Chapter- 4 ELECTROCHEMISTRY

The branch of physical chemistry which deals with the study of conversion of electrical energy into chemical energy and vice versa is called electrochemistry.

Conversion of electrical energy into chemical energy occurs in electrolytic cell and the conversion of chemical energy into electrical energy occurs in electrochemical cell or voltaic cell.

Electrochemical Cell / Galvanic cell:

- a) A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running motor or other electrical gadgets like heater, fan, geyser etc. Ex: Daniel cell or Galvanic cell.
- b) The electrochemical cell consists of two half cells such as; oxidation half cell and reduction half cell. When oxidation and reduction takes place in two separate beakers, then chemical energy is converted into electrical energy. This cell has an electrical potential equal to 1.1 V when concentration of Zn²⁺ and Cu²⁺ ions is unity (1 mol dm⁻³). Such a device is also called **voltaic** cell.



c) The two half-cells are connected by a metallic wire through a voltmeter and a switch externally and the electrolytes of the two half-cells are connected internally through a salt bridge. Electrons flow through the wire and ions flow through the salt bridge to induce current in the cell.

d) <u>In Zn-CuSO₄ cell</u>.

In left side, Zn is oxidised to Zn^{2+} ion and in right side Cu^{2+} from solution is reduced and deposited on copper electrode by receiving electron through wire. As a result concentration of Zn^{2+} ion in left side beaker and concentration of SO_4^{2-} ion in right side beaker is increased. The excess of ions flow through the salt bridge to maintain electrical neutrality and to generate current in the cell.

e) <u>Function of Salt bridge</u> :

Salt bridge is a U-shaped tube containing inert electrolyte. The electrolyte is a semisolid paste of either KCl, KNO_3 , K_2SO_4 or NH_4Cl in gelatine or agar-agar gelatine solution etc.

- (1) Salt bridge helps to maintain electrical neutrality between the two half cells.
- (2) It doesn't react with the electrolytes present in two half cells.
- (3) It allows only flow of ions through it. I.e. it complete the cell circuit
- (4) Salt bridge completes the circuit to generate emf in the cell.

In electrochemical cell, electrons flow from high oxidation potential to low oxidation potential and the current flows from low oxidation potential to high oxidation potential.

- Electrons flow from H.O.P to L.O.P or L.R.P to H.R.P
- Current flows from L.O.P. to H.O.P or H.R.P to L.R.P

In electrochemical cell where oxidation takes place is represented as anode and where reduction takes place is represented as cathode. Anode is assigned as -ve sign and cathode as +ve sign.

g) <u>Cell reaction:</u>

1) At anode (Oxidation half reaction):

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

2) At cathode (Reduction half reaction)

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

3) Full cell reaction (Oxidation half + Reduction half)

$$\begin{array}{rcl} Zn_{(s)} & \rightarrow Zn^{2+}{}_{(aq)} + 2e^{-} \\ \hline Cu^{2+}{}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)} \\ \hline Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)} \\ \hline \text{It is also written as:} \\ Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)} \end{array}$$

h) <u>Applying external potential:</u>

1) If an external opposite potential is applied in the galvanic cell and increased slowly, then the reaction continues to take place till the opposing voltage reaches the value 1.1V when, the reaction stops altogether and no current flows through the cell.

2) Any further increase in the external potential again starts the reaction but in the opposite direction. It now functions as an **electrolytic cell**, a device for

using electrical energy to carry non-spontaneous chemical reactions





Electrode Potential:-

It may be defined as the tendency of a metal to lose or gain electrons when it is placed in contact with its own ions. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction takes place.

Oxidation potential is the tendency of an electrode to lose electrons. The electrode having higher oxidation potential can lose electron easily or oxidised easily and possesses higher reducing power.

Reduction potential is the tendency of an electrode to gain electrons. The electrode having higher reduction potential is easily reduced and possesses higher oxidising power.

As oxidation and reduction are opposite to each other thus

Reduction potential = - Oxidation potential

Or Oxidation potential = – Reduction potential. $Cu^{2+} / Cu = +0.34V$ (Re duction potential) $Cu / Cu^{2+} = -0.34V$ (Oxidation potential)

Cell voltage / Cell Potential / E.M.F of cell (E^o cell)

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The *cell potential* is the difference between the electrode potentials (reduction potentials) of the cathode and anode.

E.M.F of cell(E⁰_{cell}) = Oxidation potential at left electrode + Reduction potential at right electrode

= Oxidation potential at anode + Reduction potential at cathode

= – Reduction potential at anode + Reduction potential at cathode

= Reduction potential at cathode – Reduction potential at anode

$$\Longrightarrow E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$

Ex:Let a cell reaction, $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

Half cell reactions :

Oxidation half reaction: $Cu_{(s)} \rightarrow Cu^{2+}(aq) + 2e^{-}$

Reduction half reaction: $2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$

The cell can be represented as

 $\mathbf{Cu}_{(\mathrm{s})}\,|\,\mathbf{Cu}_{(\mathrm{aq})}^{2*}\,\|\,\mathbf{Ag}_{(\mathrm{aq})}^{*}\,|\,\mathbf{Ag}_{(\mathrm{s})}$

LECT-2

f)
$$\frac{\text{Representation of Cell:}}{M_{1(s)}/M_{1(aq)}^{n+}(C_1)/M_{2(aq)}^{n+}(C_2)/M_{2(s)}}$$
$$\frac{Zn(s)/Zn_{(aq)}^{2+}(1M)}{Oxidation half} || \frac{Cu_{(aq)}^{2+}(1M)/Cu(s)}{\text{Reduction half}}$$

Similarly Cu-Ag cell can be represented as $Cu_{(s)} | Cu_{(aq)}^{2+} || Ag_{(aq)}^{+} | Ag_{(s)}$

Measurement of Electrode Potential (Standard hydrogen electrode):

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell **called standard hydrogen electrode** represented by $Pt_{(s)} / H_{2 (g)} / H^{+}_{(aq)}$, is assigned a zero potential at all temperatures corresponding to the reaction.

$$\rm H^{+}$$
 $_{(aq)} + e^{_{-}} \rightarrow \, {}^{1\!\!/_{2}} \, \rm H_{2\,(g)}$

Standard hydrogen electrode is a reference electrode and its reduction potential is arbitrarily assigned as zero volt at all temperature. A S.H.E consists of a platinum electrode coated with platinum black. The electrode is dipped in acidic solution having 1M concentration of H⁺ ions. Pure hydrogen gas at 1 bar pressure is bubbled through the solution at a temperature 298K. The hydrogen electrode can act both as anode as well as cathode.

