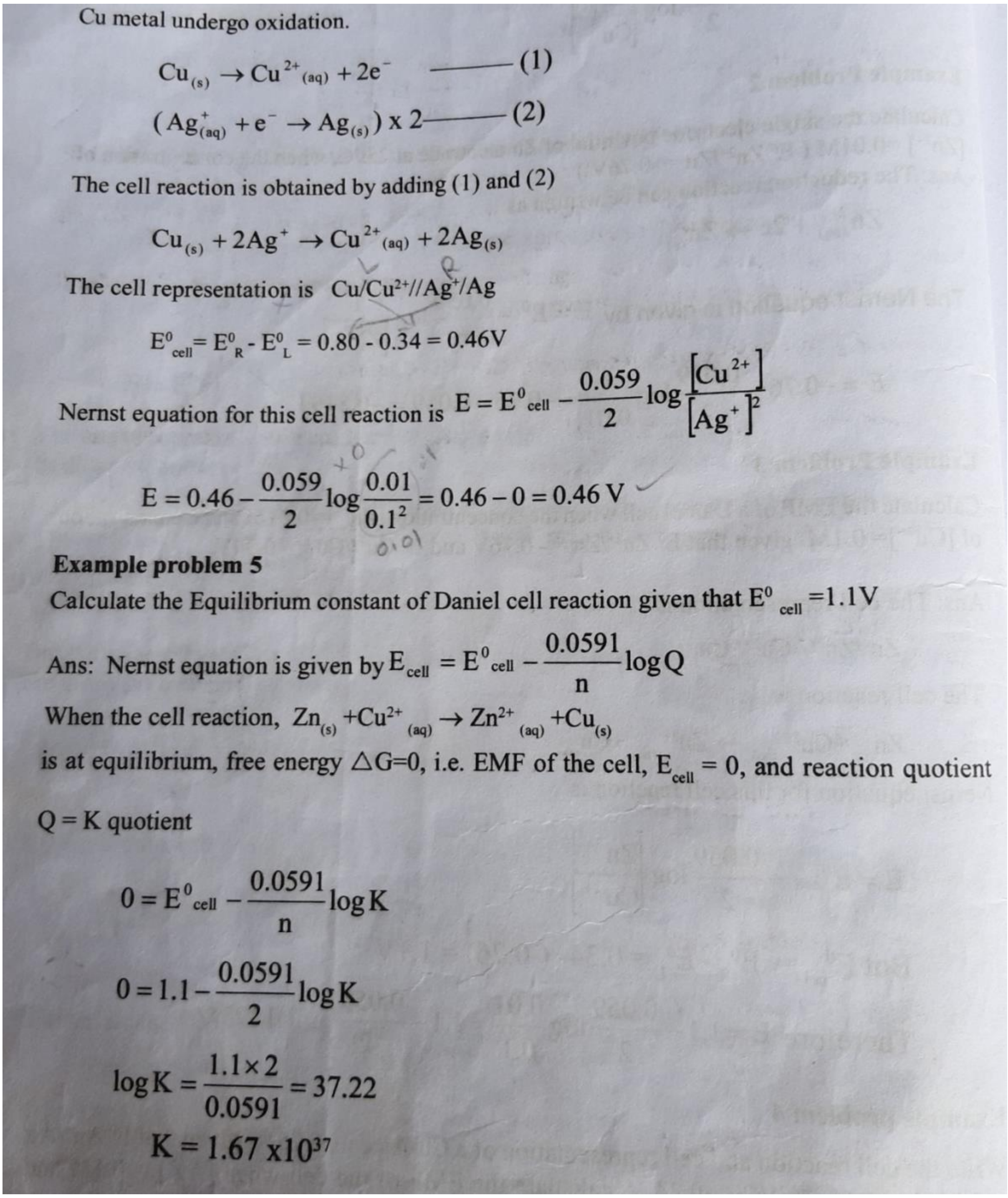
But $E^0_{cell} = E^0_R - E^0_L = 0.34 - (-0.76) = 1.1V$

$$\text{Therefore } E = 1.1 - \underset{0.0295}{\frac{0.059}{2}}\log\overset{-1}{\frac{0.01}{0.1}} = 1.1 + \frac{0.0591}{2} = 1.1295\,V$$

Example problem 4

Write the cell reaction and cell representation of a Cu-Ag cell at 25 °C given that $E^0\ Ag^+/Ag = 0.80V$ and $E^0\ Cu^{2+}/Cu = 0.34$ V. calculate the EMF of the cell when $[Ag^+] = 0.1M$ and $[Cu^{2+}] = 0.01M$

R L



Cu metal undergo oxidation.

