MIND MAP

Electrochemistry

Electrochemistry

Electrochemistry is the branch of Chemistry which deals with conversion of chemical energy into electrical energy and vice versa.

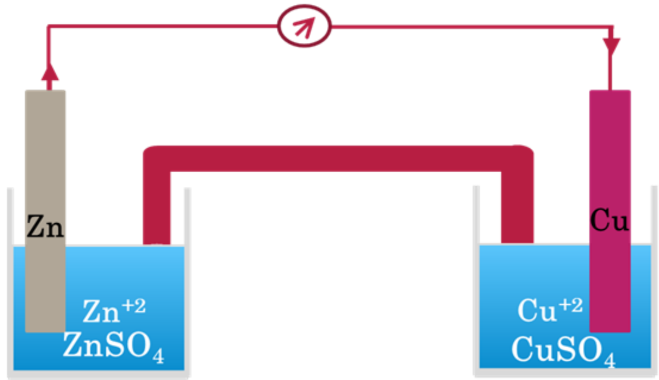
Electrochemical Cell

The chemical energy of substance converts into electrical energy.
e.g. Reaction occurring in cells/batteries.

Electrolytic Cell

Here electrical energy is converted into chemical energy.
e.g. Electrolysis, electro-refining, electro-plating etc.

Galvanic Cell (Electrochemical Cell)



Working Principle

When ever a metal strip is put in an electrolyte the process of oxidation and reduction takes place simultaneously within the system. Due to this there is a potential difference between the metal phase and the liquid phase.

On joining the metal strips through a wire (of negligible resistance) the current flows as long as the potential difference exists between the metal phase and the liquid phase.

Two solutions are connected by a salt bridge.

Representation of Galvanic Cell

Ex. Daniel cell

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq.) \mid Cu(s)$

For cell reaction

$H_2(g) + Cu\,(aq) \longrightarrow 2H^+(aq) + Cu(s)$

$Pt \mid H_2(g)\ (1\ atm) \mid H^+\ (aq) \mid\mid Cu^{2+}(aq.) \mid Cu(s)$

Electrode Potential

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

At anode

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

(Oxidation Potential)

At cathode

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

(Reduction Potential)

Standard Electrode Potential (E°)

At 298 K, concentration = 1M, P = 1 bar (Standard conditions)

The potential of standard H-electrode (SHE) ($[H^+] = 1M$ & $P_{H_2} = 1$ bar) is assumed to be 0.0V at all temperature.

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Electromotive Force of Cell or Cell Voltage

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.

$E_{cell} = E_{red}\ (cathode) - E_{red}\ (anode)$

or $E_{cell} = E_{oxi.}(anode) - E_{oxi.}(cathode)$

or $E_{cell} = E_{oxi.}(anode) + E_{red}\ (cathode)$

Nernst Equation

$$E_{cell} = E^0 - \frac{RT}{nF}\ln Q$$

Nernst equation represents effects of concentration, pressure or temperature changes on cell EMF.

Different Types of Electrodes & Their Potential

Metal – Metal Ion Electrode

$M^{+n}(aq)\,|\,M(s)$ $\quad M^{n+} + ne^- \longrightarrow M(s)$

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

Gas – Ion Electrode

$H^+(aq)\,|\,H_2(g)\,|\,Pt(s)$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

$$E = E^\circ - 0.0591\log\frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$$

Oxidation – Reduction Electrode (Redox Electrode)

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$$E = E^\circ - 0.0591\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Metal – Metal Insoluble Salt – Anion Electrode

$Cl^-\,|AgCl|Ag$

As a reduction electrode

$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - 0.0591\log[Cl^-]$$

$$\text{or } E_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + 0.0591\log\frac{K_{sp}}{[Cl^-]}$$

If $[Cl^-] = 1M \Rightarrow E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag}$