When SHE act as anode:-

$$H_{2(g)} \rightarrow 2H_{(aq)} + 2e^{-2}$$

When SHE act as cathode:-

$$2H^+_{(aq)} + 2e^- \rightarrow H^-_{2(g)}$$

Symbolic representation of SHE.

$$Pt(s) | H_{2(g)} | H_{(lm)}^{+} || H_{(lm)}^{+} | H_{2(g)} | Pt_{(s)}$$



Standard electrode potentials (E^{O}) of the electrodes are calculated By using SHE .If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, E_{R} of the given half-cell.

 $E^{\Theta} = E^{\Theta}_{R} - E^{\Theta}_{L}$ As E_{L}^{Θ} for standard hydrogen electrode is zero. $E^{\ominus} = E^{\ominus}_{R} - 0 = E^{\ominus}_{R}$ The measured emf of the cell: $Pt(s) \mid H_2(g, 1 \text{ bar}) \mid H^*(aq, 1 \text{ M}) \mid Cu^{2*}(aq, 1 \text{ M}) \mid Cu$ is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction: Cu^{2*} (aq. 1M) + 2 $e^- \rightarrow Cu(s)$ Similarly, the measured emf of the cell: $Pt(s) \mid H_2(g, 1 \text{ bar}) \mid H^*(aq, 1 M) \mid Zn^{2*}(aq, 1M) \mid Zn$ is -0.76 V corresponding to the standard electrode potential of the half-cell reaction: Zn^{2+} (aq. 1 M) + $2e^{-} \rightarrow Zn(s)$ Left electrode: $Zn(s) \rightarrow Zn^{2+}$ (aq. 1 M) + 2 e Right electrode: Cu^{2+} (aq, 1 M) + 2 $e^- \rightarrow Cu(s)$ The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

 $Zn(s) + Cu^{2*}$ (aq) $\rightarrow Zn^{2*}$ (aq) + Cu(s)

If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.

> emf of the cell = $E_{cell}^{0} = E_{R}^{0} - E_{L}^{0}$ = 0.34V - (-0.76)V = 1.10 V

Intext Questions:

- **3.1.** How would you determine the standard electrode potential of the system Mg²⁺ | Mg?
- 3.2. Can you store copper sulphate solutions in a zinc pot?
- **3.3.** Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Solution:

3.1. How would you determine the standard electrode potential of the system Mg²⁺¹ Mg?

Ans: A cell will be set up consisting of Mg/MgSO₄ (1 M) as one electrode and standard hydrogen electrode Pt, H, (1 atm)H⁺/(I M) as second electrode, measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that e⁻¹ s flow from mg electrode to hydrogen electrode, i.e., oxidation takes place on magnesium electrode and reduction on hydrogen electrode. Hence, the cell may be represented as follows :

$$Mg | Mg^{2+} (1 M) || H^{+} (1 M) | H_{2}, (1 atm), Pt$$

$$E^{o}_{cell} = E^{o}_{H^{+}/\frac{1}{2}H_{2}} - E^{o}_{Mg^{2+}/Mg}$$
Put
$$E^{o}_{H^{+}/\frac{1}{2}H_{2}} = 0$$

$$\therefore E^{o}_{Mg^{2+}/Mg} = -E^{o}_{cell}$$

LECT-3

Nernst Equation:

s

We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

$$M_{(aq)}^{n+} + ne^- \rightarrow M_{(s)}$$

The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E_{(M^{n+}/M)}^{\ominus} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E_{(M^{n+}/M)}^{\Theta} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

Substituting the value of R = $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and F = 96487 C mol^{-1} we get.

$$E_{cell} = E_{cell}^{\Theta} - \frac{0.0591}{n} \log \frac{1}{\left[M^{n+}\right]} at 298k$$

In Daniel cell, the electrode potential for any given concentration of Cu²⁺ and Zn²⁺ ions, we write

For Cathode:

$$\overline{E_{Cu^{2^{+}}/Cu}} = \overline{E_{Cu^{2^{+}}/Cu}^{\circ}} - \frac{0.0591}{2} \log \frac{1}{Cu^{2^{+}}}$$

For Anode:

$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^{o} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

The cell potential is calculated as:

$$\begin{split} \mathbf{E}_{cell} &= \mathbf{E}_{Cu^{2+}/Cu} - \mathbf{E}_{Zn^{2+}/Zn} \\ &= \left[\mathbf{E}_{Cu^{2+}/Cu}^{0} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} \right] - \left[\mathbf{E}_{Zn^{2+}/Zn}^{0} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]} \right] \\ &= \mathbf{E}_{Cu^{2+}/Xu}^{0} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} - \mathbf{E}_{Zn^{2+}/Zn}^{0} + \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]} \\ &= \mathbf{E}_{cu^{2+}/Cu}^{0} - \mathbf{E}_{Zn^{2+}/Zn}^{0} + \frac{0.0591}{2} \left[\log \frac{1}{[Zn^{2+}]} - \log \frac{1}{[Cu^{2+}]} \right] \\ &= \mathbf{E}_{cell}^{0} + \frac{0.0591}{2} \left[\log \frac{[Cu^{2+}]}{[Zn^{2+}]} \right] \\ &\Rightarrow \mathbf{E}_{cell} = \mathbf{E}_{cell}^{0} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \\ &\text{In general, if the cell reaction is} \\ & aA + bB \xrightarrow{M^{*}} cD + dD \\ &= \mathbf{E}_{cell}^{0} - \frac{2.303 RT}{nF} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \\ &At \ 25^{0}C, \\ &= \mathbf{E}_{cell}^{0} - \frac{0.0591}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \\ &\mathbf{AL} \ DCCOUP \\ &= \mathbf{E}_{cell}^{0} - \frac{0.0591}{n} \log \frac{C}{C} \\ &= \mathbf{E}_{cell}^{0} - \frac{0.0591}{n} \log 2c \\ \end{aligned}$$

