Electrochemistry

→ Electrode $\Big\langle$ +ve electrode (anode)
‒ve electrode (cathode) $\boxed{\text{I O A N}}$
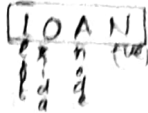
→ SRP: ‒SOP , SRP↑ reduction^n takes place.

→ Electrochemical series

Upper element always reduction & lower ion → oxidation
most powerful oxidant

$F_{2(g)} + 2e^- \rightarrow 2F^-$	2.87 V	
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_{(l)}$	1.78 V	
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	1.40 V	
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36 V	
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_{(l)}$	1.23 V	
$Br_2 + 2e^- \rightarrow 2Br^-_{(aq)}$	1.09 V	
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.99 V	
$Fe^{2+} + e^- \rightarrow Fe^{2+}_{(aq)}$	0.77 V	
$Ag^+ + e^- \rightarrow Ag_{(s)}$	0.80 V	
$I_2 + 2e^- \rightarrow 2I^-_{(aq)}$	0.54 V	
$Cu^+ + e^- \rightarrow Cu_{(s)}$	0.52 V	
$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$	0.34 V	
$2H^+ + 2e^- \rightarrow H_2 {(g)}$	0.00 V	
$Pb^{2+} + 2e^- \rightarrow Pb_{(s)}$	‒0.13 V	
$Sn^{2+} + 2e^- \rightarrow Sn_{(s)}$	‒0.14 V	
$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$	‒0.25 V	
$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$	‒0.44 V	
$Cr^{3+} + 3e^- \rightarrow Cr_{(s)}$	‒0.74 V	
$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$	‒0.76 V	
$2H_2O + 2e^- \rightarrow 2H_2 + 2OH^-$	‒0.83 V	
$Al^{3+} + 3e^- \rightarrow Al_{(s)}$	‒1.66 V	
$Mg^{2+} + 2e^- \rightarrow Mg_{(s)}$	‒2.36 V	
$Na^+ + e^- \rightarrow Na_{(s)}$	‒2.71 V	
$Ca^{2+} + 2e^- \rightarrow Ca_{(s)}$	‒2.87 V	
$K^+ + e^- \rightarrow K_{(s)}$	‒2.93 V	
$Li^+ + e^- \rightarrow Li_{(s)}$	‒3.05 V	

most powerful reduction agent

→ Electrolysis of NaCl :
aq

$NaCl \longrightarrow \underbrace{(Na^+ + Cl^- \rightarrow Cl_2}_{H_2 \nwarrow \quad OH^-}$
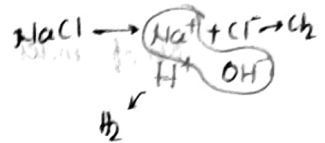
during electrolysis conc. of
$[OH^-]$ in soln ↑ pOH ↓ & pH↑

→ Electrolysis of $CuSO_4$

by using Cu electrode

$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$
$H^+ \quad OH^-$

at cathode

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$
Cu vs H_2O vs SO_4^{2-}
active electrode

at anode

$Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$

Net rxn :

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ cathode
$Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$

$\underline{Cu^{2+}_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+} + Cu_{(s)}}$
R·H·R
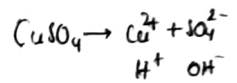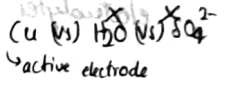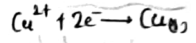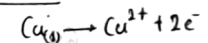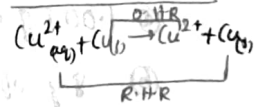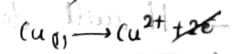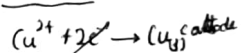
→ Electrolysis of H_2O

at cathode –
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
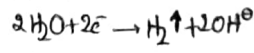
at anode –
$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \uparrow$
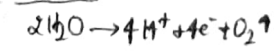
→ Faraday's law

1st law ‒ $m \propto Q$ (or) $w \propto Q$
$m = eQ$
$m = e \times c \times t$

$e =$ electrochemical equivalent ‒ amount of substance deposited at an electrode by passing 1C electricity $e = \frac{E}{F}$, $E = \frac{A}{Z}$
A = atomic mass
Z = atomic valency

Equivalent law – 1 equivalent e^- also passed through a soln always 1 equivalent substance is produced.

