1. Intro

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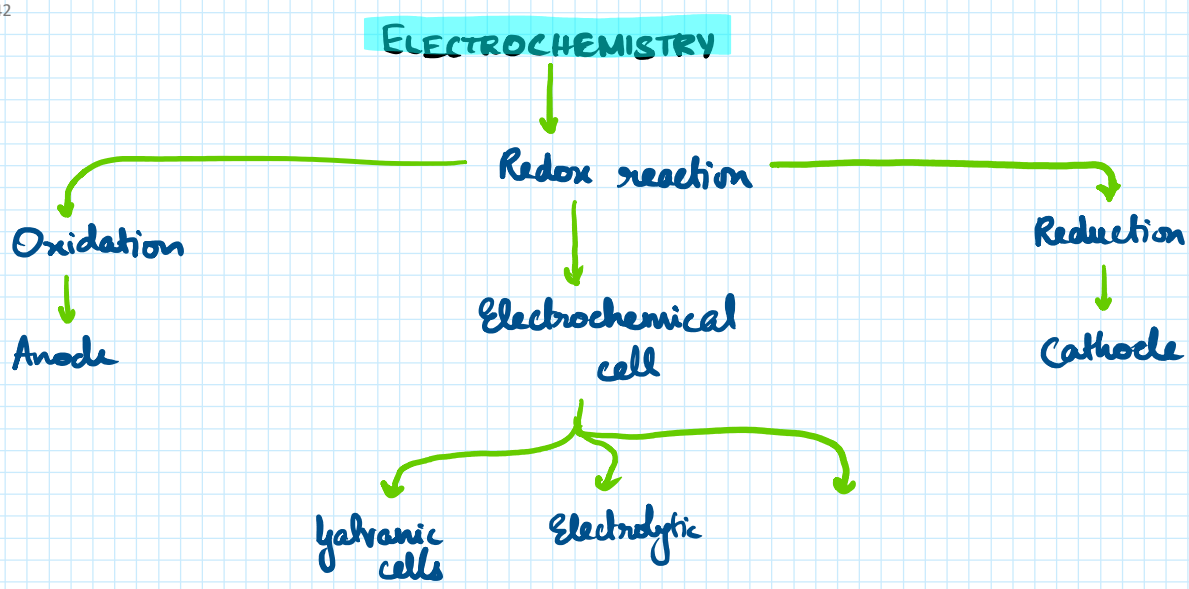
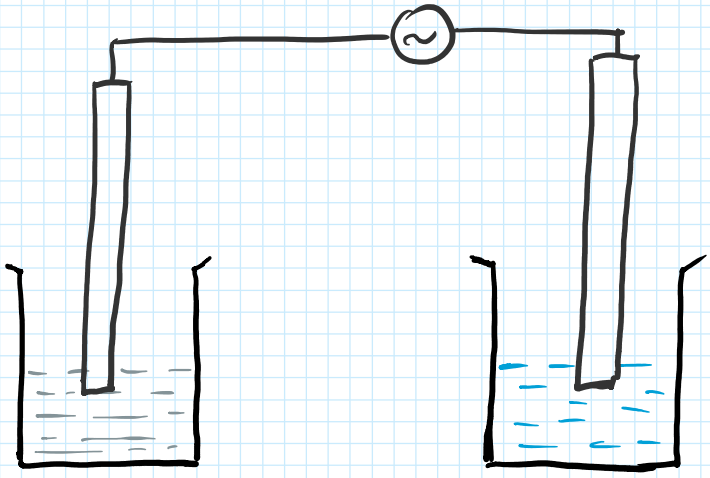


DIFFERENCE B/W GALVANIC AND ELECTROLYTIC

Galvanic	Electrolytic
• Chemical energy → electrical	Electrical → chemical
• Anode = -ve Cathode = +ve	Anode = +ve Cathode = -ve
• $\Delta G = -nEF$	$\Delta G = +nEF$
• Spontaneous reaction	Non-spontaneous reaction
Eg: Battery	Eg: Metallurgy

