ELECTRO CHEMISTRY

Electrochemical/Galvanic/ Voltaic Cell

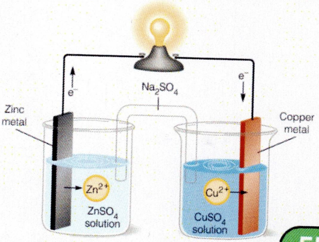
- Spontaneous Reaction → Electrical Energy
- $\Delta G < 0$ (meaning Spontaneous Redox Reaction)
- Anode (-) : Oxidation ; Cathode (+) : Reduction

Electrolytic cell

- Electrical Energy used for non-Spontaneous Reaction
- $\Delta G > 0$ (meaning non Spontaneous Reaction)
- Anode (+) : Oxidation ; Cathode (-) : Reduction

Electrochemical/Galvanic/ Voltaic Cell

Daneil Cell



Important Points : Daniel Cell (Galvanic)

- **Anode :** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- **Cathode :** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- **Overall Reaction :** $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$
- **Representation :** $Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$.
- Here || represents salt Bridge which completes circuit.
- The concentration of Zinc Sulphate increases while the concentration of Copper Sulphate decreases.
- The zinc rod loses mass while copper gains it.
- In both the compartments, the solutions remain electrically neutral. Net cell Potential, E°cell = 1.1 eV

Remember LOAN

Left side

Oxidation Anode

Negative Potential

Salt Bridge

- **U-Tube** containing solutions of inert electrolytes.
- KCl, KNO_3, K_3SO_3 or NH_4NO_3.
- KCl is not used in electrodes of Ag, Tl, Pb, Hg.
- Inner circuit completed by flow of ions through S.B.
- Maintains Electrical neutrality.
- Prevents Liquid-Liquid Junction potential.
- Ionic mobility (Cation) = Ionic Mobility (Anion)

Standard Electrode Potential (E°)

- Potential difference between electrode and solution at standard coditions of 1M at 25°C and 1 atm
- Oxidation Potential : $E^o_{Zn^{2+}/Zn}$
- Reduction Potential : $E^o_{Zn/Zn^{2+}}$

These have equal and opposite values

Standard Reduction Potential (E°_{red})

- Mostly used in questions (values provided)
- **Representation :** $E^o_{M^{n+}/M}$
- For **Hydrogen,** SRP is taken as $E^o_{H_2/H^+} = 0$

EMF of a cell

- Potential difference between two electrodes
- EMF = Red. Pot. where reduction occurs - Red. Pot. where Oxidation occurs
- **NOTE** : Use only Reduction potential to not get confused

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Standard Hydrogen Electrode

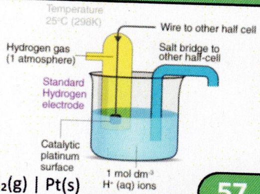
Reference electrode used to find electrode potential of other electrodes.

Anode : $H_2(g) \rightarrow 2e^- + 2H^+(aq)$

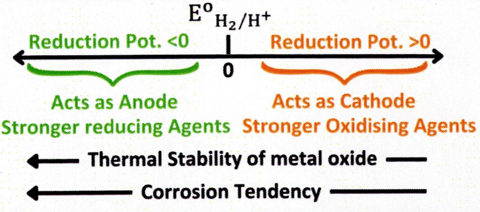
Cath. : $2e^- + 2H^+(aq) \rightarrow H_2(g)$

Representation of cell:

$Pt(s) \mid H_2(g) \mid H^+(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$



Electrochemical Series



$E^o_{H_2/H^+}$

Reduction Pot. <0

Reduction Pot. >0

0

Acts as Anode
Stronger reducing Agents

Acts as Cathode
Stronger Oxidising Agents

← Thermal Stability of metal oxide

← Corrosion Tendency

Li >K > Ca > Na > Mg > Al > Zn > Fe > Ni > Sn > Pb > H=0 > Cu > Hg > Ag > Au > Pt

Important Metal series Trick

- Lion Kings Can Not Make A Zebra Fed Near Sun Pablo
- Cute **Mercury Silver Gold Platinum**

Other Points about Electrochemical Series

- **Lithium** has most negative Reduction potential. Strongest reducing Agent
- **Fluorine** has most Positive Reduction potential. Strongest Oxidising Agent
- Reactivity Decreases on Going from Li to F.
- If we go from Li to F,
  - The Metal lying above in E.C.S displaces the other metal lying below
  - The non metal lying below in E.C.S.displaces the other metal lying above.