3.4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10. Ans. For hydrogen electrode, $H^+ + e^- \rightarrow 1/2 H_2$,

Applying Nernst equation, $E_{H^*, \frac{1}{2}H_2} = E_{H^*, \frac{1}{2}H_2}^o - \frac{0.0591}{n} \log \frac{1}{(11+1)}$

$$= 0 - \frac{0.0591}{1} \log \frac{1}{10^{-10}} \left\{ \begin{array}{c} pH = 10 \\ \Rightarrow [H^+] = 10^{-10} M \end{array} \right\}$$
$$= -0.0591 \times 10 \\ = -0.591 V$$

3.5. Calculate the emf of the cell in which the following reaction takes place: Ni(s)+2Ag⁺ (0.002 M) -> Ni²⁺ (0.160 M)+2Ag(s) Given that $E^{(-)}_{(cell)} = 1.05 V$. Ans:

Applying Nernst equation,

$$E_{cell} = E_{cell}^{0} - \frac{0.0591}{n} \log \frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

= 1.05V - $\frac{0.0591}{2} \log \frac{0.160}{(0.002)^{2}}$
= 1.05 - $\frac{0.0591}{2} \log(4 \times 10^{4})$
= 1.05 - $\frac{0.0591}{2} (4.6021)$
= 1.05 - 0.14 V
= 0.91 V

Equilibrium constant from Nernst Equation:-

Consider the reaction taking place in a Daniel cell.

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

As time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{cell} = 0 = E_{cell}^{\Theta} - \frac{2.303 \text{RT}}{2\text{F}} \log \frac{\left[\text{Zn}^{2^{+}}\right]}{\left[\text{Cu}^{2^{+}}\right]}$$
$$E_{cell}^{\Theta} = \frac{2.303 \text{RT}}{2\text{F}} \log \frac{\left[\text{Zn}^{2^{+}}\right]}{\left[\text{Cu}^{2^{+}}\right]}$$

at equilibrium
$$\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} = Kc$$
At T = 298K the above equation can be written as
$$E_{cell}^{\Theta} = \frac{0.0591}{2} \log kc = 1.1v$$

$$\log kc = \frac{(1.1v \times 2)}{0.0591v} = 37.288$$
Kc = 2 × 10³⁷ at 298K
$$Kc = 2 \times 10^{37} \text{ at 298K}$$
In general,
$$E_{cell}^{\Theta} = \frac{2.303RT}{nF} \log Kc$$

Calculate the equilibrium constant of the reaction: $\begin{aligned} \mathrm{Cu}(\mathrm{s}) \,+\, 2\mathrm{Ag}^{+}(\mathrm{aq}) \,\to\, \mathrm{Cu}^{2+}(\mathrm{aq}) \,+\, 2\mathrm{Ag}(\mathrm{s}) \\ \mathrm{E}^{\ominus}_{(\mathrm{cell})} \,=\, 0.46 \,\,\mathrm{V} \end{aligned}$

Solution
$$E_{(cell)}^{\Theta} = \frac{0.059 \text{ V}}{2} \log K_c = 0.46 \text{ V or}$$

 $\log K_c = \frac{0.46 \text{ V} \times 2}{0.059 \text{ V}} = 15.6$
 $K_c = 3.92 \quad 10^{15}$
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Electrochemical Cell and Gibbs Energy of the Reaction: Electrical work done in one second is equal to electrical potential multiplied by total charge

$$\Delta_r G = - nFE_{(cell)}$$

If the concentration of all the reacting species is unity, then

$$E_{cell} = E_{cell}^{\Theta}$$

So we have

passed.

$$\Delta_{\rm r} G^{\Theta} = -nFE_{\rm cell}^{\Theta}$$

Standard Gibb's energy of reaction $\left(\Delta_r G^{\circ}\right)$ is related to equilibrium constant (K) by the reaction

 $\Delta_{r}G^{\Theta} = -RT \ln K$ $\Rightarrow \Delta_{r}G^{\Theta} = -2.303 RT \log K$

Q. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:

 $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ Solution $\Delta_r G^{\Theta} = -nFE^{\Theta}_{(cell)}$ *n* in the above equation is 2, F = 96487 C mol⁻¹ and $E^{\Theta}_{(cell)} = 1.1$ V

Therefore, $\Delta_{\rm r} G^{\Theta} = -2$ 1.1V 96487 C mol⁻¹ = -21227 J mol⁻¹ = -212.27 kJ mol⁻¹

Conductance of Electrolytic Solutions:

(c) Specific resistance/Resistivity (ρ) :- The resistance of a conductor is directly

proportional to the length (ℓ) and area of cross section (A) of conductor.

So, $R \propto \ell, R \propto \frac{I}{A}$ $\Rightarrow R \propto \frac{\ell}{A} \Rightarrow R = \rho \frac{\ell}{A}$ $\rho \text{ is called specific resistance or resistivity of conductor.}$ $\Rightarrow \rho = \frac{RA}{\ell}$ When $\ell = 1 \text{ cm}, A = 1 \text{ cm}^2$ $\rho = R$

Hence, specific resistance is defined as the resistance offered by a conductor of 1cm^3

volume.

Unit of ρ :- Ohm cm or Ohm m.

(d) Specific Conductance (Conductivity)

It is the reciprocal of specific resistance

(b) Conductance (G) :- It is the reciprocal of resistance.

$$G = \frac{1}{R} = \frac{1}{\rho \frac{l}{A}} = k \frac{A}{l}$$

Where k = Conductivity

$$\mathbf{K} = \frac{1}{\rho} = \frac{1}{\frac{\mathbf{RA}}{\ell}}$$

$$\Rightarrow K = \frac{1}{R} \times \frac{\ell}{A} \Rightarrow K = G \times G^* \text{ where } \frac{\ell}{A} = \text{ cell constant } (G^*).$$

Unit of conductivity (K) is $ohm^{-1}cm^{-1} or ohm^{-1}m^{-1}$

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductivity depends on.

