ELECTROCHEMISTRY

ELECTROCHEMISTRY

- Deals with the chemical changes caused by the passage of electricity.
- The production of electricity caused by chemical changes is called electrochemistry.
- Focuses on Electrolytic and Electrochemical cells.

ELECTROCHEMICAL CELLS OR GALVANIC CELLS

- Device used for the conversion of chemical energy into electrical energy.
- Eg: Daniel Cell
- Electrochemical cell produces electricity using redox reactions.

CONSTRUCTION AND WORKING OF A DANIEL CELL

- The Daniel Cell consists of a zinc electrode dipped in $ZnSO_4$ solution.
- A copper electrode is dipped in $CuSO_4$ solution.
- The two solutions are connected by a salt bridge.
- The two electrodes are connected externally by a metallic wire through a voltmeter.
- A potential difference is developed which is indicated by the stream of electrons flowing from Zn to Cu.
- The cell is represented as $Zn|zn^{2+}||Cu^{2+}|Cu$
- Here oxidation takes place at the Zn electrode.
- Reduction takes place at the Cu electrode.
- The Zn electrode at which oxidation takes place is the anode.
- The copper electrode at which reduction takes place is the cathode.

Cell Reactions

- **Anode Reaction** : $Zn \longrightarrow Zn^{2+} + 2e^-$
- **Cathode Reaction** : $Cu^{2+} + 2e^- \longrightarrow Cu$
- **Overall Cell Reaction** : $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$
- The flow of electrons from Zn to Cu produces a current in the circuit.

Cell Representation

Daniel Cell is represented as

$$\underset{\text{anode}}{Zn(s) \mid Zn^{2+}(aq, +M)} \underset{\text{salt bridge}}{\|} \underset{\text{cathode}}{Cu^{2+}(aq, +M) \mid Cu(s)}$$

SALT BRIDGE AND ITS FUNCTIONS

- Salt bridge is a 'U' shaped tube containing a concentrated solution of electrolyte like KCl, KNO_3, NH_4NO_3 etc mixed with gelatin or agar agar.

Functions

- It allows the movement of ions from one solution to other without mixing of the two solutions.
- It maintains the electrical neutrality of the solution.

NOTE

- **Anode**: The electrode at which **Oxidation** takes place. (Code: **AN OX**)
- Loss of electrons occurs.
- **Cathode**: Electrode at which **Reduction** takes place. (Code: **RED CAT**)
- Gain of electrons

QUESTIONS

1. Represent galvanic cell made up of Zn and Fe electrodes.

$$Zn \mid zn^{2+} \| Fe^{2+} \mid Fe$$

2. From the position of the elements in the electrochemical series, copper(Cu) can displace silver(Ag) from silver nitrate solution.

a) Represent the cell, constructed with silver and copper electrodes.

b) Write down the reaction taking place at the anode and cathode.

a) $Cu \mid Cu^{2+} \| Ag^{+} \mid Ag$

b) Anode Reaction : $Cu \longrightarrow Cu^{2+} + 2e^{-}$

Cathode Reaction : $Ag^{+} + e^{-} \longrightarrow Ag$

ELECTRODE POTENTIAL (E)

- Tendency of an electrode to lose or gain electrons when it is in contact with its own ions in the solution is called its electrode potential.
- The electrode potential may be of two types.

1. OXIDATION POTENTIAL

- The tendency of an electrode to lose electrons is called its oxidation potential.

$$M \longrightarrow M^{n+} + ne^{-}$$

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

2. REDUCTION POTENTIAL

- The tendency of an electrode to lose electrons is called its oxidation potential.

$$M^{n+} + ne^- \longrightarrow M$$

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

STANDARD ELECTRODE POTENTIAL (E^0)

- The potential of an electrode under standard conditions i.e., 298K, 1 atm pressure and 1 Molar concentration is called standard electrode potential.

EMF OR CELL POTENTIAL

- The electrochemical cell consists of two half cells.
- The difference in potential between the two electrodes in a cell is called electromotive force or cell potential.

