

1 Electrochemical Cell

Left side	Right side
Oxidation	Reduction
Anode	Cathode
Negative	Positive

2 Representation of cell

Zn | Zn²⁺ || Cu²⁺ | Cu
R_a | P_a || R_c | P_c

Product at anode Reactant at cathode

- Electrode potential (E_{Mⁿ⁺/M})
E.P = Reduction Potential (R.P)
= -Oxidation potential (O.P)
If R.P = x, then O.P = -x
- Representation of Reduction half reaction:
Mⁿ⁺ + ne⁻ → M
- Standard Reduction Potential (SRP) (E^o_{Mⁿ⁺/M})
R.P at 1M and 298K.
SRP is calculated by using SHE
- Representation of SHE
H⁺(1M) | H₂(g, 1 bar) | Pt(s) E^o_{SHE} = 0

3 Electrochemical series

[Oxidation] → [Reduction]	E ^o (volts)
Lithium: Li ⁺ (aq) + e ⁻ ↔ Li(s)	-3.03
Potassium: K ⁺ (aq) + e ⁻ ↔ K(s)	-2.92
Calcium: Ca ²⁺ (aq) + 2e ⁻ ↔ Ca(s)	-2.87
Sodium: Na ⁺ (aq) + e ⁻ ↔ Na(s)	-2.71
Magnesium: Mg ²⁺ (aq) + 2e ⁻ ↔ Mg(s)	-2.37
Aluminum: Al ³⁺ (aq) + 3e ⁻ ↔ Al(s)	-1.66
Zinc: Zn ²⁺ (aq) + 2e ⁻ ↔ Zn(s)	-0.76
Iron: Fe ²⁺ (aq) + 2e ⁻ ↔ Fe(s)	-0.44
Lead: Pb ²⁺ (aq) + 2e ⁻ ↔ Pb(s)	-0.13
Hydrogen: 2H ⁺ (aq) + 2e ⁻ ↔ H ₂ (g)	0.00
Copper: Cu ²⁺ (aq) + 2e ⁻ ↔ Cu(s)	+0.34
Silver: Ag ⁺ (aq) + e ⁻ ↔ Ag(s)	+0.80
Gold: Au ³⁺ (aq) + 3e ⁻ ↔ Au(s)	+1.50
Fluorine: F ₂ (g) + 2e ⁻ ↔ 2F ⁻ (aq)	+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

$$E_{cell}^o = E_{Cathode}^o - E_{Anode}^o$$

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

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

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

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

5 Nernst equation

$$E_{cell} = E_{cell}^o - \frac{0.0591}{n} \log \left[\frac{\text{Product}}{\text{Reactant}} \right]$$

For Zn | Zn²⁺ || Cu²⁺ | Cu

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

For Ni | Ni²⁺ || Ag⁺ | Ag

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

R₁ | P₁ || R₂ | P₂
If R₂ ↑, P₁ ↓ then E_{cell} ↑

6 Application of Nernst Equation

- Electrode Potential
 $E_{M^{n+}/M} = E_{M^{n+}/M}^o - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$
- Nernst equation in SHE
1) $E_{H^+/H_2} = -\frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$
2) If, P_{H₂} = 1 atm
(R.P.) = E_{H⁺/H₂} = -0.0591 pH
(O.P.) = E_{H₂/H⁺} = +0.0591 pH
- Concentration Cells
Zn | Zn_{(C₁)²⁺ || Zn_{(C₂)²⁺ | Zn}}
$$E_{cell} = \frac{0.0591}{n} \log \left(\frac{C_{cathode, C_2}}{C_{anode, C_1}} \right)$$

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

7 EMF; K_c & ΔG

$$E_{cell}^o = \frac{0.0591}{n} \log K_c, \log K_c = \frac{nE_{cell}^o}{0.0591}$$

$$\Delta G = -nFE_{cell}$$

Spontaneous	Non-spontaneous
ΔG < 0	ΔG > 0
E _{cell} ^o > 0	E _{cell} ^o < 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 → A ⁺ + e ⁻	• B + 1e ⁻ → B ⁻
• A → A ⁿ⁺ + ne ⁻	• B ⁿ⁺ + ne ⁻ → B ⁻

2 Product of electrolysis

Deposition order of cation: (order of R.P)
Li⁺ < K⁺ < Ca²⁺ < Na⁺ < Mg²⁺ < Al³⁺ < Zn²⁺
< Fe²⁺ < Ni²⁺ < H⁺ < Cu²⁺ < Hg²⁺ < Ag⁺ < Au³⁺