(a) The nature and structure of the metal

(b) The number of valence electrons per atom

(c) Temperature (it decreases with the increases of temperature)

The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. The conductance of ionic solution depends on.

- (a) The nature of the electrolyte added.
- (b) Size of the ion produced and their salvation
- (c) Nature of the solvent and their viscosity
- (d) Concentration of the electrolyte
- (e) Temperature it increases with the increase of temperature.

3.9 The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 x 10⁻³ S cm⁻¹? Sol.

Cell constant = $\frac{\text{Conductivity}}{\text{Conductance}}$ = Conductivity × Resistance = 0.146 × 10⁻³ S cm⁻¹ × 1500 Ω = 0.219 cm⁻¹.

LECT-5

Measurement of the Conductivity of Ionic Solutions:

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**.



Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to 'A' and are separated by distance 'I'. Therefore, solution confined between these electrodes is a column of length I and area of cross section A. The resistance of such a column of solution is then given by the equation:

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

whose conductivity is known accurately at various concentrations. And at different temperatures The quantity I/A is called cell constant denoted by the symbol, G^* . It depends on the distance between the electrodes and their area of cross-section and has the dimension of length-1 and can be calculated if we know I and A. Measurement of I and A is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions. The cell constant, G^* , is then given by the equation:



Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. It consists of two resistances *R*3 and *R*4, a variable resistance *R*1 and the conductivity cell having the unknown resistance *R*2. The Wheatstone bridge is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

Unknown resistance
$$R_2 = \frac{R_1 R_4}{R_3}$$

Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{R} = \frac{G^*}{R}$$

(e) Molar conductivity' $(\land m)$:- It is defined as the conducting power of all the ions produced by one mole of electrolytic solution. Kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contain one mole of electrolyte.

Molar conductivity
$$\wedge_m = \frac{k}{C}$$

In the above equation, if κ is expressed in S m⁻¹ and the concentration, c in mol m⁻³ then the units of Λ_m are in S m² mol⁻¹. It may be noted that: 1 mol m⁻³ = 1000(L/m³) molarity (mol/L), and hence

$$\Lambda_{m}(S \text{ cm}^{2} \text{ mol}^{-1}) = \frac{\kappa (S \text{ cm}^{-1})}{1000 \text{ Lm}^{-3} \times \text{molarity (mol L}^{-1})}$$

If we use S cm⁻¹ as the units for κ and mol cm⁻³, the units of concentration, then the units for \ddot{E}_m are S cm² mol⁻¹. It can be calculated by using the equation:

 $\Lambda_{m}(\text{S cm}^{2} \text{ mol}^{-1}) = \frac{\kappa (\text{S cm}^{-1}) \times 1000 (\text{cm}^{3} / \text{L})}{\text{molarity (mol / L)}}$

Q. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solutions is 1.29 S/m.

Solution: The cell constant is given by the equation: Cell constant = $G^* = \text{conductivity} \times \text{resistance}$ = 1.29 S/m × 100 W = 129 m⁻¹ = 1.29 cm⁻¹ Conductivity of 0.02 mol L⁻¹ KCl solution = cell constant / resistance $= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ S m}^{-1}$ Concentration = 0.02 mol L⁻¹ = 1000 0.02 mol m⁻³ = 20 mol m⁻³ Molar conductivity = $A_m = \frac{\kappa}{c}$ $= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \quad 10^{-4} \text{ S m}^2 \text{mol}^{-1}$ Alternatively. $\kappa = \frac{1.29 \text{ cm}^{-1}}{520 \Omega} = 0.248 \quad 10^{-2} \text{ S cm}^{-1}$ and $A_m = \kappa \quad 1000 \text{ cm}^3 \text{ L}^{-1} \text{ molarity}^{-1}$ $= \frac{0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}}$

Q. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solutions of diameter 1 cm and length 50 cm is 5.55 × 103 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution: $A = \pi r^{2} = 3.14 \quad 0.5^{2} \text{ cm}^{2} = 0.785 \text{ cm}^{2} = 0.785 \quad 10^{-4} \text{ m}^{2}$ l = 50 cm = 0.5 m $R = \frac{\rho}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55 \times 10^{3} \Omega \times 0.785 \text{ cm}^{2}}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$ Conductivity = $\kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right) \text{ S cm}^{-1}$ $= 0.01148 \text{ S cm}^{-1}$ Molar conductivity. $A_{m} = \frac{\kappa \times 1000}{c} \text{ cm}^{3} \text{ L}^{-1}$ $= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^{3} \text{ L}^{-1}}{0.05 \text{ mol } \text{L}^{-1}}$ If we want to calculate the values of different quantities in terms of 'm' instead of 'cm'. $\rho = \frac{RA}{l}$ $= \frac{5.55 \times 10^{3} \Omega \times 0.785 \times 10^{-4} \text{ m}^{2}}{0.5 \text{ m}} = 87.135 \ 10^{-2} \Omega \text{ m}$ $\kappa = \frac{1}{\rho} = \frac{100}{87.135} \Omega \text{ m} = 1.148 \text{ S m}^{-1}$

LECT-6

and $A_m = \frac{\kappa}{c} = \frac{1.148 \text{ Sm}^{-1}}{50 \text{ mol m}^{-3}} = 229.6 \quad 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}.$

Variation of Conductivity and Molar Conductivity with Concentration:

Specific conductance is the conductance of 1 cm^3 of solution of an electrolyte. Thus more is the no. of ions per unit volume of the solution; more is the specific conductance / conductivity.

Specific conductance α Concentration.

However with dilution, concentration of solution decreases so that the no. of ions per unit volume decreases and hence specific conductance decreases.

