

ELECTROCHEMISTRY

① Cell → Galvanic Cell, Electrolytic Cell
 ↓
 Electrolysis
 ↓
 Faraday's Law

② Electrochemical Series.

③ Batteries, Corrosion

④ Nernst Equation → emf of cell.
 ↓
 equilibrium → Gibbs free energy

⑤ Standard Hydrogen Electrode.

⑥ Conductance in Solution.

→ Resistance → Conductance

→ Resistivity → Conductivity

↓
 molar Conductivity

↓
 Kohlrausch law.

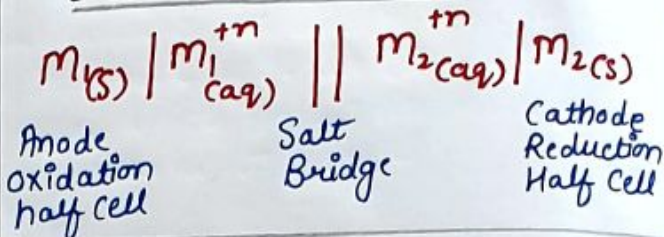
Electrochemistry — Branch of Chemistry which deal with study of production of electricity from energy released during spontaneous chemical reaction, and use of electrical energy to non-spontaneous chemical transformation.

Cells

Electrochemical Cell

Electrolytic Cell.

General Representation of an electrochemical cell



Galvanic Cell

→ It has two half cells, having beaker containing a metal strip that dips in its aqueous salt solution

→ The metal strips are called electrodes and are connected by a conducting wire.

→ Two solution are connected by a salt bridge.

→ Oxidation and Reduction half reaction occur at separate electrode and the electric current flows through the wire.

→ At Anode → (-ve) oxidation : →
 $3Zn(s) \rightarrow 3Zn^{+2}(aq) + 2e^-$

→ At Cathode → (+ve) reduction →
 $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s).$

Characteristic

Electrochemical Cell

Electrolytic Cell

Defination.

Convert Chemical energy to electric energy.

Electric energy → Chemical energy

Assembly

Combination of two half cells. electrodes and sol.ⁿ may be same or different

Single cell contains same electrode and same solutions

Nature of Electrode Spontaneity Other

Anode → -ve, Cathode → +ve

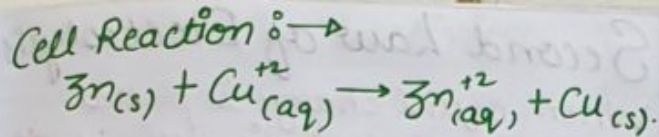
Cell Rx.ⁿ → Spontaneous

Salt Bridge required

Anode → +ve, Cathode → -ve

Cell Rx.ⁿ → non spontaneous

Salt Bridge not required



Current Flow \rightarrow

Anode \rightarrow Cathode: Internal Circuit.

Cathode \rightarrow Anode: External Circuit.

$[Zn^{2+}]$ ions in anode sol. \uparrow , mass of Cu \uparrow
mod

$[Cu^{2+}]$ ions in cathode sol. \downarrow , mass of Zn \downarrow
mod

Salt Bridge and its Function \rightarrow

\rightarrow Salt ^{bridge} is U-shaped glass filled with a jelly like substance, agar-agar (plant gel) mixed with an electrolyte like KCl, KNO_3 , NH_4NO_3 etc..

\rightarrow The electrolyte in salt bridge should be such that speed of its cation is nearly equal to speed of its anion.

\rightarrow It connects sol. of two half cell to complete the circuit.

\rightarrow It maintains the electrical neutrality of the solution.

\rightarrow If salt bridge \rightarrow removed, Voltage drops to zero.

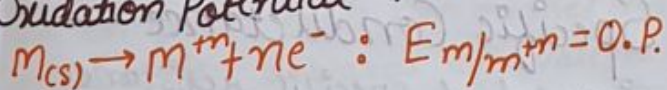
\rightarrow It prevents liquid-liquid junction potential.

Electrode Potential

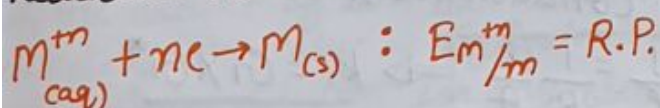
\hookrightarrow Potential difference b/w the electrode and electrolytic solution.

