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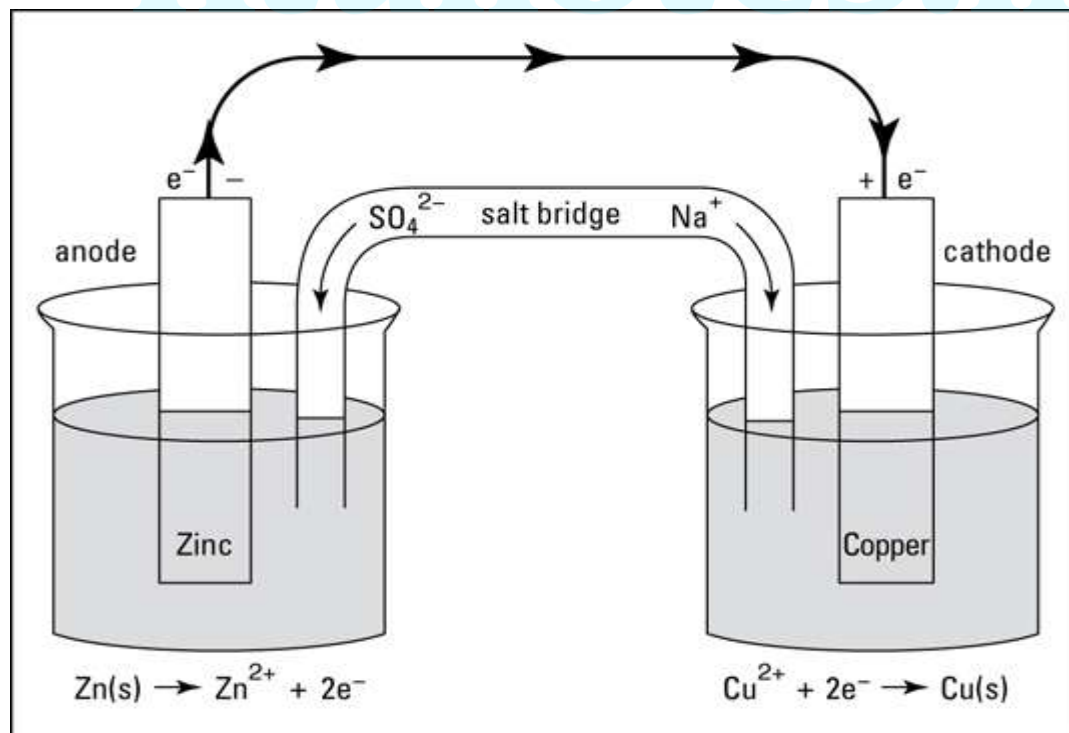
Module 1: ELECTROCHEMISTRY AND CORROSION

1.1 Introduction: Electrochemistry deals with chemical reactions produced by passing electric current through an electrolyte or the production of electric current through chemical reactions. Accordingly we have Electrochemical cell (Galvanic cell) and Electrolytic cell. Cells which convert chemical energy to electrical energy is called Electrochemical cells .E.g Daniel cell. Cells which convert electrical energy to chemical energy is called Electrolytic cells .E.g Lead acid battery.

1.2 Differences between electrolytic and electrochemical cells

Sl No	Electrochemical cell (Galvanic cell)	Electrolytic cells
1	Convert chemical energy to Electrical energy	Convert Electrical energy to chemical energy
2	Cell reaction is spontaneous	Cell reaction is Non-spontaneous
3	Cell EMF is positive	Cell EMF is Negative
4	Electrons move from anode to cathode	Electrons move from cathode to anode
5	Free energy change (ΔG) is Negative	Free energy change (ΔG) is Negative
6	Salt bridge is required	Salt bridge is not required
7	Anode is negative terminal	Anode is positive terminal
8	Cathode is positive terminal	Cathode is negative terminal
9	Source of Energy	Requires source of external energy

Daniel Cell-Redox reactions:



A Schematic representation of Daniel Cell

Anode (-ve) : Zinc metal dipped in ZnSO_4 solution: **Cathode** (+ve) : copper metal dipped in CuSO_4 solution

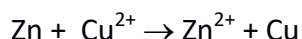
Zinc metal has a greater oxidation tendency for oxidation than that of copper, oxidation occurs at Zinc electrode and leave its electron to the zinc electrode and goes to the solution as Zn^{2+} ions;

Anode reaction : $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ----- 1

In the copper compartment the Cu^{2+} in the solution has a tendency of reduction and accepts electrons from the Cu metal and get deposited on Cu electrode consuming the electrons generated at Zn anode

Cathode reaction : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ -----2

The cell reaction is obtained by combining anode reaction(1) and Cathode reaction (2) as



Flow of electrons (negative electricity) in the cell is from Zn electrode to the copper electrode and hence flow of positive electricity ie conventional current in the cell is from copper electrode to the Zn electrode.

For the completion of the circuit, transfer of ions between anode and cathode compartments takes place through salt bridge.

Cell representation of Daniel cell is : **$\text{Zn} / \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (1\text{M}) / \text{Cu}$**

1.3 Representation of Galvanic cells:-

A cell is represented conventionally by

Two half cells. Oxidation half cell and reduction half cell

Oxidation half-cell as **$\text{M(s)} / \text{M}^{n+} (\text{c})$** , where 's' is the solid state of the metal and 'c' is the concentration of the solution.

Reduction half-cell is writtern as **$\text{M}^{n+} (\text{c}) / \text{M(s)}$** .

Anode should be represented on the Left side and cathode on the right side. Two vertical lines (||) indicated between half cells indicates salt bridge.

Note: anode is the palce where oxidation takes place ,its sign is negative (-) in electrochemical cell and positive in electrolytic cells. For cathode it is negative.

E.g cell representation of Daniel cell: **$\text{Zn} / \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (1\text{M}) / \text{Cu}$**

1.4 SALT BRIDGE:

Salt bridge is a 'U' shaped glass tube containing electrolytes like KCl, KNO₃, in a semisolid agar.

K⁺, Cl⁻ are having equal mobility and get drifted to cathode and anode respectively.

Its functions are

- (a) Maintains electrical neutrality of each half cell,
- (b) Prevents the accumulation of ions in the electrode,
- (c) Provides the continuity of electrical circuit.,
- (d) Prevents diffusion of ions from one compartment to another.

1.5 REVERSIBLE AND IRREVERSIBLE CELLS

Reversible cells are those in which chemical reactions stops when an exactly equal and opposing emf is applied, and the reaction of the cell is reversed when the opposing emf is slightly greater than that of the cell.

E.g Daniel cell

Any other cell which does not obey the above conditions is called irreversible cells. E.g : Voltaic cell (Zinc and copper rod dipped in dilute sulphuric acid).

1.6 TYPES OF ELECTRODE

1. *Metal /Metal ion electrode (M/Mn⁺)* : when a metal is immersed in the respective salt solution, a metal metal ion electrode is formed..
E.g Zinc electrode - A zinc rod dipped in zinc sulphate solution (Zn/Zn²⁺),
Silver electrode-A silver rod dipped in silver nitrate,
Copper electrode: copper rod dipped in copper sulphate solution.
2. *Gas electrode* ; In this type, gas is passed through an inert electrode like platinum which is immersed in a solution containing its own .
E.g Hydrogen electrode. It is formed by bubbling Hydrogen gas through platinum electrode immersed in HCl solution .It is represented as (Pt/H₂/H⁺) or chlorine electrode formed by bubbling chlorine gas through platinum electrode immersed in NaCl solution. It is represented as (Pt/Cl₂/Cl⁻)

Electrode reaction: (i) For Hydrogen gas electrode, $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+ + 2\text{e}^-$ or $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$;

(ii) For chlorine electrode, $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ or $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$

Here the electrode potential depends on concentration of ion and pressure at which gas is bubbled. (For schematic representation of the electrode refer "reference electrode")

3. *Metal/insoluble metal salt/common ion electrode*: In this type the metal is covered with a paste of its insoluble metal salt, which is in contact with a solution containing common ion with the insoluble salt. Here the electrode potential depends on concentration of common ion.

E.g 1 Calomel electrode : Mercury in contact with an insoluble precipitate of Hg_2Cl_2 which is in contact KCl solution, For electrical contact platinum rod is immersed in liquid Mercury, represented by $(\text{Pt}(\text{s})/\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-)$. Electrode reaction of calomel electrode. When acting as Cathode, $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg}_{(\text{l})} + 2\text{Cl}^-$

When acting as anode, $2\text{Hg}_{(\text{l})} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$

2. Silver-silver chloride electrode. Silver rod in contact with a precipitate of silver chloride (AgCl) in contact with KCl solution. Represented by Ag/AgCl . (For schematic representation of the electrode refer "reference electrodes")

4. *Redox electrode*. In this type an inert electrode like platinum is in contact with a mixture of two salts of the same metal having different oxidation states.

E.g : (1) $\text{Pt}, \text{Fe}^{2+}/\text{Fe}^{3+}$ The electrode reactions : $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. (Oxidation); or $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

(2) $\text{Pt}, \text{Sn}^{2+}/\text{Sn}^{4+}$

5. *Ion selective electrode*: In this type, sensing part of the electrode is usually made of an ion-specific membrane. The membrane may be glass membrane, crystalline membrane and ion exchange resin membrane.

Eg Glass electrode: In this electrode, glass membrane is made of an ion-exchange type of glass which are sensitive to specific ions like H^+ , Na^+ , Ag^+ , membrane.

(For schematic representation of the electrode refer "reference electrode")

1.7 Single Electrode Potential :

Theory: When a metal electrode is in contact with its own salt solution following reactions can take place due to tendency called Nernst electrolytic solution tension.

