

### 1 Electrochemical Cell

Left side	Right side
Oxidation	Reduction
Anode	Cathode
Negative	Positive

### 2 Representation of cell

Zn | Zn<sup>2+</sup> || Cu<sup>2+</sup> | Cu  
R<sub>a</sub> | P<sub>a</sub> || R<sub>c</sub> | P<sub>c</sub>

Product at anode    Reactant at cathode

- Electrode potential (E<sub>M<sup>n+/M</sup></sub>)  
E.P = Reduction Potential (R.P)  
= -Oxidation potential (O.P)  
If R.P = x, then O.P = -x
- Representation of Reduction half reaction:  
M<sup>n+</sup> + ne<sup>-</sup> → M
- Standard Reduction Potential (SRP) (E<sup>o</sup><sub>M<sup>n+/M</sup></sub>)  
R.P at 1M and 298K.  
SRP is calculated by using SHE
- Representation of SHE  
H<sup>+</sup>(1M) | H<sub>2</sub>(g, 1 bar) | Pt(s)    E<sup>o</sup><sub>SHE</sub> = 0

### 3 Electrochemical series

Equilibrium (Oxidants ↔ Reductants)	E <sup>o</sup> (volts)
Lithium: Li <sup>+</sup> (aq) + e <sup>-</sup> ↔ Li(s)	-3.03
Potassium: K <sup>+</sup> (aq) + e <sup>-</sup> ↔ K(s)	-2.92
Calcium: Ca <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Ca(s)	-2.87
Sodium: Na <sup>+</sup> (aq) + e <sup>-</sup> ↔ Na(s)	-2.71
Magnesium: Mg <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Mg(s)	-2.37
Aluminum: Al <sup>3+</sup> (aq) + 3e <sup>-</sup> ↔ Al(s)	-1.66
Zinc: Zn <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Zn(s)	-0.76
Iron: Fe <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Fe(s)	-0.44
Lead: Pb <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Pb(s)	-0.13
Hydrogen: 2H <sup>+</sup> (aq) + 2e <sup>-</sup> ↔ H <sub>2</sub> (g)	0.00
Copper: Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Cu(s)	+0.34
Silver: Ag <sup>+</sup> (aq) + e <sup>-</sup> ↔ Ag(s)	+0.80
Gold: Au <sup>3+</sup> (aq) + 3e <sup>-</sup> ↔ Au(s)	+1.50
Fluorine: F <sub>2</sub> (g) + 2e <sup>-</sup> ↔ 2F <sup>-</sup> (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

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

For Zn | Zn<sup>2+</sup> || Cu<sup>2+</sup> | Cu

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

For Ni | Ni<sup>2+</sup> || Ag<sup>+</sup> | Ag

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

R<sub>1</sub> | P<sub>1</sub> || R<sub>2</sub> | P<sub>2</sub>  
If R<sub>2</sub> ↑, P<sub>1</sub> ↓ then E<sub>cell</sub> ↑

### 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<sub>H<sub>2</sub></sub> = 1 atm  
(R.P.) = E<sub>H<sup>+</sup>/H<sub>2</sub></sub> = -0.0591 pH  
(O.P.) = E<sub>H<sub>2</sub>/H<sup>+</sup></sub> = +0.0591 pH
- Concentration Cells  
Zn | Zn<sub>(C<sub>1</sub>)<sup>2+</sup> || Zn<sub>(C<sub>2</sub>)<sup>2+</sup> | Zn</sub></sub>
$$E_{cell} = \frac{0.0591}{n} \log \left( \frac{C_{cathode, C_2}}{C_{anode, C_1}} \right)$$

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

### 7 EMF; K<sub>c</sub> & 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 <sub>cell</sub> <sup>o</sup> > 0	E <sub>cell</sub> <sup>o</sup> < 0
log K <sub>c</sub> > 0	log K <sub>c</sub> < 0
K <sub>c</sub> > 1	K <sub>c</sub> < 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 <sup>+</sup> + e <sup>-</sup>	• B + 1e <sup>-</sup> → B <sup>-</sup>
• A → A <sup>n+</sup> + ne <sup>-</sup>	• B <sup>n+</sup> + ne <sup>-</sup> → B <sup>-</sup>

### 2 Product of electrolysis

Deposition order of cation: (order of R.P)  
Li<sup>+</sup> < K<sup>+</sup> < Ca<sup>2+</sup> < Na<sup>+</sup> < Mg<sup>2+</sup> < Al<sup>3+</sup> < Zn<sup>2+</sup>  
< Fe<sup>2+</sup> < Ni<sup>2+</sup> < H<sup>+</sup> < Cu<sup>2+</sup> < Hg<sup>2+</sup> < Ag<sup>+</sup> < Au<sup>3+</sup>

