3. ELECTRO CHEMISTRY

It is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their inter conversions.

1.Daniel cell.

It is constructed by dipping a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.

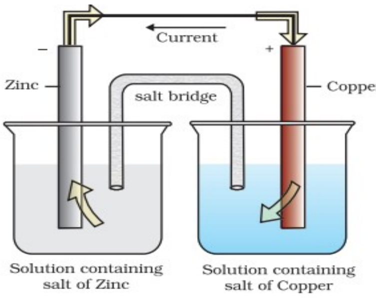
(i)$Cu^{2+} + 2e^- \rightarrow Cu(s)$ (Reduction /In right half cell)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (Oxidation /In left half cell)

Left half cell-Oxidation-Anode-Negative(LOAN)

Right half cell-Reduction-Cathode-Positive.

Here electron flow occurs from Zinc rod to Copper rod,and the conventional current flows from Copper rod to Zinc rod.



2. Electrode Potential(E_{el})

The tendency of a metal to lose or gain electron when it is in contact with its own solution is called **electrode potential,(E_{el})**. Electrode potential measured at standard conditions is known as **Standard electrode potential(E^0_{el})**.

The **cell potential** is the difference between the electrode potentials (Reduction potentials) of the cathode and anode.

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

For Daniel cell, the symbolic cell representation is $Zn_{(s)}/Zn^{2+}_{(aq)}//Cu^{2+}_{(aq)}/Cu_{(s)}$

3. Measurement of Electrode Potential is done with the help of SHE/NHE.

SHE can be represented as $Pt(s)/H_2(g)/H^+(aq)$ when it acts as anode

and as $H^+(aq)/H_2(g)/Pt(s)$ when it acts as cathode.

4. Electrochemical series

It is a series in which various electrodes are arranged in the increasing order of their Electrode Potential. Important applications of ECS are

- To compare the relative reactivity of metals.
- To predict the displacement reactions.
- To predict the liberation of H_2 gas from mineral acids

5. Nernst equation –Various forms

For a general electrode reaction $M^{n+}(aq) + ne^- \rightarrow M(s)$

- Electrode potential

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

- Cell potential for Daniel cell

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

$$E_{Cell} = E^{\ominus}_{Cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- Free energy and EMF of cell

$$\Delta_r G^{\ominus} = -nFE^{\ominus}_{(cell)}$$

- EMF of cell and Equilibrium constant

$$E^{\ominus}_{(cell)} = \frac{2.303RT}{nF} \log K_C$$

6.Variation of Molar conductivity (Λ_m) with concentration

It is the conductivity of 1 mole of an electrolytic solution kept between two electrodes with unit area of cross section and at a distance of unit length.

Molar conductivity decreases with the concentration of the electrolyte while conductivity increases with the concentration.

- For both strong and weak electrolyte, the molar conductivity increases with dilution (or decreases with increase in concentration)
- In case of weak electrolytes there is a sudden increase in molar conductivity during dilution where as in case of strong electrolyte a slight increase is observed
- When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the **limiting molar conductivity (Λ_m^0).**

- When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the **limiting molar conductivity (Λ_m^0).**

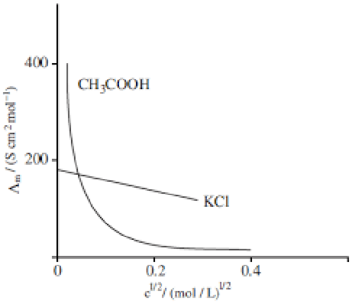
For strong electrolytes, the relation between Λm and concentration can be given as:

$$\Lambda_m = \Lambda_m^0 - A\sqrt{C}$$ **(Debye Huckel Equation)**

Where 'C' is the concentration and A is a constant .

The variation of Λ_m for strong and weak electrolytes is shown in the graphs

For strong electrolytes, the value of $\wedge_m^0$can be determined by the extrapolation of the graph.



7. Kohlrausch's law

The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual Molar ionic conductances of the anions and the cations of the electrolyte.