Molar conductance (\wedge_m)

Molar conductivity $(\land m)$ for both the strong and weak electrolyte increases on decreasing the concentration of solution. In case of strong electrolytes, molar conductance is slowly increased with decrease in concentration. Because strong electrolytes are almost ionised even at high concentration. But with increase in concentration, molar conductance slowly decreases. According to **Debye-Huckel Onsager** equation.

$$\wedge_m = \wedge_m^0 - A\sqrt{C}$$

The graph between $\wedge_m Vs \sqrt{C}$ is a straight line with intercept equal to $\wedge_m m^0$ and slope equal to -A. The value of the constant A for a given solvent and temperature depends on the type of electrolyte. i.e the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. In case of weak electrolytes molar conductance increases sharply with dilution. But suddenly decreases with decrease in dilution. Because weak electrolytes are weakly ionized. Graphically it can be represented as-



From the graph it is observed that, indicates molar conductance at zero (O) concentration or at infinite dilution. This is called limiting molar conductance. There is limiting molar conductance for strong electrolyte i.e., molar conductance of strong electrolyte is easily calculated. But it is difficult to calculate for weak electrolytes. Molar conductance of weak electrolytes can be calculated indirectly by using Kohlarausch's law.

If α is the degree of dissociation, then α is equal to

$$\alpha = \frac{{\wedge_m}^c}{{\wedge_m}^0}$$

Here \wedge_m^c = Molar conductance at certain concentration.

 $\wedge_m^{0} =$ Molar conductance at zero concentration

But we know that for a weak electrolyte like acetic acid

$$K_{\mathbf{a}} = \frac{c\alpha^2}{\left(1 - \alpha\right)} = \frac{cA_m^2}{A_m^{\circ 2} \left(1 - \frac{A_m}{A_m^{\circ}}\right)} = \frac{cA_m^2}{A_m^{\circ} \left(A_m^{\circ} - A_m\right)}$$

Kohlrausch's Law of Independent migration of Ions:-

It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

i.e
$$\wedge_{\rm m} {\rm m}^0 {\rm NaCl} = \lambda^0 {\rm Na}^+ + \lambda^0 {\rm Cl}^-$$

In general, $\wedge_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$

Hence λ^0_+ and λ^0_- are limiting molar conductivity of the cation and anion respectively.

Application of Kohlrausch's law:-

(a) To calculate the limiting molar conductivity $(\land m)$ of weak electrolytes.

$$\wedge_{m}^{0}CH_{3}COOH = \wedge_{m}^{0}HC\ell + \wedge_{m}^{0}CH_{3}COONa - \wedge_{m}^{0}NaCl$$

$$\wedge_{m}^{0}$$
H₂O = \wedge_{m}^{0} HC ℓ + \wedge_{m}^{0} NaOH - \wedge_{m}^{0} NaCl

(b) To calculate the degree of dissociation (α) and dissociation constant (Ka) of an electrostatic.

Degree of dissociation
$$(\alpha) = \frac{\wedge m}{\wedge m^0}$$

LECT-7

Electrolytic Cell and electrolysis:-

Electrolysis is a process of decomposition of an electrolyte by passing electric current. Electrolytic cell is a device in which electrical energy is converted into chemical energy by passing electric current. In an electrolytic cell anode is positive an cathode is negative.

Faraday's Laws of Electrolysis:-

1st **law:-** It states that the mass of the substance that deposited or liberated during electrolysis is directly proportional to the quantity of charge passed through the electrolyte.



 $6.023 \times 10^{23} \times 1.602 \times 10^{-19} c$

 $=96487 \text{C} \text{ mol}^{-1}$

3.15 A solution of Ni(N0₃)₂ is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Sol.

Quantity of electricity passed = $(5A) \times (20 \times 60 \text{ sec.}) = 6000C$ Ni²⁺ + 2e⁻ \longrightarrow Ni Thus, 2F, *i.e.*, 2 × 96500C of charge deposit = 1 mole of Ni = 58.7 g \therefore 6000 C of charge will deposite = $\frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g of Ni.}$

2nd Law:- When two or more electrolytic cells are connected in series and same quantity of charge is passed through them the mass of the substances deposited is directly proportional to their chemical equivalent weight.

i.e $\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3}$

 w_1 , w_2 , w_3 are masses and E_1 , E_2 , E_3 are equivalent masses of substances 1, 2 and 3 respectively.

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3.16 Three electrolytic cells A, B, C containing solutions of ZnS0₄, AgNO₃ and CuS0₄, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 45 g of silver deposited at the cathode of call B. How long did the current flow? What mass of copper and zinc were deposited?

Sol. Given: I = 1.5 A, W = 1.45 g of Ag, t = ?, E = 108, n = 1Using Faraday's 1st law of electrolysis W = ZItor, $W = \frac{E}{nF}$ It or, $t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73$ seconds. Now for Cu, $W_1 = 1.45$ g of Ag, $E_1 = 108$, $W_2 = ?$, $E_2 = 31.75$ From Faraday's 2nd law of electrolysis $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

 $\frac{1.45}{W_2} = \frac{108}{31.75} \therefore W_2 = \frac{1.45 \times 31.75}{108}$

Products of electrolysis: - It depends on

- (a) Nature of material being electrolyses and the type of electrodes being used.
- (b) If the electrode is inert (i.e. platinum or gold or graphite) it does not participate in the chemical reaction and acts only as source for electrons.
- (c) If the electrode is reactive it participates in the electrode reaction. Thus the product of electrolysis may be different for reactive and inert electrodes.

(d) The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.

(a) Product of Electrolysis of molten NaCl

 $\operatorname{NaCl}_{(s)} \rightarrow \operatorname{Na}_{(melt)}^{+} + \operatorname{Cl}_{(melt)}^{-}$

At Cathode:- $Na^+_{(melt)} + 1e^- \rightarrow Na_{(s)}$

At Anode:- $2Cl_{(melt)}^{-} \rightarrow Cl_{2(g)} + 2e^{-}$

So during electrolysis of molten NaCl, sodium metal will be deposited at cathode and chlorine gas will be liberated at anode.

(b) Product of Electrolysis of Aqueous NaCl.