$1 eye^- = mole\ reaction \rightarrow 96500c = 1F = N_A \times Q_e$

Chemical equivalent (E): Amount of substance liberated by passing of 1F electricity

$$e = E/F = E/96500$$

No of moles $= \dfrac{no.\ of\ atoms\ deposited}{N_A} = \dfrac{no\ of\ gas\ molecules\ deposited}{N_A}$

$$= \dfrac{volume\ of\ gas\ (at\ STP)}{22.4}$$
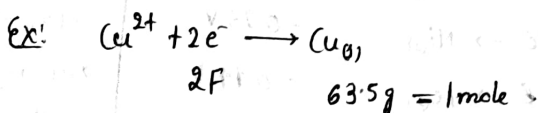
$N = M \times n \Rightarrow n = \dfrac{N}{n\ factor} \times vol\ of\ soln\ inL$

$$n = \dfrac{Q}{n\ factor \times F} = \dfrac{C \times t}{n\ factor \times 96,500}$$

$$n_{eq} = \dfrac{wt}{GEW} = N \times V_{(inL)} = \dfrac{C \times t}{96,500}$$

2nd law – same quantity of electricity passed through different electrolytes amount of substance liberated α chemical equivalents

$$m \alpha E \Rightarrow \dfrac{m}{E} = const.$$

Ex: $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$

$2F$ $63.5g = 1\ mole$

→ 1F will deposite at STP

ⓐ $1.008\ g\ of\ H_2$

ⓒ $9g\ of\ Al$ $\boxed{1C = 6.25 \times 10^{18}\ e^-s}$

ⓑ $8g\ of\ O_2 = 5.6\ lt$

→ Thickness of coated layer

$d = m/v$

$m = (a \times b \times c) \times e$

$\boxed{m = \dfrac{(2)E \times c \times t}{F} = (a \times b \times c) \times e}$

efficiency of cell, $\eta = \dfrac{m_{obs}}{m_{theo}} \times 100$ $m_{obs} = \dfrac{E \times c \times t}{F}$

→ Resistance $(R) = \rho(l/a) = S(l/a)$

conductance $(C\ or\ G) \Rightarrow C = 1/R = ohm^{-1}\ or\ mho\ (or\ U\ \sigma) = Siemen\ (s)\ (\Omega^{-1})$

specific conductance $K\ (or)\ G^o\ (or)\ 1/s$

$K = C \times l/a$ $U - ohm^{-1}\ cm^{-1} = Siemen\ m^{-1}$

→ at temp T↑ conductivity of metal ↓ but electrolytic ↑↑

→ Molar conductance (Λ_m):

Λ_m ↪ k/c

$$\Lambda_m = k \cdot V_{(in\ ml)} = \frac{k \times 1000}{M_{(molarity)}} \qquad M = \frac{n}{V_{(in\ l)}}$$

$$\Lambda_m = \frac{(c \times V_a) \times 1000}{M} = \frac{(1/R \times V_a)(1000)}{M} \qquad Unit → ohm^{-1}\ cm^2\ mole^{-1}$$

Siemen m^2 mole^{-1}

→ Equivalent conductance (Λ_e):

$$\Lambda_e = k \cdot V_{(in\ ml)} = \frac{k \times 1000}{N} \qquad \Lambda_e = ohm^{-1}\ cm^2\ equivalent^{-1}$$