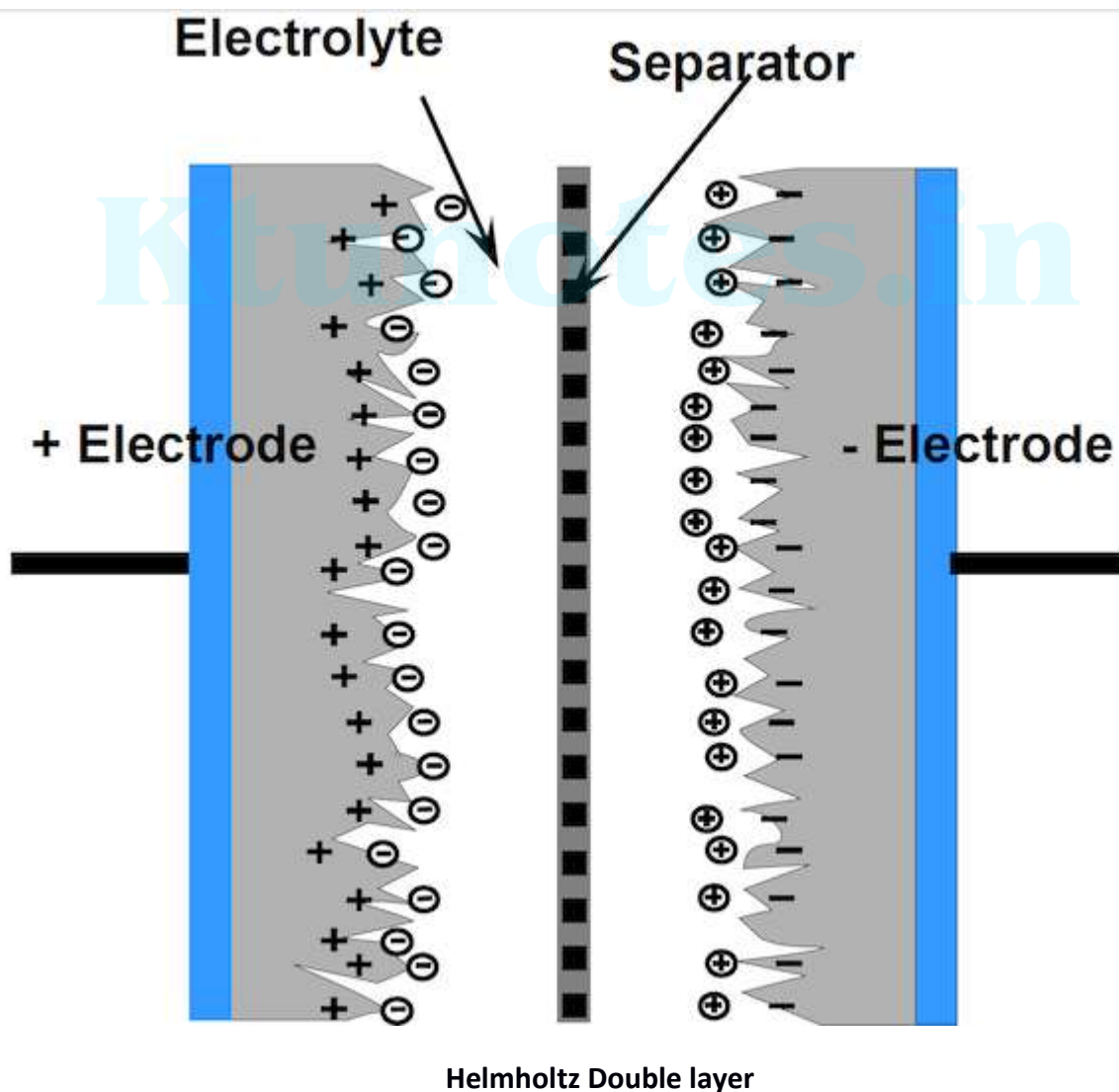
$\text{M} \rightarrow \text{Mn}^+ + \text{ne}^-$ (Oxidation); Case 1 ;

$\text{Mn}^+ + \text{ne}^- \rightarrow \text{M}$ (Reduction) Case 2

In first case some metal ions enter into the electrolyte solution leaving behind the electrons on the metal electrode. Thus electrode gets negative charge and solution side gets positive charge due to excess positive metal ions.

In the second case the positive metallic ions from the solution take electrons from the electrode and get deposited as metal on the electrode surface. Now the electrode gets a positive charge and the solution side gets a negative charge (due to deficiency of positive metal ions)

Equilibrium is reached in the vicinity of electrode, due to the electrostatic force and further transfer of metal ions does not take place. Thus the positive charge and negative charge remain close to the metal surface forming a double layer. This double layer is called "HELMHOLTZ ELECTRICAL DOUBLE LAYER (SEP)". As a result, difference in potential is set up between the metal and the solution this potential is called Single electrode potential.(E).



If the tendency of the electrode is to lose electrode is called Oxidation potential, and the tendency of the electrode is to gain electrode is called reduction potential. At equilibrium the potential difference becomes constant, and this 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 (E^0) of the metal.

1.8 REFERENCE ELECTRODES: These are the standard electrodes with reference to these, the electrode potentials of any other electrode can be determined. Reference electrodes are of two types.

(i) Primary reference electrode, e.g Standard Hydrogen electrode,

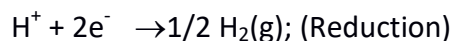
(ii) Secondary reference electrode .e.g Calomel electrode.

1.8.1 STANDARD HYDROGEN ELECTRODE (SHE)

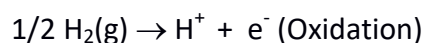
Description: It consists of an inert platinum dipped in 1M H^+ (HCl) solution, which is in contact with H_2 gas at 1 atm pressure at 298 K. SHE is taken as the standard reference electrode and the electrode potential is taken as ZERO.

The electrode is represented as $Pt/H_2(g) 1 atm / H^+(1M)$.

SHE is a reversible electrode which can act as anode or cathode depending on the potential of the electrode to which it is coupled. If the potential of the coupled electrode is less than zero (Eg Zn, Mg, Li), reduction takes place in SHE and it acts as cathode and the electrode reaction is as shown below.



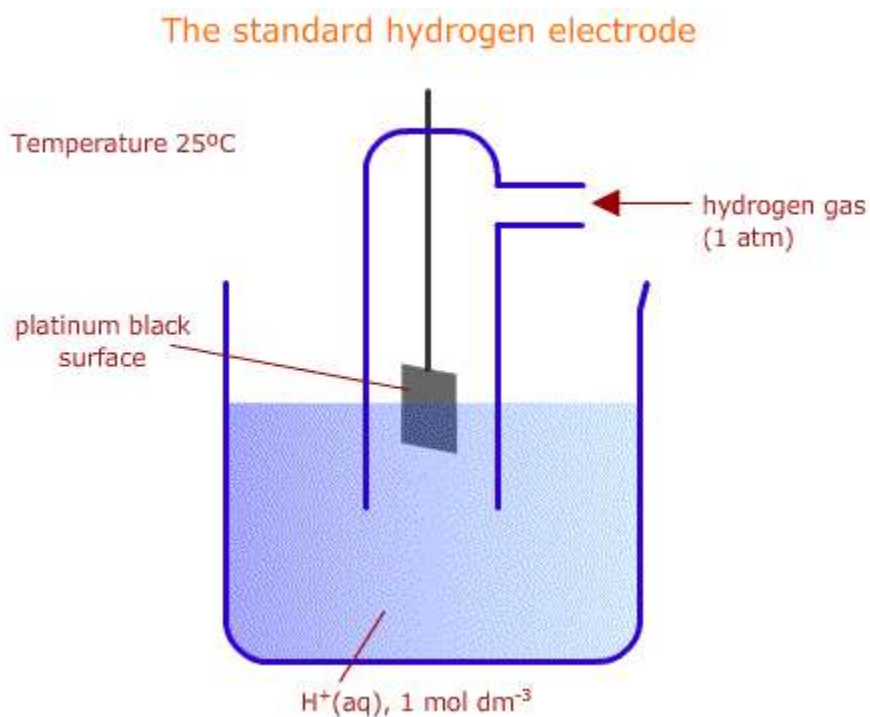
When the potential of the coupled electrode is greater than zero, (E.g Cu, Ag, F) oxidation reaction takes place in SHE and it acts as anode as shown,



SHE is a Primary reference electrode and is used for finding single electrode potential of other electrodes.

The -ve or +ve values are obtained for standard reduction potential or standard electrode potential depending on whether the half cell act as anode or cathode with respect to SHE. For example standard electrode potential of zinc electrode is -ve since the electrode act as anode with respect to SHE.

The schematic representation of a standard Hydrogen electrode is shown below.



Advantages of SHE

A primary reference electrode.

Shows no salt error, negligible internal resistance,

Can be used over the entire pH range.

Highly accurate.

Limitations of SHE

It is difficult to set up and transport.

Pressure of H_2 gas is to be maintained at 1 atm all the time

Electrode potential changes with pressure

Cannot be used in redox systems.

Will be poisoned by compounds like Hg, AS, S, Fe^{3+} , MnO_4^- etc.

1.8.2 CALOMEL ELECTRODE

Calomel electrode is an example of metal –metal insoluble metal salt electrode and a solution of its common ion(mercury-mercurous chloride electrode electrode,KCl.)

Construction: It consists of a glass tube at the bottom of which, a small amount of Hg is placed .This is covered with a paste of solid mercurous chloride (Hg_2Cl_2 or calomel)which is further in contact with a solution of KCl. A Pt wire dipped into the Hg layer is used for making electrical contact. The side tube is used for making electrical contact with a salt bridge. The electrode may be represented as

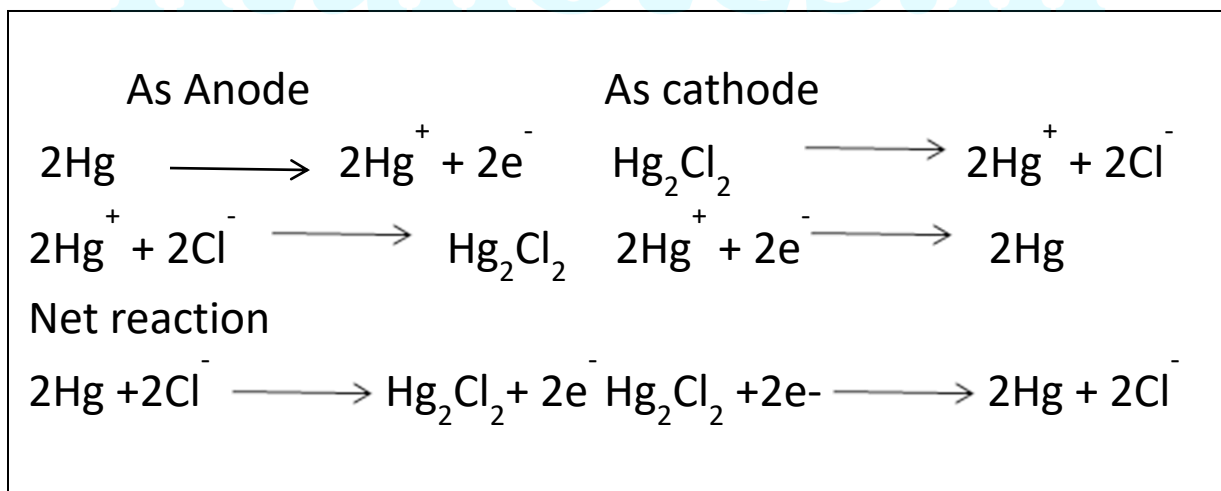
$\text{Pt-Hg/Hg}_2\text{Cl}_2(\text{s})/\text{KCl}$.