Galvanic Cell



Helmholtz electrical double layer

Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

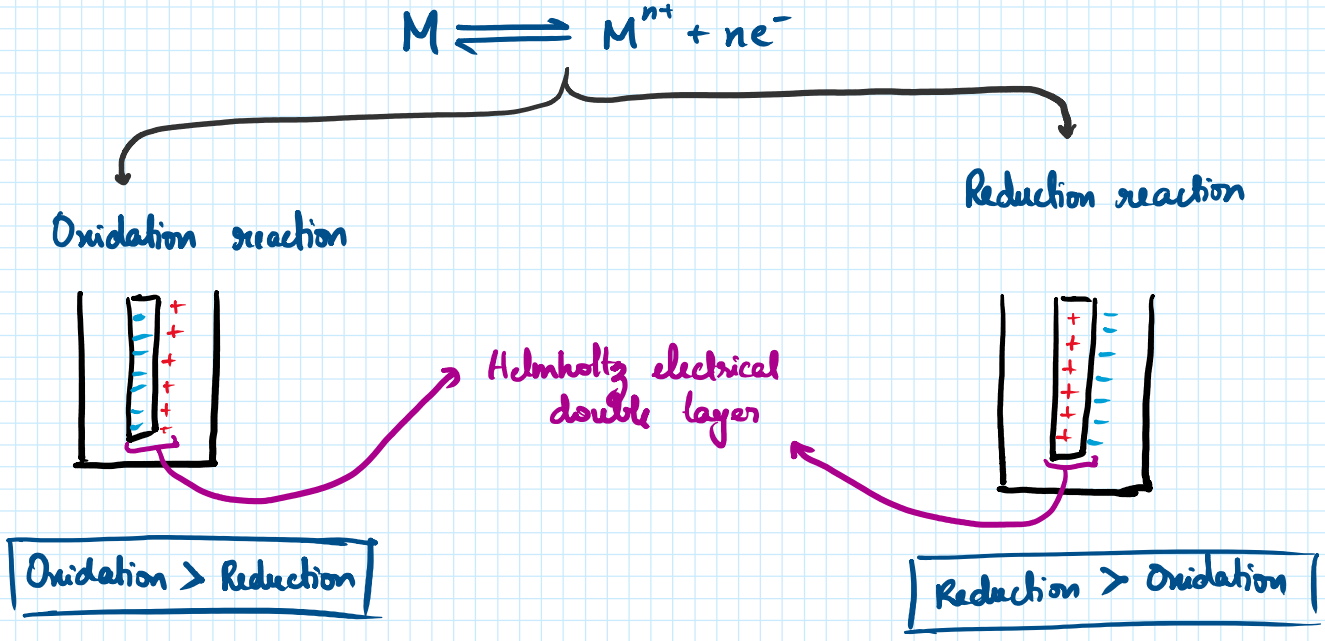
Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

ORIGIN OF ELECTRODE POTENTIAL

Definition of E:

Definition of E° (1 M, 25°C):



Electrode potential depends upon:

- Nature of metal
- Temperature
- Pressure
- Concentration of electrolyte

ELECTROCHEMICAL SERIES

		E°
Li	$Li + e^- \longrightarrow Li$	-3.05 V
K	$K^+ + e^- \longrightarrow K$	-2.9 V
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76 V
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.44 V
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.0 V
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34 V
Ag	$Ag^+ + e^- \longrightarrow Ag$	+0.8 V

LKG PROBLEMS

① $Cu|Cu^{2+}||Ag^{+}|Ag$ ② $Zn|Zn^{2+}||Cu^{2+}|Cu$

Write half reactions, overall reactions. Calculate E°_{cell}.

Soln: ① $E^{\circ}(Cu) = +0.34\,V$ $E^{\circ}(Ag) = +0.8\,V$

$E^{\circ}(Cu)$ → anode; $E^{\circ}(Ag)$ → cathode

Anode: $Cu \longrightarrow Cu^{2+} + 2e^{-}$

Cathode: $(Ag^{+} + e^{-} \longrightarrow Ag) \times 2$

$$Cu + 2Ag^{+} \longrightarrow 2Ag + Cu^{2+}$$

$$E^{\circ}_{cell} = E^{\circ}_{cath} - E^{\circ}_{anode}$$

$$= 0.8 - 0.34$$

$$= 0.46\,V$$

Nernst

Derivation

Based on reduction reaction

$$M^{n+} + ne^{-} \longrightarrow M$$

$$Q = \frac{[M]}{[M^{n+}]} = \frac{1}{[M^{n+}]}$$

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Work done by the system

$W_{max} = nEF$

$W_{max} = -\Delta G$

$$\left.\begin{aligned} \Delta G &= -nEF \\ \Delta G^\circ &= -nE^\circ F \end{aligned}\right\} \text{——} (1)$$