Let the molar ionic conductances of anion and cation at infinite dilutions are λ_+ and λ_- respectively,Then

$$\Lambda_m^0 = \upsilon_+ \lambda_+^0 + \upsilon_- \lambda_-^0$$

Where $\upsilon_+$and υ_- represents the total number of cations and anions produced by one unit formula of an electrolyte.

Applications

Determination of $\wedge_m^0$of weak electrolytes.

By knowing the $\wedge_m^0$ values of strong electrolytes, we can calculate $\wedge_m^0$ of weak electrolytes. For e.g. we can determine the $\wedge_m^0$of acetic acid (CH_3COOH) by knowing the $\wedge_m^0$ of CH_3COONa, NaCl and HCl as follows:

$$\wedge_m^0(CH_3COONa) + \wedge_m^0(HCl) - \wedge_m^0(NaCl) = \wedge_m^0\ CH_3COOH$$

Determination of degree of dissociation of weak electrolytes

By knowing the molar conductivity at a particular concentration ($\wedge_m$) and limiting molar conductivity ($\wedge_m^0$), we can calculate the degree of dissociation (α) as,

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

8.Faraday's laws of electrolysis

Faraday's first law

It states that the amount of substance deposited or liberated at the electrodes (m) is directly proportional to the quantity of electricity (Q) flowing through the electrolyte.

Faraday's second law

It states that when same quantity of electricity is passed through solutions of different substances, the amount of substance deposited or liberated is directly proportional to their own equivalent masses.

Products of electrolysis

Electrolyte	Product at Anode	At cathode
Aq.NaCl	Chlorine	Hydrogen
Molten NaCl	Chlorine	Sodium

9. Batteries/ Commercial cells

Non- rechargeable cells – Primary cell Drycell, Mercury cell
Rechargeable cells – Secondary cells Lead storage cell,Ni-Cd cells.

Cells	Anode	Cathode	Electrolyte	Overall cell reaction
Dry Cell (Leclanche cell)	Zn container	Graphite $+MnO_2$	Ammonium chloride (NH_4Cl).	$2Zn(s) + MnO_2 + NH_4^+ \rightarrow 2Zn^{2+} + MnO(OH) + NH_3$
Mercury cell (Button cell)	Zinc – mercury amalgam	Paste of HgO and carbon	Paste of KOH and ZnO	$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
Lead storage cell	Lead	Grid of lead packed with lead dioxide (PbO_2)	38% H_2SO_4	$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

✔ Mercury cell has a constant potential of 1.35 V since the overall reaction does not involve any ion in solution. Mercury cell is suitable for hearing aids, watches, etc.

✔ In Lead storage battery cell reaction can be reversed by passing current through it in the opposite direction. *The most important secondary cell is, which is used in automobiles and inverters.*

10. Fuel cells

- These are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol,etc. directly into electrical energy.
- One example for fuel cell is ***Hydrogen – Oxygen fuel cell***, which is used in the Apollo space programme.
- Here hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous Sodium hydroxide solution.

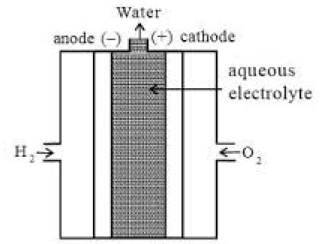


Fig. : A simple fuel cell

The electrode reactions are:

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Anode: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Overall reaction is: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Advantages

- The cell works continuously as long as the reactants are supplied.
- It has higher efficiency
- It is eco-friendly (i.e. pollution free)
- Water obtained from $H_2 – O_2$ fuel cell can be used for drinking.

11. Corrosion

It is the slow destruction of the metal due to the attack of various atmospheric gases with the metallic surface .Some common examples are: The rusting of iron, tarnishing of silver, formation of green coating on copper and bronze (verdigris) etc.

Rusting of iron is an electrochemical phenomenon. Chemically rust is hydrated ferric oxide ($Fe_2O_3 . x H_2O$)

Methods to prevent corrosion

- Barrier protection By coating the metal surface with paint, varnish etc.
- Sacrificial protection By coating the metal surface with another electropositive metal like Zinc, Magnesium etc. The coating of metal with zinc is called Galvanisation and the resulting iron is called Galvanized iron.
- Anti-rust solutions.
- Cathodic protection.