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^- \text{ ——— } (1)$$

$$(Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}) \times 2 \text{ ——— } (2)$$

The cell reaction is obtained by adding (1) and (2)

$$Cu_{(s)} + 2Ag^+ \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

The cell representation is Cu/Cu²⁺//Ag⁺/Ag

$$E^0_{cell} = E^0_R - E^0_L = 0.80 - 0.34 = 0.46V$$

Nernst equation for this cell reaction is $E = E^0_{cell} - \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$

$$E = 0.46 - \frac{0.059}{2}\log\frac{0.01}{0.1^2} = 0.46 - 0 = 0.46\text{ V}$$

0.01

Example problem 5

Calculate the Equilibrium constant of Daniel cell reaction given that $E^0_{cell} = 1.1V$

Ans: Nernst equation is given by $E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log Q$

When the cell reaction, $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

is at equilibrium, free energy $\Delta G = 0$, i.e. EMF of the cell, $E_{cell} = 0$, and reaction quotient

Q = K quotient

$$0 = E^0_{cell} - \frac{0.0591}{n}\log K$$

$$0 = 1.1 - \frac{0.0591}{2}\log K$$

$$\log K = \frac{1.1 \times 2}{0.0591} = 37.22$$

$$K = 1.67 \times 10^{37}$$

Potentiometric titrations

- Potentiometric titrations are the measurement of EMF, for recording the end point of volumetric titration by using a potentiometer.
- According to Nernst equation the potential of an electrode depends upon the concentration of the electrolyte ions

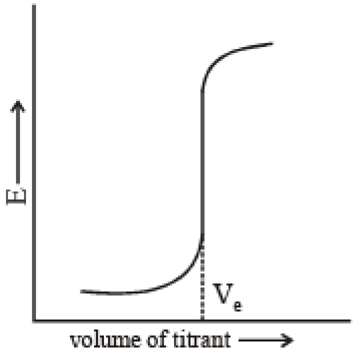
$$E = E0 + \frac{0.0591}{n}\log[Mn+]$$

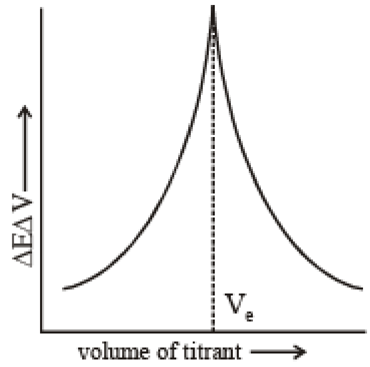
- In a titration ,there is a change in ionic concentration which can be followed by measuringthe potential of a suitable electrode.

$E_{cell} = E_C - E_a = E_{reference} - E_{indicator} = 0.2422 - E_{indicator}$

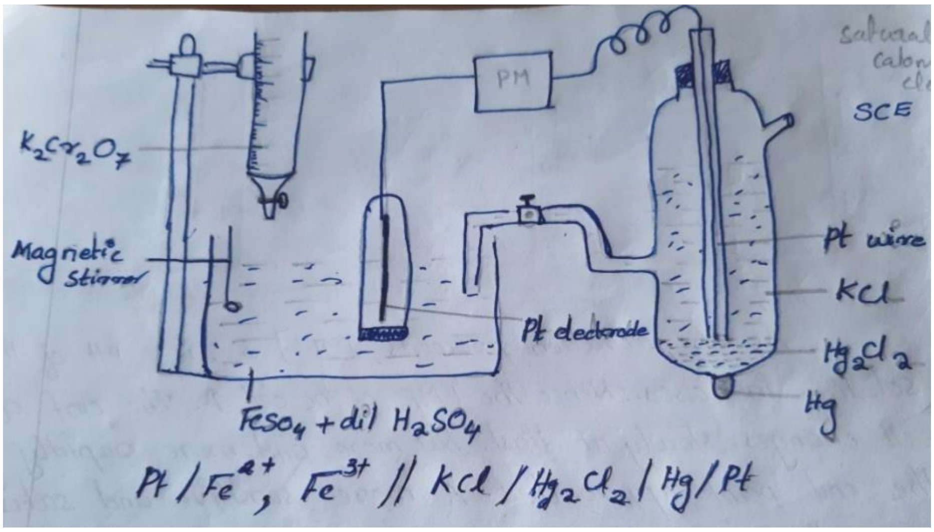
(where $E_{reference}$ is the electrode potential of reference electrode, i.e. $E_{SCE} = 0.2422$, $E_{indicator}$ is the electrode potential of indicator electrode made up of Pt or Au)

- $E_{cell}$is recorded at intervals as the titrant is added.
- The volume of the titrant added is plotted against EMF.(This method based on the fact thatnear the end point, there is sudden change in the EMF of the cell formed)
- E_{cell} depends on the concentration of interested ions with the indicator electrode is in contact.





Redox titration



- Redox titration can also be carried out potentiometrically.
- Take 25ml of ferrous sulphate solution in to the beaker.
- Add 20ml of dilute sulphuric acid.
- The indicator electrode dipped in to the solution in the beaker.

(Pt wire immersed in a solution containing both the oxidized and reduced forms of thesame species (redox electrode)-it act as indicator electrode).

