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Electrochemistry.

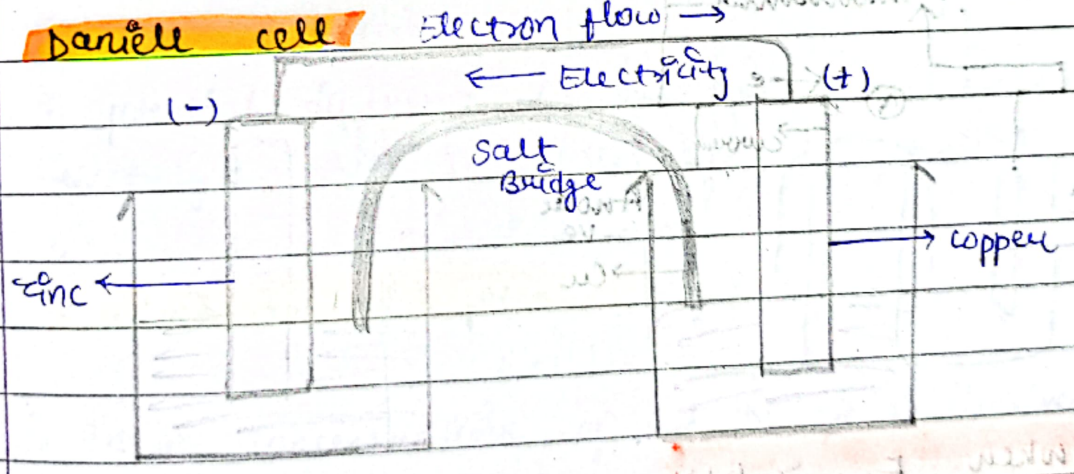
⇒ Electrochemistry is the study of production of electricity from energy released during spontaneous chemical rxn and its application.

* **Chemical Rxn** → Redox
* **Electrolyte** → It is a salt solution in which completely pass the electricity is called electrolyte.

Ex: $CuSO_4$, $ZnSO_4$ etc.

* **Electrochemical cell**: It is a device that can generate electricity from the chemical rxn.

* **Daniell cell**

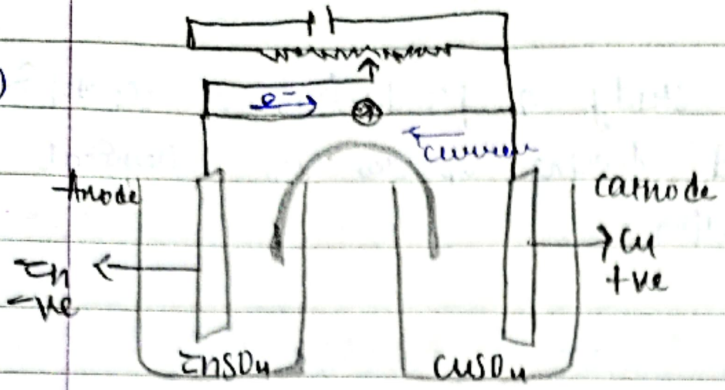


Rxn: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

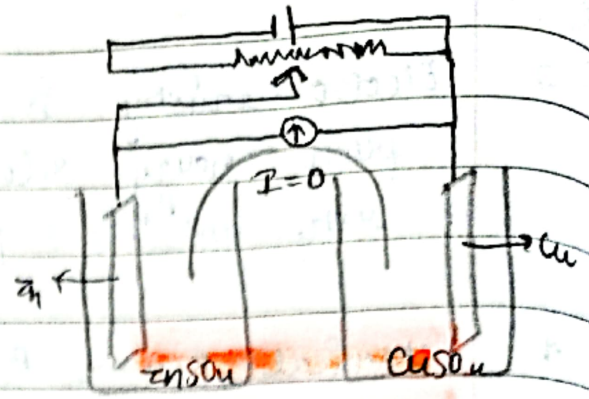
Electric potential = 1.1 V

Cases

(a)



(b)