The electrode reaction is given by : $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg}_{(\text{l})} + 2\text{Cl}^-$; $E^0 = 0.2810\text{V}$ -----3

The calomel electrode can act as anode or cathode depending on the electrode potential of the coupled electrode. If the electrode potential of the coupled electrode is lower than the calomel electrode, then calomel electrode undergoes reduction and act as cathode. If the electrode potential of the coupled electrode is greater than the calomel electrode, then calomel electrode undergoes oxidation and act as anode and the reverse of the above reaction (3) takes place.

The anode and cathode reactions are as follows.

Thus the electrode reaction sare represented as follows



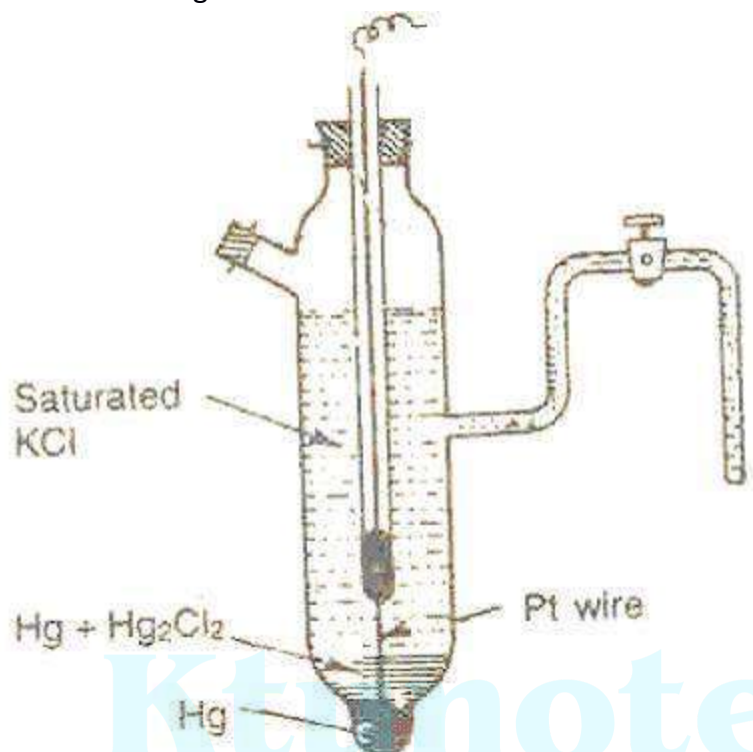
The Nernst equation of this electrode at 25°C is given by

$$E_{\text{cal}} = E_{\text{cal}}^0 - 0.0591 (\log [\text{Cl}^-]^2) / 2$$

Thus the potential of the calomel electrode varies with the concentration of the concentration of KCl solution as shown in the Table below. Normally a saturated KCl solution is used since the emf will not vary with chemical react ion and it is also easy to set up.

KCl concentration	0.1 N (DNCE)	1N (NCE)	Saturated (SCE)
Electrode potential (Volts)	0.3335	0.2810	0.2422

A schematic diagram of a calomel electrode is shown below.



Working : Measurement of electrode potential using Calomel electrode. The experimental set up used for the measurement of electrode potential of other electrodes is shown below.

Determination of single electrode potential using calomel electrode:

The test electrode (e.g., Zn^{2+}/Zn) is coupled with a saturated calomel electrode.

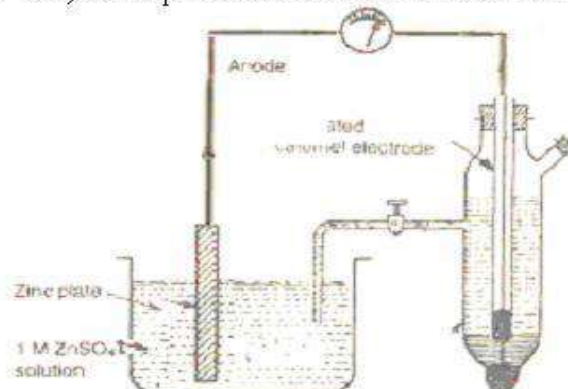
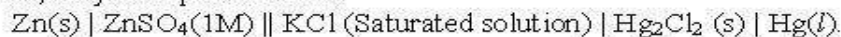


Fig. Determination of electrode potential of zinc electrode using calomel electrode as reference electrode.

The cell, so formed, may be represented as



The calomel electrode is written on the right as reduction takes place at this electrode. The emf of this cell measured potentiometrically.

$$\begin{aligned} \text{Then } E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{cal}} - E_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.2422 - E_{\text{Zn}^{2+}/\text{Zn}} \\ \text{i.e., } E_{\text{Zn}^{2+}/\text{Zn}} &= 0.2422 - E_{\text{cell}} \end{aligned}$$

By measuring E_{cell} , $E_{\text{Zn}^{2+}/\text{Zn}}$ can be calculated.

1.8.3 GLASS ELECTRODE:

A glass electrode is a type of ion-selective electrode made of doped glass membrane that is sensitive to a specific ion. It is universally used for pH measurement. For pH measurement H^+ ion selective glass electrode is used.

Construction: The glass electrode assembly consists of a long glass tube with a thin glass bulb filled with 0.1 M HCl. The glass is low melting and having high electrical conductivity. The composition of Na_2O in this glass is slightly more than ordinary soda glass. The inner surface of the glass is in contact a AgCl coated silver electrode or simply a platinum contact electrode. HCl in the bulb furnishes a constant H^+ ion concentration..

Glass electrode representation is:



electrode reaction is $\text{H}^+ + \text{Na}^+_{(\text{galas})} \rightarrow \text{Na}^+ + \text{H}^+_{(\text{galas})}$,

The Nernst equation for glass electrode is

$$E_G = E_G^0 - 0.0591 \text{ pH} ,$$

where E_G^0 constant for a particular variety of glass,(0.5 or 0.6 depending on the variety of glass.).

E_G^0 can be determined by coupling with saturated calomel electrode.

This cell can be represented as $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}_{(\text{satd})} \parallel \text{H}^+_{(\text{unknown})}/\text{glass}/\text{H}^+_{(0.1\text{M})}/\text{Pt}$

Measurement of pH: For measuring the pH of a test solution the glass bulb is immersed in the test solution such that the outer surface of the glass bulb comes in contact with the test solution. The glass membrane serves as ion-selective resin and, equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution.

In order to measure the potential of glass electrode ,it has to be coupled with a secondary reference electrode like Calomel electrode as shown above. The EMF of the cell is measured and the pH can be calculated as follows.

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

$$E_{\text{cell}} = E_G^0 - 0.0591 \text{ pH} - 0.2422$$

$$E_{\text{cell}} = (E_G^0 - 0.2422) - 0.0591 \text{ pH} \text{ .----- (A)}$$

(A) Has the form $Y = mx + C$, representing the equation for a straight line

The constants and the intercept C can be determined by calibrating the pH meter with two buffer solutions of known pH.

The intercept $C = E_G^0 - 0.2422$, and the slope is 0.0591 at 25 °C.

Problem:

A glass electrode –calomel electrode assembly shows an emf of 208 mV and -32mV with buffer solutions of pH 4 and 9.2 respectively. Find the pH of the test solution if it shows an emf of 78mV

The graph between emf on Y axis and pH on X axis ,with the given data ,we can form equations of two straight lines as shown below.

$$208 = C + 4m \quad (1)$$

$$-32 = C + 9.2m \quad (2)$$

$$(1) - (2) \rightarrow 240 = -5.2m , \therefore m = -46.15$$

Substituting in (1) gives

$$208 = C + 4(-46.15), \therefore C = 392.6$$

From the value of C and m we can write the emf of the test solution as

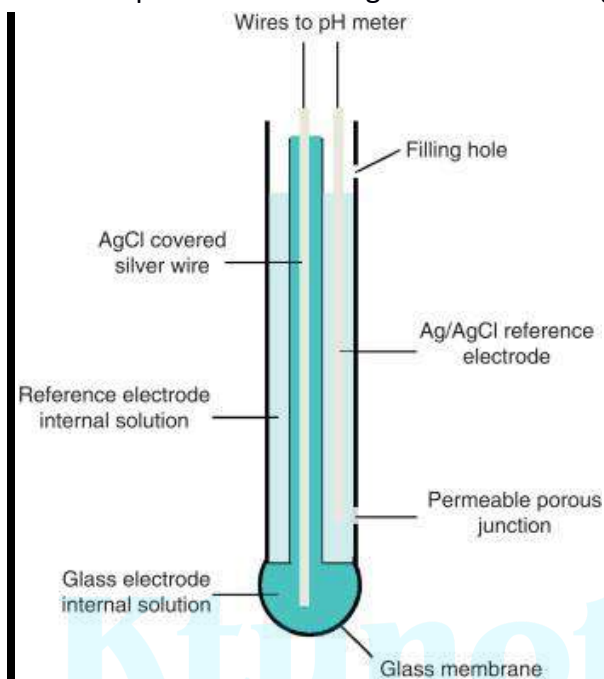
$$78 = C + m \times \text{pH} \quad (3)$$

Knowing the calibration constants m and C unknown constants can be determined by substituting in the equation (3), we have

$$78 = 392.6 + (-46.15) \times \text{pH}$$

$$\text{pH} = 6.81$$

A schematic representation of a glass electrode is given below.



1.9 Electrochemical series and its application

Electrochemical series is the series in which the standard electrode potentials are arranged in descending order.

According to IUPAC only reduction reactions and reduction potentials are taken into consideration.