- It is coupled with SCE (it act as reference electrode)

$Pt /Fe^{2+,}Fe^{3+}// KCl / Hg_2Cl_2/Hg/Pt$

- Connect the electrode to a potentiometer, and measure the potential.
- Fill the burette with $K_2Cr_2O_7$
- Add 1ml of $K_2Cr_2O_7$ to the beaker. Stir the solution and measure the potential.
- Continue step above, till the potential shows a tendency to increase rapidly.

- Plot ΔE/ΔV against volume and determine the endpoint.

Addition of $K_2Cr_2O_7$ to Fe^{2+} ion solution results the oxidation of Fe^{2+} to Fe^{3+} ions.

$$(Fe^{2+} \rightarrow Fe^{3+} + e)$$

During titration the electrode potential is controlled by Fe^{2+} ions. After the end point Fe^{2+} ion is zero, as a result of this the electrode potential there after suddenly changes.

Conductivity

Conductors

- A substance or material that allows the passage of electricity, such substances are called conductors.
- Substance or material that does not allow the passage of electricity, are called non-conductors or insulators.

Types of conductors

Conductors are two types

1. Metallic conductor-Conduct electric current due to movement of electrons.Eg: metals, semiconductros.
2. Electrolytic conductors-1.Conduct electric current due to movement of ions. Eg: salt solutions.

Conductance(C)-Reciprocal of resistance. C=1/R,

Units are ohm^{-1} (mho) and siemen(s).

Specific resistance or resistivity (ρ)

We know that resistance (R) is directly proportional to $\frac{}{a}$

$R \propto \frac{l}{a}$ $R = \rho \frac{l}{a}$

Specific resistance is the resistance of a conductor of unit length and unit area of cross section.

Unit is Ωcm. $\rho = R\frac{a}{l}$

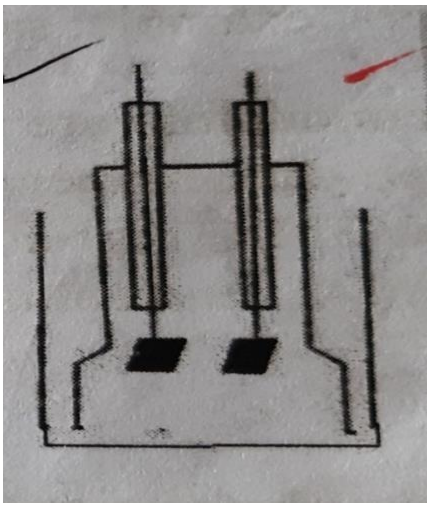
Specific conductance or conductivity(κ)

It is the reciprocal of specific resistance. It is defined as the conductance of $1cm^3$ of a conductor held between two electrodes of $1cm^2$ area.

$$\kappa = \frac{1}{\rho} \text{ i.e. } \kappa = \frac{l}{Ra}$$

Conductivity cell

It consists of two electrode plates coated with pt black. It is connected to pt wire, which are sealed through two glass tubes. The tubes are strongly fixed such that distance between electrodes remains unchanged.



Cell constant

It is the ratio of distance between two electrodes (l) and area of the electrodes (a)

Cell constant $x=\frac{l}{a}$, unit - m^{-1}or cm^{-1}

Determination of cell constant

- Direct measurement of l and a are difficult.
- In actual practice the cell constant is obtained by measuring the conductance of 0.1N KCl solution
- The specific conductance of 0.1N KCl is $0.012886\Omega^{-1}cm^{-1}$

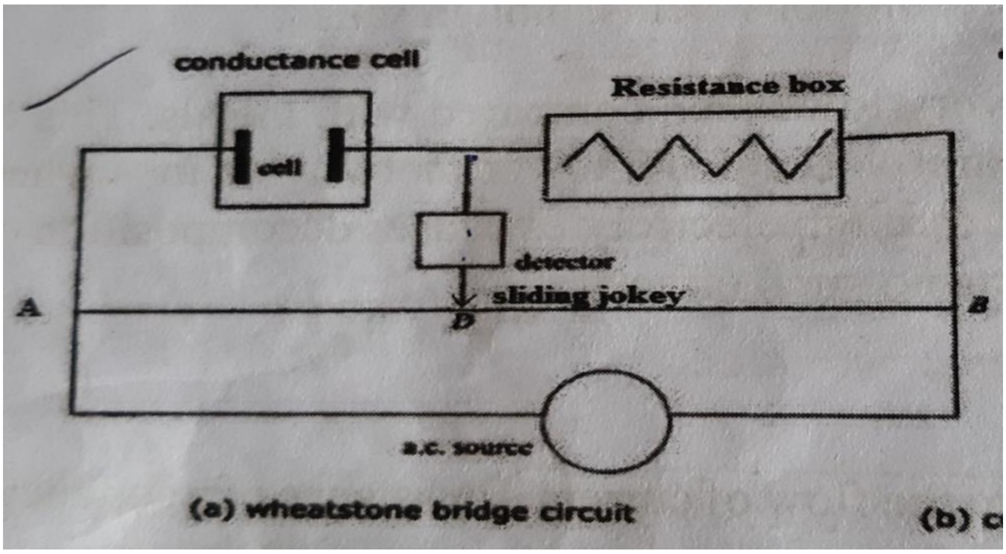
$$\text{Cell constant} = \frac{\text{specific conductance}}{\text{conductance}}$$

Experimental arrangement and procedure for the determination of conductance.