When $E_{ext} < 1.1$ V

(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn

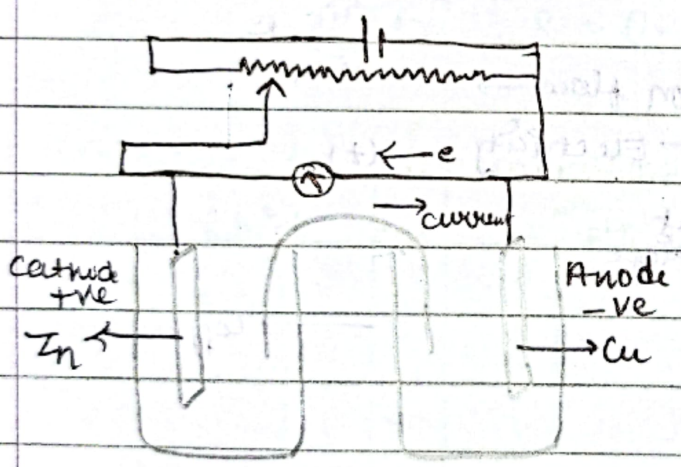
(ii) Zn dissolves at anode and copper deposits at cathode

When $E_{ext} = 1.1$

(i) No flow of electrons or current

(ii) No chemical rxn occurs.

(c)



When $E_{ext} > 1.1$ V

(i) Electrons flow from Cu to Zn & current flows from Zn to Cu

(ii) Zinc is deposited at zinc electrode & Cu dissolves at copper electrode.

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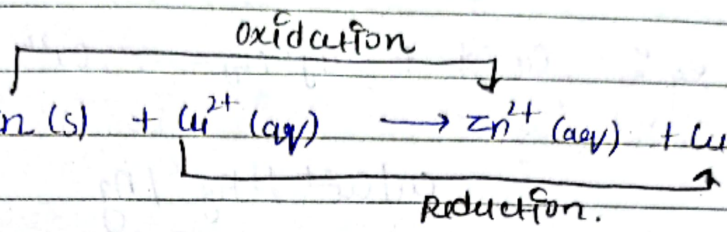
* Galvanic Cell

⇒ Galvanic cell is an electrochemical cell that converts the chemical energy of the spontaneous redox rxn into electrical energy.

Redox:



Oxidation half: $Zn \longrightarrow Zn^{2+} + 2e^{\ominus}$

Reduction half: $Cu^{2+} + 2e^{\ominus} \longrightarrow Cu$

* Electrode Potential

→ Depends upon: ① Nature of the metal
② Concentration of the ions in the solution
③ Temp.

⇒ A potential difference develops blw the electrode and the electrolyte which is called electrode potential.

* Standard electrode potential. [1 M]

⇒ When the concentrations of all the species involved in a half-cell is unity then the electrode potential is k/a standard electrode potential.

* Cell Potential.

⇒ The cell potential is the difference blw the electrode potential of cathode and anode.

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{right} - E_{left}$$

Cell representation.

→ Salt Bridge.

anode || cathode
oxidation reduction.

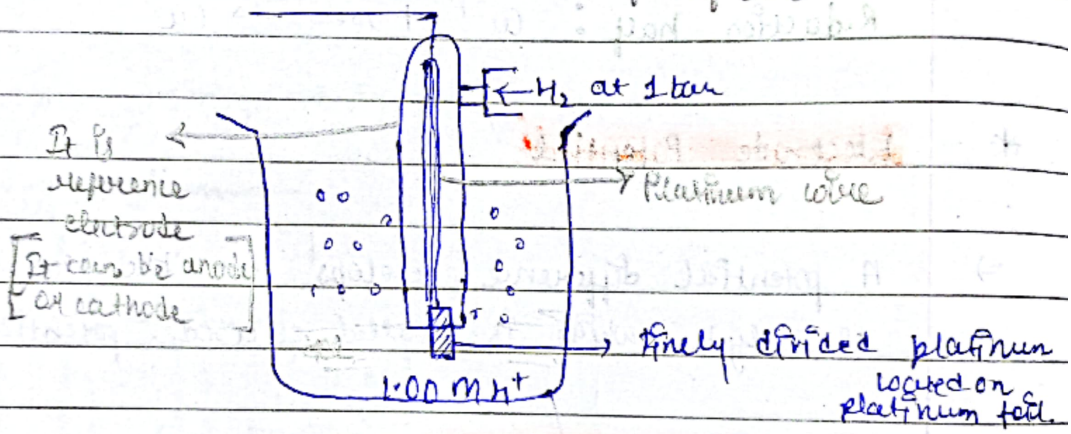
Eg: $Zn / Zn^{2+} || Cu^{2+} / Cu$ → Daniell cell

Eg: $Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+} + 2Ag(s)$

$Cu / Cu^{2+} || Ag^{+} / Ag$

Standard hydrogen electrode.