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

$$E_{cell} = E_{Right} - E_{Left}$$

Standard EMF, $E^0_{cell} = E^0_{Right} - E^0_{Left}$

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$$

QUESTION

1. Consider the reaction, $2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$. The standard electrode potentials for $Ag^+ \longrightarrow Ag$ and $Cd^{2+} \longrightarrow Cd$ couples are 0.80 volt and -0.40 volt, respectively.

(i) What is the standard potential E° for this reaction?

(ii) For this electrochemical cell, which electrode is negative electrode?

(i) Oxidation Half Reaction: $Cd \longrightarrow Cd^{2+} + 2e^-$ (i)

Reduction Half Reaction: $2Ag^+ + 2e^- \longrightarrow 2Ag$

$E^oAg^+/Ag = 0.80$ volt (Reduction potential)

$E^oCd^+/Cd = -0.40$ volt (Reduction potential)

$$E^0_{cell} = E^0_{cathode} - E^0_{Anode}$$

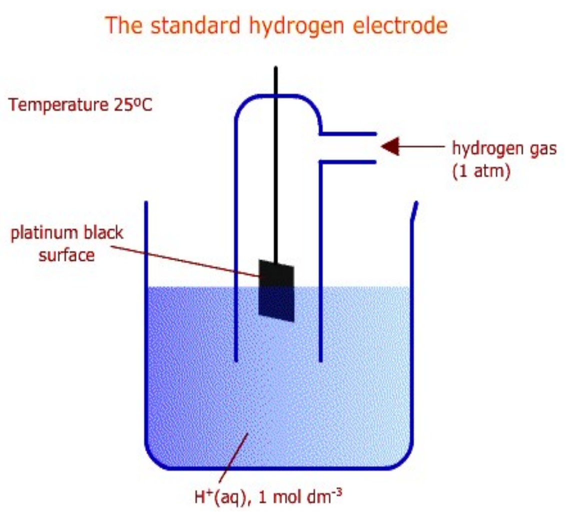
$$E^0_{cell} = E^0_{Cd^{2+}/Cd} - E^0_{Ag^+/Ag}$$

$$E^0_{cell} = 0.80 + 0.40 = 1.20\ V$$

ii) Silver Electrode

STANDARD HYDROGEN ELECTRODE (SHE)

- SHE consists of Pt wire sealed in a glass tube and has a Pt foil attached to it.



- The foil is coated with finely divided Pt.
- It is dipped into an acid solution containing H^+ ions having 1M concentration.
- Pure hydrogen gas at 1 atm pressure is bubbled into the solution at constant temperature.
- The Standard Hydrogen Electrode can be represented as

  $Pt, H_2 | H^+$ when it acts as anode

  $H^+ | H_2, Pt$ when it acts as cathode

CELL REACTIONS

- If SHE acts as anode, $H_2 \longrightarrow 2H^+ + 2e^-$
- If SHE acts as cathode, $2H^+ + 2e^- \longrightarrow H_2$
- If SHE acts as a reversible electrode, $H_2 \rightleftharpoons 2H^+ + 2e^-$
- For convenience the potential of SHE is arbitrarily fixed as zero.

MEASUREMENT OF STANDARD ELECTRODE POTENTIAL

- The electrode, whose standard electrode potential is to be measured, is coupled with a SHE through a voltmeter.
- The voltmeter reading indicates the potential difference between the two electrodes.
- Since the potential of SHE is taken as zero, the measured emf is equal to the potential of the electrode.

  Eg: $Pt, H_2 | H^+ \| Cu^{2+} | Cu$

- The voltmeter reading is 0.34 volts.

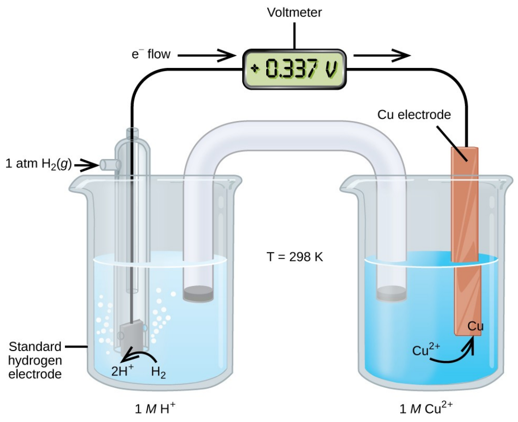
$$EMF = E_{Right} - E_{Left}$$

$$EMF = E_{Cu} - E_{SHE}$$

$$EMF = 0.34V$$

$$0.34 = E_{Cu} - 0$$

$$E_{Cu} = 0.34V$$



ELECTROCHEMICAL SERIES

- The arrangement of various elements in the increasing order of their standard reduction potential by taking hydrogen as a standard is called electrochemical series.

