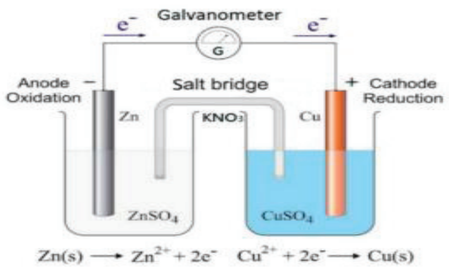
UNIT II ELECTROCHEMISTRY

Electrochemical cell: A device in which chemical energy of the redox reaction is converted into electrical energy. e.g., Daniel cell or Galvanic cell The overall cell reaction is:



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

The Daniel cell is represented as :

$Zn(s)|\ Zn^{2+}(aq)(C_1)\ ||\ Cu^{2+}(aq)\ (C_2)|\ Cu(s)$

Oxidation half   Reduction half

Salt Bridge and Its Functions: It consists KCl, KNO_3 or NH_4Cl .It helps in flow of ions by completing the circuit and maintains electrical neutrality.

Measurement of electrode potential: Potential of individual half-cell cannot be measured but we can measure the difference between the two half-cell potentials that gives the emf of the cell by using SHE (Standard Hydrogen electrode).

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Riglit} - E^0_{Left}$

Nernst equation: It is an equation which gives the relationship between electrode potential and the concentration of ions. For an electrode reaction (reduction reaction), $M^{n+}(aq) + ne^- \rightarrow M(s)$,

Nernst equation can be written as:

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

Where, $E_{Mn+/M}$ = Electrode potential,

$E^o_{Mn+/M}$ = Standard electrode potential

R = 8.314JK /mol,

T = Temperature in kelvin,

n = No. of electrons gained, F = Faraday constant (96500 C /mol)

Substituting the value of R and F we get

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \quad \text{at 298 K}$$

Thus, the reduction potential increases with the increase in the concentration of ions.

Nernst equation can be written as for a general reaction

aA+ bB → cC + dD

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Electrochemical cell and Gibbs Free Energy:

The work done by a reversible galvanic cell is equal to decrease in its free energy.

Mathematically, $\Delta rG = -nFE$cell

If concentration of all the reacting species is unity, then Ecell = $E°$cell

and we get, $\Delta rG = -nFE°$cell

$\Delta rG = -RT\ln Kc$ or $\Delta rG = -2.303RT\log Kc$

Measurement of Conductance: The resistance of electrolytic solution is determined by Wheatstone bridge method having variable resistance (R1), fix resistance (R3 andR4) and unknown resistance (R2 = R) of electrolyte solution. A null point detected by P detector such that, $R1/R2 = R3/R4$ or $R2 = R1R4/R3$ The reciprocal of $R2$ gives the conductance (G)of the solution as,

$\kappa = \frac{1 \times l}{R \times A} = G \times G^*$ $l/A = G^*$ (called as cell constant.

Conductance of Electrolytic solutions:

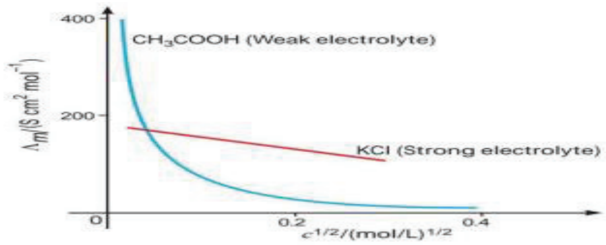
Resistance (R) - Obstruction to the flow of current, $R = \rho\, l/A$, Its SI unit is ohm.

Resistivity(ρ) - Electrical resistance of a conductor of unit cross-sectional area and unit length.

$\rho = R\,A/l$, Its SI unit is ohm metre

Limiting molar conductivity: When concentration approaches zero i.e., at infinite dilution, the molar conductivity is known as limiting molar conductivity ($\Lambda°\,m$).

Variation of Conductivity and Molar Conductivity with Concentration:



For strong and weak electrolytes:. Λn increases as concentration decreases but does not reach a constant value even at infinite dilution. Hence, their $\Lambda°$m cannot be determined experimentally.

Kohlrausch's Law: It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. $\Lambda^o = v_+\lambda_+^o + v_-\lambda$

Applications of Kohlrausch's law:

(a) Calculation of molar conductivities of weak electrolyte at infinite dilution i.e.,

$\Lambda°(CH3COOH) = \Lambda°m(CH3COONa) + \Lambda°m(HCl) - \Lambda°m(NaCl)$

(b) Determination of degree of dissociation of weak electrolytes: Degree of dissociation $(\alpha) = \Lambda m / \Lambda°m$

(c) Determination of dissociation constant (K) of weak electrolytes: $Ka = C\alpha^2/ 1\text{-}\alpha$.

Faraday's first law of electrolysis: The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.