NaCl
$$\longrightarrow$$
 Na⁺_(aq) + Cl⁻_(aq)

$$H_2O_{(\ell)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$$

At Cathode:- $2H^{+}_{(aq)} + 2e^{-} \rightarrow H^{-}_{2(g)}$

This is because standard reduction potential of $\, H^{\scriptscriptstyle +} \, / \, H_2^{\,}$ is greater than $\, E^\Theta N a^{\scriptscriptstyle +} \, / \, N a$

At anode :- $2Cl_{(aq)}^{-} \rightarrow Cl_{2(g)} + 2e^{-}$

This is because of over potential of oxygen. Therefore,

$$2NaCl_{(aq)} + 2H_2O_{(\ell)} \xrightarrow{electrolysis} H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$$

(c) Product of electrolysis of dilute H₂SO₄

During electrolysis of dilute H_2SO_4 the product are $\underset{2(aq)}{H_2SO_{4(aq)}}$ at cathode and $O_{2(g)}$ at anode $H_2SO_{4(aq)} \rightarrow 2H_{(a)}^+ + SO_{4(aq)}^{2-}$

At anode:-
$$H_2O_{(\ell)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+ + 2e$$

At cathode:
$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

At higher concentrations of H₂SO₄, oxidation takes place at anode as

$$2SO_4^{2-}$$
 (aq) $\rightarrow S_2O_8^{2-}$ (aq) + 2e⁻

(d) Product of electrolysis of aqueous copper sulphate using platinum electrode:-

During electrolysis, copper is deposited at cathode and oxygen is liberated at anode

 $\mathrm{CuSO}_{4(\mathrm{aq\,})} \to \mathrm{Cu}_{(\mathrm{aq\,})}^{2+} + \mathrm{SO}_{4(\mathrm{aq\,})}^{2-}$

 $\mathrm{H_2O}_{(\ell)} \to \mathrm{H^+_{(aq)}} + \mathrm{OH^-_{(aq)}}$

At cathode:- $\operatorname{Cu}_{(aq)}^{2+} + 2e^{-} \rightarrow \operatorname{Cu}_{(s)}$

At anode:- $4OH_{(aq)} \rightarrow 2H_2O_{(\ell)} + O_{2(g)} + 4e^-$

(e) Product of Electrolysis of AgNO3 using silver electrodes:-

During electrolysis impure silver will be oxidized at anode and pure silver will be deposited at cathode.

At Cathode:- $Ag^+_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

At Anode :- $Ag_{(s)} \rightarrow Ag_{(aq)}^+ + 1e^-$

BATTERIES

Electrochemical cells using salt bridge have high internal resistance. As a result we can not draw large current from them and their voltage drops sharply. Thus an electrochemical cell to be used as commercial cell do not drop voltage during use. If a number of cells are connected in series then the arrangement is called battery. The commercial cells are classified as three types such as-

ii) Secondary cells

iii) Fuel cells

PRIMARY CELLS:

Primary cells are those in which redox reaction occurs only once and the cell becomes dead after some times and can not be used again. In other words the cell reaction is not reversible. Such primary cells are called dry cells. These cells are used in torches, radio receivers, electronic calculators, hearing aids, etc. Example of Primary cells:- i) Leclanche cell ii) Alkaline battery iii) Mercury battery iv) Nickel-Cadmium(Nicad) battery.



It consists of

<mark>Ano</mark>de <mark>– Z</mark>in<mark>c co</mark>ntainer

Cathode: - Carbon (graphite) rod surrounded by powered MnO₂ and carbon

Electrolytic: - Moist paste of NH₄Cl and ZnCl₂

The reaction that takes place is

Anode:- $Zn_{(s)} \rightarrow Zn^{2+} + 2e^{-}$

Cathode:- $MnO_2 + NH_4^+ + 1e^- \rightarrow MnO(OH) + NH_3$

In the reaction at cathode manganese is reduced from the +4 oxidation state to the +3 oxidation state ammonia produced in the reaction forms complex with Zn^{2+} to give $\left[Zn(NH_3)_4\right]^{2+}$. The cell potential is nearly 1.5v. It is used in transistor.

(b) Mercury Cell:- it consists of

Anode:- Zinc - mercury amalgam Cathode :- Paste of HgO and carbon Electrolyte paste of KOH and ZnO The electrode reaction for the cell is

Anode: $Zn(Hg) + 2OH^{-} \rightarrow ZnO_{(s)} + H_2O + 2e^{-}$

Cathode:- $HgO + H_2O + 2e^- \rightarrow Hg_{(\ell)} + 2OH^-$

Overall reaction:- $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(\ell)}$

The cell potential is remains constant during its life as the overall reaction does not involve any ion in solution whose concentration changes during its life time. The cell potential is approximately 1.35V. It is used in low current device like hearing acids watches etc.

LECT-8

Secondary Cell/ Battery:-Those type of cell which after use can be recharged by passing current through it in the opposite direction so that it can be used again.

Example:- Lead storage battery.

Nickel – cadmium cell.

(a) Lead storage battery:- It consists of

Anode:- Lead

Cathode:- Grid of lead packed with PbO₂

Electrolyte:- 38% solution of H₂SO₄. The cell reaction when the battery is in use.

Discharging Process :

At anode : Pb is oxidised to Pb²⁺ which then ng your Tomorrow react with SO42-ions generated from H2SO4 to form PbSO₄.

$$\begin{array}{c} Pb_{(S)} \rightarrow Pb^{2+} + 2e^{-} \\ \\ Pb^{2+} + SO_{4}^{2-} \rightarrow PbSO_{4(S)} \\ \hline Pb_{(S)} + SO_{4}^{2-} \rightarrow PbSO_{4(S)} + 2e^{-} & \dots \dots \dots (1) \end{array}$$

At cathode : The reactions are :

$$\begin{array}{c} PbO_{2} \rightarrow Pb^{4+} + 2O^{2-} \\ 4H^{+} + 2O^{2-} \rightarrow 2H_{2}O \\ Pb^{4+} + 2e^{-} \rightarrow Pb^{2+} \\ \hline Pb^{2+} + SO_{4}^{-2-} \rightarrow PbSO_{4(S)} \\ \hline PbO_{2(S)} + 4H^{+} + SO_{4}^{-2-} + 2e^{-} \rightarrow \\ PbSO_{4(S)} + 2H_{2}O \quad \dots \dots (2) \end{array}$$

The net cell reaction in the discharging process is obtained by adding equation (1) and (2)

$$\begin{array}{c} Pb_{(S)} + SO_{4}^{\ 2^{-}} \rightarrow PbSO_{4(S)} + 2e^{-} \\ PbO_{2(S)} + 4H^{+} + SO_{4}^{\ 2^{-}} + 2e^{-} \rightarrow \\ PbSO_{4(S)} + 2H_{2}O \\ \hline \hline Pb_{(S)} + PbO_{2(S)} + 2H_{2}SO_{4} \rightarrow 2PbSO_{4(S)} + 2H_{2}O \end{array}$$

cell potential is approximately 12V. It is used in automobiles and invertors. On charging the battery the reaction is reversed and PbSO4 on anode and cathode is converted into Pb and PbO2 respectively.