\rightarrow At 1 bar, 298K, 1M concentration, the potential difference is % standard electrode potential.

Oxidation Potential \rightarrow



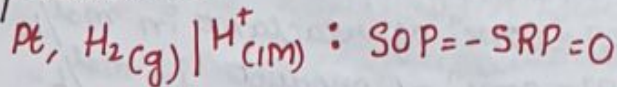
Reduction Potential \rightarrow



Reference Electrode

Standard Hydrogen Electrode (SHE) is taken as standard reference electrode. Its electrode potential is assumed to be 0.00 Volt.

Representation \rightarrow



Electrochemical Series:

arrangement of elements based on decreasing Value of reduction potential

Increasing strength of Oxidising agent.

Li	Sn
K	Pb
Ba	H₂
Na	Cu
Mg	I ₂
Al	Fe
Mn	Hg
H ₂ O	Ag
Zn	Br ₂
Cu	Pt
Fe	O ₂
Cd	Cl ₂
Co	F ₂
Ni	

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Application \rightarrow

Oxidising power $\propto SRP \propto \frac{1}{SOP}$

Reducing power $\propto SOP \propto \frac{1}{SRP}$

\rightarrow Metal above Hydrogen displaces H_2 from dil. Acid Solution.

Nernst Equation:

Relation b/w electrode potential, emf of cell, temperature, consⁿ of ion in solution represented by the equation.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \left[\frac{\text{product}}{\text{Reactant}} \right]$$

at 25°C $\rightarrow E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[P]}{[R]}$

E_{cell} = EMF of cell at new concentration

R = Gas Constant

n = number of electrons

E°_{cell} = Standard emf of cell (1M, 25°C, 1atm)

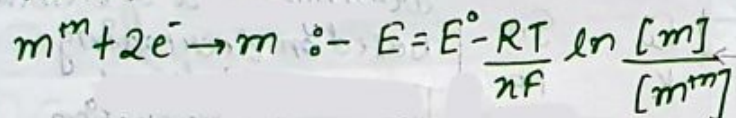
T = absolute temperature

F = Faraday Constant

$[R]$ = Concⁿ of reactant in mol/L

$[P]$ = concⁿ of product in mol/L

For the reaction \rightarrow



$[M^m] \uparrow \uparrow \rightarrow E_{\text{red}} \uparrow \uparrow$

$[M^m] \downarrow \downarrow \rightarrow E_{\text{oxi}} \uparrow \uparrow$

Spontaneity of Cell:

Spontaneous Cell: $-\Delta G < 0$; $\Delta E > 0$

Non-Spontaneous Cell: $-\Delta G > 0$; $\Delta E < 0$

At equilibrium: $-\Delta G = 0$; $\Delta E = 0$

$$\Delta G = -RT \ln^a$$

Quantitative aspect of electrolysis \rightarrow

First Law

The mass of a standard substance oxidised or reduced at an electrode is directly proportional to the amount of charge supplied.

$$W \propto Q$$

$$W = ZQ$$

$$W = ZIt$$

W = amount of substance deposited

Q = Charge in Coulomb

I = Current

t = time

Z = electrochemical equivalent

$$Z = \frac{E}{96500}$$

Second Law of Electrolysis

When equal charge is passed through 2 electrolytic cell and this cell are connected in series the mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Electrolytic Conductance

① Resistance (R) \rightarrow Metallic and electrolytic conductors obey Ohm's Law, according to which the resistance of a conductor is the ratio of applied potential difference (V) to the current (I) following.

$$R = \frac{V}{I} \quad ; \text{Unit} = \Omega (\text{ohm})$$

② Specific Resistance / Resistivity (ρ) \rightarrow The resistance offered by 1cm³ electrolytic solution is resistivity

$$R = \frac{\rho l}{A} \quad ; \text{Unit} = \Omega \text{cm}$$

③ Conductance (G) \rightarrow It is property by virtue of which it favours flow of current.

$$G = \frac{1}{R} \quad ; \text{Unit} = \Omega^{-1}, \text{mho/ohm}^{-1}, \text{Siemens}$$

④ Specific Conductance \rightarrow Reciprocal of specific resistance \rightarrow Conductance \times Cell Constant

$$\frac{1}{\rho} = \frac{1}{R} \frac{l}{A} \Rightarrow k_1 = G \times G^* \quad \text{Unit} = \text{ohm}^{-1} \text{cm}^{-1}$$