Nernst Equation

- **Half Cell Nernst Equation :** $M^{n+} + ne^- \rightarrow M$

$$E = E^o{}_{cell} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]} \quad \text{at 298K}$$

- **Half Cell Nernst Equation :** $B^{n+} + A \rightarrow A^{n+} + B$

$$E = E^o{}_{cell} - \frac{0.059}{n}\log\frac{[A^{n+}]}{[B^{n+}]} \quad \text{at 298K}$$

- **At Any other Temperature**

$$E = E^o{}_{cell} - \frac{RT}{nF}\ln\frac{[A^{n+}]}{[B^{n+}]}$$

Relation between ΔG and EMF of cell

- ΔG is an extensive (Additive) Property, E° is an intensive (non Additive) Property.

$$\Delta G = -nRT\ln K_c$$
$$= -nFE^o{}_{cell}$$

- If two half cells Having Potentials $E_1°$ & $E_2°$ are combined to give third half cell with $E_3°$. Then,

$$E_3{}^o = \frac{n_1E_1{}^o + n_2E_2{}^o}{n_3}$$

Where, n = Number of electrons involved

Other Formulas

Temp. Coeff	**Enthalpy Change of rxn**	**Entropy change**
$\left(\frac{\partial E}{\partial T}\right)_P$	$= -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$	$nF\left(\frac{\partial E}{\partial T}\right)_P$

Concentration Cells, Here ($E^\circ=0$)

Electrolytic Concentration Cells

Same Substance used with different concentration

Cathode : $M^{n+}(c_2) + ne^- \rightarrow M(s)$

Anode : $M(s) \rightarrow M^{n+}(c_1) + ne^-$

Overall Reaction :

$M^{n+}(c_2) \rightarrow M^{n+}(c_1)$

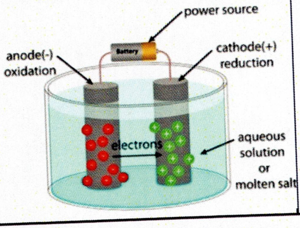
$$E = \frac{0.059}{n}\log\frac{c_2}{c_1}$$

Electrode Concentration Cells

E.g. Two hydrogen electrodes at different pressure dipped in sam solution of H^+ ion

$$E = \frac{0.059}{n}\log\frac{p_2}{p_1}$$

Electrolytic Cell



- Cells which bring Chemical Change during passage of electric current.
- Cations go to Cathode
- Anions go to Anode

According to Preferential Discharge Theory,

- In case of Cations, **Higher E°(red), Migration faster.**
- In case of Anions, **$SO_4^{2-} < NO_3^- < Cl^- < Br^- < I^- < OH^-$**

Product of Electrolysis

Ionic Comp.	Cathode	Anode	Electrode
$CuSO_4$	Cu	O_2	Pt/graphite
$CuSO_4$	Cu	Cu	Cu Electrode
$AgNO_3$	Ag	O_2	Pt/graphite
NaCl	H_2	Cl_2	Pt/graphite
Conc. H_2SO_4	$2H^+ + 2e^- \rightarrow H_2$	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	Pt/graphite
$AgNO_3$	$Ag^+ + e^- \rightarrow Ag$	$Ag \rightarrow Ag^+ + e^-$	Ag (inert)

Faraday's Law of Electrolysis

1st Law of Faraday

Weight of Metal deposited $\propto$ Quantity of charge passed

$W \propto Q$	$W = ZQ$	$W = Z \times i \times T$

Z = Electrochemical Equivalent; i=current ; t = time

Other important formula from exam P.O.V.	$W = \frac{\text{eq. weight}}{96500} \times Q$

2nd Law of Faraday

Passage of the same charge through diff. electrolytes brings in equal equivalents of ion to be ox. or red.	$\frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C}$

Formulas for Conductance

Resistance V = Voltage, I = Current	$R = \frac{V}{I}$	**Ohm**
Resistivity A= area of Cross sec l = dist. b/w electrodes	$\rho = \frac{RA}{l}$	**Ohm-m**
Conductance	$G = \frac{1}{R}$	**ohm^{-1}** **Siemen (S)**
Conductivity	$k = \frac{l}{RA}$	**$\text{ohm}^{-1}\ \text{m}^{-1}$** **$\text{S m}^{-1}$**
Cell Constant	$\text{c. c.} = \frac{l}{A} = k \times R = \frac{k}{G}$	

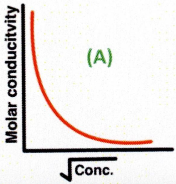
Types of Conductivities

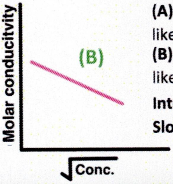
Molar Conductivity	$\Lambda_m = \frac{k \times 1000}{C}$	**$\text{S cm}^2\ \text{mol}^{-1}$**
Molar Conductivity	$\Lambda_{eq} = \frac{k \times 1000}{N}$	**$\text{S cm}^2\ \text{mol}^{-1}$**
Relationship	$\Lambda_m = \Lambda_{eq} \times \text{n. f.}$	n-factor is total +ve or -ve charge