The net cell reaction during charging is

$$\begin{split} PbSO_{4(S)} + 2e^{-} &\rightarrow Pb_{(S)} + SO_{4}^{2-} \\ PbSO_{4(S)} + 2H_{2}O_{(i)} &\rightarrow PbO_{2(S)} + 4H^{+} + SO_{4}^{2-} + 2e^{-} \\ \hline 2PbSO_{4(S)} + 2H_{2}O &\rightarrow Pb_{(S)} + PbO_{2(S)} + 2H_{2}SO_{4} \end{split}$$

(b) Nickel Cadmium Cell (NiCad cell):-

It consists of Anode:- Cadmium Cathode:- Metal grid containing N, O₂ Electrolyte:- Most KOH/ NaOH. The overall cell reaction that takes place as

```
Cd (s) + 2Ni(OH)<sub>3</sub> (s) \rightarrow CdO (s) + 2Ni(OH)<sub>2</sub> (s) + H<sub>2</sub>O (l)
```

Nickel-cadmium cell has longer life than the lead storage cell but more expensive to manufacture.

Fuel cell:- It is a device in which the energy produced due to combustion of fuel like hydrogen, methane and methanol is converted into electrical energy.

Example:- Hydrogen – oxygen Fuel cell:-

It consists of porous carbon electrodes incorporated with catalyst like finely divided platinum or palladium metal. The electrode reaction that taking place are

Cathode:-
$$O_{2(g)} + 2H_2O_{(\ell)} + 4e^- \rightarrow 4OH_{(aq)}^-$$

Anode:-
$$2H_{2(aq)} + 4OH_{(aq)} \rightarrow 4H_2O_{(\ell)} + 4e^-$$

Overall:
$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$$

It is used in Apollo space programme.

Advantages of Fuel cell:-

(a) It has high efficiency of about 70%

(b) It does not cause pollution

(c) The by-product water produced can be used for drinking purpose



<u>Corrosion of Metals</u>: The process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting in to the formation of compounds such as oxides, sulphides, carbonates, sulphates etc. is called corrosion. Example: Rusting of iron ,Tarnishing of silver, development of green coating on copper and bronze etc. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. Corrosion of iron (rusting) is said to be an electrochemical phenomena as it involves the formation of electrochemical cell on the surface of iron.



At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction as:

Anode
$$2Fe_{(s)} \rightarrow 2Fe^{2+} + 4e^{-}$$
 $E_{(Fe^{2+}/Fe)}^{\Theta} = -0.44 \text{ V}$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H+ (which is believed to be available from H2CO3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere. This spot behaves as cathode with the reaction:

Cathode: $O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2 O(l) E^{\odot}_{H^+|O_2|H_2O} = 1.23 V$ The overall reaction being:

 $2\mathrm{Fe}(\mathrm{s}) + \mathrm{O}_2(\mathrm{g}) + 4\mathrm{H}^+(\mathrm{aq}) \longrightarrow 2\mathrm{Fe}^{2+}(\mathrm{aq}) + 2 \mathrm{H}_2\mathrm{O}(\mathrm{l}) \qquad E_{\mathrm{(cel)}}^{\ominus} = 1.67 \mathrm{V}$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide as Fe_2O_3 .x H_2O with further production hydrogen ion.

$$2\operatorname{Fe}_{(aq)}^{2+} + 2\operatorname{H}_{2}\operatorname{O}_{(\ell)} + \frac{1}{2}\operatorname{O}_{2(g)} \rightarrow \operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 4\operatorname{H}^{+}(aq)$$

Fe₂O_{2(s)} + xH₂O \rightarrow Fe₂O₂.xH₂O

Chemically rust is hydrated ferric oxide.

Prevention of Rusting:-

- (a) Barrier protection:- it can be done by painting oiling, or greasing
- (b) Sacrificial Protection:- it can be done by coating a highly reactive metal on the surface of iron. Example: Galvanization
- (c) Electrical protection (catholic protection) :- it is used to prevent underground pipes from rusting. Using metal like zinc, aluminum, magnesium
- (d) Using antirust solution:- It is the alkali solution of phosphate and chromate of sodium and potassium. These solutions form a protective insoluble film of iron phosphate which prevents rusting.

Questions for Electrochemistry:-

Lectures – 1

- 01. Can you store copper sulphate solution in a zinc pot.?
- 02. What would happen, if no salt bridge were used in as electro chemical cell like $Zn CuSO_4$ cell?

03. Wh<mark>y does a Galvanic Cell beco</mark>me dead after some time?

04. Give the standard electrode potentials $K^+ / K = -2.93v$, $Ag^+ / Ag = 0.80v$

 $Mg^{2+}/Mg = -2.37v$, $Hg^{2+}/Hg = 0.79v$ $Cr^{3+}/Cr = -0.74v$. Arrange these methods in their increasing order of reducing power.

05. Depict the Galvanic cell in which the following reaction takes place. Further show

$$Zn_{(s)} + 2Ag_{(aq)}^+ \rightarrow Zn_{(aq)}^{2+} + 2Ag_{(s)}$$

(a) Which of the electrode is negatively charged?

- (b) The carriers of the current in the cell
- (c) Individual reaction at each electrolysis.

06. Depict the Galvanic Cell in which the case reaction is $Cu + 2Ag^+ \rightarrow 2Ag + Cu^{2+}$

Lecture – 2

- 01. Why it is not possible to measure the single electrode potential?
- 02. How would you determine the standard electrode potential of the system Mg^{2+}/Mg ?
- 03. Consider a cell given below

 $Cu / Cu^{2+} || Cl^{-} | Cl_{2}, Pt$ Write the cell reaction that occurs at anode and cathode.