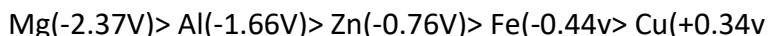
1.9.1 Applications of Electrochemical series

1. To predict reactivity of metals

Electrodes having negative values of standard electrode potential with respect to hydrogen have tendency to undergo oxidation whereas electrodes having positive values have tendency to undergo reduction in aqueous solution.

e.g. among the metals, $\text{Al}(-1.66\text{V})$, $\text{Cu}(+0.34\text{V})$, $\text{Fe}(-0.44\text{V})$, $\text{Mg}(-2.37\text{V})$, $\text{Zn}(-0.76\text{V})$, [Figures in bracket is E^0 value], according to their order in which they displace each other can be

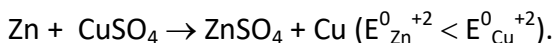
shown as below. When the reduction potential becomes low, the metal shows more tendency to lose electrons and can be displaced.



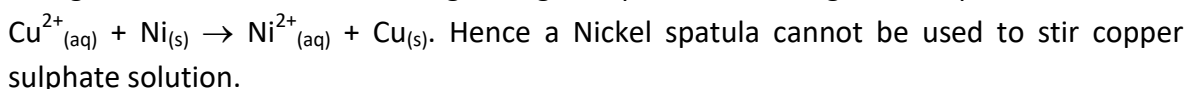
2. To explain Displacement reactions

(a) To predict whether a given metal will displace another, from its salt solution. A metal having lower E^0 value will displace the metal having higher E^0 value from its salt solution.

E.g : Zn metal ($E^0 = -0.76\text{V}$) can displace Cu ($E^0 = +0.34\text{V}$) from CuSO_4 solution as per the reaction



when we use Ni spatula to stir CuSO_4 solution, Nickel having lower reduction potential (-0.23V) than copper (0.34V), nickel loses electron and Ni^{2+} ions are formed, while Cu^{2+} ions get reduced to Cu metal and get Cu get displaced according to the equation,



Similarly it is not possible to store CuSO_4 solution in an iron vessel, since reduction potential of Cu^{2+}/Cu is greater than that of Fe^{2+}/Fe ($0.34\text{V} > -0.23\text{V}$)

(b) Metals having negative reduction potentials can displace hydrogen from acids

For example metals like Fe, Zn, Al etc can liberate H_2 gas when react with acids.



(c) A non-metal having higher reduction potential can displace a non-metal having lower reduction potential.

For example

On passing fluorine gas through sodium chloride solution, displacement reaction takes place generating chlorine gas and sodium fluoride.

Reason : Fluorine and chlorine are non-metal and $E^0_{\text{F}_2/\text{F}^-}$ of Fluorine ($+2.87\text{V}$) is higher than that of chlorine, $E^0_{\text{Cl}_2/\text{Cl}^-}$ ($+1.33\text{V}$). ($E^0_{\text{F}_2/\text{F}^-} > E^0_{\text{Cl}_2/\text{Cl}^-}$)

3. Determination of standard emf of a cell : Standard emf of a cell can be judged based on the standard reduction potentials of the respective cell.

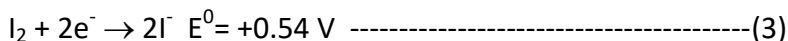
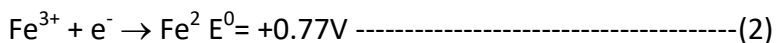
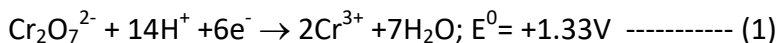
For example, the emf of the Daniel cell can be determined from the standard reduction potential of Zinc and copper electrodes.

$$\begin{aligned} E^0_{(\text{Daniel})} &= E^0_{(\text{Cu}^{2+}/\text{Cu})} - E^0_{(\text{Zn}^{2+}/\text{Zn})} \\ &= 0.34 - (-0.76) \\ &= 1.10 \text{ V} \end{aligned}$$

4. To predict the spontaneity of redox reactions. The spontaneity of a chemical reaction can be understood based on the standard reduction potential. The reaction having more cell emf is more spontaneous.

For example, On the addition of potassium dichromate solution to acidified mixture of ferric chloride and potassium iodide, oxidation of I^- to I_2 takes place first than oxidation of Fe^{2+} to Fe^{3+} .

This can be understood from the E^0 values of the corresponding reactions



For oxidation of I^- to I_2 (1) and (3) to take place, its $EMF = 1.33 - 0.54 = 0.79V$, while for oxidation of Fe^{2+} to Fe^{3+} to take place, (1) and (2) should take place and its $EMF = 1.33 - 0.77 = 0.56V$.

Since $0.79 > 0.54$, reaction (1) and (3) take place first before (1) and (2).

Similarly, while acidified potassium permanganate solution can liberate chlorine gas for NaCl solution, acidified potassium dichromate solution is not capable of liberating Chlorine gas from NaCl. which can be explained on the basis of electrode potentials. (EMF of cell (permanganate- Cl_2/Cl^-) is positive while EMF of cell (dichromate- Cl_2/Cl^-) is negative hence ΔG is positive and non spontaneous.

5. *Analysis of products of electrolysis:* The emf of the cell constituted by the oxidizing and reducing specie/ ion, should be less negative.

For example,

Predict the product of Electrolysis of a mixture of aqueous solution of KCl and KI using platinum electrode.,

Here the electrode used is inert and do not take part in the reaction. Hence the product of electrolysis depend only on the oxidizing and reducing species present in the electrolytic cell, and their E^0 values.

H_2 is liberated at cathode (-ve terminal) and I_2 is liberated at anode (+ve terminal)

6. *Decomposition potential:*

Decomposition potential can be calculated from the electrochemical series.

For example, In acid medium Water can be decomposed into Hydrogen and oxygen by applying 1.23V since the E^0 values of O_2 and H are 1.23V and 0 respectively.

1.10 RELATION BETWEEN FREE ENERGY AND EMF OF THE CELL

Free Energy(ΔG) : Energy available per mole that can be converted into mechanical work.

Decrease of free energy is equal to electrical energy produced in a reversible cell.

Electrical energy produced per mole = quantity of charge in mole X EMF

For a reaction involving “n” electrons, Quantity of charge in one mole = nF,

∴ Electrical energy produced per mole = nFE

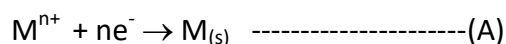
Since, Decrease of free energy is converted into electrical energy,

$$\Delta G = -nFE \quad \text{where } (F = 6.023 \times 10^{23} \times 1.6 \times 10^{-19} = 96500 \text{ C})$$

1.11.0 NERNST EQUATION FOR A SINGLE ELECTRODE

Gives relation between electrode potential and concentration of the ion of the electrolyte.

Consider a general electrode reaction



In the case of a reversible reaction free energy change and its equilibrium constant are interrelated as per vanthoff's equation

$$\Delta G = \Delta G^0 + RT \ln Q \text{ ----- (1)}$$

,where Q is the reaction quotient(ratio of activities of products to reactants).

$$\text{Since, } \Delta G = -nFE, \text{ -----(2)}$$

Substituting (2) in (1) we get,

$$-nFE = -nFE^0 + RT \ln Q \quad (E^0 \text{ is the standard electrode potential, measured at 298K, and 1 bar pressure})$$

Dividing both sides by -nF, we get

$$E = E^0 - (RT/nF) \ln Q \text{ -----(3)}$$

Substituting the constant, R=8.314 JK⁻¹, T= 298 K, and F=96500 C, and converting into logarithm to base 10, (3) becomes

$$E = E^0 - (8.314 \times 298 \times 2.303/n \times 96500) \log Q$$

$$\text{ie } E = E^0 - (0.0591/n) \log Q$$

$$Q = [M_s] / (M^{n+} \times [e]), \text{ since } [e] = 1, \text{ and } [M_s] = 1,$$

$$Q = 1/[M^{n+}].$$

$$\text{Therefore the (4) becomes, ie } E = E^0 - (0.0591/n) \log (1/[M^{n+}]). \text{ ----- (4)}$$

is the Nernst equation for a single electrode whose electrode reaction is as (A).

1.11.1 NERNST EQUATION FOR AN ELECTROCHEMICAL CELL

Gives the effect of concentration of the electrolyte species on the EMF of the cell.

An electrochemical cell is obtained by coupling two half cells. A Daniel cell is formed by coupling a Zinc electrode (Zinc rod dipped in Zinc sulphate solution- Zn/Zn^{2+}) and Copper electrode (copper rod dipped in coppersulphate solution- Cu/Cu^{2+}) separated by a salt bridge, as

$\text{Zn}_s/\text{Zn}^{2+}_{(\text{aq})} || \text{Cu}^{2+}/\text{Cu}_s$; Zn electrode act as anode and Cu electrode act as cathode.

$$E_{\text{cell}} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})} \text{ ----- (5)}$$

Nernst equation for cathode, $E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{\text{Cu}^{2+}/\text{Cu}} - (0.0591/2) \log(1/\text{Cu}^{2+}) \text{ ----- (6)}$: for Daniel cell reaction $n=2$

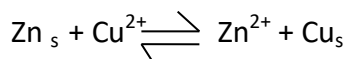
Nernst equation for anode, $E_{(\text{Zn}^{2+}/\text{Zn})} = E^0_{\text{Zn}^{2+}/\text{Zn}} - (0.0591/2) \log(1/\text{Zn}^{2+}) \text{ ----- (7)}$

Substituting (6) & (7) in (5) we get,

$$\begin{aligned} E_{\text{cell}} &= \{ E^0_{\text{Cu}^{2+}/\text{Cu}} - (0.0591/2) \log(1/\text{Cu}^{2+}) \} - \{ E^0_{\text{Zn}^{2+}/\text{Zn}} - (0.0591/2) \log(1/\text{Zn}^{2+}) \} \\ &= \{ E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}} \} - \{ (0.0591/2) \log(1/\text{Cu}^{2+}) - (0.0591/2) \log(1/\text{Zn}^{2+}) \} \\ &= E^0_{\text{cell}} - (0.1591/2) \log \{ (1/\text{Cu}^{2+}) - \log(1/\text{Zn}^{2+}) \} \\ &= E^0_{\text{cell}} - \{ (0.1591/2) \log (1/\text{Cu}^{2+}) / (1/\text{Zn}^{2+}) \} \\ &= E^0_{\text{cell}} - (0.1591/2) \log \{ (1/ [\text{Cu}^{2+}]) \times ([\text{Zn}^{2+}]/1) \} \end{aligned}$$

$$E_{\text{cell}} = E^0_{\text{cell}} - (0.1591/2) \log \{ [\text{Zn}^{2+}] / [\text{Cu}^{2+}] \} \text{ at } 25^\circ\text{C} \text{ ----- (8)}$$