Electrode Gas Concentration Cell

$Pt, H_2(P_1)\,|\,H^+(C)\,|\,H_2(P_2), Pt$

Anode $\frac{1}{2}H_2(p_1) \longrightarrow H^+(c) + e^-$

Cathode $H^+(c) + e^- \longrightarrow \frac{1}{2}H_2(p_2)$

Net $\frac{1}{2}H_2(p_1) \rightleftharpoons \frac{1}{2}H_2(p_2)$

At 25^0C, $E_{cell} = \frac{0.0591}{2}\log\left(\frac{p_1}{p_2}\right)$

For spontanity of such cell reaction, $p_1 > p_2$

Electrolyte Concentration Cells

$Zn(s)|ZnSO_4\ (C_1)||ZnSO_4\ (C_2)|Zn(s)$

Anode $Zn(s) \longrightarrow Zn^{2+}(C_1) + 2e$

Cathode $Zn^{2+}(C_2) + 2e \longrightarrow Zn(s)$

Net $Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1)$

From Nernst equation, we have

$$E = \frac{2.303\,RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontanity of such cell reaction, $C_2 > C_1$

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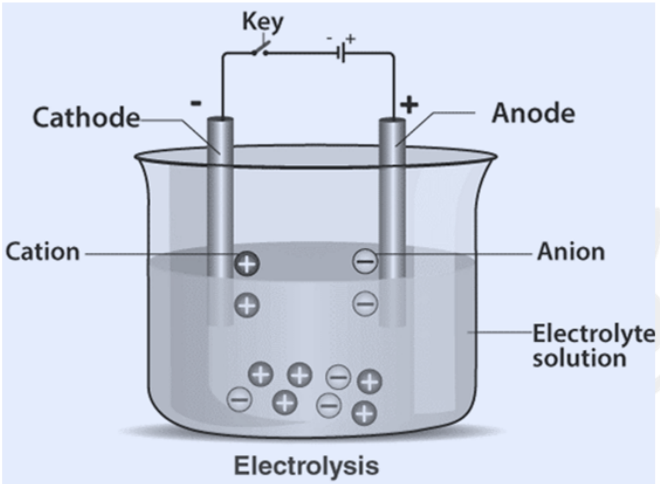
Electrolysis

The process of decomposition of an electrolyte by the passage of electricity is called electrolysis or electrolytic dissociation. When an electric potential is applied between the electrodes, the positively charged ions move towards the cathode and negative ions move towards the anode.



Products of Electrolysis

Electrolysis of Fused Sodium Chloride

At anode $Cl^- \xrightarrow{-e^-} Cl$

$Cl + Cl \longrightarrow Cl_2$

At cathode $Na^+ \xrightarrow{+e^-} Na$

Electrolysis of Aqueous Solution of KBr

At anode $2Br^-(aq.) \longrightarrow Br_2(g) + 2e^-$

At cathode

$2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Electrolysis of Aq. $PbBr_2$

Cathode

$Pb^{2+} + 2e^- \longrightarrow Pb(s)$ $E^0 = 0.126V$

Anode

$2Br^- \longrightarrow Br_2 + 2e^-$ $E^0 = -1.08\ V$

Electrolysis of Aq. $CuSO_4$

Cathode

$Cu^{2+} + 2e^- \longrightarrow Cu(s)$ $E^0 = 0.34\ V$

Anode

$2H_2O(\ell) \longrightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23V$

Electrolysis of Aq. NaCl

Cathode

$2e^- + 2H_2O(l) \longrightarrow H_2(g) + 2OH^-$ $E^0 = -0.83\ V$

Anode

$2Cl^- \longrightarrow Cl_2 + 2e^-$ $E^0_{OX} = -1.30V$

(due to OVER VOLTAGE)

Electrolysis of Aq. $CuSO_4$ Using Cu Electrode

Anode (oxidation)

$Cu(s) \longrightarrow Cu^{2+} + 2e^-$ $E^0 = -0.34\ V$

Cathode (reduction)

$Cu^{2+} + 2e^- \longrightarrow Cu$ $E^0 = +0.34\ V$

$\therefore$ Both oxidation and reduction of Copper occurs and density of solution remains constant.

