# ELECTROCHEMISTRY

PHYSICS WALLAH

## 1 Electrochemical Cell

| Left side | Right side |
|---|---|
| Oxidation | Reduction |
| Anode | Cathode |
| Negative | Positive |

## 2 Representation of cell

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

$R_a|\ P_a||\ R_c|\ Pc$

↙ Product at anode ↘ Reactant at cathode

- Electrode potential ($E_{M^{n+}/M}$)

E.P= Reduction Potential (R.P) = -Oxidation potential (O.P)

If R.P=x, then O.P=-x

Representation of Reduction half reaction:

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

- Standard Reduction Potential(SRP) ($E^0_{M^{n+}/M}$)

R.P at 1M and 298K.
SRP is calculated by using SHE

Respresentation of SHE

$H^+_{(1M)}|\ H_{2\ (g,1\ bar)}\ |\ Pt_{(s)}$ , $E^0_{SHE}=0$

## 3 Electrochemical series

| Equilibrium (Oxidants ⇌ Reductants) | $E^\circ$ (volts) |
|---|---|
| Lithium: $Li^+(aq) + e^- \leftrightarrow Li(s)$ | -3.03 |
| Potassium: $K^+(aq) + e^- \leftrightarrow K(s)$ | -2.92 |
| Calcium: $Ca^{2+}(aq) + 2e^- \leftrightarrow Ca(s)$ | -2.87 |
| Sodium: $Na^+(aq) + e^- \leftrightarrow Na(s)$ | -2.71 |
| Magnesium: $Mg^{2+}(aq) + 2e^- \leftrightarrow Mg(s)$ | -2.37 |
| Aluminum: $Al^{3+}(aq) + 3e^- \leftrightarrow Al(s)$ | -1.66 |
| Zinc: $Zn^{2+}(aq) + 2e^- \leftrightarrow Zn(s)$ | -0.76 |
| Iron: $Fe^{2+}(aq) + 2e^- \leftrightarrow Fe(s)$ | -0.44 |
| Lead: $Pb^{2+}(aq) + 2e^- \leftrightarrow Pb(s)$ | -0.13 |
| Hydrogen: $2H^+(aq) + 2e^- \leftrightarrow H_2(g)$ | 0.00 |
| Copper: $Cu^{2+}(aq) + 2e^- \leftrightarrow Cu(s)$ | +0.34 |
| Silver: $A^+(aq) + e^- \leftrightarrow Ag(s)$ | +0.80 |
| Gold: $Au^{3+}(aq) + 3e^- \leftrightarrow Au(s)$ | +1.50 |
| Flourine: $F_2 + 2e^- \longleftrightarrow 2F^-$ | +2.87 |

Metal Reducing Activity Increasing ↑ ↓ Metal Oxidizing Activity Increasing

SRP↑=O.A.
SRP↓= R.A.

Metals with high SRP = less reactive
Metals with low SRP = highly reactive

## 4 EMF of a cell

$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$

$E_{cell} = RP_{Cathode} - RP_{Anode}$

$E_{cell} = RP_{Cathode} + OP_{Anode}$

$E_{cell} = OP_{Anode} - OP_{Cathode}$

In cell, Cathode with high RP, Anode with low RP makes spontaneous reactions

## 5 Nernst equation

$E_{cell} = E^0_{Cell} - \frac{0.0591}{n} \log\left[\frac{Product}{Reactant}\right]$

For $Zn|\ Zn^{2+}||\ Cu^{2+}|\ Cu$

$E_{cell} = E^0_{Cell} - \frac{0.0591}{2} \log\left[\frac{Zn^{2+}}{Cu^{2+}}\right]$

For $Ni|\ Ni^{2+}||\ Ag^+|\ Ag$

$E_{cell} = E^0_{Cell} - \frac{0.0591}{2} \log\left[\frac{Ni^{2+}}{(Ag^+)^2}\right]$