Debye huckel Molar Conductivity

Relation between Molar conductivity and concentration

$\Lambda_m = \Lambda_m{}^o - A\sqrt{c}$	A depends on electrolyte nature





(A) Weak electrolyte
like CH_3COOH
(B) Strong electrolyte
like KCl
Intercept : Λ_m
Slope : -A

Kohlrauch's law

If the limiting molar conductivity of the cations is denoted by $\boldsymbol{\lambda_+^\circ}$ and that of the anions by $\boldsymbol{\lambda_-^\circ}$ then the limiting molar conductivity of electrolyte is:

$\Lambda_m{}^o = v_+\lambda_+{}^o + v_-\lambda_-{}^o$	v = no. of ions present
eg. $BaCl_2$	$\Lambda_{m(BaCl_2)}{}^o = \lambda^o{}_{Ba^{2+}} + 2 \times \lambda^o{}_{Cl^-}$
Application to calculate D.O.D of weak Electrolytes using conductivity	$\alpha = \dfrac{\Lambda_m}{\Lambda_m{}^o}$
$K_a = \dfrac{C\alpha^2}{(1-\alpha)} = \dfrac{C\Lambda_m{}^2}{\Lambda_m{}^o\,(\Lambda_m{}^o - \Lambda_m)}$	**Equilibrium constant**

Batteries

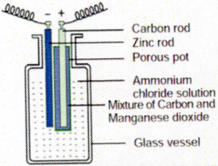
Primary : Leclanche cell

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

NH_3 forms a complex with Zn^{2+}

Cell Potential Energy = 1.5 V

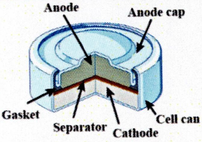


Primary : Mercury cell

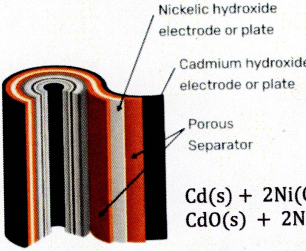
Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

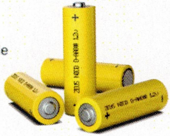
Cathode : $HgO + H_2O + 2e^- \rightarrow HgI + 2OH^-$

Cell Potential Energy = 1.35 V



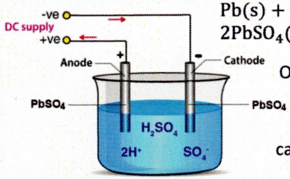
Secondary : Ni-Cd Battery





$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(s)$

Secondary : Pb Storage Batttery



$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O\ (l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2 respectively.

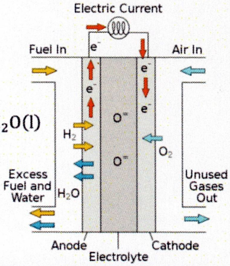
Fuel Cells

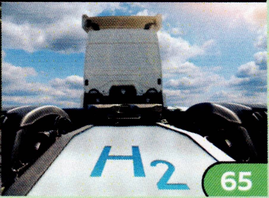
Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

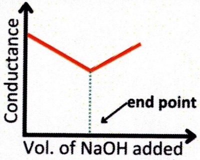
Overall : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, directly into electrical energy are called fuel cells.



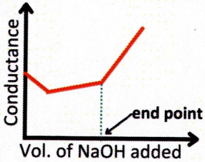


Strong Acid HCl - Strong Base NaOH



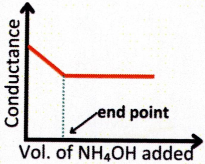
The fast-moving hydrogen ions are replaced by slow-moving sodium ions and the conductance decreases gradually up to the equivalent point.

Weak Acid CH_3COOH - Strong Base NaOH



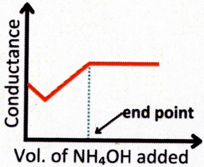
Slight decrease in the conductance of the solution due to the substitution of free H+ ions by slow-moving Na+ ions.Then increase due to formation of CH_3COONa

Strong Acid HCl - Weak Base NH_4OH



The fast-moving H+ ions are replaced by slow-moving NH4+ ions. Therefore, the conductance decreases until the endpoint is reached.

Weak Acid CH_3COOH - Weak Base NH_4OH



The conductance slightly decreases due to the substitution of H+ ions by slow-moving NH4+ions. On further addition of NH4OH solution, the conductance of solution increases til the endpoint due to the formation of highly ionized