[It gives the value of electrode potential of half cell]



- Standard hydrogen electrode consist of platinum electrode coated with platinum black.
- The electrode is dipped in acidic solution & pure hydrogen gas is bubbled through it.
- The concentration of both reduced & oxidised forms of hydrogen is maintained at unity (same).
- Molarity = 1 molar
- Pressure = 1 bar.

] Condition should be for SHE

$$E^{\circ} = E^{\circ}_{R} - E^{\circ}_{L}$$

As E°_{L} for standard hydrogen electrode is zero.

$$E^{\circ} = E^{\circ}_{R} - 0$$

$$E^{\circ} = E^{\circ}_{R}$$

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Measured emf of the cell :

$Pt(s) \mid H_2(g, 1\,bar) \mid H^+(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu$

Q Find the Standard electrode potential.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$E^\circ_{cell} = ?$ $\quad Cu^{2+} = 0.34$ $\quad Zn^{2+} = -0.76$

$$E^\circ_{cell} = E_{cathode} - E_{anode}$$
$$= 0.34 - (-0.76)$$
$$= 0.34 + 0.76$$
$$= 1.10\ V$$

Exercise 2.4 (i) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd$

$E^\circ_{cell} = ?$ $\quad Cd^{2+} = -0.40$ $\quad Cr^{3+} = -0.74$

$$E^\circ_{cell} = -0.40 - (-0.74)$$
$$= -0.40 + 0.74$$
$$= 0.34\ V$$

(ii) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

$E^{2+}_{Fe} = 0.77$ $\quad Ag = 0.80$

$$E^\circ_{cell} = 0.80 - 0.77$$
$$= 0.03V$$

✳ **Nernst equation**

Nernst eqn shows that for electrode reaction:

$$M^{n+}(aq) + ne^{\ominus} \longrightarrow M(s)$$

the electrode potential at any concentration measured with respect to standard hydrogen electrode.

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

E_{cell} = emf of cell, E°_{cell} = standard electrode potential

F = Faraday constant [96500]

⇒ **Nernst eqn.**

(i) $$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[P]}{[R]}$$

(ii) $$E_{cell} = E^{\circ}_{cell} - \left(\frac{2.303RT}{nF}\right) \log \frac{[P]}{[R]}$$

(iii) $$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[P]}{[R]}$$

(iv) For standard hydrogen electrode.

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{1}{[R]}$$

(v) $$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log K_c$$

$$aA + bB \longrightarrow cC + dD$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \left[\frac{\text{Oxidant}}{\text{Reduct}}\right]$$

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4 For equilibrium constant from Nernst eqn [In the form of K_c]

Acc. to N. eq/n

$$0 = E^\circ_{cell} - \frac{0.059}{n} \log K_c$$

$$\boxed{E^\circ_{cell} = \frac{0.059}{n} \log K_c}$$

$$\frac{n E^\circ_{cell}}{0.059} = \log K_c$$

$$K_c = \text{exponential} \left[\frac{n E^\circ_{cell}}{0.059}\right]$$

$$\boxed{K_c = e^{\left(\frac{n E^\circ_{cell}}{0.059}\right)}}$$

Ex 2.1 $Mg + 2Ag^+ \longrightarrow Mg^{2+} + 2Ag$

$E^\circ_{cell} = 3.17\ V$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \left[\frac{Oxd}{Red}\right]$$

$$= 3.17 - \frac{0.059}{2} \log \frac{Mg^{2+}}{(Ag^+)^2}$$

$$= 3.17 - \frac{0.059}{2} \log \left(\frac{0.130}{(0.0001)^2}\right)$$

$$= 3.17 - 0.0295 \log 13 \times 10^6$$

$$= 3.17 - 0.0295 \log 13 \times 10^6$$

$$= 3.17 - 0.0295 \log 1.3 + \log 10^6$$

$$= 3.17 - 0.0295 [1.113 + 6]$$

$$= 3.17 - 0.0295 [7.113]$$

$$= 3.17 - 0.144$$

$$= 2.96\ V$$

Ex 2.2 $E^\circ_{cell} = 0.46\ V$

$$E^\circ_{cell} = \frac{0.059}{2} \log K_c$$

$$0.46 = \frac{0.059}{2} \log K_c$$

$$\frac{0.46 \times 2}{0.059} = \log K_c$$

$$\frac{0.92}{0.059} = \log K_c$$

$$15.59 = \log K_c$$

$$[42.37 = K_c]$$

0.46 / 0.9 (2)