Measurement of electrical conductance of electrolytic solution done by determination of electrical resistance. Since $C=\frac{1}{R}$

Procedure

The determination of electrical resistance is carried out by using Wheatstone bridge



(a) wheatstone bridge circuit

- One arm of the bridge is connected to conductivity cell containing test solution.
- A known resistance(R) is taken out of the resistance box.

- AC current source is connected between A and B in the presence of AC source galvanometer cannot be used as the null point detector.
- Head phone is used as a null point detector, which produce a sound corresponding to AC current.
- Sliding the jockey along AB line, at the balancing point sound intensity become zero.
- The length XA and XB is measured from the scale.
- At the null point:-

$$\frac{\text{Resistance of the conductivity cell}}{\text{Known resistance}} = \frac{Balancing\ length\ AD}{Balancing\ length\ DB}$$

From this resistance of conductivity cell can be determined.

$\therefore$ Conductance of solution (C) $= \frac{1}{\text{resistance of conductivity cell}}$

Specific conductance of solution = conductance × cell constant

Problem

Calculate the conductivity of given sodium chloride solution at 298K ,which shows a conductance of 560 micro mho in the given cell at 298K.A standard solution of 0.1M KCl shows a conductance of 1200 micro mho in that cell.(Given that conductivity of 0.1M KCl at 298 K is 0.001288 ohm^{-1}cm^{-1}.

Specific conductance of KCl solution = conductance × cell constant

Cell constant $= \frac{\text{Sp.conductance of standard KCl solutin}}{\text{conductance of standard KCl in the given cell}} = \frac{0.01288}{1200\times10-6} = \underline{\underline{10.73\text{cm}^{-1}}}$

Conductivity of given NaCl solution = conductance × cell constant = $560\times10^{-6}\times10.73$

$= \underline{\underline{6.01\times10^{-3}\text{ohm}^{-1}\ \text{cm}^{-1}}}$

Types of cell

Cells which are used as a source of electrical energy .There are of three types.

1. Primary cells-In which cell reactions cannot be reversed. So it cannot be recharged.

Eg: Daniel cell, Weston cadmium cell

2. Secondary cells(storage or accumulation cell)-In which cell reaction can be reversed by applying an external source of current.

Eg:Lithium-ion cell,Lead storage battery,Ni-Cd battery.

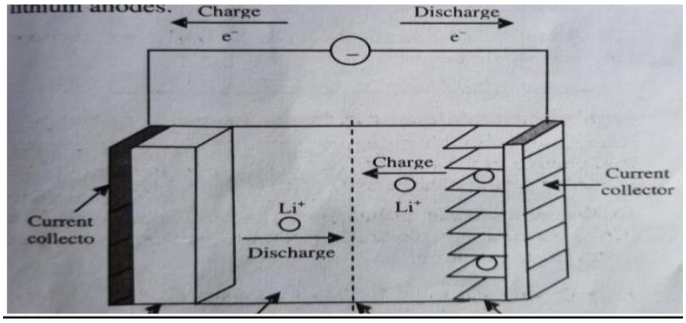
Lithium-ion cell

- It is a rechargeable battery
- It has three functional components:

1. Anode-lithiated graphite or lithiated carbon(Li_xC_G)

   Lithium ions are inserted in between the layer of carbon atoms.
2. Cathode –lithiated transition metal oxide($LiMO_2$)Eg:$LiFeO_2$
3. Electrolyte-the solution of lithium salt in an organic solvent.

Working



The lithium ion moves from the anode to cathode during discharging and from cathode to anode while charging.

Discharging: During discharging the cell act as an electrochemical cell where the chemical energy is converted to electrical energy. When the cell acts as an electrochemical cell,$LiMO_2$ is the cathode and graphite is the anode.

$$Li_xC_G \rightarrow xLi^+ + xe^- + C_G \text{(Oxidation)}$$

These Li + ions produced during oxidation diffuses through the electrolyte and reaches at the cathode for reduction.

$$Li_{(1-x)}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$$

Charging

$$LiMO_2 \rightarrow Li_{(1-x)}MO_2 + xLi^+ + xe^-$$

$$C_G + xLi^+ + xe^- \rightarrow Li_xC_G$$

The net cell Reactions is,

$Li_xC_G + Li_{(1-x)}MO_2 \rightarrow LiMO_2 + C_G$ (Discharging)

$LiMO_2 + C_G \rightarrow Li_xC_G + Li_{(1-x)}MO_2$(Charging)

Advantages

- Li-ion batteries are lighter than other equivalent batteries.
- Can handle hundreds of charge discharge cycles
- They do not use poisonous materials like Pb,Hg,Cd etc
- Available in different size and shape.
- They have no memory effect-which means that if do not have completely discharge them before recharging.