→ $\Lambda_m = v \cdot f \times \Lambda_e$ ⇒ $\Lambda_e = \frac{\Lambda_m}{v \cdot f}$ → Valency factor

v.f for $AlCl_3 = 3$
$Fe_2(SO_4)_3 = 6$

→ Kohlrausch law: Λ_e° (or) $\Lambda^\infty = \lambda_+^\circ + \lambda_-^\circ = \lambda_c^\circ + \lambda_a^\circ$
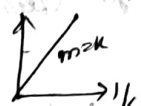
(Conductance at infinite dilution)

$$\Lambda_e^\circ\ (Fe_2(SO_4)_3) = \frac{1}{3}\lambda_{Fe^{3+}}^\circ + \frac{1}{2}\lambda_{SO_4^{2-}}^\circ$$

Ex: $\Lambda_{NH_4OH}^\circ = \Lambda_{NH_4Cl}^\circ + \Lambda_{NaOH}^\circ - \Lambda_{NaCl}^\circ$

$= \lambda_{NH_4^+}^\circ + \lambda_{Cl}^\circ + \lambda_{Na^+}^\circ + \lambda_{OH^-}^\circ - \lambda_{Na^+}^\circ - \lambda_{Cl}^\circ$

$\Lambda_{NH_4OH}^\circ = \lambda_{NH_4^+}^\circ + \lambda_{OH^-}^\circ$

→ $\alpha = \frac{\Lambda^c}{\Lambda^\circ} = \frac{\Lambda^c}{\Lambda^\infty} = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\Lambda_e^c}{\Lambda_e^\infty}$ $\qquad \Lambda_m → \Lambda_m$ at conc. $= C$

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

→ $k = c\alpha^2$ ⇒ $\quad \alpha = \frac{\Lambda^c}{\Lambda^\infty}$

→ solubility of sparingly soluble salts:

$$S_{(in\ mol/lt)} = \frac{k_{salt} \times 1000}{\Lambda_m} \qquad k_{salt} = k_{soln} - k_{solvent}$$

→ mobility (u) = $\dfrac{V}{\left(\frac{V_{(potential)}}{l}\right)}$ $\qquad T_+ + T_- = 1 \Rightarrow \dfrac{u_+}{u_+ + u_-} + \dfrac{u_-}{u_+ + u_-} = 1$

→ Factors affecting conductance:

conc. $\alpha \dfrac{1}{conductance}$ $\quad \alpha$ specific conductance α dilution αu α temp. α viscosity

α size of ions

→ Debye–Huckel Onsager eqn:
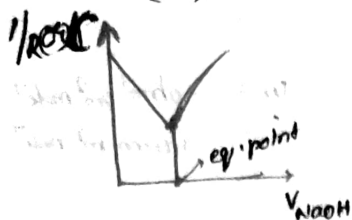
$$\Lambda_c = \Lambda_0 - b\sqrt{c}$$

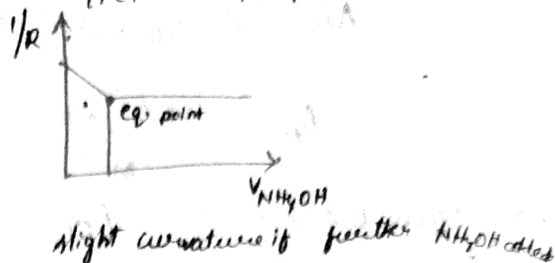where $b = \dfrac{82.4}{\eta(DT)^{1/2}} + \dfrac{8.2 \times 10^5}{(DT)^{3/2}}\Lambda_0$
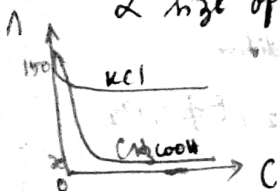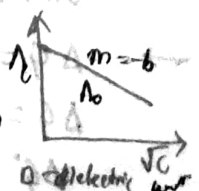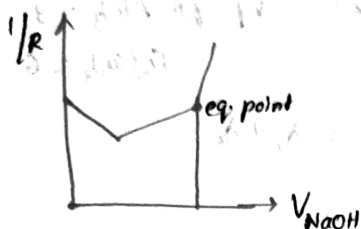
→ Conductometric Titration
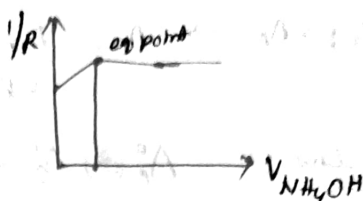
① **Strong acid vs strong base**
(HCl)   (NaOH)