* **Gibbs energy of reaction for cell**

For general Form

$$[\Delta G = -nFE_{cell}]$$

For standard Form

$$[\Delta_r G^\circ = -nFE^\circ_{cell}]$$

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -2.303 \times RT \log K$$

$$K = e^{\left[\frac{-\Delta G^\circ}{RT}\right]}$$

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Ex 2:3 $E^\circ_{cell} = 1.1V$ $\Delta_r G^\circ = ?$

$$\Delta G^\circ = -nFE^\circ_{cell}$$
$$= -2 \times 96500 \times 1.1$$
$$= -193000 \times 1.1$$

$$\boxed{\Delta G^\circ = -212300 \text{ J/mol}}$$

96500 × 2 = 193000

193000 × 11 = 2123000

* Conductance of Electrolytic solutions

Terms:

① **Resistance (R)**: It is the property of conductor to resist the flow of electrons.

$$\boxed{R = \frac{\rho l}{A}}$$

Where, ρ = Resistivity $[\Omega \cdot m]$
R = Resistance $[\Omega]$
l = length of conductor
A = thickness of conductor or wire.

⇒ **Factors affecting the resistance of conductor**

1) Nature of material
2) length of conductor
3) Thickness of conductor OR Area of cross-section
4) Temperature.

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② **Resistivity** (ρ) : It is the property of material and reciprocal of conductivity.

SI unit = Ωm

$$\rho = \frac{1}{K} \qquad \rho = \frac{R l}{A}$$

K = conductivity.
↳ kapa

③ **Conductivity** (K) : It is inverse of resistivity k/a conductivity

$$K = \frac{1}{\rho}$$

SI unit = $S cm^{-1}$

④ **Conductance** (G) : It is the inverse of resistance k/a conductance.

$$G = \frac{1}{R} = \frac{A}{\rho L}$$

SI unit = Seimens [S] or Ω^{-1}

NOTE : $1 S cm^{-1} = 100 S m^{-1}$

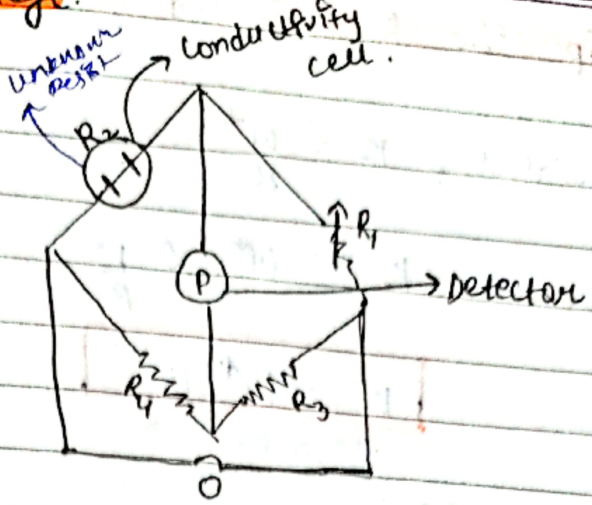
* **Electrical conductance depends on :**

① The nature and structure of the metal
② The number of valence electrons per atom
③ The temperature [It decreases with increase of temp.]

* **Ionic Conductance depends on :**

① The nature of the electrolyte added
② Size of the ions produced and their solvation
③ The nature of the solvent and its viscosity.
④ The concentration of the electrolyte.
⑤ temperature [It increases with the increase of temp.]

* Wheatstone Bridge.