Is the Nernst equation for the Daniel cell whose cell reaction is



Nernst equation for a general equilibrium reaction ,

$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ is given by

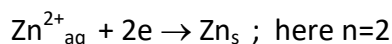
$$E_{\text{cell}} = E^0_{\text{cell}} - 2.303RT/nF \log \{ ([\text{C}]^c [\text{D}]^d) / ([\text{A}]^a [\text{B}]^b) \} \text{ ----- (9)}$$

1.11.2 Numerical on Nernst equation:

Worked out examples (WE)

M1WE1 . Calculate the single electrode potential of Zn electrode at 25 °C , when the concentration of $[Zn^{2+}] = 0.01M$ ($E_{Zn^{2+}/Zn}^0 = -0.76V$)

The electrode reaction for the electrode Zn/Zn^{2+} is



Applying Nernst equation for the single electrode (5) above, we have

$$\text{ie } E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0 - (0.0591 / 2) - \log 1 / [Zn^{2+}]$$

$$\text{ie } E_{Zn^{2+}/Zn} = -0.76 - 0.0591/2 \log 1 / 0.01$$

$$\text{ie } E_{Zn^{2+}/Zn} = -0.76 - 0.0591/2 \log 10^2$$

$$\text{ie } E_{Zn^{2+}/Zn} = -0.76 - 0.0591/2 \times 2 \log 10$$

$$\text{ie } E = -0.76 - 0.0591 \times 2 / 2$$

$$\text{ie } E = -0.76 - 0.0591$$

$$\text{ie } E = -0.891V$$

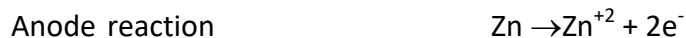
M1WE2. Calculate the EMF of a Daniel cell when the concentration of $[Zn^{2+}] = 0.01M$ and concentration of $[Cu^{2+}] = 0.01M=0.1M$ given that ($E_{Zn^{2+}/Zn}^0 = -0.76V, E_{Cu^{2+}/Cu}^0 = +0.34V$)

Since $E_{Cu^{2+}/Cu}^0 > E_{Zn^{2+}/Zn}^0$, Copper electrode has higher tendency for reduction and gets reduced act as cathode while zinc electrode has less tendency for reduction and thus gets oxidized and act as anode, when Zinc and copper electrodes are coupled.

Thus the Daniel cell can be represented as



Electrode reactions are



$$E_{cell}^0 = E_R^0 - E_L^0 \text{ OR}$$

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

$$E_{\text{cell}}^0 = E_{\text{Cu}}^{0, 2+} - E_{\text{Zn}}^{0, 2+}$$

$$E_{\text{cell}}^0 = +0.34 - (-0.76) = 1.1\text{V}$$

Nernst equation for the above cell reaction can be shown as

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.1591/2) \log \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\} \text{ at } 25^\circ\text{C}$$

$$= 1.1 - (0.0591/2) \log(0.01/0.1)$$

$$= 1.1 - [0.0591/2] [\log (10/100)]$$

$$= 1.1 - [0.0295][\log 0.1]$$

$$= 1.1 - [0.0295][-1]$$

$$= 1.1 + 0.0295$$

$$= 1.1295 \text{ V}$$

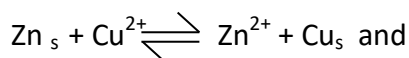
1.11.3 APPLICATIONS OF NERNST EQUATION

1. To calculate electrode potential of an unknown metal
2. To study the effect of concentration of electrolytes on electrode potential.
3. To calculate potential of a cell under non-standard conditions
4. Determination of pH of a solution from the measurement of electrode potential.
5. Determination of valency of an ionic species in an electrochemical reaction.
6. Calculation of equilibrium constant of a cell reaction
7. To predict corrosion tendency of metals.
8. Solubility of a sparingly soluble salt at different temperature can be determined.
9. To calculate potential of a cell under non-standard conditions.

1.11.4 VARIATION OF EMF WITH TEMPERATURE

Variation of EMF of a cell with temperature of the electrolyte

To understand the effect of temperature of the electrolytic solution, consider Daniel cell reaction



Nernst equation for Daniel cell is

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF) \log \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\}$$

The effect of temperature on EMF can be understood by considering three cases as below.

Case 1 : when $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$,

The Nernst equation becomes,

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF) \log \{1\} = E_{\text{cell}}^0 - 0 = E_{\text{cell}}^0$$

Hence **EMF of the cell will be independent of temperature.**

Case 2: when $[\text{Zn}^{2+}] > [\text{Cu}^{2+}]$, Logarithmic term becomes negative, and $E_{\text{cell}} < E_{\text{cell}}^0$. Therefore the EMF of the cell decreases with rise in temperature.

Case 3: when $[\text{Zn}^{2+}] < [\text{Cu}^{2+}]$, Logarithmic term becomes positive, and $E_{\text{cell}} > E_{\text{cell}}^0$. Therefore the EMF of the cell increases with rise in temperature.

1.11.5 Practice problems on Nernst equation(PPNE)

M1PPNE1: Calculate the standard electrode potential of Cu, if its electrode potential at 25°C is 0.296V, and the concentration of Cu^{2+} is 0.015M.

M1PPNE2: A cell is constructed by coupling Zn electrode dipped in 0.5M ZnSO_4 and Ni electrode dipped in 0.05M NiSO_4 . Write the cell representation, cell reaction. Calculate the EMF of the cell, given E^0 of Zn and Ni as -0.76V and -0.25 V respectively.

M1PPNE3 Calculate the equilibrium constant of the reaction $\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{3+} + \text{Ag}$ at 25°C, given $E^0_{\text{Fe}^{3+} / \text{Fe}^{2+}} = 0.75\text{V}$ and $E^0_{\text{Ag}^+ / \text{Ag}} = 0.85\text{V}$.

1.16 POTENTIOMETRIC TITRATIONS

Principle: Potentiometric titrations make use of measurement of change in electrode potential upon addition of the titrant against the volume of titrant against the volume of titrant added. In this measurement of electrode potential, a cell is constructed in which at least one of the electrodes is reversible with respect to one of the ions taking part in the titration reaction. A small change in the concentration of active ion in the solution changes the electrode potential. This change in electrode potential is measured and plotted against volume of titrant. During the course of titration, the indicator electrode is measured by coupling with a reference electrode like saturated calomel electrode.

There are three types of potentiometric titrations: Acid Base titration and Oxidation-reduction titrations (Redox) titrations and Precipitation titration.

Oxidation-reduction titrations (Redox) titrations: A redox titration is a titration of a reducing agent by an oxidation agent or titration of an oxidizing agent by a reducing agent. Redox titration determines the concentration of an unknown solution (analyte) that contains an oxidizing or reducing agent. It can be followed by an inert electrode (a Platinum electrode or foil).

- Types of Redox titrations: Permanganometry uses potassium permanganate, Dichrometry uses potassium dichromate, Iodometry used Iodine, Bromometry uses Bromine, Cerimetry employs cerium(IV) salts.

Consider the general reduction reaction,

Oxidation state + ne \rightarrow Reduced state.

The potential of the indicator electrode is

$$E = E^0 - (0.0591/n) \log [\text{reduced state}]/\text{Oxidised state}.$$

This titration involves transfer of electrons from the substance being oxidized to the substance being reduced.

End point of redox titration can be determined by potentiometric titration.

Consider the oxidation of Fe^{2+} to Fe^{3+} by acidified $\text{K}_2\text{Cr}_2\text{O}_7$, by using platinum electrode. The apparatus for the titration of a ferrous salt with acidified Ce^{4+} .

The reduction potential of Ce^{4+} (1.6V) $>$ Fe^{2+} (0.77V) hence Ce^{4+} undergo reduction and is capable of oxidizing Fe^{2+} to Fe^{3+} .

The redox reaction is $\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$

Procedure:

20mL ferrous sulphate solution is taken in a beaker and 20 mL of Sulphuric acid is added to provide acidic medium.

A platinum electrode is inserted into it.

A saturated calomel electrode is coupled with it

Potential difference is measured using a Digital voltmeter.

Standard ceric ammonium sulphate is taken in the burette and added to the acidified ferrous sulphate solution taken in the beaker in 1 ml installments and the EMF is noted for each addition.

EMF is plotted against the volume of ceric solution. As Ce^{4+} is added into ferrous solution, the concentration of Fe^{3+} increases and that of Fe^{2+} decreases. When the end point is reached, Fe^{2+} is not available, and then $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple sets up and the potential increases sharply.

The end point is the point where the rate of change of EMF ($\Delta E/\Delta V$) is maximum.

Before the end point, redox potential developed is due to $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple ($E^\circ = 0.77\text{v}$) which is less than the redox potential developed after the end point $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple ($E^\circ = 1.60\text{v}$)

For the same reason, oxidation of Fe^{2+} solution can be followed potentiometrically by using acidified Potassium dichromate and potassium permanganate solution.