Van't Hoff equation

$$\Delta G = \Delta G^\circ + RT \ln Q \text{ ——} (2)$$

Substituting (1), Q in (2)

$$-nEF = -nE^\circ F + RT \ln\left(\frac{1}{[M^{n+}]}\right)$$

Dividing both sides by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln\left(\frac{1}{[M^{n+}]}\right)$$

$$\boxed{E = E^\circ - \frac{2.303RT}{nF} \log\left(\frac{1}{[M^{n+}]}\right)}$$

Substitute constants

$$\boxed{E = E^\circ - \frac{0.0591}{n} \log\left(\frac{1}{[M^{n+}]}\right)} \quad [OR] \quad \boxed{E = E^\circ + \frac{0.0591}{n} \log([M^{n+}])}$$

Q. $Zn|Zn^{2+}||Cu^{2+}|Cu$. Derive Nernst eqn. for this reaction

Soln: Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$W_{max} = nEF$

$W_{max} = -\Delta G$

$\Delta G = -nEF$
$\Delta G^\circ = -nE^\circ F$ } — (1)

Vant Hoff eqn.

$\Delta G = \Delta G^\circ + RT \ln Q$

$-nEF = -nE^\circ F + RT \ln\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$

$E = E^\circ - \frac{RT}{nF} \ln\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$

$$\boxed{E = E^\circ - \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Q. Given cell

$Ni|Ni^{2+}(0.5)||Ag^+(0.2M)|Ag$

$E^\circ_{Ni^{2+}/Ni} = -0.25\,V$

$E^\circ_{Ag^+/Ag} = 0.8\,V$

(i) Write half reaction and overall reaction
(ii) Derive Nernst eqn.
(iii) Calculate E°_{cell}, E_{cell} at 25°C
(iv) Calculate ΔG
(v) Predict the nature of the reaction

Soln: (i) Anode: $Ni \longrightarrow Ni^{2+} + 2e^-$

Cathode: $(Ag^+ + e^- \longrightarrow Ag) \times 2$

$Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

(iii) $E^\circ_{cell} = E^\circ_{cath} - E^\circ_{anode}$

$= 0.8 - (-0.25)$

$= 1.05\,V$

$E_{cell}(25°C) = 1.05 - \frac{0.0591}{2} \log\left(\frac{0.5}{(0.2)^2}\right)$

$= 1.017\,V$

$= 1.017\ V$

(iv) $\Delta G = -nEF$

$= -2 \times 1.017 \times 96500$

$= -196281\ J$

$F = 96500\ C$

(v) Spontaneous reaction

Q $Cr \mid Cr^{3+}(0.02M) \| Pb^{2+}(0.01M) \mid Pb$

$E^\circ_{Cr/Cr^{3+}} = -0.744V$

$E^\circ_{Pb^{2+}/Pb} = -0.126V$

Ans. Anode: $(Cr \longrightarrow Cr^{3+} + 3e^-) \times 2$

Cathode: $(Pb^{2+} + 2e^- \longrightarrow Pb) \times 3$

$2Cr + 3Pb^{2+} \longrightarrow 2Cr^{3+} + 3Pb$

$E^\circ_{cell} = E^\circ_C - E^\circ_A$

$= -0.126 - (-0.744)$

$= 0.618\ V$

$E_{cell}(25^\circ C) = E^\circ_{cell} - \frac{0.0591}{6} \log \frac{(0.02)^2}{(0.01)^3}$

$= 0.618 - \frac{0.0591}{6} \log \frac{(0.02)^2}{(0.01)^3}$

$= 0.5923\ V$

$\Delta G = -nEF$

$= -6(0.5923)(96500)$

$= -342941.7\ J$

Since ΔG is -ve $\longrightarrow$ non-spontaneous reaction

Q. Emf of the cell is 2.78 V.

$Mg|Mg^{2+}(0.014\ M)\ ||\ Cu^{2+}|Cu$ at 25°C

Measured $E^{\circ}_{Mg} = -2.37\ V$

Calculate electrode potential of Cu.

Soln. $E_{Mg} = E^{\circ}_{Mg} - \frac{0.0591}{2} \log \frac{1}{0.014}$

$= -2.37 - \frac{0.0591}{2} \log \frac{1}{0.014}$

$= -2.425$

$E_{cell} = E_C - E_A$

$2.78 = E_{Cu} - (-2.425)$

$2.78 - 2.425 = E_{Cu}$

$E_{Cu} = 0.355\ V$