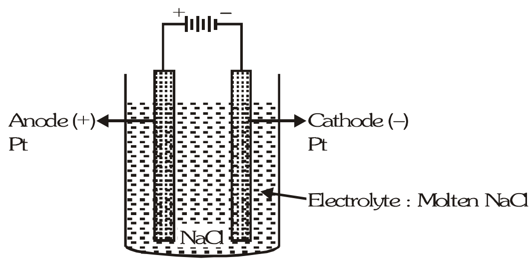
ELECTRO CHEMISTRY

CELL
- Electrolytic cell
- Electrochemical cell

➢ Electrolytic cell : Converts electrical energy into chemical energy



Cathode : $Na^{+}_{(aq.)} + e \longrightarrow Na(s)$

Anode : $Cl^{-}_{(aq.)} \longrightarrow \frac{1}{2} Cl_2(g) + e$

➢ ***Deposition of material at any electrode follow faraday's law of electrolysis.***

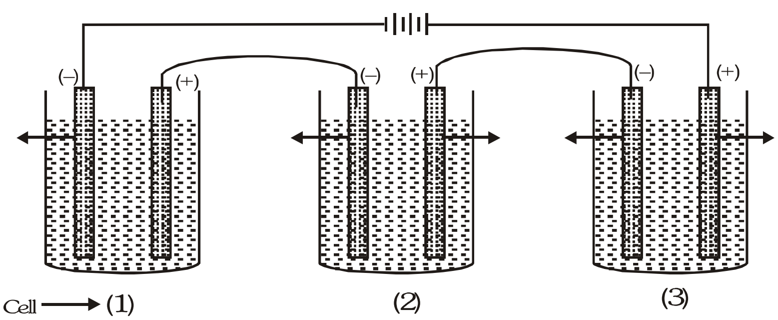
Faraday's I[st] Law :

$$w = Z\,it$$

$$w = \frac{M}{n - \text{factor} \times 96500}\ it$$

where
- w = mass deposite (gm)
- M = molar mass
- i = current (Amp.)
- t = time (sec.)

Faraday's second law :



➢ At any electrode for material deposited.

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3}$$

Note : Order of discharge potential.

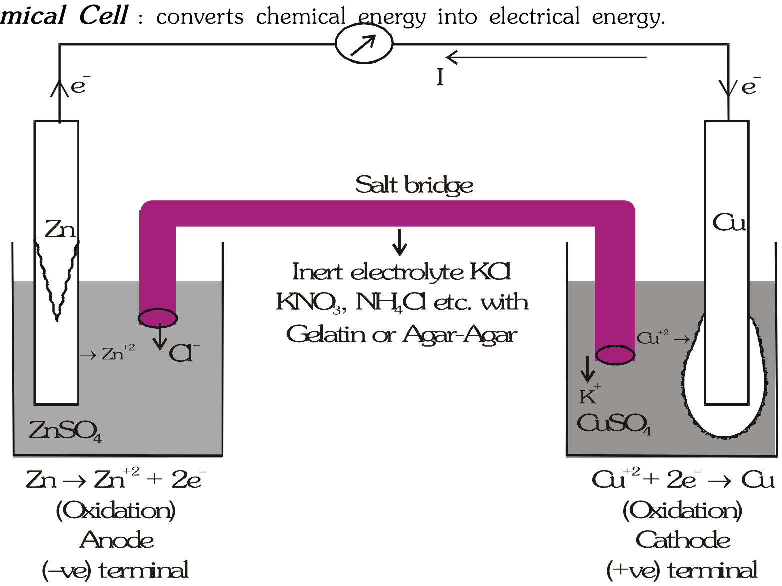
Cathode : $Au^{+3} > Ag^{+} > Cu^{+2} > Zn^{+2} > H_2O > Al^{+3} > Mg^{+2} > Na^{+} > Li^{+}$

Anode : $SO_4^{2-} < NO_3^{-} < H_2O < Cl^{-} < Br^{-} < I^{-}$

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl_2	Na
(iii)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu
(vi)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(vii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(viii)	Aqueous $AgNO_3$	Pt of Graphite	O_2	Ag

➢ ***Electrochemical Cell*** : converts chemical energy into electrical energy.



$$\underbrace{Zn(s)\,/Zn^{+2}_{(aq.)}}_{\text{Anode}} \quad \underbrace{//}_{\text{Saltbridge}} \quad \underbrace{Cu^{2+}_{(aq.)}\,/Cu(s)}_{\text{Cathode}}$$

➢ $E_{Cell} = SRP_{cathode} - SRP_{Anode}$

$= SRP_{cathode} + SOP_{at\ anode}$

Half cell reaction :

Anode: $Zn(s) \longrightarrow Zn^{+2}_{(aq.)} + 2e$

Cathode : $Cu^{+2}_{(aq.)} + 2e \longrightarrow Cus$

➢ ***Cell reaction :*** $Zn(s) + Cu^{+2}_{(aq.)} \longrightarrow Zn^{+2}_{(aq.)} + Cu(s)$