⇒ Wheatstone Bridge is a electrical circuit network which help to determine unknown resistance.

$$\frac{R_2}{R_4} = \frac{R_1}{R_3}$$

$$R_2 = \frac{R_1 \times R_4}{R_3}$$

* Cell constant:

⇒ It is the ratio of length per unit cross-sectional area of conductor.

$$G^* = \frac{l}{A} = RK$$

* Relationship b/w K, G^* and R [Resistance]

$$R = \rho \frac{l}{A}$$

$$\frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

$$K = \frac{G^*}{R}$$

Specific conductivity

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* Relationship b/w K, G^* and G

We know that, $K = \frac{G^*}{R}$

$$K = G^* \times \frac{1}{R}$$

$$\boxed{K = G^* \cdot G}$$

* Molar conductivity.

⇒ It is defined as ratio of conductivity to the molar concentration of electrolyte.

$$\boxed{\Lambda_m = \frac{K}{C}}$$

SI unit = Sm^2/mol.

$$\Lambda_m \left[S cm^2 mol^{-1}\right] = \frac{K\,(S cm^{-1})}{1000\, L\, m^{-3} \times \text{molarity}\,(mol\, L^{-1})}$$

$$\Lambda_m \left[S cm^2 mol^{-1}\right] = \frac{K\,(S cm^{-1}) \times 1000\,(cm^3/L)}{\text{molarity}\,(mol/L)}$$

$1\, S m^2 mol^{-1} = 10^4\, S cm^2 mol^{-1}$

$1\, S cm^2 mol^{-1} = 10^{-4}\, S m^2 mol^{-1}$

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Eg° 2.4

$C_1 = 0.1$ mol/L | $R_1 = 100\ \Omega$ | $K_1 = 1.29$ S/m

$C_2 = 0.02$ mol/L | $R_2 = 520\ \Omega$ | $K_2 = ?$

$G^* =$ Conductivity × Resistance

$= \frac{1.29}{100} \times 100$

$= 129\ m^{-1}$

Conductivity $K_2 = \frac{G^*}{R} = \frac{129}{520} = 0.248\ S m^{-1}$

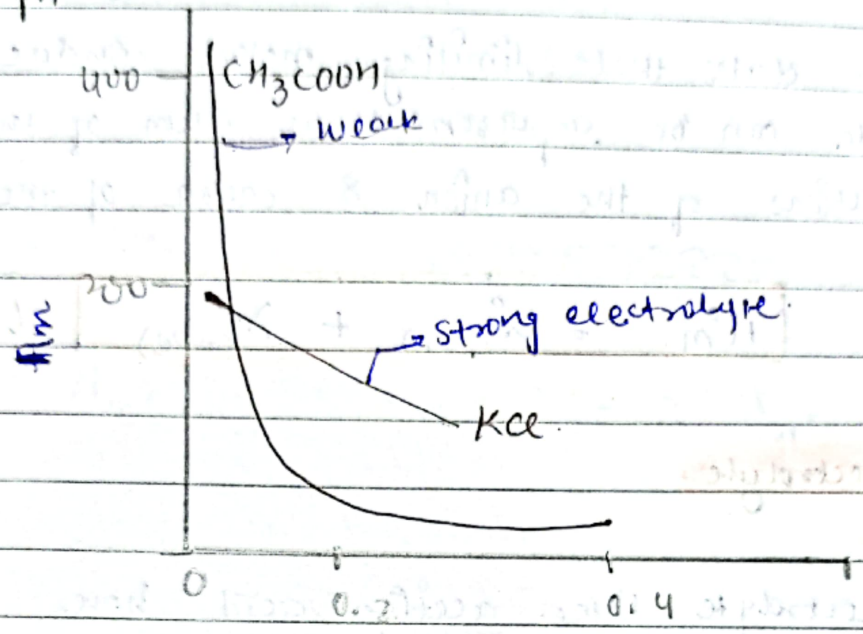
$K_2 = 0.248\ S m^{-1}$

$\Lambda_m = \frac{K}{C} = \frac{0.248 \times 1000}{0.02 \times 1000} = \frac{248}{2} = 124$

$\Lambda_m = 124\ S cm^2/mol$

* Variation of conductivity & molar conductivity.

- conductivity & molar conductivity change with concentration of electrolyte.
- conductivity always decrease with decrease in concentration for both weak & strong electrolyte.
- graph :



$$\Lambda_m = \frac{K}{C}$$

$$\Lambda_m \propto K$$
$$K \propto C$$

- Molar conductivity increase with decrease in concentration and increase with conductivity.

