



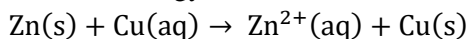
Class : 11

2023 - 24

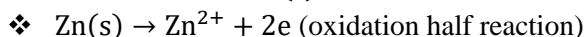
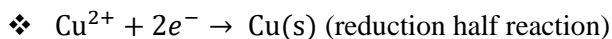
ELECTROCHEMISTRY

GALVANIC CELLS :

- ❖ Galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.



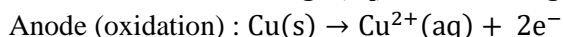
This reaction is a combination of two half reactions whose addition gives the overall cell reaction :



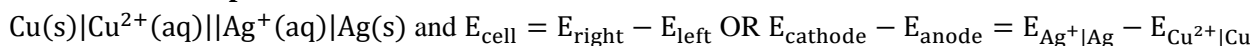
- ❖ The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.
- ❖ A potential difference develops between the electrode and the electrolyte which is called **electrode potential**.
- ❖ When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as standard **electrode potential**.
- ❖ The half-cell in which oxidation takes place is called anode and it has a negative potential with respect to the solution.
- ❖ Half-cell in which reduction takes place is called cathode and it has a positive potential with respect to the solution.
- ❖ The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.
- ❖ It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell.
- ❖ A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.
- ❖ This is illustrated by the following example:



Half-cell reactions :

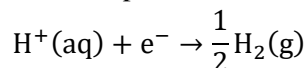


The cell can be represented as :

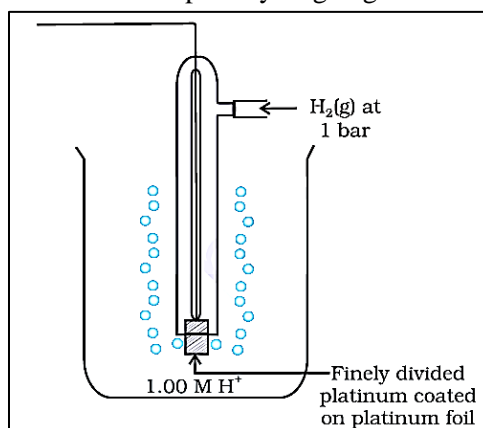


- ❖ **Measurement of Electrode Potential :**

- ❖ According to convention, a half-cell called standard hydrogen electrode represented by $\text{Pt(s)}/\text{H}_2(\text{g})/\text{H}^+(\text{aq})$ is assigned a zero potential at all temperatures corresponding to the reaction.



- ❖ This consist of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution of concentration of 1.0 M H^+ ion and pure hydrogen gas at 1 bar is bubbled through it.



Standard Hydrogen Electrode (SHE)

- ❖ To measure the standard reduction electrode potential value of $E_{\text{Cu}^{2+}|\text{Cu}}^0$, we will make standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode ($\text{Cu}^{2+}|\text{Cu}$)
 $\text{Pt(s)}|\text{H}_2(\text{g}, 1 \text{ bar})|\text{H}^+(\text{aq}, 1 \text{ M})||\text{Cu}^{2+}(\text{aq}, 1 \text{ M})|\text{Cu}$
 The measured *emf* of this cell is +0.34 V which is equal to the value of $E_{\text{Cu}^{2+}|\text{Cu}}^0$.

NERNST EQUATION :

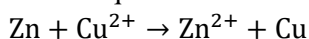
For the electrode reaction : $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightarrow \text{M}(\text{s})$ the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by :

$$E_{(\text{M}^{n+}|\text{M})} = E_{(\text{M}^{n+}|\text{M})}^0 - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

concentration of solid M is taken as unity, and we have

$$E_{(\text{M}^{n+}|\text{M})} = E_{(\text{M}^{n+}|\text{M})}^0 - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

Nernst equation for **Daniell cell** i.e.,



$$E_{(\text{cell})} = E_{(\text{cell})}^0 - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{M}^{n+}]}$$

EQUILIBRIUM CONSTANT FROM NERNST EQUATION :

$$E_{(\text{cell})}^0 - \frac{2.303 RT}{nF} \log K_C$$

ELECTROCHEMICAL CELL AND GIBBS ENERGY OF THE REACTION :

- If the *emf* of the cell is E and of is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -nFE_{(\text{cell})}$$

- $E_{(\text{cell})}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n .