- 04. Define electrochemical series.
- 05. What does the negative value of E_{cell}^{θ} indicate?
- Lecture 3
- 01. Write Nernst equation for single electrode potential $M^{n_+} + ne^{-1} \rightarrow M$
- 02. Write the relationship between E_{cell}^{θ} and Gibb's energy of reaction.
- 03. Write the relationship between Gibb's energy charge of reaction and equilibrium constant.
- 04. Calculate the equilibrium constant of the reaction. $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
 - $E_{cell}^{\theta} = 0.46V$
- 05. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Lecture – 4

- 01. Calculate the emf of the cell in which the following reaction takes place. $Ni_{(s)} + 2Ag^+_{(0.002m)} \rightarrow Ni^{2+}_{(0.160m)} + 2Ag_{(s)}$. Given that $E^{\theta}_{cell} = 1.05V$
- 02. The standard electrode potential for Daniell cell is 1.1v. Calculate the standard Gibb's energy for the reaction. $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$.
- 03. In the button cells widely used in watches and other devices the following reaction takes place. $Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn_{(aq)}^{2+} + 2Ag_{(s)} + ZOH_{(aq)}$.
- 04. Calculate the standard cell potentials of galvanic cell in which the following reaction takes place.

(a)
$$2Cr_{(s)} + 3Cd_{(aq)}^{2+} \rightarrow 2Cr_{(aq)}^{3+} + 3Cd$$
 (b) $Fe_{(aq)}^{2+} + Ag_{(aq)}^{+} \rightarrow Fe_{(aq)}^{3+} + Ag_{(s)}$

Calculate the $\Delta r G^{\theta}$ and equilibrium constant for the reaction.

Given
$$E^{\theta}_{Cr^{3+}/Cr} = -0.74V, E^{\theta}_{Cd^{2+}/Cd} = -0.40V$$
 $E^{\theta}_{Fe^{3+}/Fe^{2+}} = 0.77V, E^{\theta}_{Ag^+/Ag} = 0.80V$

05. Calculate the emf of the cell in which the following reaction takes place.

$$Ni_{(s)} + 2Ag^{+}_{(0.002m)} \rightarrow Ni_{(0.160m)} + 2Ag_{(s)}$$
, Given that $E^{\theta}_{cell} = 1.05W$

Lecture – 5

01. Write the relationship between conductivity (K) conductance (G) and Cell constant $\left(G^{*}
ight)$

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- 02. Define cell constant and write the unit
- 03. State Kohlrausch's law of independent migration of ions.
- 04. Suggest a way to calculate the \wedge_m^0 of water
- 05. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

- 06. The conductivity of 0.20 m solution of KCl at 295 K is 0.0248s cm⁻¹. Calculate its molar conductivity.
- 07. Calculate the \wedge_m^0 for CaCl₂ and MgSO₄ from the following data

$$\lambda^{0}Ca^{2+} = 119.0 Scm^{2}mol^{-1}, \lambda^{0}Cl^{-} = 76.3 Scm^{2}mol^{-1}$$

 $\lambda^{0}Mg^{2+} = 106.0Scm^{2}mol^{-1}, \lambda^{0}SO_{4}^{2-}Scm^{2}mol^{-1}$

- 08. \wedge_m^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0s cm²mol⁻¹ respectively. Calculate \wedge_m^0 for HAc.
- 09. Why does conductivity of a solution decreases with dilution?
- 10. The molar conductivity of $0.025 mol L^{-1}$ methanoic acid (HCOOH) is 46.1Scm² mol⁻¹. Calculate its degree of dissociation and dissociation constant.

Given $\lambda^0 H^+ = 349.6 S \, cm^2 mol^{-1} \, \lambda^0 H COO^- = 54.6 S \, cm^2 mol^{-1}$

Lecture – 6

- 01. State Faraday's 1st law of electrolysis.
- 02. How much charge is required for the following reduction?
 - (a) 1 mol of Al^{3+} to Al (b) 1 mol of MnO_4^- to Mn^{2+}

03. How much electricity inter of Faradays is required to produce?

- (a) 20.0 g of Ca from molten $CaCl_2$ (b) 40.0 g of Al from Al_2O_3
- 04. If a current of 0.5 ampere flows through a metallic wire for 240 cms, then how many electrons would flow through the wire?
- 05. Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + be^- \rightarrow 2Cr^{3+} + 7H_2O$. What is the quantity of electricity in coulombs needed to reduce 1 mole of $Cr_2O_7^{2-}$?

- 06. A solution of CuSO₄ is electrolyses for 10 minutes with a current of 1.5 ampere. What is the mass of copper deposited at the cathode?
- 07. Produce the product of electrolyses of
 - (a) A dilute solution of H_2SO_4 with platinum electrodes.
 - (b) An aqueous solution of CuCl₂ with platinum electrodes
 - (c) An aqueous solution of $AgNO_3$ with platinum electrodes.
- 08. How will the pH of brine (aqueous NaCl solution) be affected when it is electrolyzed?

Lecture – 7

- 01. What is a primary battery? Write the out takes place at anode and cathode in a dry cell.
- 02. Why is mercury cell maintaining constant potential during its life time?
- 03. What are secondary batteries? Write the reaction that takes place during the charging and discharging of lead strong cell.
- 04. What are the advantages of nickel cadmium cell over lead strong batteries?
- 05. For the given cells. Lead storage cell, mercury cell, fuel cell, dry cell. Answer the following.
 - (a) Which cell is used in hearing aids?
 - (b) Which cell is used in automobiles and invertors?
 - (c) Which cell does not have long life?
- 06. Write the formula of complex entity formed when Zn^{2+} react with NH_3 in a dry cell.

Lecture – 8

01. What is a Fuel cell? Write the reaction involve in hydrogen oxygen Fuel cell. What are advantages?

02. Suggest two materials other than hydrogen that can be used as fuels in fuel cell.

- 03. Explain how rusting of iron is envisaged as setting up of an electrostatic cell?
- 04. Name the metal which can be used for cathode protection of iron.
- 05. Define Galvanisation? Name metal which as used for sacrificial protection of iron.
- 06. Why is resting of iron is faster in saline water then the ordinary water?
- 07. Why is alkaline medium inhibits the rusting of iron?