* Limiting Molar Conductivity $[\Lambda_m^\circ]$

⇒ When concentration approaches zero the molar conductivity is known as limiting molar conductivity.

* **For strong electrolytes**

$$\Lambda_m = \Lambda_m^\circ - AC^{1/2}$$

⇒ NaCl, $CaCl_2$, HCl, $MgSO_4$
1:1 2:1 2:2] Ratio of charge.

* **Kohlrausch law of Independent migration of ions**

⇒ The law states that limiting molar conductivity of an electrolyte can be represented as sum of the individual contributions of the anion & cation of the electrolyte.

$$\Lambda_m^\circ = \lambda^\circ_{(+ve)} + \lambda^\circ_{(-ve)}$$ [For strong electrolyte]

* **Weak electrolyte:**

⇒ Weak electrolyte like acetic acid have lower degree of dissociation at higher concentration & hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation

* **Degree of Dissociation**

$$\alpha = \frac{\Lambda_m}{\lambda_m^\circ}$$

⇒ Ratio of molar conductivity to the limiting molar conductivity.

* **Dissociation of weak electrolyte.**

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

Application of Kohlrausch law

we can find Λ_m, Λ_m° with the help of this law

Ex: 2.7

$$\Lambda^\circ_{m(CaCl_2)} = \lambda^\circ_{Ca^{2+}} + 2\lambda^\circ_{Cl^-}$$
$$= 119.0 + 2(76.3)$$
$$= 119 + 152.6$$
$$= 271.6 \text{ S cm}^2/\text{mol}$$

$$\Lambda^\circ_{m(MgSO_4)} = \lambda^\circ_{Mg^{2+}} + \lambda^\circ_{SO_4^{2-}}$$
$$= 106 + 160$$
$$= 266 \text{ S cm}^2/\text{mol}$$

Ex: 2.8

$$\Lambda^\circ_{m(HAc)} = \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{NaAc} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$

$$= \Lambda^\circ_{m\,HCl} + \Lambda^\circ_{m\,NaAc} - \Lambda^\circ_{m(NaCl)}$$
$$= 425.9 + 91.0 - 126.4$$
$$= 390.5 \text{ S cm}^2/\text{mol}$$

Ex: 2.9

$C = 0.001028$ mol/L $K = 4.95 \times 10^{-5}$

$K_a = ?$ $\Lambda^\circ_m = 390.5$

$$\Lambda_m = \frac{K}{C} = \frac{4.95 \times 10^{-5} \times 1000}{0.001028} = 48.15 \text{ S cm}^2/\text{mol}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ} = \frac{48.15}{390.5} = 0.1233$$

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.00128 \times 0.1233}{1 - 0.1233} = 1.78 \times 10^{-5} \text{ mol/L}$$

* Electrolytic cell

⇒ In an electrolytic cell external source of voltage is used to bring about a chemical rxn. The electrochemical processes are of great importance in the laboratory and the chemical industry.

⇒ If DC voltages applied to the two electrodes, then Cu^{2+} ions discharge at cathode [-vely charged] & the following rxn takes place.

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

* Electrolysis

* Faraday's law of electrolysis.

⇒ **Faraday's 1st law**: The amount of chemical rxn which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte [solution or melt].

$$Q = It \quad \text{or} \quad I = \frac{ne}{t} \quad \text{or} \quad Q = ZIT$$

amount of

⇒ **Faraday's 2nd law**: The different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights [Atomic mass of metal ÷ No. of electrons required to reduce the cation]

$$Z = \frac{M \rightarrow \text{molar mass}}{e^- \text{[ions]}}.$$

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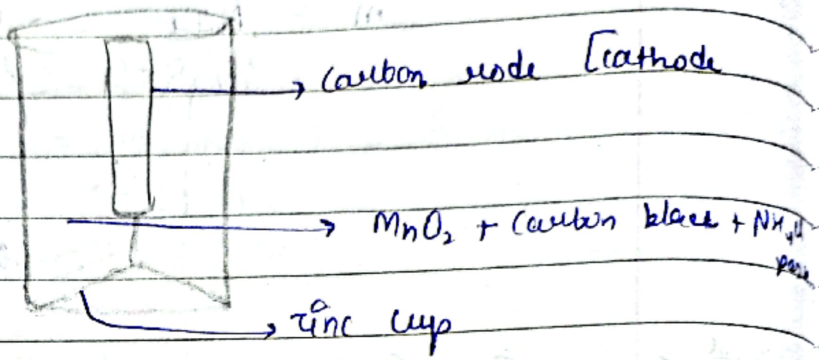
* **Batteries**

→ The combination of two or more cells is kla batteries.

