ELECTROCHEMISTRY

1 Electrochemical Cell

Left side	Right side
Oxidation	Reduction
Anode	Cathode
Negative	Positive

2 Representation of cell

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

$R_a | P_a || R_c | P_c$

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) ($E^o_{M^{n+}/M}$)
  R.P at 1M and 298K.
  SRP is calculated by using SHE
  Respresentation of SHE
  $H^+_{(1M)} | H_{2\,(g,1\,bar)} | Pt_{(s)}$ $E^o_{SHE}=0$

3 Electrochemical series

Table 1: Electrochemical Series

Metal Reducing Activity Increasing ↑ — Metal Oxidizing Activity Increasing ↓

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

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

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

$\Delta G = -nFE_{cell}$

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

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

1F=96500 C

- 1mol ⇐ 23g ⇐ Na^+
- $O_2 \Rightarrow 8g \Rightarrow \frac{1}{4}$ 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
- $\frac{1}{3}$mol ⇐ 9g ⇐ Al^{3+}
- $Ag^+ \Rightarrow 108g \Rightarrow 1$ mol
- $Cu^{2+} \Rightarrow 31.75g$= 1/2 mole

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

1F displaces & gives 1 equivalent of product

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)

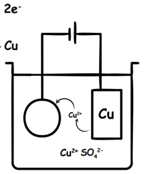
$Li^+ < K^+ < Ca^{2+} < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Ni^{2+} < H^+ < Cu^{2+} < Hg^{2+} < Ag^+ < Au^{3+}$

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



4 Electrolytic conduction

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

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

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

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

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

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

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

N>M ∴ $\lambda_m > \lambda_{eq}$

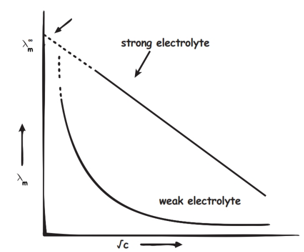
For H_2SO_4, Z = 2 ($2H^+$)
NaCl, Z = 1 ($1Na^+$)
$Al_2(SO_4)_3$, Z = 6 ($2Al^{3+}$)

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 ∝ $\frac{1}{\text{Hydrated Radii}}$

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

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

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

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