Deposition order of anion  
SO<sub>4</sub><sup>2-</sup> < NO<sub>3</sub><sup>-</sup> < OH<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>

Note: 1) For conc. H<sub>2</sub>SO<sub>4</sub>  
Anode: H<sup>+</sup> + 1e<sup>-</sup> → 1/2 H<sub>2</sub>  
Cathode: 2SO<sub>4</sub><sup>2-</sup> → S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + 2e<sup>-</sup> (peroxo disulphate ion)

2) Very dil. NaCl(H<sub>2</sub>O >> NaCl)  
Anode: H<sup>+</sup> + 1e<sup>-</sup> → 1/2 H<sub>2</sub>  
Cathode: 2OH<sup>-</sup> → 1/2 O<sub>2</sub> + H<sub>2</sub>O + 2e<sup>-</sup>

3) For CuSO<sub>4</sub> with Cu electrode  
Anode: Cu → Cu<sup>2+</sup> + 2e<sup>-</sup>  
Cathode: Cu<sup>2+</sup> + 2e<sup>-</sup> → Cu

Electroplating

# ELECTROCHEMISTRY

## 3 Faraday's law

Product formed

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

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

1F = charge of 1 mole of e<sup>-</sup> = 96500 C

Na<sup>+</sup> + e<sup>-</sup> → Na ⇒ 1F  
Mg<sup>2+</sup> + 2e<sup>-</sup> → Mg ⇒ 2F  
Al<sup>3+</sup> + 3e<sup>-</sup> → Al ⇒ 3F

1F displaces & gives 1 equivalent of product

1F = 96500 C

- 1mol ⇔ 23g ⇔ Na<sup>+</sup>
- 1mol ⇔ 9g ⇔ Al<sup>3+</sup>
- Ag<sup>+</sup> ⇒ 108g ⇒ 1mol
- Cu<sup>2+</sup> ⇒ 31.75g ⇒ 1/2 mole
- O<sub>2</sub> ⇒ 8g ⇒ 1/4 mole = 5.6L
- H<sub>2</sub> ⇒ 1g ⇒ 1/2 mole = 11.2L
- Cl<sub>2</sub> ⇒ 35.5g ⇒ 1/2 mole = 11.2L

### 4 Electrolytic conduction

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

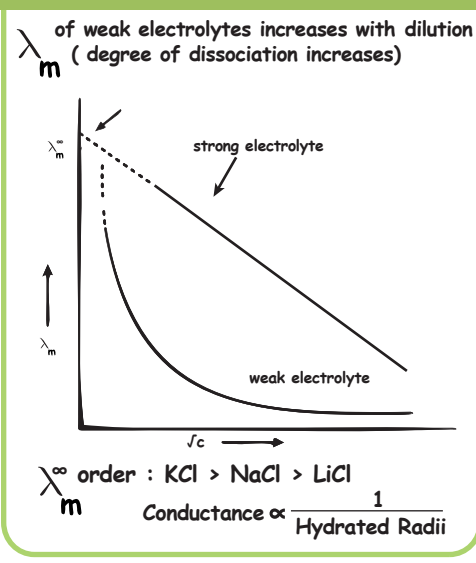
Conductivity (K) = 1/ρ

Molar Conductivity (λ <sub>m</sub> )	Equivalent Conductivity (λ <sub>eq</sub> )
λ <sub>m</sub> = 1000 K / M	λ <sub>eq</sub> = 1000 K / N
K → Scm <sup>-1</sup>	K → Scm <sup>-1</sup>
M → mol L <sup>-1</sup>	N → eq L <sup>-1</sup>
λ <sub>m</sub> → Scm <sup>2</sup> mol <sup>-1</sup>	λ <sub>eq</sub> → Scm <sup>2</sup> eq <sup>-1</sup>

1Scm<sup>2</sup> mol<sup>-1</sup> = 10<sup>-4</sup> Sm<sup>2</sup> mol<sup>-1</sup>  
λ<sub>m</sub> = λ<sub>eq</sub> × Z  
N > M ∴ λ<sub>m</sub> > λ<sub>eq</sub>

For H<sub>2</sub>SO<sub>4</sub>, Z = 2 (2H<sup>+</sup>)  
NaCl, Z = 1 (1Na<sup>+</sup>)  
Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Z = 6 (2Al<sup>3+</sup>)

λ<sub>m</sub> for SE increases with dilution (interionic attraction decreases)

$$\lambda_m = \lambda_m^\infty - b\sqrt{c}$$
 (Debye-Huckel Onsagar equation)  
At √c = 0, λ<sub>m</sub> = λ<sub>m</sub><sup>∞</sup> (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 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

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

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

Application

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

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

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