APPLICATIONS OF ELECTROCHEMICAL SERIES

1. CALCULATION OF STANDARD EMF OF CELLS

- The EMF of a cell is given by the equation

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

- It is possible to calculate the standard electrode potentials of cells from the electrochemical series.
- Standard EMF of the cell is calculated by applying the formula

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

NOTE

- The electrode with higher reduction potential acts as cathode while that with lower reduction potential will act as anode.

2. TO CALCULATE THE RELATIVE STRENGTH OF OXIDISING AND REDUCING AGENT

- Substances with lower reduction potentials have greater tendency to undergo oxidation.
- They are strong reducing agents.
- Substances with higher reduction potentials have greater tendency to undergo reduction.
- They are strong oxidising agents.
- In general, Substances with higher reduction potentials are strong oxidising agents while substances with lower reduction potentials are strong reducing agents.

3. PREDICTING THE FEASIBILITY OF A REDOX REACTION

- Electrochemical series helps to predict the feasibility of a redox reaction.
- In a redox reaction, the species undergoing reduction should have relatively higher E^0 value than the species which undergo oxidation.
- If the condition is fulfilled, the redox reaction is feasible.
- If the EMF of the cell is +ve, the redox reaction is feasible.
- If the EMF is —ve, the redox reaction is not feasible.

4. TO PREDICT WHETHER A METAL CAN LIBERATE HYDROGEN FROM ACIDS

- The metals which are placed above hydrogen is the electrochemical cells are capable of liberating hydrogen from acids.
- i.e., metals having —ve electrode potentials can liberate hydrogen from acids.

NOTE

- Higher the reduction potential value, reduction tendency is more, it gets reduced, act as an **oxidizing agent**
- The electrode with higher reduction potential acts as **cathode.**
- Electrode of lower reduction potential act as **anode.**
- Higher oxidation potential- **Reducing agent**

QUESTIONS

1. Can copper displace H_2 from dilute acids?

- Copper cannot displace H_2 from dilute acids, because the standard reduction potential of copper will be higher than that of hydrogen.

2. When a zinc piece is dipped in $CuSO_4$ solution, the blue color of the solution is discharged. Account for the observation on the basis of electrode potential values.

- The standard reduction potential of copper is higher than that of zinc.
- The metal having lower reduction potential can displace the metal having higher reduction potential from the solution of metal ions.

3. Standard electrode potentials of some electrodes are given below

$E^0_{Zn} = -0.76V$, $E^0_{Cu} = +0.34V$, $E^0_{H_2} = 0.00V$, $E^0_{Fe} = -0.44V$

a) Represent the galvanic cell made up of Zn and Fe electrodes.

$Zn|zn^{2+} \| Fe^{2+}|Fe$

b) Calculate the standard e.m.f. of the above cell.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.44-(-0.76)$$

$$E^0_{cell} = 0.32V$$

c) When a Zn piece is dipped in copper sulphate solution, the blue colour of the solution is discharged. Account for the observation on the basis of electrode potential values.

The standard reduction potential of copper is higher than that of Zn. The metal having lower reduction potential can displace the metal having higher reduction potential from the solution of metal ions.

d) Can copper displace H_2 from dilute acids? Why?

Copper cannot displace H_2 from dilute acids because the standard reduction potential of copper will be higher than that of hydrogen.

4. The standard electrode potentials of some electrodes are given below:

$E^0(Zn^{2+}/Zn) = -0.76V$, $E^0(Cu^{2+}/Cu) = 0.34V$, $E^0(Ag^+/Ag) = 0.8V$, $E^0(H^+/H_2) = 0$ V.

a) Can $CuSO_4$ solution be kept in silver vessel?

