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

Table 1: Electrochemical Series	
Equilibrium (Oxidants ↔ Reductants)	E° (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 & ΔG

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

$\Delta G = -nFE_{cell}$

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

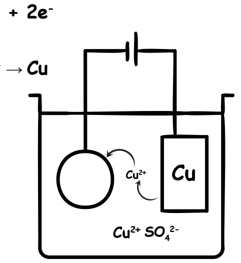
Deposition order of cation: (order of R.P)

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

Deposition order of anion

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

Note:

1) For conc. H_2SO_4	3) For $CuSO_4$ with Cu electrode
Anode: $H^+ + 1e^- \rightarrow 1/2\ H_2$ Cathode: $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ (peroxo disulphate ion)	Anode: $Cu \rightarrow Cu^{2+} + 2e^-$ Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
2) Very dil. NaCl(H_2O>>NaCl)	
Anode: $H^+ + 1e^- \rightarrow 1/2\ H_2$ Cathode: $2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$	 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

1F=96500 C

- $O_2 \Rightarrow 8g \Rightarrow \frac{1}{4}$ mol=5.6L
- $H_2 \Rightarrow 1g \Rightarrow \frac{1}{2}$ mole= 11.2L
- $Cl_2 \Rightarrow 35.5g \Rightarrow \frac{1}{2}$ mole= 11.2L
- $Cu^{2+} \Rightarrow 31.75g$= 1/2 mole
- $Ag^+ \Rightarrow 108g \Rightarrow 1$ mol
- $\frac{1}{3}mol \Leftarrow 9g \Leftarrow Al^{3+}$
- $1mol \Leftarrow 23g \Leftarrow Na^+$

4 Electrolytic conduction

Resistance(R)= $\rho\frac{l}{A}$

Unit of R = Ω
$\rho = \Omega m$
$C = \Omega^{-1}$=S=mho
$K = \Omega^{-1}m^{-1}$ or Sm^{-1}
$1Scm^{-1} = 100\ Sm^{-1}$

Conductance(C) = $\frac{1}{R}$

Conductivity(K) = $\frac{1}{\rho}$

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

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

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

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

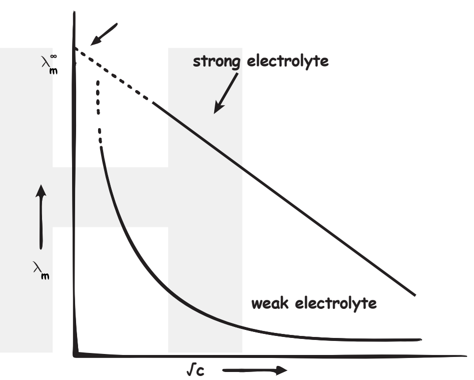
For H_2SO_4, Z = 2 ($2H^+$)
NaCl, Z = 1 ($1Na^+$)
$Al_2(SO_4)_3$, Z = 6 ($2Al^{3+}$)

λ_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)

λ_m of weak electrolytes increases with dilution (degree of dissociation increases)



λ^∞_m order : KCl > NaCl > LiCl

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

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

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

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