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

- *Nearest equation :*

$$E_{Cell} = E_{Cell} - \frac{0.059}{n}\log Q \qquad \text{at 298 K}$$

- Max electrical work done = nFE = $-\Delta G$

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DIFFERENT TYPE OF ELECTRODES/HALF CELL

Type	*Example*	*Half-cell reaction*	*Electrode potential (reduction)*
Metal - Metal ion	M/M^{n+}	$M^{n+} + ne^- \longrightarrow M(s)$	$E = E + \frac{0.0591}{n} \log [M^{n+}]$
Gas - ion	$Pt / H_2 (P\ atm) / H^+ (XM)$	$H^+ (aq) + e^- \longrightarrow \frac{1}{2} H_2 (P\ atm)$	$E = E - 0.0591 \log \frac{\sqrt{P_{H_2}}}{[H^+]}$
Oxidation - reduction	$Pt / Fe^{2+} , Fe^{3+}$	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	$E = E - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$
Metal - insoluble salt Anion	$Ag/AgCl, Cl^-$	$AgCl (s) + e^- \longrightarrow Ag (s) + Cl^-$	$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - 0.0591 \log [Cl^-]$
Calomel electrode	$Cl^-(aq)/Hg/Hg_2Cl_2$	$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq.)$	$E = E - 0.0591 \log [Cl^-]$

- Gibb's Helmhaltz equation :

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]$$

$$\Rightarrow \qquad \Delta H = -nFE + nFT\left[\frac{\partial \Delta G}{\partial T}\right]_P$$

'THE ELECTROCHEMICAL SERIES'

Element	*Electrode Reduction Reaction*	*Standard electrode Reduction potential E^0, Volts*
Li	$Li^+ + e \rightarrow Li$	– 3.05
K	$K^+ + e^- \rightarrow K$	– 2.93
Ba	$Ba^{+2} + 2e^- \rightarrow Ba$	– 2.90
Ca	$Ca^{+2} + 2e^- \rightarrow Ca$	– 2.87
Na	$Na^+ + e^- \rightarrow Na$	– 2.71
Mg	$Mg^{+2} + 2e^- \rightarrow Mg$	– 2.37
Al	$Al^{+3} + 3e^- \rightarrow Al$	– 1.66
Mn	$Mn^{+2} + 2e^- \rightarrow Mn$	– 1.18
H_2O	***$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$***	***– 0.828***
Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	– 0.76
Cr	$Cr^{+3} + 3e^- \rightarrow Cr$	– 0.74
Fe	$Fe^{+2} + 2e^- \rightarrow Fe$	– 0.44
Cd	$Cd^{+2} + 2e^- \rightarrow Cd$	– 0.40
Ni	$Ni^{+2} + 2e^- \rightarrow Ni$	– 0.25
Sn	$Sn^{+2} + 2e^- \rightarrow Sn$	– 0.14
Pb	$Pb^{+2} + 2e^- \rightarrow Pb$	– 0.13
H_2	$2H^+ + 2e^- \rightarrow H_2$	0
Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+ 0.34
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+ 0.54
Hg	$Hg_2^{+2} + 2e \rightarrow 2Hg$	+ 0.79
Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.80
Hg	$Hg^{+2} + 2e^- \rightarrow Hg$	+ 0.85
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.08
O_2	***$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$***	***+ 1.229***
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
Au	$Au^{+3} + 3e \rightarrow Au$	+ 1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.87

CONDUCTION IN ELECTROLYTES

	Conductance	*Specific Conductivity*	*Molar Conductivity*
Symbol Unit	C Ω^{-1}	κ $\Omega^{-1}\ cm^{-1}$	Λ_m $\Omega^{-1}\ cm^2 mol^{-1}$
Specific	conductance of volume within electrode	conductance of unit volume	conductance of that volume which contain exactly one mole
Change with concentraction	decrease with decrease in concentration	Decrease with decrease in concentration	Increase with in decrease in concentration
Formula	$C = \frac{1}{R}$	k = C cell constant	$k = \Lambda_m = K \quad V$ V = Volume of solution contain 1 mole of electrolyte
Factors	(i) nature of electrolyte (ii) concentration of electrolyte (iii) Type of cell.	(i) nature of electrolyte (ii) concentration of electrolyte	(i) nature of electrolyte (ii) concentration of electrolyte

➢ ***KOHLRAUSEH'S LAW*** :

$$\Lambda_m^\infty(A_xB_y) = x\lambda_+^\infty + y\lambda_-^\infty$$

$$\Lambda_m^\infty(K_2SO_4) = 2\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty(Na_3PO_4) = 3\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty[Fe_2(SO_4)_3] = 2\lambda_+^\infty + 3\lambda_-^\infty$$

➢ ***FORMULA***

(1) $R = \rho \; \frac{\ell}{A}$

(2) $\lambda_m = k \; \frac{1000}{M}$

(3) $\lambda_{eq.} = k \times \frac{1000}{N}$

(4) for strong electrolyte $\lambda_m = \lambda_{m_\infty} - b\sqrt{C}$