Electrolysis of $AgNO_3(aq)$ using Ag electrodes

Anode

$Ag(s) \longrightarrow Ag^+(aq) + e^-$ $E^0 = -0.80V$
(impure)

Cathode

$Ag^+ + e^- \longrightarrow Ag(s)$ (pure) $E^0 = 0.8V$

Both oxidation and reduction of Ag occurs and mass transfer of Ag occurs from anode (impure Ag) to cathode (pure Ag).

Faraday's Laws of Electrolysis

Faraday's First Law of Electrolysis

The amount of a substance deposited or dissolved at an electrode is directly proportional to the charge passing through the electrolytes.

$$W = ZIt = \frac{E}{96500} It$$

Z is known as electrochemical equivalent.

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Electrochemistry

Faraday's Second Law of Electrolysis

Amounts of different substances deposited in different solutions at electrodes by passage of the same quantity of electricity are proportional to their equivalent masses(E).

$W \propto E$ (equivalent masses) $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

Electrolytic Conductance

Electrolytic Conductors

Substances whose aqueous solution conducts the electric current and which are decomposed by the passage of current are called electrolytes.
In this case, conduction takes place by movement of ions.

Resistance (R)

$R = \frac{V}{I}$

R is expressed in ohms.

$R = \rho\frac{\ell}{A}$

ρ is a constant and is called resistivity or specific resistance.

Conductance (G)

$G = \frac{1}{R}$

G is expressed in mho or Ω^{-1} or Siemen(s).

$\kappa = \frac{1}{\rho}$ Specific Conductance or Conductivity (κ)

$\kappa = \frac{G\ell}{A}$

$\frac{\ell}{A}$ = Cell constant

Equivalent Conductance (Λ_{eq})

It is defined as the product of specific conductance (k) and the volume (V in mL) of the solution which contain one gram equivalent of the electrolyte.

$\therefore \Lambda_{eq} = k \times V \quad \Lambda_{eq} = \frac{k \times 1000}{N}$

Molar conductance (Λ_m)

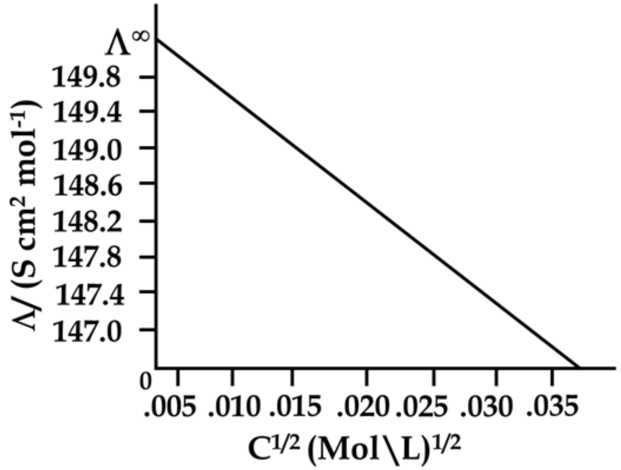
It is defined as the product of specific conductance (k) and the volume (V in mL) which contains one mole of the electrolyte.