Since the standard reduction potential of silver is higher than that of copper, $CuSO_4$ solution can be kept in silver vessel.

b) Zn or Cu, which can displace hydrogen from dil. H_2SO_4?

Zinc has lower standard reduction potential than hydrogen and hence it can displace hydrogen from dil. H_2SO_4.

c) What is the reaction taking place at SHE when it is connected with Ag^+/Ag electrode to form a galvanic cell?

SHE is acting as the anode and hence the following reactions take place.

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

5. From the position of elements in the electrochemical series, Cu can displace Ag from $AgNO_3$ solution.

a) Represent the cell constructed with Cu and Ag electrodes.

$Cu|Cu^{2+} \parallel Ag^{+}Ag$

b) Write down the cell reaction taking place at the anode.

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

c) Write down the reaction taking place at the cathode

$Ag^+ + 1e^- \longrightarrow Ag$

c) Write the Nernst equation for the above cell reaction.

$$E_{cell} = E^0_{cell} + \frac{2.303RT}{nF} \log \frac{[Ag^+]}{[Cu^{2+}]}$$

NERNST EQUATION

- Nernst gave a relationship between electrode potentials and the concentration of electrolyte solutions known as Nernst equation.
- Consider a general redox reaction, $M^{n+} + ne^- \rightleftharpoons M$
- The Nernst equation for the above reaction can be written as

$$E_{M^{n+}|M} = E^0_{M^{n+}|M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}|M} = E^0_{M^{n+}|M} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]} \qquad [\ln x = 2.303 \log x]$$

Where $E_{M^{n+}|M}$ = Electrode Potential

$E^0_{M^{n+}|M}$ = Standard Electrode Potential

R = Gas Constant

T = Temperature

n = No. of electrons gained

$$E_{M^{n+}|M} = E^0_{M^{n+}|M} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}|M} = E^0_{M^{n+}|M} - \frac{0.059}{n} \log \frac{[M]}{[M^{n+}]}$$

NERNST EQUATION FOR DANIEL CELL

Consider the redox reaction $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

The Nernst Equation for the above cell reaction is

$$E_{Cell} = E^0_{Cell} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

QUESTION

1. To find the standard potential of M^{3+}/M electrode, the following cell is constituted: $Pt|M|M^{3+}$(0.0018 mol-1L)||Ag^+(0.01 mol-1L)|Ag. The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction $M^{3+} + 3e^- \longrightarrow M = 0.80$ volt.

Solution:

The cell reaction is: $M + 3Ag^+ \longrightarrow 3Ag + M^{3+}$

Applying Nernst equation,

$$E_{cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{\left[Mg^{2+}\right]}{\left[Ag^+\right]^3}$$

$$0.42 = E^0_{Cell} - \frac{0.0591}{n} \log \frac{\left[0.0018\right]}{\left[0.01\right]^3}$$

$0.42 = E^0_{cell} - 0.064$

$E^0_{cell} = (0.042+0.064) = 0.484$ volt

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$$

$$E^0_{Anode} = E^0_{Cathode} - E^0_{Cell}$$

$= (0.80-0.484) = 0.32$ volt

CALCULATION OF EQUILIBRIUM CONSTANT FROM NERNST EQUATION

- Consider a redox reaction $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$
- The equilibrium constant $K_C = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$
- The Nernst equation for the above cell reaction can be represented as

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- At equilibrium, $E_{cell} = 0$

$$0 = E^0_{cell} - \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^0_{cell} = \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^0_{cell} = \frac{2.303RT}{nF} \log K_C$$

$$E^0_{cell} = \frac{0.059}{n} \log K_C$$

$$\log K_C = \frac{nE^0_{cell}}{0.059}$$

QUESTIONS

1. You are supplied with the following substances: Copper rod, Zinc rod, Salt bridge, two glass beakers, a piece of wire, 1M $CuSO_4$ solution, 1M $ZnSO_4$ solution.

a) Represent the cell made using the above materials.

The cell is represented as $Zn|zn^{2+} \| Cu^{2+}|Cu$

b) Write the Nernst equation for the above cell.