* **Primary Batteries**: The Rxn occurs only once and after use one partial of the battery becomes dead and can't be used again.

① **Dry cell or Leclanche**



→ **Anode Rxn**:

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

→ **Cathode Rxn**:

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

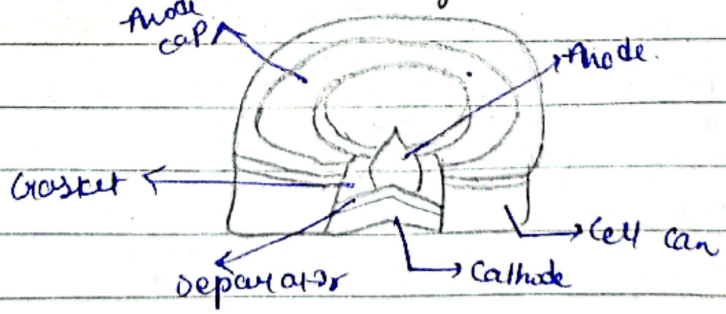
→ Anode: zinc container.

→ Cathode: carbon [graphite] rod surrounded by powdered manganese dioxide & carbon

→ Electrolyte: moist paste of Ammonium chloride & zinc chloride.

Used in: Transistors and clocks.

② **Mercury cell**



→ **Anode Rxn**: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

→ **Cathode Rxn**: $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$

⇒ **Overall Rxn** : $Zn + HgO \rightarrow ZnO + Hg$

⇒ Anode : zinc - mercury amalgam

⇒ Cathode : paste of $HgO + C$

⇒ Electrolyte : paste of KOH and ZnO.

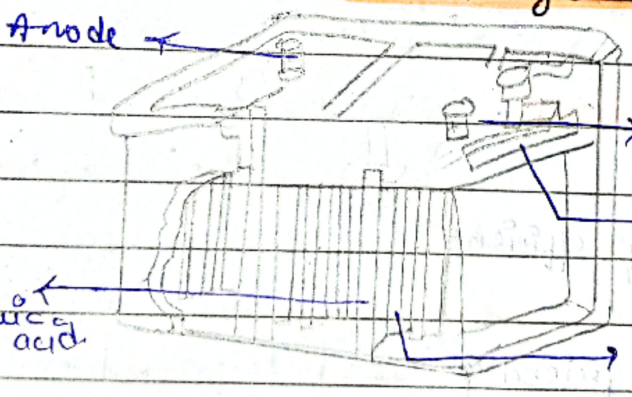
⇒ used in : Hearing aids, watches.

Q why mercury's cell, cell potential is constant?

Ans The cell potential is approx. 1.35 V and remains constant during its life as the overall rxn does not involve any ion in solution whose concentration can change during its life time.

* **Secondary Battery** : A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again.

① **Lead Storage cell**.



⇒ **Anode Rxn** : $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

⇒ **Cathode Rxn** : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$.

⇒ **Overall Rxn** :

⇒ $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

For recharge Reverse the Reaction

This Rxn is for discharge

Anode : lead

Cathode : grid of lead packed with lead dioxide [PbO_2]

Electrolyte : 38% sol. of sulphuric acid.

⇒ Used in : Automobiles and inverters.

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

⇒ Used in : Thermal Power plants.

⇒ **Anode Rxn** : $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

⇒ **Cathode Rxn** : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

⇒ **Overall Rxn** : $2H_2 + O_2 \longrightarrow 2H_2O$.

* **Benefits of Fuel cells**.

- They are energy efficient
- They are eco friendly
- They are less polluting.

Corrosion

=) Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal.

=) The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.

Anode : $2Fe \longrightarrow 2Fe^{2+} + 4e^-$

Cathode : $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Overall : $2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$

Prevention of corrosion :

One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by :

=) Covering the surface with paint or by some chemicals [Eg : bisphenol].