$\Lambda_m = k \times V$ and $\Lambda_m = \frac{\kappa \times 1000}{M}$

Debye Huckel Onsager Equation

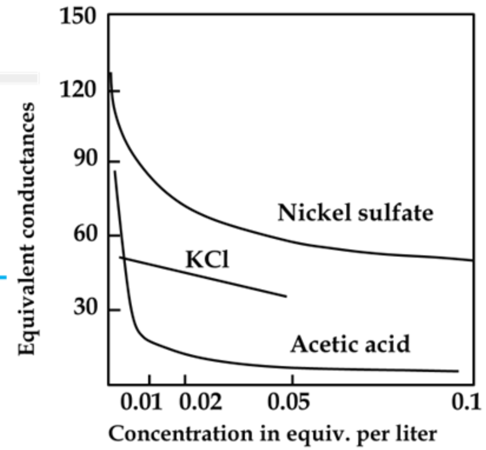
$\Lambda = \Lambda^0 - A\,C^{1/2} \quad A = \text{constant}$

Variation of Λ against $C^{1/2}$



For strong electrolytes Λ^0 or Λ^∞ can be calculated graphically from y−intercept.

Weak Electrolytes



$KCl \longrightarrow$ Strong

$Ni_2SO_4 \longrightarrow$ Modertae

$CH_3COOH \longrightarrow$ Weak electrolyte

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Kohlrausch's Law

At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated.

$\Lambda_{eq}^{\infty} = \Lambda_a + \Lambda_c$ Λ_a=Conductivity of Anion

Λ_c=Conductivity of Cation

Λ_{eq}^{∞}=Conductivity at infinite dilution

Degree of dissociation $\alpha = \dfrac{\Lambda_{eq}}{\Lambda_{eq}^{0}}$

$= \dfrac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$

Solubility(S) and Λ_M^{∞}

Λ_m, Saturated $= \Lambda_M^{\infty} = \dfrac{\kappa \times 1000}{\text{Solubility}}$

$S = \dfrac{\kappa \times 1000}{\Lambda_M^{0}}$

Primary Cells:

Dry Cells(Leclanche cell)

Anode $Zn(s) \longrightarrow Zn^{+2} + 2e^-$

Cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the cathode reaction, Manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $[Zn(NH_3)_4]_{2+}$ ion.

Mercury Cells

Anode Zn amalgam (Zn - Hg)

Cathode HgO + graphite

Electrolyte Aq. paste of (KOH + ZnO)

Anode: $Zn\text{-}Hg(s) + 2(OH^-)(aq) \longrightarrow ZnO(s) + Hg(l) + H_2O$

Cathode: $H_2O(s) + HgO + 2e^- \longrightarrow Hg(l) + 2OH^-(aq)$

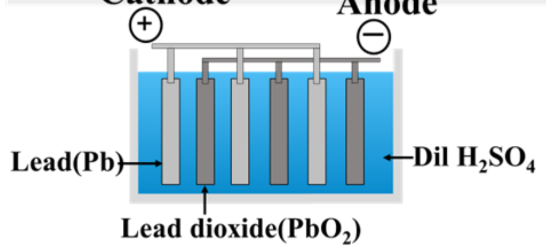
$Zn\text{-}Hg(s) + HgO \longrightarrow ZnO(s) + 2Hg(l)$

Secondary Cells:

$E^0 = 1.35$ eV

Lead storage battery

It consists of a lead as anode and a grid of lead packed with lead dioxide as cathode.



The lead is oxidised to Pb^{+2} ion and lead plates acquire a negative charge.

At Anode

$Pb \longrightarrow Pb^{+2} + 2e^-$

Pb^{+2} ions combine with Sulphate ions of solution to form insoluble lead Sulphate ($PbSO_4$), which begins to coat lead electrode.

$Pb^{+2} + SO_4^{2-} \longrightarrow PbSO_4$ (Precipitation)

The electrons given by Pb are used at cathode (PbO_2 electrode).

At Cathode

$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$ (Precipitation)

Overall cell reaction

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

E^0_{cell} is 2.041 volt

Fuel Cells:

Electrical cells that are designed to convert the free energy from the combustion of fuels such as hydrogen, Carbon monoxide or Methane directly into electrical energy are called Fuel Cells.

The electrode reactions are

Anode

$[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-]$

Cathode

$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

This cell runs continuously as long as the reactants are supplied.