If the concentration of all the reacting species is unity, then $E_{(\text{cell})} = E_{(\text{cell})}^0$ and we have

$$\Delta_r G^\circ = nFE_{(\text{cell})}^0$$

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

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS :

- The electrical resistance is represented by the symbol 'R' and it is measured in ohm (Ω)

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

The constant of proportionality, ρ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm metre ($\Omega \text{ m}$)

- The inverse of resistance, R, is called conductance G

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

- The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm (also known as mho) or Ω^{-1} .
- The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, κ .
- The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1} .
- Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on
 - ❖ the nature and structure of the metal
 - ❖ the number of valence electrons per atom
 - ❖ temperature (it decreases with increase of temperature).
- The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance, The conductivity of electrolytic (ionic) solutions depends on :

- ❖ the nature of the electrolyte added
- ❖ size of the ions produced and their solvation
- ❖ the nature of the solvent and its viscosity
- ❖ concentration of the electrolyte
- ❖ temperature (it increases with the increase of temperature).

- **Measurement of the Conductivity of Ionic Solutions:**

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

The quantity A is called cell constant denoted by the symbol, G^* .

$$G^* = \frac{l}{A} = R \kappa$$

- **Molar conductivity :** It can be defined as the conductance of the one mole of the electrolytic solution containing electrodes of conductivity cell at unit distance.

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{C} \text{ OR } \kappa V$$

$$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1}) = \frac{\kappa (\text{S cm}^{-1}) \times 1000 (\text{cm}^3/\text{L})}{\text{molarity (mol/L)}}$$

- **Variation of Conductivity and Molar Conductivity with Concentration:**

- ❖ Conductivity always decreases with decrease in concentration both for weak and strong electrolytes because the number of ions per volume that carry the current in a solution decreases on dilution.
- ❖ Molar conductivity increases with decrease in concentration. This because the total volume, V , of solution containing one mole of electrolyte also increases.
- ❖ It has been found that decrease in k on dilution of a solution is more than compensated by increase in its volume.
- ❖ When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ_m° .

- **Strong Electrolytes:** For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation :

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

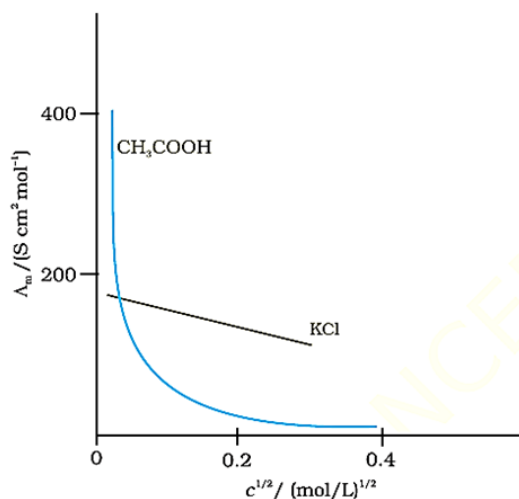


Fig.: Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

- ❖ **Kohlrausch law of independent migration** of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda_m^\circ (\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

If an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by :

$$\lambda_m^\circ = v_+ \lambda_+^\circ + v_- \lambda_-^\circ$$

Weak Electrolytes :

- ❖ For Weak electrolytes Λ_m increases steeply (Fig. 3.6) on dilution, due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte.
- ❖ Any concentration c , if α is the degree of dissociation, then it can be approximated to the ratio of molar conductivity Λ_m at the concentration c to limiting molar conductivity Λ_m° . Thus we have :

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

$$\text{Also, } K_a = \frac{c\alpha^2}{(1-\alpha)}$$

- **Applications of Kohlrausch law:**

- ❖ It is possible to calculate Λ_m° for any electrolyte from the λ° of individual ions.
- ❖ Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the Λ_m° and Λ_m at a given concentration (c).

Conductance of Electrolytic Solutions :

- In an electrolytic cell external source of voltage is used to bring about a chemical reaction.
- Michael Faraday was the first scientist who described the quantitative aspects of electrolysis.
- **Faraday's Laws of Electrolysis :**
 - ❖ **First Law :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
 - ❖ **Second Law :** The amounts of 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 / Number of electrons required to reduce the cation).

$$Q = It$$

Q is in coulombs when I is in ampere and t is in second.

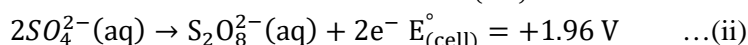
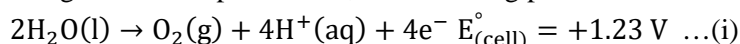
The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction.

This quantity of electricity is called Faraday and is represented by the symbol F .

$1F = 96500 \text{ C mol}^{-1}$.