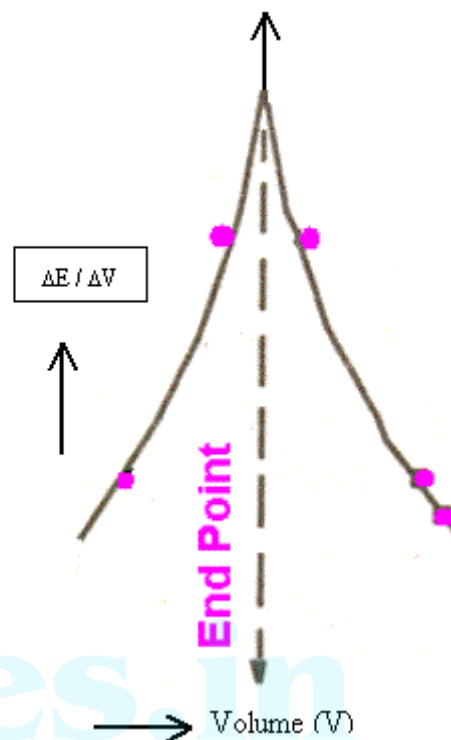
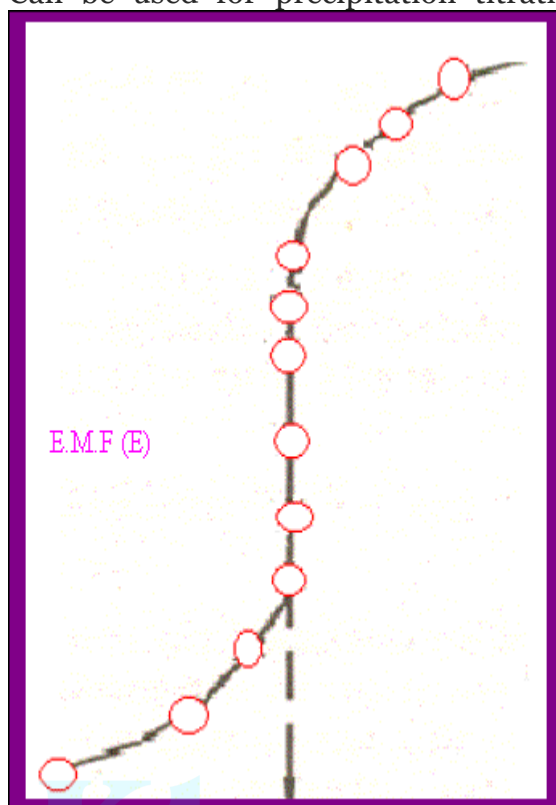
$E^\circ_{(\text{Mn}^{+7}/\text{Mn}^{+2})} = 1.51\text{ v}$ and $E^\circ_{(\text{Cr}^{+6}/\text{Cr}^{+2})} = 1.33\text{ v}$ for which the redox reactions are



Advantages of Potentiometric titration:

- Can be used for coloured solutions,
- Simple cheap, reliable and readily available apparatus,
- Mixture of solutions can be analysed,

- Can be used for precipitation titrations. **Potentiometric Titration Curves**



First derivative Potentiometric curve

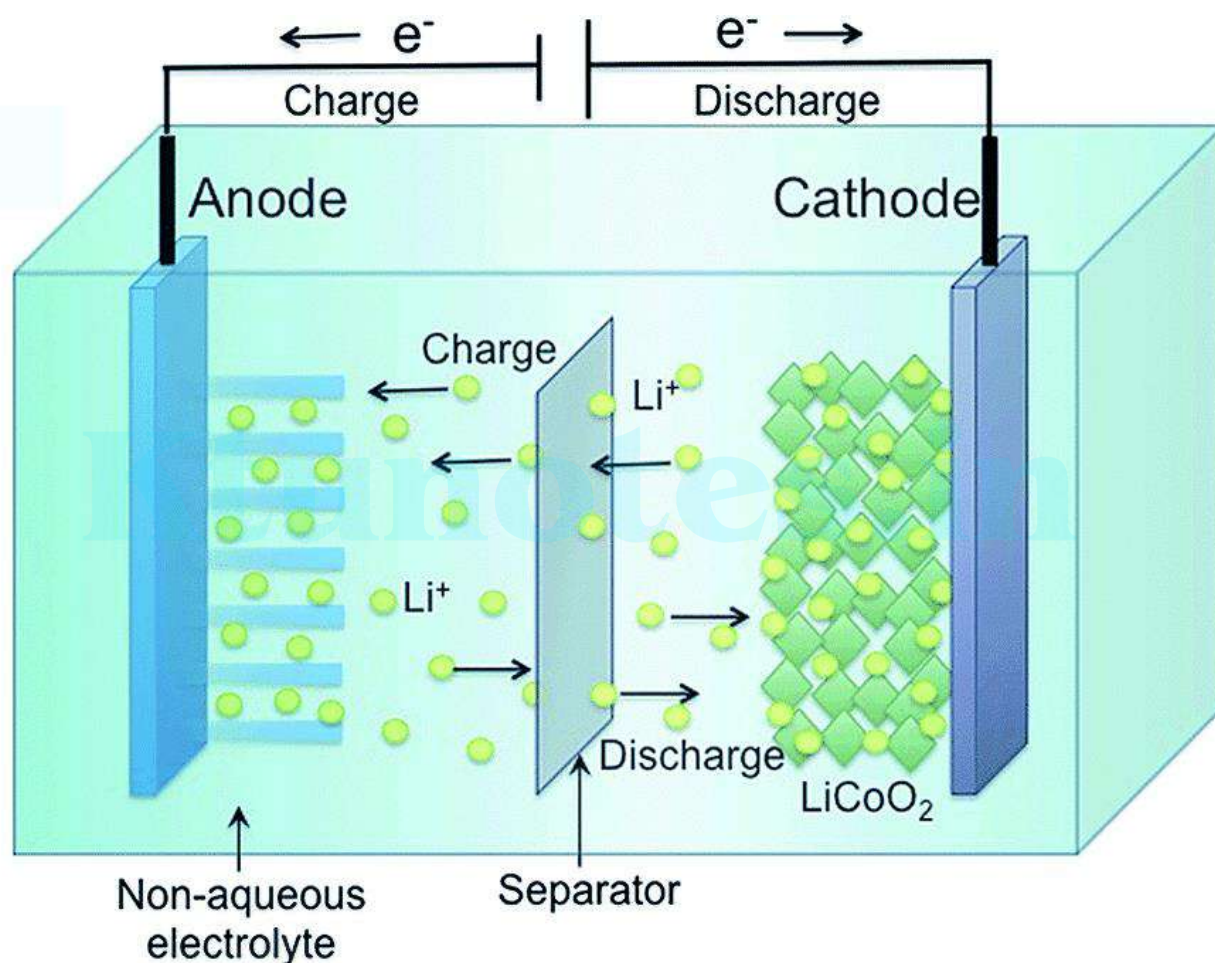
1.17 Electrochemical cell -Types

Commercial cells are used as source of electrical energy. They are three types.

Primary cells: Cells whose reactions are not based on reversible reactions. Fuel cells, E.g Daniel cell

Secondary cells: Galvanic cells in which cell reactions can be reversed by applying an external source of electric current .E.g : Lead-Acid Battery, Li ion cell etc.

Lithium-ion cell



Lithium ion cell is a rechargeable battery in which Li-ion moves between anode and cathode during charging and discharging.

Li is a better element because Li has a higher negative value for reduction potential and a lower atomic mass than any other element, due to which only 6.94g of Li is needed to provide 1 mole of electrons.

Construction:

Electrodes: Crystalline mixed oxide [LiCoO_2 or $\text{Li}_2\text{O} \cdot \text{Co}_2\text{O}_3$], and Lithiated Graphite

(Li embedded graphite)

Electrolyte: Li salt solution in an organic solvent such as ether or a solid phase polymer

A solid electrolyte separates the anode and cathode compartments.

Working:

S.No	CHARGING	DISCHARGING
1	Act as Electrolytic cell	Act as Electrochemical Cell
2	Electrical Energy is converted into Chemical Energy	Chemical Energy is converted into Electrical Energy
3	Anode : LiCoO_2 Anode reaction: $\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$	Anode: Graphite(lithiated) Anode reaction: $\text{Li}_x\text{C}_G \rightarrow \text{C}_G + x\text{Li}^+ + xe^-$
4	Cathode : Graphite(lithiated) Cathode Reaction $\text{C}_G + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_G$	Cathode : LiCoO_2 Cathode Reaction $\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2$

When $x < 1$ mole,

Li^+ ions get removed from crystal lattice, and Co^{3+} ion get oxidized to Co^{4+} , Hence electrical neutrality is maintained.

When $x = 1$ mole

Anodic material becomes $\text{Li}_{1-1}\text{CoO}_2$ ie CoO_2 which is an explosive material. Hence Li ion battery is allowed to charge only upto 90%.

Hence automatic circuit breakers are there to prevent from charging more than 90% ie $x = 0.9$ mole

Lithium ion cell of different types exists. Few are LiCoO_2 and LiFePO_4 . Li ion cell based on LiCoO_2 has an EMF of 3.7 V. Has high energy weight ratio. This is not suitable for making large size battery because of possibility of explosion and are used in cell phones, laptop computers, digital cameras.

While the cell based on LiFePO_4 is having a potential of 3.3 V and is suitable for making large size battery suitable for automobile application.

Anode material is graphite because every 6 carbon atom in graphite can accommodate a lithium atom.

1.18 Conductivity :

The substances which allows the passage of electric current through them is called Conductors, while those which do not allow flow of electric current are called insulators.

Conductors are of two types (1) Electronic conductors (metals, and semiconductors),

(2) Electrolytic conductors (salt solution, acids, molten salts)

Electrical Resistance (R) : Measures obstruction of flow of current. Resistance of a conductor is proportional to length (l) and inversely proportional to area of cross section (a) of the conductor.

$$R \propto l/a$$

$R = \rho l/a$, where ρ is called specific resistance Or Resistivity.

Unit of specific resistance (ρ) is ohm cm.

Electrical conductance (C) : Measure of the ease with which the current flows through a conductor or a solution. The reciprocal of resistance is called conductance, ($C = 1/R$)

The unit of conductance is Ohm^{-1} or mho. SI unit of conductance is Siemens (S)

Specific conductance or conductivity (κ)

The reciprocal of specific resistance (ρ) is called specific conductance. ($\kappa = 1/\rho$)

Defined as the conductance of one cm^3 of a conductor or solution held between two electrodes of 1 cm^2 area placed on the opposite pairs of faces of cube of edge length 1 cm.