$1/R$ or C

eq. point

V_{NaOH}

② **strong acid (vs) weak base**
HCl NH_4OH

$1/R$

eq. point

V_{NH_4OH}

slight curvature if further NH_4OH added

③ **Weak acid vs strong base**
CH_3COOH NaOH

$1/R$

eq. point

V_{NaOH}

④ **Weak acid (vs) Weak base**

$1/R$

eq point

V_{NH_4OH}

Mix of weak + strong acid $(HCl + CH_3COOH)$ & base (NaOH)

$1/R$

V_1 V_2 V_{NaOH}
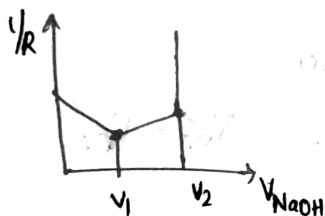
for **precipitation**
aq. $AgNO_3$ Vs KCl

$1/R$

eq point

V_{KCl}

→ **Salt Bridge :** U-shaped tube contains inert electrolyte like KCl, KNO_3,
NH_4Cl & NH_4NO_3 in agar-agar gel. (Denoted by ||).

i) C^+ & A^- have same mobility

ii) ions of inert electrolyte do not mix & do not participate in electrochemical change

Function of it — complete ckt, maintain neutrality b/w 2 half cells

→ **Representation of cell :**

$$Zn_{(s)} | ZnSO_{4 \ (aq)} \ || \ CuSO_{4 \ (aq)} | Cu_{(s)}$$

anode (−)   salt bridge   cathode (+)

separation b/w phases
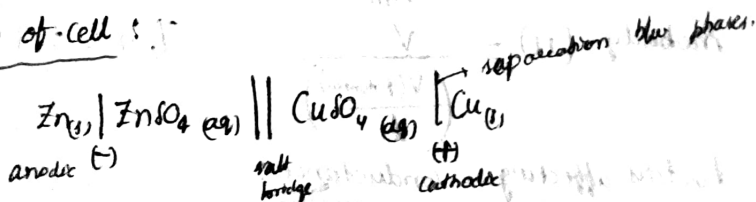
→ $\boxed{E_{cell} = O.P_{(anode)} + R.P_{(cathode)}} = -R.P_{(anode)} + R.P_{(cathode)}$

S.R.P ↑ Oxidising power ↑

→ $\Delta G = -nF E_{cell}$

$\Delta G = \Delta G° + RT \log_e Q$

$\Delta G° = -RT \log_e K_{eq}$

→ $E°_{cell}$ is not additive.

$E_1 = x_1 , \ E_2 = x_2 , \ E \neq x_1 + x_2$

use ΔG.

, NERNST Eqn — $E_{cell} = E^\circ_{cell} + \dfrac{0.059}{n} \log Q$

$Q = \dfrac{[product]}{[reactants]}$

at eq. $\Delta G^\circ = 0$, $E^\circ_{cell} = 0$

$E_{cell} = \dfrac{0.059}{n} \log Q$

i) for an electrolyte

$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \dfrac{0.059}{n} \log \dfrac{1}{[M^{n+}]}$

ii) for conc. cell. — anode & cathode are made of same material so,

$\boxed{E^\circ_{cell} = 0}$

ⓐ electrolyte $Zn_{(1)} / Zn^{2+} \;||\; Zn^{2+} / Zn_{(2)}$, ⓑ electrode $Pt(H_2)/H^+ \;||\; H^+/H_2(Pt)$

