ELECTROCHEMISTRY

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In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).

Rusting of Iron: According to electrochemical theory, rusting can be represented as:

Oxidation at Anode: $Fe \rightarrow +Fe^{2+} + 2e^-; E^\circ_{oxi} = -0.44\ V$

Reduction at Cathode: $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$

$2H^+(aq) + 2e^- \rightarrow 2H$

$2H + \frac{1}{2}O_2 \rightarrow H_2O$

$2H^+ + \frac{1}{2}O_2 + 2e \rightarrow H_2O; E^\circ_{red} = 1.23\,V$

Overall reaction of corrosion cell:

$$Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O; E^\circ_{cell} = 1.67\,V$$

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{Rust}}{Fe_2O_3.xH_2O}$$

Prevention of Corrosion

- The metal surface is coated with paint which keeps it out of contact with air, moisture etc.
- By applying film of oil and grease on the surface of the iron tools and machinery.
- The iron surface is coated with non-corroding.

Faraday's First Law: When an electric current is passed through an electrolyte, the amount of substance deposited or liberated at an electrode is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation. $W \propto Q$

A coulomb is the quantity of charge when a current of one ampere is passed for one second.

Q = current in amperes × time in seconds = I × t

$W \propto I \times t$

$W = Z \times I \times t$

where Z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

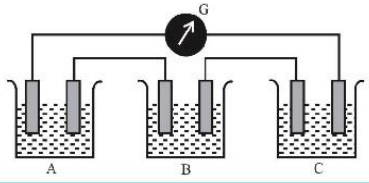
Electro-chemical equivalent

$$(Z) = \frac{\text{equivalent wt. of element}}{96500}$$

Faraday's Second Law: It states that when same quantity of electricity is passed through different electrolytes, then the quantity of deposit is directly proportional to respective equivalent weight. (Equivalent wt. of electrolytes).

$W \propto E$

$$\frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C}$$



Regardless whether a cell is a voltaic or an electrolytic-cell,
—The anode is the electrode at which oxidation occurs
—The cathode is the electrode at which reduction occurs

	Voltaic cell	Electrolytic-cell
Anode	Oxidation, Negative (–) terminal	Oxidation positive (+) terminal
Cathode	Reduction Positive (+) terminal	Reduction negative (–)terminal

- Electrode potential

$E_{cell} = E^o_{right} - E^o_{left}$

For SHE, $E^\circ_{cell} = 0$

- **Nernst equation:**

For reaction, $M^{n+} + ne^- \rightarrow M(s)$

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

- **For reaction :**

$aA + bB \rightarrow cC + dD$

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

At equilibrium $E_{cell} = 0$

$$E^o_{cell} = \frac{2.303RT}{nF}\log K_c$$

$$\Delta_r G = -nFE_{cell} \text{ or } \Delta_r G = -nFE^o_{cell}$$

- **Electrochemical series:** Arrangement of elements in order of increasing value of E^o red. Reducing nature decreases form top.

Name of cell/Battery	Anode (–)	Cathode (+)	Electrolyte	Reaction at electrodes	E_{cell}
• Dry cell (primary cell)	Zn container	Graphite rod	Powdered $MnO_2 + C$ + Paste of $NH_4Cl + ZnCl_2$	**Anode:** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ **Cathode:** NH_3 forms complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$ $MnO_2 + 2NH_4^+ + e^- \rightarrow MnO(OH) + NH_3 \cdot NH_3$ Forms Complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$	1.25 to 1.5 V
• Mercury cell (primary cell)	Zn-Hg amalgam	Paste of HgO andC	Paste of KOH + ZnO	**Anode:** $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ **Cathode:** $HgO + H_2O + 2e^- \rightarrow Hg(1) + 2\bar{O}H$	1.35 V
• Lead storage Battery (secondary cell)	Pb	Pb + PbO_2	38% by mass H_2SO_4 (d=1.30 g cm^{-3})	**Anode:** $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ **Cathode:** $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(1)$ On applying a potential slightly greater than the potential of battery, battery can be recharged.	12 V consists of 6 cell each producing 2 V
• Ni-Cd Secondary cell Or Ni-Cd cell (Rechar-geable)	Cd	NiO_2	Moist KOH	**Anode :** $Cd(s) + 2OH(aq) \rightarrow Cd(OH)_2(s) + 2e^-$ **Cathode :** $NiO_2(s) + 2H_2O + 2e^- \rightarrow Ni(OH)_2(s) + 2OH(aq)$	1.4 V
• Fuel cell (H_2-O_2)	Porous carbon containing catalyst (finely divided Pt and Pd)	Porous carbon containing catalyst (finely divided Pt and Pd)	Concentrated NaOH solution	**Anode :** $2H_2(g) + 4OH^-(aq) 4H_2O(1) + 4e^-$ **Cathode :** $O_2(g) + 2H_2O(1) + 4e^- \rightarrow 4OH^-(aq)$	0.09 V