Relation between conductivity (κ) and conductance (C)

We know

$$\kappa = 1/\rho,$$

$$C = 1/R,$$

$$= a / (\rho \times l)$$

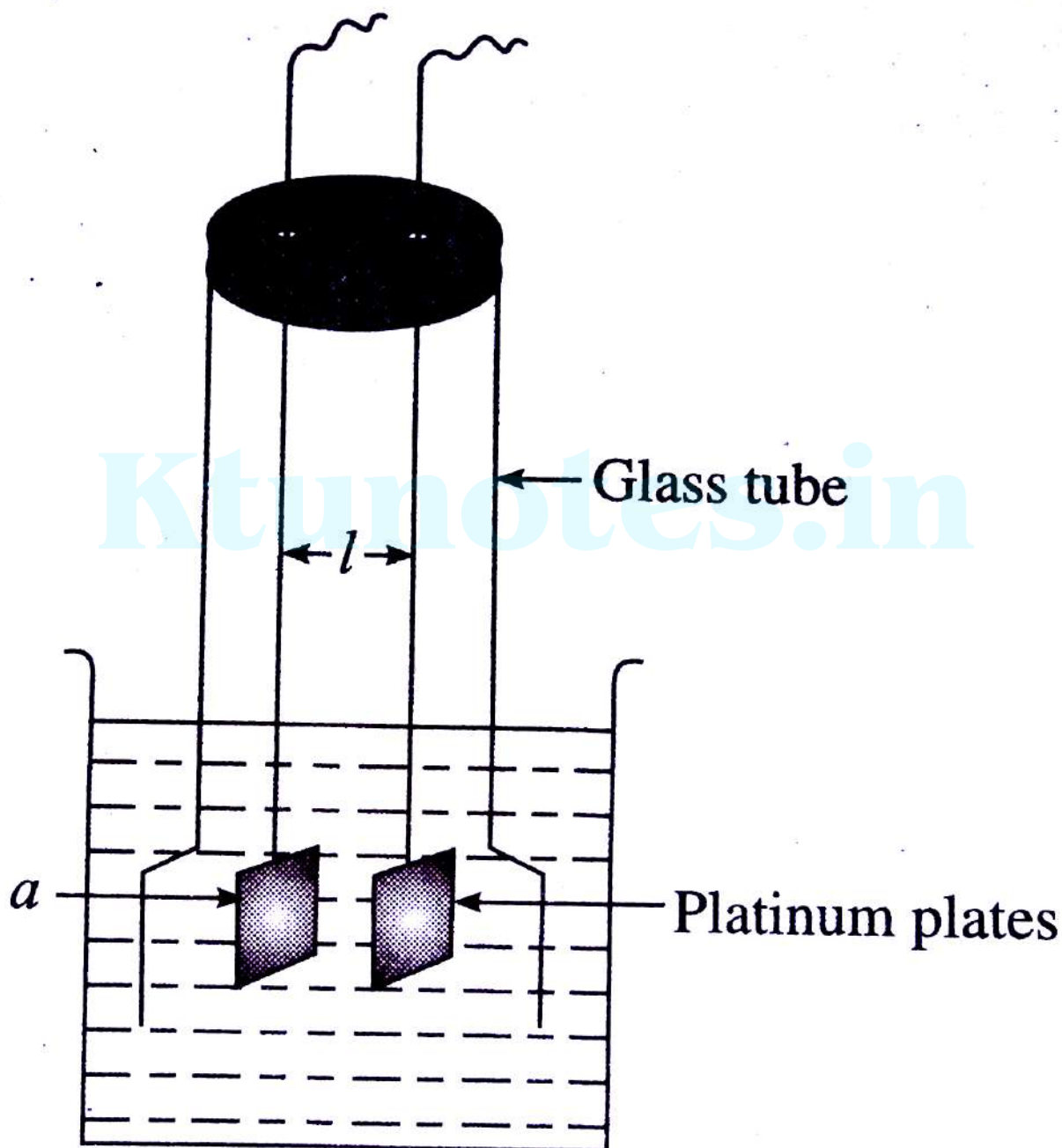
$$= \kappa \times (a/l)$$

$$\boxed{\kappa = C \times (l/a)} \quad \text{where} \quad l/a = \text{cell constant}$$

ie **Conductivity (κ) = conductance (c) x cell constant**

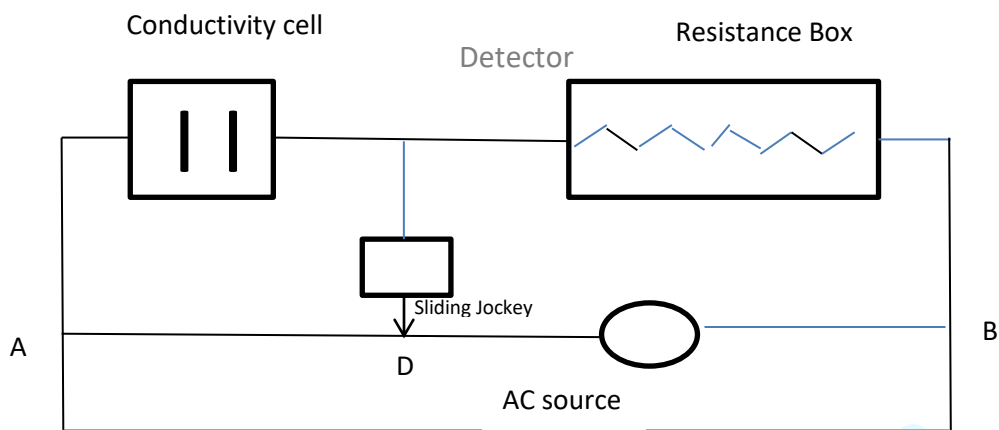
Cell constant: It is defined ratio of the distance between two electrodes (l) to area (a) of the electrodes. Unit of cell constant is cm^{-1} or m^{-1} . Cell constant is determined experimentally by measuring the conductance of a 0.1 M solution of KCl of known conductivity (specific conductance). The conductivity of 0.1 M KCl solution is $0.01288 \text{ S cm}^{-1}$. Conductivity of a solution is measured using conductivity cell shown below.

. The schematic representation of a conductivity cell.



Conductivity cell consists of two electrode plates coated with finely divided platinum black, which are welded with the ends of platinum wire that are sealed strongly, through two glass tubes. The tubes are strongly fixed such that distance between electrodes remain unaltered

Measurement of Conductivity of a solution: Modified wheatstones bridge is used for determining conductance and hence the conductivity of solution. The circuit diagram is as shown below.



Wheatstone Bridge circuit

Procedure :

- One arm of the bridge is conducted to conductivity cell containing the test solution.
- A known resistance is R taken out of the resistance box.
- An alternating current source is used here . This is to prevent electrolysis.
- When A/c current is used galvanometer cannot be used as nul point detector..A Head phone is used which produces a maximum sound as detector.
- At balancing point the sound intensity becomes zero.

Calculation

- Acc to wheatstone's principle,at the balancing point,

$$\frac{\text{Resistance of the conductivity cell}}{R}$$

$$\frac{\text{Balancing length AD}}{\text{Balancing length DB}}$$

$$\text{Conductance of the cell (C)} = \frac{1}{\text{Resistance of the conductivity cell}}$$

Numerical:

1. Calculate the conductivity of given sample of water at 298 K which shows a conductance of 560 μS in the given cell at 298K. A standard solution of 0.1M KCl shows a conductance of 12.34 mS in that cell. (conductivity of 0.1M KCl at 298 K is 0.01288S cm^{-1}).

We know Conductivity (κ) = conductance (c) x cell constant

ie Having given the conductivity and conductance of 0.1M KCl, we can calculate the cell constant first then using the cell constant the conductivity of the given sample of water can be calculated with the conductance value.

To find cell constant

Conductivity (κ) of 0.1 MKCl = conductance (c) of 0.1MKCl x cell constant

$$\text{Cell constant} = 0.01288\text{S cm}^{-1} / 12.34 \times 10^{-3} \text{ S} = 1.043 \text{ cm}^{-1}$$

$$\text{Conductivity of the given sample of water} = 560 \mu\text{S} \times 1.043 \text{ cm}^{-1} = \mathbf{584 \mu\text{S cm}^{-1}}$$

1.18.1 Practice problems on Conductivity (PPC)

M1PPC1 : The specific conductance of a N/10 KCl solution at 25°C is $0.0002765 \text{ ohm}^{-1}\text{cm}^{-1}$. If the resistance of the cell containing this solution is 500 ohm, what is the cell constant?

M1PPC2: A conductivity cell has two parallel plates of 1.25 cm^2 area placed at 10.50 cm apart, when filled with a solution of an electrolyte, the resistance was found to be 2000 ohms. Calculate the cell constant and the specific conductance of the solution.

M1PPC 3 : Resistance of a N/2 solution of an electrolyte in a cell is found to be 45Ω . Calculate specific conductance of the solution if the electrodes in the cell are of 3.8 cm^2 area and 2.2 cm apart.

Applications of conductivity measurement

- Used for measuring salinity of water
- Acid-base titrations can be carried out by conductivity measurement
- To determine degree of dissociation of weak acids and bases
- Determination of solubility of sparingly soluble salts

1.19 CORROSION

Corrosion is the process of disintegration of a metal by chemical or an electrochemical reaction with surroundings. Eg. tarnishing of silver, copper, rusting of Iron.

Cause: A pure metal which is in a higher energy state will have a natural tendency to revert back to a thermodynamically stable state in the form of their oxides, sulphides, carbonates, chlorides etc.

Theories of corrosion:

1. Chemical corrosion, 2. Electrochemical corrosion

1. Chemical or Dry corrosion: E.g : (a) Oxidation corrosion ie high temperature of Iron, (b) corrosion by other gases like chlorine, (c) Liquid metal corrosion in liquid mercury or sodium.
2. Electrochemical corrosion or wet corrosion: E.g : (a) Hydrogen evolution type and (b) Oxygen absorption type. (Both in acid and Alkaline medium)

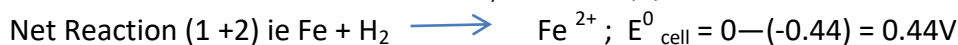
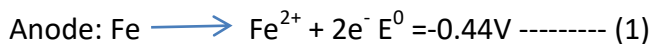
Mechanism of Electrochemical corrosion: Takes place under moist conditions through the formation of Galvanic cells.

This type of corrosion involves, 1. Anodic oxidation, 2. Cathodic reduction, 3. Diffusion of metallic and nonmetallic ions towards each other, 4. Formation of separate anodic and cathodic areas due to the deposition of products between which current flows through the conducting medium.

This mechanism can be outlined in the following four aspects.

1.19.1.0 Hydrogen evolution corrosion in acid medium: This occurs when metals are in contact with acid solution in absence of sufficient oxygen. E.g : Fe or Al in contact with HCl. This is because hydrogen electrode potential in acid medium ($E^0_{H^+/H_2}$) = 0, is higher than electrode potential in acid medium ($E^0_{Fe^{2+}/Fe}$) = -0.44 V. The reactions involved in this

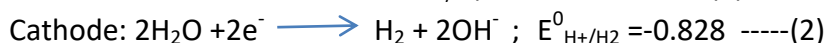
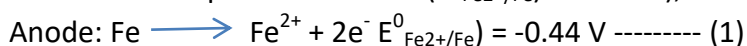
type of corrosion are as follows⊗ Here electrode with higher E^0 value will be reduced and act as cathode.