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

c) Calculate the standard EMF of the cell if $E^0_{Zn^{2+}/Zn} = -0.76$ V and $E^0_{Cu^{2+}/Cu} = +0.34$V.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.34 - (-0.76)$$

$$E^0_{cell} = 0.46V$$

d) Find the value of Kc (equilibrium constant) in the Daniel cell at 298K.

$$E^0_{cell} = E^0_{Right} - E^0_{Left}$$

$$E^0_{cell} = 0.34 - (-0.76) = 1.10V$$

$$E^0_{cell} = \frac{0.059}{n} \log K_C$$

$$1.10 = \frac{0.059}{n} \log K_C$$

$$1.10 = \frac{0.059}{2} \log K_C$$

ELECTROCHEMICAL CELL AND GIBBS FREE ENERGY

- The free energy of a cell reaction is related to the cell potential as

$$\Delta G = -nFE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

- Where ΔG is the free energy change.
- In the standard state, the reaction is given as

$$\Delta G^0 = -nFE^0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

- But $E^0 = \frac{2.303RT}{nF} \log K$
- Substituting the value of E^0 in equation (2)

$$\Delta G^0 = -nF \times \frac{2.303RT}{nF} \log K$$

$$\Delta G^0 = -2.303 RT \log K$$

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

OHMS LAW

- Law states that the strength of the current flowing conductor is directly proportional to potential difference (V) applied across the conductor and is inversely proportional to the resistance of the conductor.

i.e., $I \alpha V$

$I = \frac{V}{R}$ where V = potential difference and R is the resistance

RESISTANCE (R)

- It is the measure of obstruction to the flow of current.
- The resistance of any conductor is proportional to the length 'ℓ' and inversely proportional to the area of cross section.

i.e., $R \alpha \frac{\ell}{a}$

$$R = \rho . \frac{\ell}{a}$$

$\rho = R . \frac{a}{\ell}$ where 'ρ' is the resistivity

- The unit of resistance is Ω.

SPECIFIC RESISTANCE

- Specific resistance is the resistance of a conductor of unit length and unit area of cross section.
- Its unit is Ω cm.

CONDUCTANCE (C)

- It is the reciprocal of resistance.
- It implies the ease with which the current flows through the conductor.

$$C = \frac{1}{R}$$

- Its unit is Ω^{-1} or Siemens 'S'.

SPECIFIC CONDUCTANCE (κ)

- It is the conductance of a conductor of unit length and unit area of cross section.
- It is denoted by κ

$$\kappa = C.\frac{\ell}{a}$$

- Its unit is Ω^{-1} cm^{-1}.

EQUIVALENT CONDUCTANCE (λ)

- It is the conducting power of all the ions produced by dissolving 1g equivalent of an electrolyte in solution.
- It is denoted by the symbol λ.

$$\lambda = \frac{\kappa \text{ X } 1000}{C}$$

where 'C' is the concentration

- Its unit is Ω^{-1} cm^2 $equiv^{-1}$

MOLAR CONDUCTANCE (λ_m)

- It is the conducting power of all the ions produced by dissolving 1g mole of an electrolyte in solution.
- It is denoted by the symbol λ_m

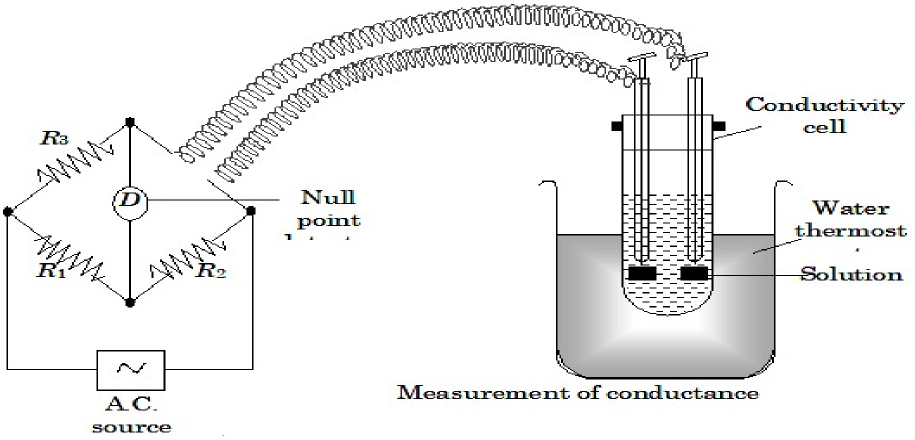
$$\lambda_m = \frac{\kappa \text{ x } 1000}{M}$$