- **Products of Electrolysis :**

- ❖ Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. For sulphuric acid, the following processes are possible during the electrolysis at the anode :



For dilute sulphuric acid, reaction (i) is preferred but at higher concentrations of H_2SO_4 , reaction (ii) is preferred.

Batteries :

- **Primary Batteries:** A commercial dry cell consists of a graphite (carbon) cathode in a zinc container, the latter acts as the anode.
- **Secondary Batteries:** These batteries can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery.
 - ❖ **Anode :** $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
 - ❖ **Cathode :** $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{e}^- + 2\text{H}^+ \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 - ❖ **Overall reaction :** $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

On charging the battery the reaction is reversed and PbSO_4 on anode and cathode is converted into Pb and PbO_2 .

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.

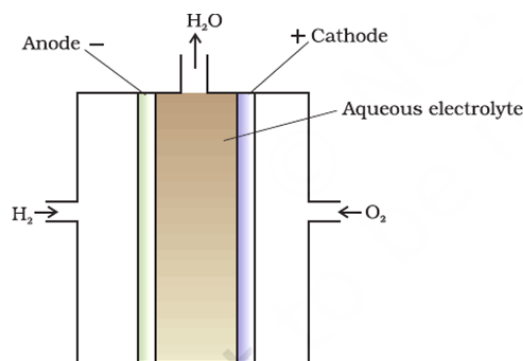
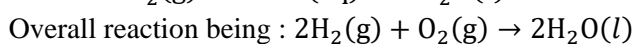
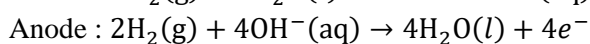
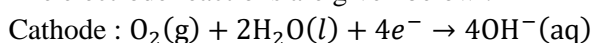


Fig. : Fuel cell using H_2 and O_2 produces electricity.

- The cell was used for providing electrical power in the Apollo space programme.
- The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts.

The electrode reactions are given below :

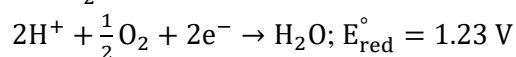
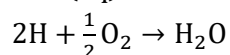
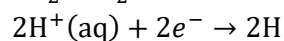
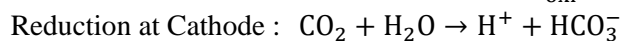
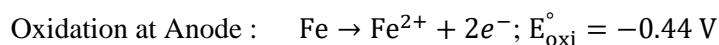


Fuel cell produce electricity with an efficiency of about 70% compared.

Name of cell/Battery	Anode (-)	Cathode (+)	Electrolyte	Reactions at electrodes	E_{cell}
• Dry cell (primary cell)	Zn container	Graphite rod	Powdered $MnO_2 + C$ + Paste of $NH_4Cl + ZnCl_2$	Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ Cathode: NH_3 forms complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$ $MnO_2 + 2NH_3 + e^- \rightarrow MnO(OH) + NH_3$, NH_3 Forms Complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$	1.25 to 1.5 V
• Mercury cell (primary cell)	Zn-Hg amalgam	Paste of HgO and C	Paste of KOH + ZnO	Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ Cathode: $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$	1.35 V
• Lead storage Battery (secondary cell)	Pb	Pb + PbO_2	38% by mass H_2SO_4 ($d=1.30 \text{ g cm}^{-3}$)	Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ On applying a potential slightly greater than the potential of battery, battery can be recharged.	12 V consists of 6 cell each producing 2 V
• Ni-Cd Secondary cell Or Ni-Cd cell (Rechargeable)	Cd	NiO_2	Moist KOH	Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$ Cathode: $NiO_2(s) + 2H_2O + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$	1.4 V
• Fuel cell (H_2-O_2)	Porous carbon containing catalyst (finely divided Pt and Pd)	Porous carbon containing catalyst (finely divided Pt and Pd)	Concentrated NaOH solution	Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$ Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.09 V

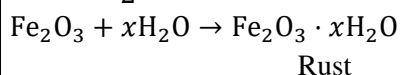
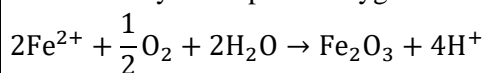
Corrosion :

- **In corrosion**, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).
- **Rusting of Iron** : According to electrochemical theory, rusting can be represented as :



Overall reaction of corrosion cell :

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.



Prevention of Corrosion :

- ❖ The metal surface is coated with paint which keeps it out of contact with air, moisture etc.
- ❖ By applying film of oil and grease on the surface of the iron tools and machinery.
- ❖ The iron surface is coated with non-corroding metals such as nickel, chromium, aluminium, etc.



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