Disadvantages

- They will destroyed 2or 3years from the date of manufacture whether you used them or not.
- They are extremely sensitive to high temperature.
- Expensive to manufacture.
- If they get completely discharged, then destroyed.

Applications

- Used in notebook computers
- Mobile phone and other electronic devices.
- Used in small digital music devices,MP_3 player.
- Digital camera.
- Laptops.
- Military applications.

CORRASION

Introduction

- All metals and alloys are susceptible to corrosion.
- Au shows excellent resistance under atmosphere condition, but gets corroded when exposed to Hg at ambient temperature.
- On the other hand iron readily gets rusted in the atmosphere but it does not corrode in Hg.

Definition

- Corrosion is a process which involves the slow destruction of a metal as a result of its reaction with moisture and other gases present in the atmosphere.
- Corrosion always occurs at anodic areas.
- More reactive metals are corroded more easily.
- Corrosion is enhanced by the presence of a) impurities b)air and moisture c)electrolytes and strains in metals like dents, scratches etc.

Corrosion of iron is called **rusting**. Rust is a hydrated form of ferricoxide, $\mathbf{Fe_2O_3xH_2O}$. Tarnishing of silver, formation of green coating on copper and bronze etc are other examples of corrosion.

Factors affecting corrosion

There are two factors influencing the rate of corrosion process

1.Nature of the metal 2.Nature of environment

Nature of the metal	Nature of environment
1. Position in the Galvanic series	Temperature
2. Relative anodic and cathodic area	Humidity
3. Purity of the metal	PH of the solution
4. Physical state of the metal	Conductance of the medium
5. Nature of surface film	Formation of oxygen concentration cell
6. Solubility of corrosion products	Nature of impurities

TYPES OF CORROSION

Based on environment corrosion is classified into Two types.

1. Dry or Chemical Corrosion

2. Wet or Electrochemical Corrosion

Dry or Chemical Corrosion

Direct chemical action of environment/atmosphere gases such as O_2, halogen, H_2S, SO_2, N_2 or anhydrous inorganic liquid with metal surfaces of immediate proximity.

Wet or Electrochemical Corrosion

The corrosion of metals in aqueous environment is more common than dry corrosions. This types of corrosion takes place when

- A metal is in contact with a conducting liquid
- Two dissimilar metals or alloys are immersed or dipped partially in a conducting solution.

According to electrochemical theory

- Separate anodic and cathodic areas are developed, between which current flows through the conducting medium.
- At the anodic area (in the metal part) oxidation and generation of electrons takes place.
- These electrons formed in anodic area moves through the conducting medium, and it is called corrosion current.
- Environment is the cathodic area where the electrons are received (reduction) non metallic ions like OH^- or O^{2-} are formed.
- Diffusion towards the metallic ions formed in the anodic area and non metallic ions in the cathodic area takes place and the corrosion product is formed in between the anodic and cathodic area.

.

Mechanism of corrosion (Rusting)

In this type of corrosion one part of the metal becomes anode, flow of electronic current between the anodic and cathodic areas takes place in through an electrolyte in contact with it.

The anodic reaction involves the dissolution of metal to metallic ions with the liberation of electrons.

Hence corrosion (loss of metal) always takes place at the anodic area.

Hydrogen evolution corrosion in acid medium

This occurs when metals are in contact with acidic solution in the absence of sufficient oxygen concentration, e.g. Fe or Al in contact with HCl. Hydrogen evolution corrosion takes place in case of iron immersed in acid medium, this is due to the fact that hydrogen electrode in acid medium($E^0_{H+/H2}$=0V) is higher than electrode potential of iron($E^0_{Fe2+/Fe}$= -0.44V)

At anode,

$Fe \rightarrow Fe^{2+} + 2e^-$; $E^0_{Fe2+/Fe} = -0.44V$

At cathode,

$2H^+ + 2e^- \rightarrow H_2$;$E^0=0V$

Net reaction,

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$; $E^0cell = 0 - -0.44 = 0.44v$

Hydrogen evolution corrosion in alkaline medium

Hydrogen evolution corrosion does not take place in the case of iron immersed in alkaline medium. This is due to the fact that hydrogen electrode potential in alkaline medium ($E^0_{H2/OH-}$ =-0.828V,pH=14) is lower than electrode potential of Fe($E^0_{Fe2+/Fe}$= -0.44V).Whereas metals like Al can give Hydrogen evolution corrosion in alkaline medium also. This is due to the fact that hydrogen electrode potential in alkaline medium ($E^0_{H2/OH-}$ =-0.828V, pH=14)is higher than electrode potential of aluminium($E^0_{Al3+/Al}$= -1.66V).