$R_1|\ P_1||\ R_2|\ P_2$

If $R_2 \uparrow, P_1 \downarrow$ then $E_{cell} \uparrow$

## 6 Application of Nernst Equation

- Electrode Potential

$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$

- Nernst equation in SHE

1) $E_{H^+/H_2} = -\frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$

2) If, $P_{H_2} = 1$ atm

(R.P.)= $E_{H^+/H_2} = -0.0591$ pH

(O.P.)= $E_{H_2/H^+} = +0.0591$ pH

- Concentration Cells

$Zn\ |\ Zn^{2+}_{(C_1)}\ ||\ Zn^{2+}_{(C_2)}\ |\ Zn$

$E_{cell} = \frac{0.0591}{n} \log\left|\frac{cathode.C_2}{anode.C_1}\right|$

$\frac{C_2}{C_1} > 1 \Rightarrow \log\left(\frac{C_2}{C_1}\right) > 0 \quad \therefore E_{cell} > 0$

## 7 EMF: $K_c$ & $\Delta G$

$E^0_{cell} = \frac{0.0591}{n} \log K_c$, $\log K_c = \frac{nE^0_{cell}}{0.0591}$

$\Delta G = -nFE_{cell}$

| Spontaneous | Non-spontaneous |
|---|---|
| $\Delta G < 0$ | $\Delta G > 0$ |
| $E^0_{cell} > 0$ | $E^0_{cell} < 0$ |
| $\log K_c > 0$ | $\log K_c < 0$ |
| $K_c > 1$ | $K_c < 1$ |

Galvanisation is applying coating of Zn

## 1 Electrolytic cell



| ANODE | CATHODE |
|---|---|
| • Anion goes to anode | • Cation goes to cathode |
| • +ve electrode | • -ve electrode |
| • Oxidation | • Reduction |
| • $A \rightarrow A^+ + e^-$ | • $B + 1e^- \rightarrow B^-$ |
| • $A \rightarrow A^{n+} + ne^-$ | • $B^n + ne^- \rightarrow B^-$ |

## 2 Product of electrolysis

Deposition order of cation: (order of R.P)

$Li^+ < K^+ < Ca^{2+} < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Ni^{2+} < H^+ < Cu^{2+} < Hg^{2+} < Ag^+ < Au^{3+}$

Deposition order of anion

$SO_4^{2-} < NO_3^- < OH^- < Cl^- < Br^- < I^-$

Note:

1) For conc. $H_2SO_4$

Anode: $H^+ + 1e^- \rightarrow 1/2\ H_2$

Cathode: $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ (peroxo disulphate ion)

2) Very dil. NaCl($H_2O$ >> NaCl)

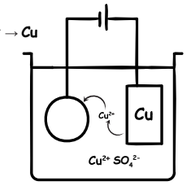
Anode: $H^+ + 1e^- \rightarrow 1/2\ H_2$

Cathode: $2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$

3) For $CuSO_4$ with Cu electrode

Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$




Electroplating

## 3 Faraday's law

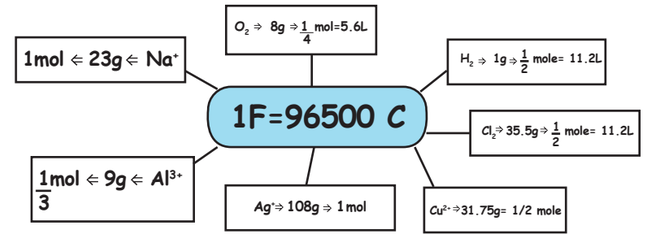
Product formed

$m = \frac{EM}{96500} \times It$

$EM = \frac{AM}{valency}$

1F=charge of 1 mole of $e^-$

=96500 C




$Na^+ + e^- \rightarrow Na \Rightarrow 1F$
$Mg^{2+} + 2e^- \rightarrow Mg \Rightarrow 2F$
$Al^{3+} + 3e^- \rightarrow Al \Rightarrow 3F$