Conductance of Electrolytic Solutions:

- Conductance (G) = $\frac{1}{\text{Resistance}}$

Unit: ohm^{-1} or Siemens

- Specific conductivity (κ) = $G\frac{l}{a}\left(\frac{l}{a} = \text{cell constant}\right)$

Unit = $ohm^{-1}\ cm^{-1}$ or Scm^{-1}

- Molar conductance $(\Lambda_m) = \frac{1000 \times \kappa}{M}$

Unit = $Scm^2\ mol^{-1}$

- Equivalent conductance $(\Lambda_{eq}) = \frac{1000 \times \kappa}{N}$

Unit = $cm^2 ohm^{-1}\ g - eq^{-1}$

Conductance (G), molar conductance (Λ_m) and equivalent conductance (Λ_{eq}) increase with dilution where as specific conductance (κ) decrease with dilution

Effect of concentration on Λ_m:

- **For strong electrolytes,** Λ_m increases slowly with dilution and can be represented by the equation: $\Lambda_m = \Lambda^o_m - AC^{1/2}$ **(Debye-Huckel Onsager equation)**

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '$-A$.'

Thus, Λ_m decreases linearly with $\sqrt{C}$, when C = 0, $\Lambda_m = \Lambda^\circ_m$ and Λ°_m can be determined experimentally.

- For weak electrolytes, Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, there Λ°_m cannot be determined experimentally.
- **Kohlrausch's Law :**

$\Lambda^\infty_{eq} = \lambda^\circ_+ + \lambda^\circ_-$

Where = λ°_+ is the limiting equivalent conductivity of the cation and λ°_- is the limiting equivalent conductivity of the anion. These contributions are called limiting equivalent conductances at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

Applications of Kohlrausch's Law:

- **Calculation of Molar Conductivity at Infinite Dilution for Weak Electrolytes:** In order to calculate Λ^∞_m or Λ^∞_m of a weak electrolyte say CH_3COOH, we determine permentally Λ_m values of the strong electrol

$\Lambda^\infty_{m(CH_3COOH)} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$ …(i)

for strong electrolytes :

$\Lambda^\circ_{m(CH_3COOK)} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{K^+}$ …(ii)

$\Lambda^\circ_{m(HCl)} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$ …(iii)

$\Lambda^\circ_{m(KCl)} = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-}$ …(iv)

$\therefore$ eqn (ii) + eqn. (iii) – eqn (iv) = eqn (i)

i.e.,

$\Lambda^\infty_{m(CH_3COOK)} + \Lambda^\infty_{m(HCl)} - \Lambda^\infty_{m(KCl)}$

$= \Lambda^\infty_{m(CH_3COOH)}$

- **Calculation of the Degree of Dissociation :**

Λ^c_m is the molar conductivity of a solution at any concentration C and Λ°_m the molar conductivity at infinite dilution (i.e., zero concentration), we will have

$\alpha = \frac{\text{no.of dissociat edions}}{\text{no. of totalions present}}$;

Degree of dissociation $(\alpha) = \frac{\Lambda^c_m}{\Lambda^\circ_m}$

- **Calculation of Dissociation Constant of a Weak Electrolyte :**

$$K_c = \frac{C\alpha^2}{1-\alpha}$$