At anode,

$Al \rightarrow Al^{3+}+3e^-$; E^0= -1.66V

At cathode,

$2H_2O +2e^- \rightarrow H_2 +2OH^-$;E^0=-0.828V

Here corrosion cell potential is $E^0_{cell}=E_{cathode}- E_{anode}$= -0.828- -1.66=0.832V

Oxygen absorption corrosion in acid medium

This occurs when metals are in contact with water having dissolved oxygen in acidic or even neutral environment e.g.rusting of iron.

At anode,

$Fe \rightarrow Fe^{2+}+2e^-$; $E^0_{Fe2+/Fe}$= -0.44V

At cathode,

$O_2+4H^++4e \rightarrow 2H_2O$;E^0=+1.23V

Here corrosion cell potential in acid medium is $E^0_{cell}=E_{cathode}- E_{anode}$=1.23- -0.44=1.67V

Fe^{2+} produced here can further oxidised to Fe^{3+} in acidic or neutral environments, since oxygen electrode potential is greater than $E^0_{Fe3+/Fe2+}$= +0.77V.

Fe^{3+} produced here forms an insoluble precipitate of $Fe(OH)_3$ called yellow rust. If the amount of moisture is less black rust Fe_3O_4 is formed. The rust formation leads to intense localised corrosion called Pitting corrosion. This is due to the formation of separate cathodic and anodic area. The precipitate adhered area is not in contact with oxygen called anodic area. In this area iron oxidises and pits are formed.Oxygen contacting area is called cathodic area.

Oxygen absorption corrosion in alkaline medium

This occurs when metals are in contact with water having dissolved oxygen in alkaline environment.

At anode

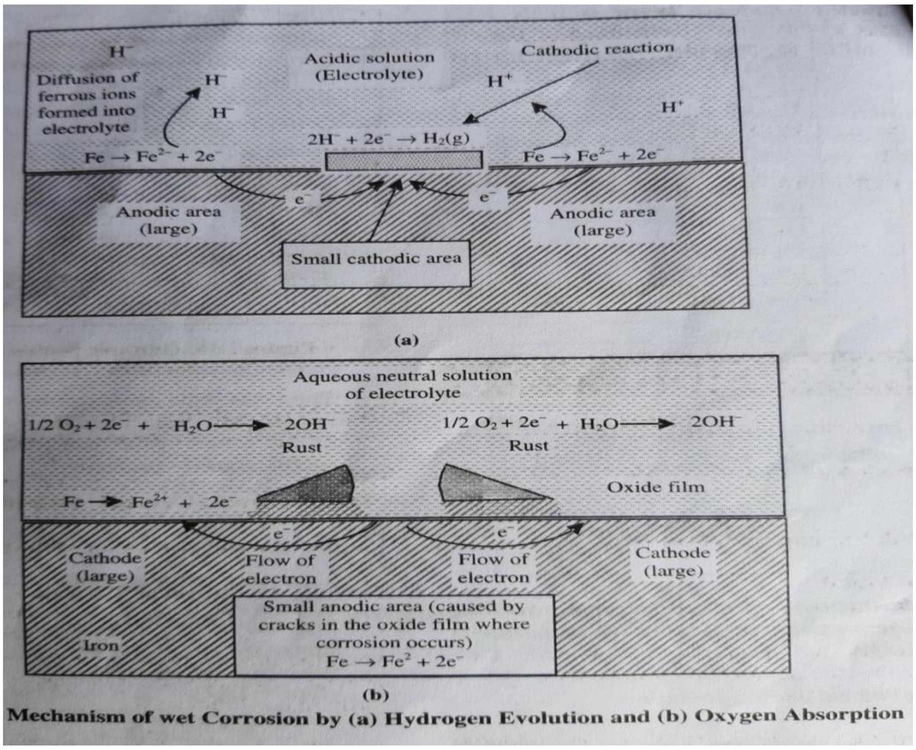
$Fe \rightarrow Fe^{2+}+2e^-$; $E^0_{Fe2+/Fe}$= -0.44V

At cathode

$O_2+2H_2O+4e^- \rightarrow 4[OH^-]$; E^0 =+0.40V

Here corrosion cell potential in acid medium is $E^0_{cell}=E_{cathode}- E_{anode}$=0.40- -0.44=0.84V.