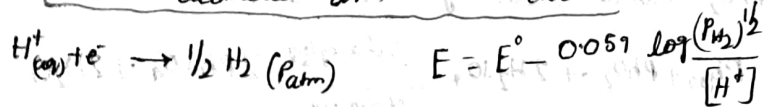$E = \dfrac{0.059}{2} \log \dfrac{C_2}{C_1}$ $\qquad E = \dfrac{0.059}{2} \log \left(\dfrac{P_1}{P_2}\right)$

→ different types of electrodes:

i) **Metal-Metal ion** electrode $M_{(s)} / M^{n+}_{(aq)}$

$E = E^\circ + \dfrac{0.0591}{n} \log [M^{n+}]$

ii) **Gas-ion** electrode as reduction electrode

$H^+_{(aq)} + e^- \rightarrow \tfrac{1}{2} H_2 \,(Patm)$ $\qquad E = E^\circ - 0.059 \log \dfrac{(P_{H_2})^{1/2}}{[H^+]}$

iii) **Oxidation - reduction** electrode $Pt / Fe^{2+}, Fe^{3+}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$
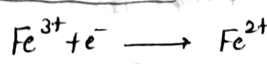
$E = E^\circ - 0.059 \log \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

iv) **Metal — Metal insoluble salt**

$AgCl + e^- \longrightarrow Ag_{(s)} + Cl^-$
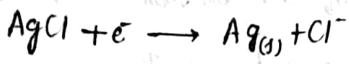
$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/Ag} - 0.059 \log [Cl^-]$

Calomel electrode

metal + insoluble salt + soluble anion

Ex) $Hg_{(l)} + Hg_2Cl_2 + Cl^-_{(aq)}$ $\qquad Q = [Cl^-]^2$ $\qquad E = E_0 - \dfrac{0.059}{n} \log Q$
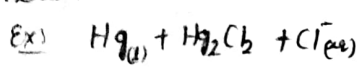
$E = E_0 - \dfrac{0.059}{n} \log [Cl^-]^2$

$E_{cell} = 0.059 \left[pH_{anode} - pH_{cathode} \right]$

Fuel cell: Chemical energy $\xrightarrow{stage\,I}$ Heating $\xrightarrow{stage\,II}$ mechanical energy $\to$ electrical energy

Net rxn: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
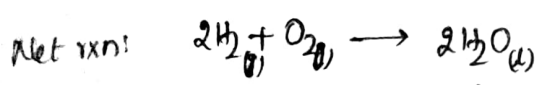
efficiency of fuel cell $= \dfrac{\Delta G_m}{\Delta H_m}$, practically $= 70\%$

Corrosion –

$$Fe \xrightarrow{air} Fe_2O_3 \cdot xH_2O$$

$$Ag \xrightarrow{air} Ag_2O + Ag_2S$$

$$\underbrace{}_{black\ shade}$$

$$Cu \xrightarrow{air} CuCO_3 \cdot Cu(OH)_2$$

Thermodynamics

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \frac{\partial (\Delta G)}{\partial T} \Rightarrow Temp\ coeff.$$

$$\Delta H = nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

Cells –

Charging → E passed → chemical rxn occurs } electrolytic cell.

Discharging → E produced ← due to chemical rxn } Galvanic cell.

Galvanic cell is reversible cell to electrolytic cell.

Lead storage battery –

Pb – anode, PbO_2 – cathode, electrolyte $-38\%\ H_2SO_4$

Net rxn – $Pb_{(s)} + PbO_2 + 2H_2SO_4 \underset{charging}{\overset{discharging}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$

discharging – $Pb \downarrow PbO_2 \downarrow \quad PbSO_4 \uparrow \quad H_2O \uparrow$

→ for cell spontaneity – $\Delta G = -ve, E^\circ_{cell} = +ve, K_{eq} > 1$

→ Cell will oxidise only the SRP of cell less than that of respective electrodes.

→ Completely discharged cell means $E_{cell} = 0\ V$

Dry cell

$$\underset{+4}{MnO_2} + NH_4^+ + e^- \longrightarrow \underset{+3}{MnO(OH)} + NH_3$$