=) Cover the surface by other metals [Sn, Zn etc].

=) An electrochemical method is to provide a sacrificial electrode of another metal [like Mg, Zn etc] which corrodes itself but saves the object.

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* Numericals based on Nernst eqn.

Q1 Calculate the electrode potential of a copper wire dipped in 0.1 M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 volt

Ans $Cu^{2+} + 2e^- \longrightarrow Cu$

So $n = 2$.

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\text{oxidation}]}{[\text{Reduction}]} \rightarrow (Cu^{2+})$$

$$= 0.34 - \frac{0.059}{2} \log \frac{1}{0.1}$$

$$= 0.34 - 0.0295$$

$$= 0.310 \text{ volt}$$

Q A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. $[E^\circ_{Zn^{2+}/Zn} = -0.76V]$

Ans $Zn^{2+} + e^- \longrightarrow Zn$

So $n = 2$

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$

$$[Zn^{2+}] = \frac{95}{100} \times 0.1M = 0.095M$$

$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.059}{2} \log \frac{1}{0.095}$$

$$= -0.76 - 0.0295 \quad [\log 1000 - \log 95]$$

$$= 0.76 - 0.0295 \quad [3 - 1.977]$$

$$= -0.76 - 0.03021$$

$$= -0.790 \text{ volt.}$$

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Q The EMF of the following cell is found to be 0.20 V at 298 K $Cd | Cd^{2+}$ (?) $|| Ni^{2+}$ (2.0 M) $| Ni$

What is the molar concentration of Cd^{2+} ions in the solution

$E^\circ_{Cd^{2+}/Cd} = -0.40\ V$, $E^\circ_{Ni^{2+}/Ni} = -0.25\ V$

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

$$E^\circ_{cell} = -0.25 - (-0.40) = 0.15\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cd^{2+}]}{[Ni^{2+}]}$$

$$0.20 = 0.15 - \frac{0.059}{2} \log \frac{[Cd^{2+}]}{2}$$

$$[Cd^{2+}] = \text{antilog } \bar{2}.6121$$

$$= 0.0409\ M$$

Q At what pH of HCl solution will hydrogen gas electrode show electrode potential of $-0.118\ V$? H_2 gas is bubbled at 298 K & 1 atm pressure

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2$$

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{1} \log \frac{1}{[H^+]}$$

$$= 0 + 0.059 \log [H^+]$$

$$-0.118 = -0.059 \times pH$$

or

$$pH = 2$$

* Numericals based on calculation of ΔG° & k_c from E°_{cell}

Q (a) Calculate the standard free energy & maximum work obtainable for the reaction

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

$E^\circ_{Zn^{2+}/Zn} = -0.76\ V$; $E^\circ_{Cu^{2+}/Cu} = +0.34V$

$F = 96500$

Ans $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.34 - (-0.76)$

$= 1.10$ volt

$n = 2$

$\Delta G^\circ = -nFE^\circ_{cell}$

$= -2 \times 96500 \times 1.10V$

$= -212,300$ J/mol.

(b) Also calculate the equilibrium constant for the rxn.

$\Delta G^\circ = -RT \ln k_c$

$= -2.303\ RT \log k_c$

$-212300 = -2.303 \times 8.314 \times 298 \times \log k_c$

$k_c = \text{antilog } 37.2074$

$= 1.6 \times 10^{37}$

Q Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition rxn:

$\frac{2}{3} Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2$ is $\Delta G = +960$ kj $F = 96500$

$\Delta G = +960$ kj $= 960000$ J $n = 4$

$\Delta G = -nFE$

$960000 = -4 \times 96500 \times E$

$E = -2.487\ V$

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Q The E° values corresponding to the following two reduction electrode processes are :

i) $Cu^+/Cu = +0.52\ V$

ii) $Cu^{+2}/Cu^+ = +0.16V$

Formulate the galvanic cell for their combination. what will be the standard cell potential for it ? calculate ΔG° for cell rxn [F = 96500]

Ans

$$Cu^+ + e^- \longrightarrow Cu$$

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

Overall : $2Cu^+ \longrightarrow Cu + Cu^{2+}$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= 0.52 - 0.16$$

$$= 0.36\ V$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$= -1 \times 96500 \times 0.36$$

$$= -34740\ J/mol$$