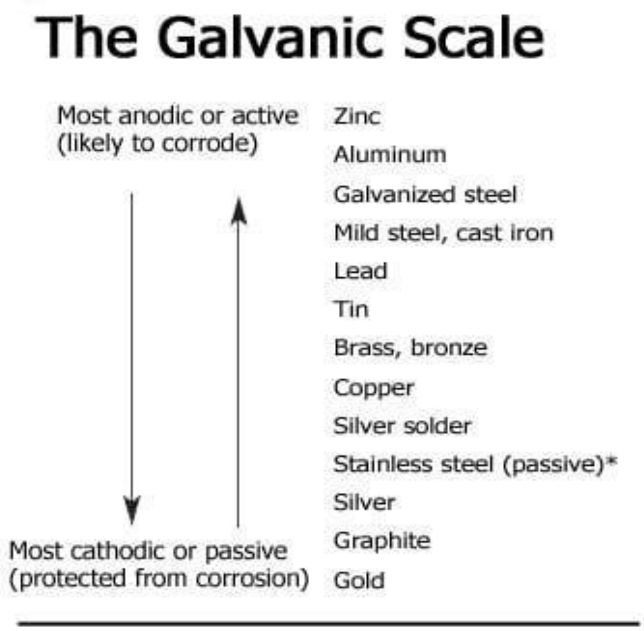
Fe2+ cannot oxidised to Fe3+ in alkaline environment, since oxygen electrode potential is less than $E^0_{Fe3+/Fe2+}$= +0.77V in alkaline medium. Here no insoluble precipitate of $Fe(OH)_3$ is produced, thus no intense localised corrosion.



Mechanism of wet Corrosion by (a) Hydrogen Evolution and (b) Oxygen Absorption

Galvanic series

Galvanic series which gives real and useful information regarding corrosion behaviour of metals and alloys in a given environment.
Or it is a series obtained by arranging metals and alloys in the order of corrosion tendencies.



The Galvanic Scale

Most anodic or active (likely to corrode)

- Zinc
- Aluminum
- Galvanized steel
- Mild steel, cast iron
- Lead
- Tin
- Brass, bronze
- Copper
- Silver solder
- Stainless steel (passive)*
- Silver
- Graphite
- Gold

Most cathodic or passive (protected from corrosion)

EMF series	Galvanic series
The position of a given metal in electrochemical series is fixed.	Position may shift.
There is no information regarding position of alloys.	Alloys are included.
It tells the relative displacement tendencies.	Predicts relative corrosion tendencies.
Electrode potential is measured by using SHE as reference electrode.	Electrode potential is measured by using SCE as reference electrode.

CATHODIC PROTECTION

Cathodic protection is a method of preventing a metallic object from corrosion.It is an electrochemical process in which the metal which is to be protected is forced to act as cathode.

A metal surface buried or immersed can contain anodic and cathodic areas.Corrosion occurs only in the anodic area.Therefore the entire surface of the metal can be turned into a cathode,then the corrosion can be prevented.

Two main methods of applying cathodic protection are

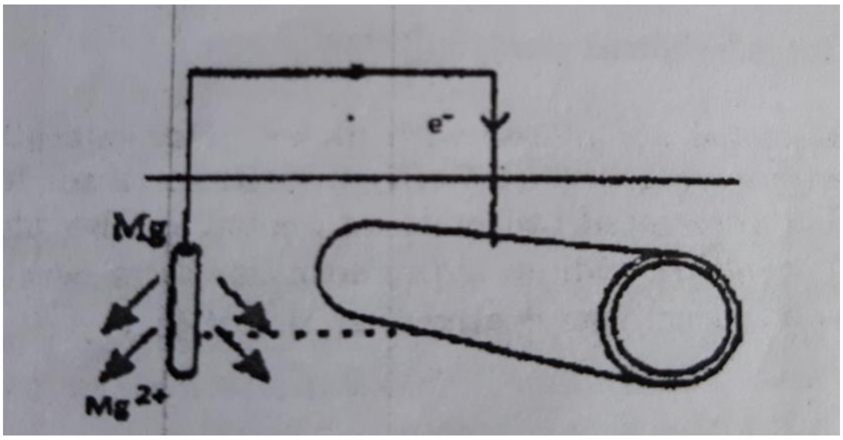
i. Sacrificial anode protection

ii. Impressed current cathodic protection.

i. Sacrificial anode protection

In this method, the metallic structure which is to be is protected is connected to a more anodic metal through a wire,so the entire corrosion is concentrated on the anodic metal, and the metallic structure is protected sacrificially.

Example for anodic metals; Mg,Zn,Al and its alloys.



Sacrificial anode systems are based on the position of themetal in the galvanic series.Metals at the top of the series are more prone to corrosion.

Sacrificial anode systems are more reliable than the impressed current system because lesser quantity of the component is destroyed and no power supply is required.