Since corrosion cell potential is positive, this corrosion reaction is feasible.

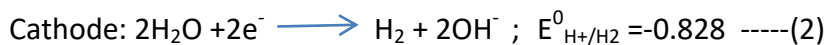
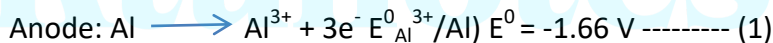
1.19.1.1 Hydrogen evolution corrosion in alkaline medium:

Corrosion of Iron will not take place when Iron is immersed in an alkaline medium because hydrogen electrode potential in alkaline medium ($E^0_{\text{H}_2/\text{OH}^-} = -0.82\text{V}$), is lower than electrode potential of iron ($E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$),



$E^0 = -0.388\text{V}$ Since E^0 value is negative, the reaction is not feasible.

while metals like aluminium can give hydrogen evolution corrosion in alkaline medium also because of the reason that electrode potential of hydrogen in alkaline medium ($E^0_{\text{H}_2/\text{OH}^-} = -0.82\text{V}$) is higher than Aluminium ($E^0_{\text{Al}^{3+}/\text{Al}} = -1.66\text{V}$)

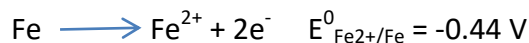


$E^0 = -0.388\text{V}$ Since E^0 value is negative, the reaction is not feasible.

1.19.2.0 Oxygen absorption corrosion in acid medium: This occurs when metals are in contact with water having high Dissolved oxygen in acidic or neutral medium

E.g : Fe rusting

Anode



Cathode



E^0 for Net cell reaction in acid medium is $E^0_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}} = 1.23 - (-0.44) = 1.67\text{V}$, (+ve),

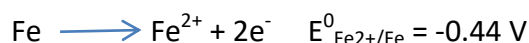
this indicates the feasibility of the reaction. Hence Fe corrodes when immersed in water having dissolved oxygen in acidic or neutral environment.

1.19.2.1 Oxygen absorption corrosion in alkaline medium :

This type of corrosion occurs when metals are in contact with water having high dissolved oxygen in alkaline medium

Anode

Anode



Cathode



E^0 for Net cell reaction in acid medium is $E^0_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}} = 0.40 - (-0.44) = 0.84 \text{ V}$, (+ve),

Here Fe^{2+} thus produced cannot be further oxidized to Fe^{3+} . Because oxygen electrode potential in alkaline medium ($E^0_{\text{O}_2/\text{OH}^-} = 0.40 \text{ V}$) which is less than $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$. Hence no insoluble precipitate of $\text{Fe}(\text{OH})_3$ is formed, and hence no localised corrosion.

1.20 Factors affecting Corrosion

1. Nature of the metal ie purity, position in the galvanic series, relative anodic and cathodic area, surface of the metal, overvoltage) and
2. Nature of corrosive environment (like Temperature, Humidity, pH, conductance of the medium, Presence of impurities and its nature, affect the rate of corrosion.

1.21 GALVANIC SERIES

Galvanic series is a series in which the metals and alloys are arranged in the order of their corrosion tendencies. It is different from Electrochemical series. Following are the differences between Galvanic series and Electrochemical series. It is a scale of Nobility

S.No	Electro chemical Series	Galvanic series
1	E^0 is measured for metals and non-metals	E^0 is measured for metals and alloys
2	E^0 is measured by dipping pure metals in their salt solutions of 1M concentration	E^0 is measured by dipping pure metals and alloys in unpolluted seawater
3	E^0 is measured by using standard hydrogen electrode as reference electrode	E^0 is measured by using calomel electrode as reference electrode
4	Position of the metal is fixed	Position of the metal and alloy may change
5	Predicts relative displacement tendencies	Predicts relative corrosion tendencies
6	Alloys are not included	Alloys are included

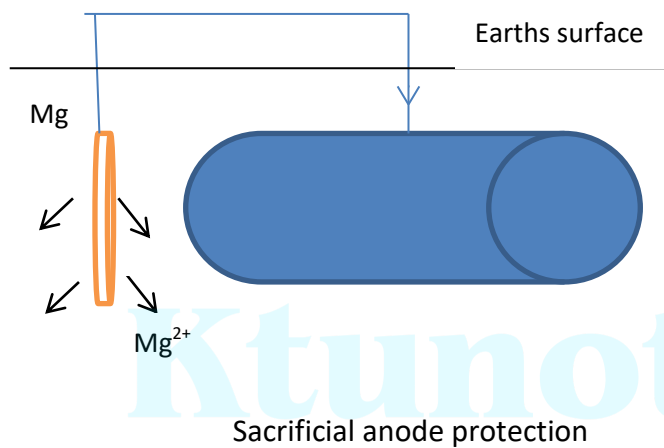
1.22 CATHODIC PROTECTION:

Cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell.

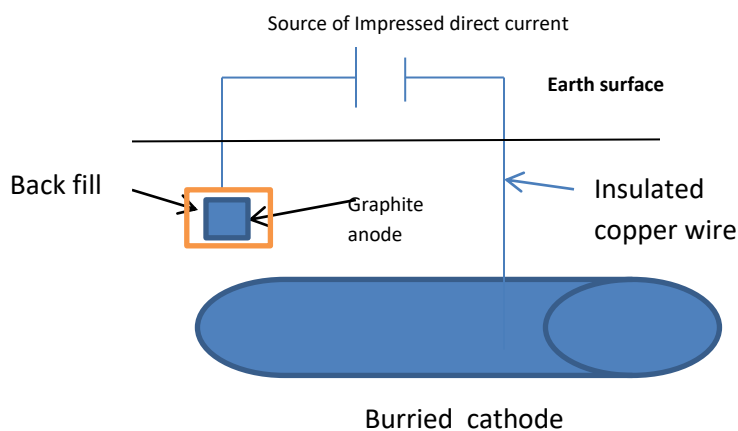
A simple method of **protection** connects the metal to be **protected** to a more easily corroded "sacrificial metal" to act as the anode.

There are two types of cathodic protection.

1. Sacrificial anodic protection or Galvanic protection. Here the underground pipelines cables, ship hulls are protected by connecting some sacrificial anode like Mg, Zn, and Al rods with the pipe as shown in the figure.



2. Impressed current cathodic protection: In this method impressed current is applied to convert the corroding metal from anode to a cathode. A DC current is applied to an anode (inert graphite) which is buried inside the soil and to the corroding metal structure. e.g. Ships docked in harbor are protected by this method.



1.23 ELECTROLESS PLATING

Electroless plating is defined as a controlled autocatalytic deposition of a continuous layer of a noble metal from its salt solution on a catalytic surface of the base metal without using electrical energy. This method is used for thin coating.

Principle: It is an autocatalytic process. Here substrate develops a potential in plating bath containing metallic ions, reducing agent, complexing agent, stabilizer, and other components. A non-galvanic plating method in which several reactions takes place without the use of external power.

Here hydrogen is released by a reducing agent (sodium hypophosphite), and oxidized, thus producing a negative charge on the surface of the metal

Important requirement is that the kinetics of electron transfer from the reducing agent to the metal is low to prevent deposition in bulk and enable that the metal ions are reduced only at the surface.

Stability of electroless plating depends on the substrate material, pretreatment process, solution type, pH and temperature of plating.

Process: There are three steps involved

1. Surface preparation: Surface is activated first by any one of the following method such as Etching (removal of impurities), Electroplating, Chemical treatment (plastics objects are treated with SnCl_2 ,and PdCl_2 .).
2. Preparation of plating bath: The plating bath is prepared with the following
 - a. Soluble salt of the metal
 - b. Complexing agents like EDTA to prevent excess deposition
 - c. Reducing agents like sodiumthiosulphate ,formaldehyde etc
 - d. Exaltants or accelerators (Succinates, glycinate, fluorides, etc, to enhance the plating rate.
 - e. Stabilizers (Calcium ions, lead ions, thiourea, to prevent decomposition of the bath and to impart stability to the solution.
 - f. Buffer solution (Rochelle salt, Boric acid to maintain pH.

3. Procedure: The article to be plated is immersed in the bath containing the metal salt and reducing agent in a series of tanks. The rate of decomposition is controlled by the amount of reducing agent and the type of chelating agent.

Advantages of Electroless plating:

- Electroless plating can be made on both metals and plastics.
- Electric power and accessories are required.
- Gives uniform coating
- Coating provides better wear resistance
- Coating provides less porous and hence better corrosion resistance
- Flexibility in plating volume and thickness.

This method of Electroless plating is applied for copper plating and Nickel.

1.23.1 Electroless copper plating: To deposit a layer of copper on a metal surface without electrical power. This is used to render conductivity in printed circuit boards.

Procedure: The object is to be degreased first using organic solvent and, then acid treated. Then immersed in plating bath containing cupric salt, reducing agent(HCHO), suffer and complexing agent, pH above 12

Anode reaction: $2\text{HCHO} + 4\text{OH}^- \longrightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$; $E^0 = 0.056\text{ V}$

: Cathode reaction: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$, $E^0 = 0.34\text{ V}$

Net reaction (1) +(2)

$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \longrightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2$

Uses: To coat double or multilayered printed circuit boards.

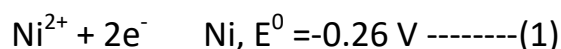
As base coating for subsequent electroplating.

1.23.2 Electroless Nickel plating :

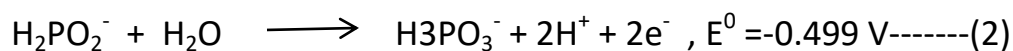
Procedure: Substrate (Al, Fe,Cu,Brass,Glass,plastic,quartz,) are pretreated first with SnCl_2 in acid medium ,then with PdCl_2 .

Pretreated substrate is immersed in the plating bath containing Nickel salt solution and reducing agent like sodium hypophosphite.. Cell reactions are as follows.

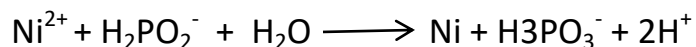
At Cathode,



At Anode



Net reaction : (1) +(2)



BY using buffer solution uniform fine grained coating can be obtained.

Uses: In Aerospace components like pistons, engine shafts,engine mounts for corrosion resistance, wear resistance.

In packaging and handling machinery

In chemical manufacturing and in making automotive components.