$m = Z \times I \times t$ where Z = Electrochemical equivalent

Faraday's second law of electrolysis: amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

$W1/E1 = W2/E2$

Battery: Combination of galvanic cells in series and used as a source of electrical energy.

(i) Primary batteries are non-chargeable batteries such as Leclanche cell and Dry cell.

(ii) Secondary batteries are chargeable cells involving reversible reaction.

Example, Lead storage battery and Nickel-cadmium cells.

Dry cell (Leclanche cell): The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO2 and C. The space is filled with paste of NH4Cl and ZnCl2.

At anode: Zn(s) → Zn2+(aq) + 2e– At cathode: MnO2 (s) + NH4 +(aq)+ 2e– → MnO(OH) + NH3

The net reaction: $Zn + NH_4^+(aq) + MnO2 \rightarrow Zn^{2+} + MnO(OH) + NH_3$

Mercury cell: consists of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

Anode: Zn(Hg) + 2OH-→ ZnO(s) + H2O + 2e –

Cathode: HgO(s) + H2O + 2e- → Hg (l) + 2OH–

Lead storage battery: Anode – lead . cathode – lead oxide

At anode : Pb(s) +SO4 2–(aq) → PbSO4 (s) +2e–

At cathode: PbO2 (s) + 4H+(aq) + SO4 2–(aq) + 2e– → PbSO4 (s) + 2H2O(l)

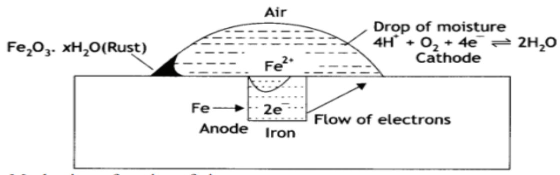
Complete cell reaction: $Pb(s) + PbO2\ (s) + 2H2\ SO4\ (aq) \rightarrow 2PbSO4\ (s) + 2H_2O(l)$

Recharge reaction of cell: PbSO4 (s) + 2H2O(l) → Pb(s) + PbO2 (s) + 2H2SO4 (aq)

Nickel–cadmium cell which has longer life than the lead storage cell but is costly.
overall reaction $Cd(s) + 2Ni(OH)_3 (s) \rightarrow CdO(s) + 2Ni(OH)_2 (s) + H_2O(l)$

Fuel cells: Electrical cells that are designated to convert the energy from the combustion of fuelssuch as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells. the cell reactions are: Anode: $2H_2 (g) + 4OH^- (aq) \rightarrow 4H_2O (l) + 4e^-$,
Cathode: $O_2 (g) + 2H_2O(l) + 4e^- \rightarrow 4OH^- (aq)$ Net reaction: $2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

Corrosion: The process of slow conversion of metals into their undesirable compounds by reaction with moisture and other gases present in the atmosphere. Rusting of iron:



Mechanism of rusting of air.

Oxidation: $Fe(s) \rightarrow Fe^{+2} (aq) + 2e^-$
Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Atmospheric oxidation $2Fe^{+2}(s) + \frac{1}{2} O_2 (g) + 2H_2O(l) \rightarrow Fe_2O_3 + 4H^+(aq)$, $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.xH_2O$

Prevention of Corrosion: (i) Barrier protection: By covering the surface with paint or a thin film of grease or by electroplating. (ii) Sacrificial protection: By galvanization. (iii) Alloying

Name of cell/ battery	Anode	Cathode	Electrolyte
Dry cell	Zinc	Graphite; MnO_2 + C (touching cathode)	$NH_4Cl + ZnCl_2$ (touching anode)
Mercury cell (used in watches,hearing aids)	Zinc-mercury amalgam	Paste of HgO & carbon	Paste of KOH & ZnO
Lead storage battery	Lead	Lead dioxide PbO_2	H_2SO_4 (38%)
Ni-Cd cell	Cadmium	$[Ni(OH)_3]$	KOH solution
H_2O_2 Fuel cell	Porous carbon containing catalysts (H_2 passed)	Porous carbon containing catalysts (O_2 passed)	Conc. Aq. NaOH solution

MULTIPLE CHOICE QUESTIONS (1 MARKS)

Q1. Which metal is used as electrode which do not participate in the reaction but provides surface for conduction of electrons? (a) Cu (b) Pt (c) Zn (d) Fe

Q2. An electrochemical cell can behave like an electrolytic cell when
(a) Ecell = 0 (b) Ecell > Eext (c) Eext > Ecell (d) Ecell = Eext

Q3. Fused NaCl on electrolysis gives ………….. on cathode.
(a) Chlorine (b) Sodium (c) Sodium amalgam (d) Hydrogen

Q4. The charge required for reducing 1 mole of MnO_4^- to Mn^{2+} is
(a) 1.93×10^5 C (b) 2.895×10^5 C (c) $4.28 \times {}^5$C (d) 4.825×10^5 C

Q5. Which of the following is supplied to the cathode of a fuel cell?
(a) Hydrogen (b) Nitrogen (c) Oxygen (d) Chlorine