Advantages

*1.*No external power is required

2.Easy to install and inexpensive

3.Minmum maintenance required

Applications

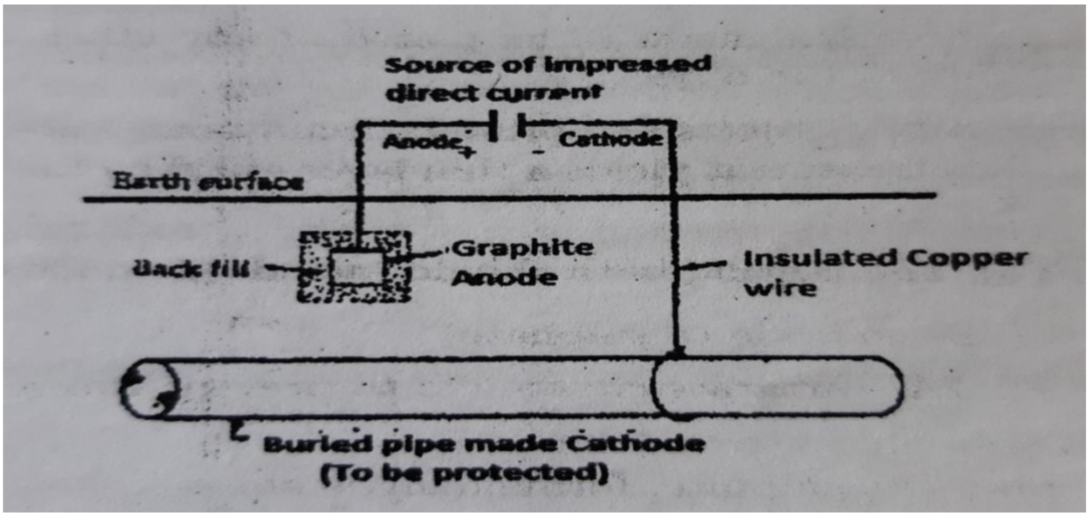
Protection of buried pipelines, underground cables, marine structures,ship body,open water tank coolers, condensers etc.

ii.Impressed current cathodic protection

This widely used system is usually developed to protect a structure which is immersed in a high resistivity electrolyte such as fresh water or sandy soils. This method requires large amount of current.

As a result of corrosion an electric flow occurs from the anodic region to the cathodic part, which is known as corrosion current. An impressed current is applied in opposite direction to neutralize corrosion current and convert the corroding metal from anode to cathode.

Usually impressed current is derived from a battery or DC source with an insoluble anode like graphite or silica.



Applications

Impressed current cathodic protection is applied to

(i)Open water boxes,coolers,water tanks etc.

(ii)Concrete buildings,bridges etc.

(iii) Vessels,pipelines and tanks which are used to store or transport liquids.

(iv) Marine cathodic protection covers many areas jetties,harbours,offshore structures etc.

Electroless plating

Electroless plating is a chemical, autocatalytic, metal coating process without the use of electricity.

In this process metal piece which is to be plated is immersed in a mixture of a reducing agent and a complex compound. It produces a deposition of continuous coating layer, on the surface,by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited

Metal ions + Reducing agent→Metal plated over a catalytically active surface + oxidised product.

Electroless plating is used to deposit a conductive surface on a non- conductive object to improve its electroplating

Electroless Nickel plating

Electroless nickel plating has better corrosion resistance than electroplated ones.

Nickel sulphate salt and hypophosphate reducing agent are taken in the furnace. Buffer, complexing agent and air are applied, catalytic surface(metal)which is to be plated is introduced and then heated. The electroless plating of nickel take place as follows.

Ni salt: $NiSO_4$

Reducing agent: Hydrated Na

Hypophosphite($NaH_2PO_2.H_2O$)Buffer: Na. Acetate

Overall reaction: $NiSO_4 + NaH_2PO_2.H_2O \rightarrow Ni\ (plating) + NaH_2PO_3 + H_2SO_4$

In the case of nickel plating, the deposits are dense and relatively hard. This method is conducted on metals like iron, steel, aluminium etc.

Applications

1.Electroless Ni plating is extensively used in electronic applications

2.its used in domestic (eg.Jewellery,perfume bottle top etc)

3.Automotive fields

4.Electroless Ni plated polymers (ABS) are used in decorative as well as functional applications.

Advantages

1.No electricity required.

2.Can be used to obtain uniform coating on irregular shaped articles.

3.The deposits are more compact and highly adherent.

4.No elaborate arrangements are required.

Electroless -Copper plating.

Electroless copper plates much more slowly, and is a much more expensive process, than electrolytic copper plating.

Copper sulphate and formaldehyde reducing agent are taken in the furnace.buffer,complexing agent and air are applied, catalytic surface(metal)which is to be plated is introduced and then heated.The electroless plating of copper take place as follows.

Cusolution:$CuSO_4$

Reducingagent:formaldehyde (HCHO)

Buffer: NaOH
Reactions: at cathode $Cu^{2+}+2e^- \rightarrow Cu$
At anode $2HCHO+4OH^- \rightarrow 2HCOO^-+2H_2O+H_2+2e^-$

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

Advantages of Electroless plating

- Even coating, does not use electrical power.
- Flexibility in plating volume and thickness.
- Complex filtration method is not required.
- Matte, semibright or bright finishes available.
- Improved hardness, strength, ductility and resistance to corrosion.

Applications

Electroless plating is used in

- The plating of printed circuit boards.
- Oil field valves, optical surfaces, door knobs, kitchenutensils, bathroomfixtures, electrical ormechanical tools and office equipments.
- Numerous consumer goods are coated by this method to create durable and attractive surfaces.

Limiations

1. The complexing agent creates difficulties.
2. Formaldehyde is a human health hazard.

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