Deposition order of anion
SO₄²⁻ < NO₃⁻ < OH⁻ < Cl⁻ < Br⁻ < I⁻

Note: 1) For conc. H₂SO₄
Anode: H⁺ + 1e⁻ → 1/2 H₂
Cathode: 2SO₄²⁻ → S₂O₈²⁻ + 2e⁻ (peroxo disulphate ion)

2) Very dil. NaCl(H₂O >> NaCl)
Anode: H⁺ + 1e⁻ → 1/2 H₂
Cathode: 2OH⁻ → 1/2 O₂ + H₂O + 2e⁻

3) For CuSO₄ with Cu electrode
Anode: Cu → Cu²⁺ + 2e⁻
Cathode: Cu²⁺ + 2e⁻ → Cu

Electroplating

ELECTROCHEMISTRY

3 Faraday's law

Product formed

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

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

1F = charge of 1 mole of e⁻ = 96500 C

Na⁺ + e⁻ → Na ⇒ 1F
Mg²⁺ + 2e⁻ → Mg ⇒ 2F
Al³⁺ + 3e⁻ → Al ⇒ 3F

1F displaces & gives 1 equivalent of product

1F = 96500 C

- 1mol ⇔ 23g ⇔ Na⁺
- O₂ ⇒ 8g ⇒ 1/4 mole = 5.6L
- H₂ ⇒ 1g ⇒ 1/2 mole = 11.2L
- Cl₂ ⇒ 35.5g ⇒ 1/2 mole = 11.2L
- 1mol ⇔ 9g ⇔ Al³⁺
- Ag⁺ ⇒ 108g ⇒ 1mol
- Cu²⁺ ⇒ 31.75g ⇒ 1/2 mole

4 Electrolytic conduction

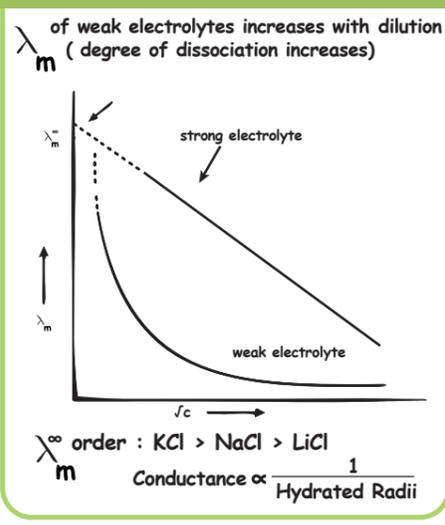
Resistance (R) = ρ l / A Unit of R = Ω
ρ = Ωm
Conductance (C) = 1/R C = Ω⁻¹ = S = mho
Conductivity (K) = 1/ρ K = Ω⁻¹m⁻¹ or Sm⁻¹
1Scm⁻¹ = 100 Sm⁻¹

Molar Conductivity (λ _m)	Equivalent Conductivity (λ _{eq})
λ _m = 1000 K / M	λ _{eq} = 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

1Scm² mol⁻¹ = 10⁻⁴ Sm² mol⁻¹
λ_m = λ_{eq} × Z
N > M ∴ λ_m > λ_{eq}

For H₂SO₄, Z = 2 (2H⁺)
NaCl, Z = 1 (1Na⁺)
Al₂(SO₄)₃, Z = 6 (2Al³⁺)

λ_m for SE increases with dilution (interionic attraction decreases)

$$\lambda_m = \lambda_m^\infty - b\sqrt{c}$$
 (Debye-Huckel Onsagar equation)
At √c = 0, λ_m = λ_m[∞] (limiting molar conductivity)


5 Kohlrausch's law

$$\lambda_{eq}^\infty(AB_2) = \lambda_{eq}^\infty(A^{2+}) + 2\lambda_{eq}^\infty(B^-)$$

$$\lambda_{eq}^\infty(AB_2) = \lambda_{eq}^\infty(A^{2+}) + \lambda_{eq}^\infty(B^-)$$

For Al₂(SO₄)₃

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

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

Application

$$\lambda_{eq}^\infty NH_4OH = \lambda_{eq}^\infty NH_4Cl + \lambda_{eq}^\infty NaOH - \lambda_{eq}^\infty NaCl$$

$$\lambda_{eq}^\infty CH_3COOH = \lambda_{eq}^\infty CH_3COONa + \lambda_{eq}^\infty HCl - \lambda_{eq}^\infty NaCl$$

$$\lambda_{eq}^\infty BaSO_4 = \lambda_{eq}^\infty BaCl_2 + \lambda_{eq}^\infty Na_2SO_4 - 2\lambda_{eq}^\infty NaCl$$