5) Molar Conductivity

The conductance of all ion produced by one mole of electrolyte present in the given volume of solution.

$$\Lambda_m = \frac{KA}{l}$$

Unit of $\Lambda_m = \text{sm}^2 \text{mol}^{-1} / \text{cm}^2 \text{mol}^{-1}$

6) Equivalent Conductance

Conductance of all the ion produced by one gram equivalent of the electrolyte in given volume of solution

$$\Lambda_m = K \cdot V = \frac{K \times 1000}{M}, \quad \Lambda_{eq} = KV = \frac{K \times 1000}{N}$$

$$\Lambda_{eq} = \frac{\Lambda_m}{\text{Valency factor.}}$$

Factor affecting electrolytic Conductance

- ① Inter ionic attraction
- ② Polarity of Solvent.
- ③ Viscosity of medium.
- ④ Temperature
- ⑤ Hydrated ion

Debye Huckel Onsager Equation

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c} \rightarrow \text{only for strong electrolyte.}$$

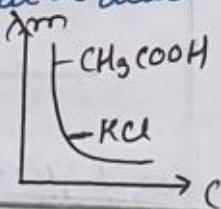
Λ_m = molar conductance at c .

Λ_m^∞ = molar conductance at ∞ dilution.

b = constant

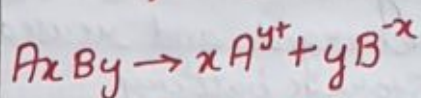
Kohlrausch's Law

→



At infinite dilution when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of ion with which it is associate the value of equivalent conductance at infinite dilution for any electrolyte is sum of contribution of its constituent ions.

$$\Lambda_{eq}^\infty = \lambda_c^\infty + \lambda_a^\infty$$



$$\therefore \Lambda_{eq}^\infty = \frac{1}{x} \lambda_{m(c)}^\infty + \frac{1}{y} \lambda_{a(c)}^\infty$$

Application of Kohlrausch Law

① To calculate degree of dissociation (α) = $\frac{\Lambda_{eq}}{\Lambda_{eq}^\infty}$

② To calculate solubility (s) = $\Lambda_m = \frac{K \cdot 1000}{\text{Solubility}}$

Corrosion → Process of metal surface into salt like oxides, sulphides, due to atmospheric gases.

Rust → It is hydrated ferric oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

Factors which enhance Corrosion

- ① Presence of impurities in metal.
- ② Presence of moisture.
- ③ Presence of electrolyte.

→ Corrosion can be prevented by Barrick protection, sacrificial protection.

Battery and Cell

Batteries → Source of electrical energy which may have one or more cells connected in series

① Primary Batteries →

R_x^n occurs only once and after use over a period of time, battery becomes dead and cannot be reused

ex- Dry cell and Leclanche cell
Mercury Cell

② Secondary Batteries

Cells can be recharged and reused.
eg. → Lead Storage battery
Nickel Cadmium Cell



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① Dry Cell :

Anode → Zinc Container

Cathode → Graphite Rod

Paste → $\text{NH}_4\text{Cl} + \text{ZnCl}_2$

Rxⁿ → $2\text{MnO}_2 + 2\text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$

Cell potential → 1.25V - 1.5V

② Mercury Cell :

Anode → Zn-Hg amalgam

Cathode → $\text{HgO} + \text{C}$

Paste → $\text{KOH} + \text{ZnO}$

Rxⁿ → $\text{Zn(Hg)} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$

Cell potential → 1.35V

① Lead Storage :

Anode → Spongy Lead

Cathode → Pb with PbO_2

Rxⁿ → $\text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{2-} \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

When recharged, cell Rxⁿ are reversed

② Nickel-Cadmium Storage Cell

Anode → Cadmium

Cathode → Metal NiO_2

Rxⁿ → $\text{Cd} + \text{NiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + \text{Ni(OH)}_2$

Cell potential → 1.4V

Nickel-Cadmium Cell has longer life than the lead storage cell

Fuel Cells → Galvanic Cells which are energy of combustion of fuel like H_2 , CH_4 ,

→ Pollution free and have high efficiency

ex. → Hydrogen, Oxygen fuel cells

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