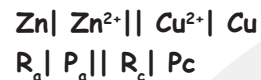


1 Electrochemical Cell

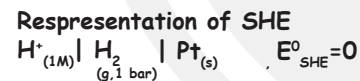
Left side Right side
Oxidation Reduction
Anode Cathode
Negative Positive

2 Representation of cell



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:
 $M^{n+} + ne^- \rightarrow M$
- Standard Reduction Potential (SRP) ($E_{M^{n+}/M}^0$)
R.P at 1M and 298K.
SRP is calculated by using SHE



3 Electrochemical series

Table 1: Electrochemical Series

Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)
Lithium: $\text{Li}^+ (\text{aq}) + e^- \leftrightarrow \text{Li} (s)$	-3.03
Potassium: $\text{K}^+ (\text{aq}) + e^- \leftrightarrow \text{K} (s)$	-2.92
Calcium: $\text{Ca}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Ca} (s)$	-2.87
Sodium: $\text{Na}^+ (\text{aq}) + e^- \leftrightarrow \text{Na} (s)$	-2.71
Magnesium: $\text{Mg}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Mg} (s)$	-2.37
Aluminium: $\text{Al}^{3+} (\text{aq}) + 3e^- \leftrightarrow \text{Al} (s)$	-1.66
Zinc: $\text{Zn}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Zn} (s)$	-0.76
Iron: $\text{Fe}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Fe} (s)$	-0.44
Lead: $\text{Pb}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Pb} (s)$	-0.13
Hydrogen: $2\text{H}^+ (\text{aq}) + 2e^- \leftrightarrow \text{H}_2 (g)$	0.00
Copper: $\text{Cu}^{2+} (\text{aq}) + 2e^- \leftrightarrow \text{Cu} (s)$	+0.34
Silver: $\text{Ag}^+ (\text{aq}) + e^- \leftrightarrow \text{Ag} (s)$	+0.80
Gold: $\text{Au}^{3+} (\text{aq}) + 3e^- \leftrightarrow \text{Au} (s)$	+1.50
Fluorine: $\text{F}_2 + 2e^- \leftrightarrow 2\text{F}^-$	+2.87

SRP \uparrow = O.A.
SRP \downarrow = R.A.
Metals with high SRP = less reactive
Metals with low SRP = highly reactive

4 EMF of a cell

$$E_{\text{cell}}^0 = E_{\text{Cathode}}^0 - E_{\text{Anode}}^0$$

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

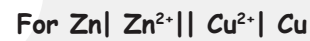
$$E_{\text{cell}} = RP_{\text{Cathode}} + OP_{\text{Anode}}$$

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

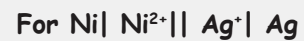
In cell, Cathode with high RP, Anode with low RP makes spontaneous reactions

5 Nernst equation

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



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



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

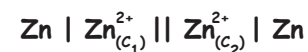


If $\text{R}_2 \uparrow, \text{P}_1 \downarrow$ then $E_{\text{cell}} \uparrow$

6 Application of Nernst Equation

- Electrode Potential
 $E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$
- Nernst equation in SHE
1) $E_{\text{H}^+/\text{H}_2} = -\frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$
2) If, $P_{\text{H}_2} = 1 \text{ atm}$
(R.P.) = $E_{\text{H}^+/\text{H}_2} = -0.0591 \text{ pH}$
(O.P.) = $E_{\text{H}_2/\text{H}^+} = +0.0591 \text{ pH}$

Concentration Cells



$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{\text{cathode } C_2}{\text{anode } C_1} \right)$$

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

7 EMF: K_c & ΔG

$$E_{\text{cell}}^0 = \frac{0.0591}{n} \log K_c, \log K_c = \frac{nE_{\text{cell}}^0}{0.0591}$$

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

Spontaneous	Non-spontaneous
$\Delta G < 0$	$\Delta G > 0$
$E_{\text{cell}}^0 > 0$	$E_{\text{cell}}^0 < 0$
$\log K_c > 0$	$\log K_c < 0$
$K_c > 1$	$K_c < 1$

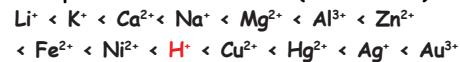
Galvanisation is applying coating of Zn

1 Electrolytic cell

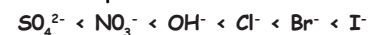
ANODE	CATHODE
• Anion goes to anode	• Cation goes to cathode
• +ve electrode	• -ve electrode
• Oxidation	• Reduction
• $A \rightarrow A^+ + e^-$	• $B + 1e^- \rightarrow B^-$
• $A \rightarrow A^{n+} + ne^-$	• $B^{n+} + ne^- \rightarrow B^-$

2 Product of electrolysis

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



Deposition order of anion



Note:

1) For conc. H_2SO_4 Anode: $\text{H}^+ + 1e^- \rightarrow 1/2 \text{H}_2$ Cathode: $2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2e^-$ (peroxo disulphate ion)	3) For CuSO_4 with Cu electrode Anode: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$ Cathode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
2) Very dil. $\text{NaCl} (\text{H}_2\text{O} \gg \text{NaCl})$ Anode: $\text{H}^+ + 1e^- \rightarrow 1/2 \text{H}_2$ Cathode: $2\text{OH}^- \rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O} + 2e^-$	Electroplating

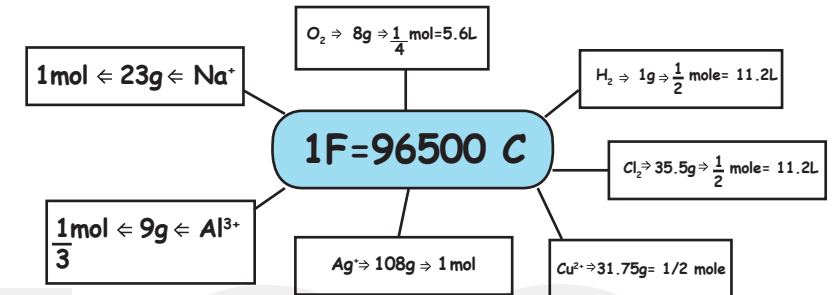
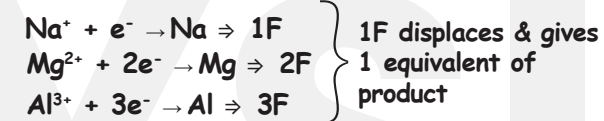
3 Faraday's law

Product formed

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

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

$$1F = \text{charge of 1 mole of } e^- = 96500 \text{ C}$$



4 Electrolytic conduction

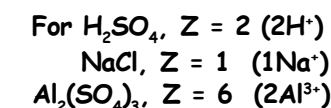
Resistance (R) = $\frac{\rho l}{A}$ Unit of R = Ω
 $\rho = \Omega m$
Conductance (C) = $\frac{1}{R}$ $C = \Omega^{-1} = S = \text{mho}$
Conductivity (K) = $\frac{1}{\rho}$ $K = \Omega^{-1} m^{-1} \text{ or } Sm^{-1}$
 $1 \text{ Sm}^{-1} = 100 \Omega^{-1} m^{-1}$

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

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

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

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

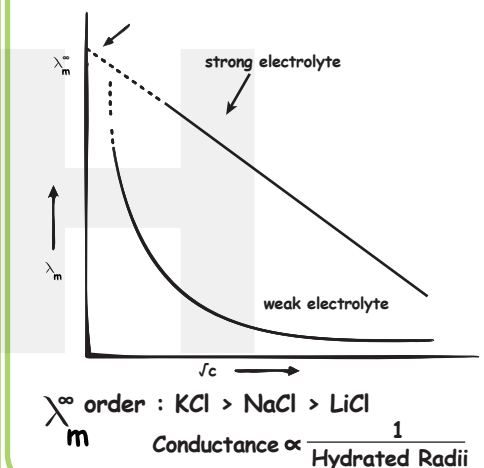


λ_m for SE increases with dilution (interionic attraction decreases)

$$\lambda_m = \lambda_m^\infty - b\sqrt{c} \quad (\text{Debye-Huckel Onsager equation})$$

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

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



5 Kohlrausch's law

$$\lambda_m^\infty (\text{AB}_2) = \lambda_m^\infty (\text{A}^{2+}) + 2 \lambda_m^\infty (\text{B}^-)$$

$$\lambda_{eq}^\infty (\text{AB}_2) = \lambda_m^\infty (\text{A}^{2+}) + \lambda_{eq}^\infty (\text{B}^-)$$

For $\text{Al}_2(\text{SO}_4)_3$

$$\lambda_m^\infty (\text{Al}_2(\text{SO}_4)_3) = 2 \lambda_m^\infty (\text{Al}^{3+}) + 3 \lambda_m^\infty (\text{SO}_4^{2-})$$

$$\lambda_{eq}^\infty (\text{Al}_2(\text{SO}_4)_3) = \lambda_{eq}^\infty (\text{Al}^{3+}) + \lambda_{eq}^\infty (\text{SO}_4^{2-})$$

Application

$$\lambda_m^\infty \text{NH}_4\text{OH} = \lambda_m^\infty \text{NH}_4\text{Cl} + \lambda_m^\infty \text{NaOH} - \lambda_m^\infty \text{NaCl}$$

$$\lambda_m^\infty \text{CH}_3\text{COOH} = \lambda_m^\infty \text{CH}_3\text{COONa} + \lambda_m^\infty \text{HCl} - \lambda_m^\infty \text{NaCl}$$

$$\lambda_m^\infty \text{BaSO}_4 = \lambda_m^\infty \text{BaCl}_2 + \lambda_m^\infty \text{Na}_2\text{SO}_4 - 2 \lambda_m^\infty \text{NaCl}$$