} 1F displaces & gives 1 equivalent of product

## 4 Electrolytic conduction

Resistance(R)= $\rho \frac{l}{A}$ Unit of R = Ω, ρ = Ωm

Conductance(C) = $\frac{1}{R}$ C = $\Omega^{-1}$=S=mho

Conductivity(K) = $\frac{1}{\rho}$ K = $\Omega^{-1}m^{-1}$ or $Sm^{-1}$

$1Scm^{-1} = 100\ Sm^{-1}$

| Molar Conductivity ($\lambda_m$) | Equivalent Conductivty ($\lambda_{eq}$) |
|---|---|
| $\lambda_m = \frac{1000\ K}{M}$ | $\lambda_{eq} = \frac{1000\ K}{N}$ |
| $K \rightarrow Scm^{-1}$ | $K \rightarrow Scm^{-1}$ |
| $M \rightarrow mol\ L^{-1}$ | $N \rightarrow eq\ L^{-1}$ |
| $\lambda_m \rightarrow Scm^2\ mol^{-1}$ | $\lambda_{eq} \rightarrow Scm^2\ eq^{-1}$ |

$1Scm^2\ mol^{-1} = 10^{-4}\ Sm^2 mol^{-1}$

$\boxed{\lambda_m = \lambda_{eq} \times Z}$

$N > M \therefore \lambda_m > \lambda_{eq}$

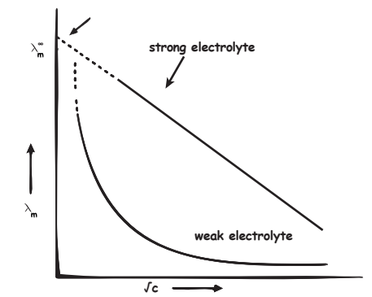
For $H_2SO_4$, Z = 2 ($2H^+$)
NaCl, Z = 1 ($1Na^+$)
$Al_2(SO_4)_3$, Z = 6 ($2Al^{3+}$)

$\lambda_m$ for SE increases with dilution (interionic attraction decreases)

$\boxed{\lambda_m = \lambda^\infty_m - b\sqrt{c}}$ (Debye-Huckel Onsagar equation)

At $\sqrt{c}=0$, $\lambda_m = \lambda^\infty_m$ (limiting molar conductivity)

$\lambda_m$ of weak electrolytes increases with dilution ( degree of dissociation increases)




$\lambda^\infty_m$ order : KCl > NaCl > LiCl

$\lambda^\infty_m$ Conductance $\propto \frac{1}{\text{Hydrated Radii}}$

## 5 Kohlrausch's law

$\lambda^\infty_M(AB_2) = \lambda^\infty_M(A^{2+}) + 2\lambda^\infty_M(B^-)$

$\lambda^\infty_{eq}(AB_2) = \lambda^\infty_M(A^{2+}) + \lambda^\infty_{eq}(B^-)$

For $Al_2(SO_4)_3$

$\lambda^\infty_M(Al_2(SO_4)_3) = 2\lambda^\infty_M(Al^{3+}) + 3\lambda^\infty_M(SO_4^{2-})$

$\lambda^\infty_{eq}(Al_2(SO_4)_3) = \lambda^\infty_{eq}(Al^{3+}) + \lambda^\infty_{eq}(SO_4^{2-})$

Application

$\lambda^\infty_M\ NH_4OH = \lambda^\infty_M NH_4Cl + \lambda^\infty_M NaOH - \lambda^\infty_M NaCl$

$\lambda^\infty_M\ CH_3COOH = \lambda^\infty_M CH_3COONa + \lambda^\infty_M HCl - \lambda^\infty_M NaCl$

$\lambda^\infty_M\ BaSO_4 = \lambda^\infty_M BaCl_2 + \lambda^\infty_M Na_2SO_4 - 2\lambda^\infty_M NaCl$