where 'M' is the molarity

- Its unit is Ω^{-1} cm^2 mol^{-1}

MEASUREMENT OF THE CONDUCTIVITY OF IONIC SOLUTIONS

- The conductance of a solution is the reciprocal of resistance.
- Therefore, the experimental determination of conductance involves the measurement of resistance.
- The resistance is commonly measured with the help of Wheatstones Bridge.
- One arm of the bridge is made as the conductivity cell.
- The solution whose resistance is to be measured is placed in the conductivity cell.
- The cell is placed in the thermostat to keep the temperature constant.
- The electrodes of the cell are made up of platinum coated with platinum black.
- An alternating current of frequency 1000—3000 cycles per second is used.
- When the current flows through the circuit, the resistances R_1, R_2, R_3 are so adjusted to get no current.
- This is indicated by the null point detector. At this point $\frac{R_{Soln}}{R_3} = \frac{R_2}{R_1}$
- Since R_1, R_2, R_3 are known, the resistance of the solution is calculated and its reciprocal gives the conductance of the solution.



CALCULATION OF SPECIFIC CONDUCTANCE (κ)

- The specific conductance is related to the conductance by the relation $\kappa = C.\frac{\ell}{a}$
- The quantity $\frac{\ell}{a}$ is called cell constant. It s unit is cm^{-1}.

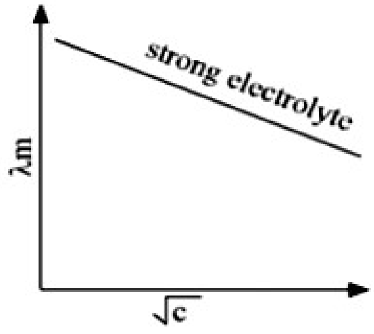
$$\kappa = \frac{1}{R} x \frac{\ell}{a}$$

$$\kappa = \frac{\text{Cell constant}}{R}$$

VARIATION OF MOLAR CONDUCTANCE WITH CONCENTRATION

- Molar conductance of a solution increases with dilution and reaches a limiting value.
- The maximum value of molar conductance at high dilution is known as **molar conductance at infinite dilution**, λ_m^0 .
- The equivalent conductance of a solution increases with dilution and reaches a limiting value.
- This maximum value of equivalent conductance at high dilution is known as **equivalent conductance at infinite dilution**, λ^0 .
- The variation of molar conductance with concentration can be studied by plotting the values of λ against square root of concentration.

a) For Strong Electrolytes



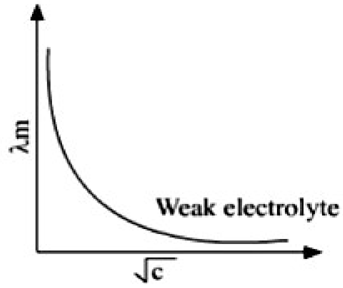
- For strong electrolytes, the number of ions in the solution do not increase because, these are almost completely ionised in solutions at all concentration.
- However, in concentrated solutions of strong electrolytes the density of ions is relatively high which results in the significant inter ionic interaction.
- Such interactions effectively reduce the speed of the

ions and are responsible for the lower value of λ_m .

- On increasing the dilution, the ions move apart and inter ionic interactions are decreased. As a result, λ_m increases.

b) For Weak Electrolytes

- For weak electrolytes, the variation in the value of molar conductance with dilution can be explained on the basis of number of ions furnished by it in the solution.
- The number of ions furnished by the electrolyte in solution depends upon the degree of ionisation of the electrolyte.
- On dilution, the degree of ionisation of the electrolyte increases, thereby increasing the value of λ_m .
- When the limiting value of molar conductance is reached, whole of the solute dissociate into ions. $\alpha = \frac{\lambda_m}{\lambda_m^0}$,



- $\alpha = \frac{\text{Molar conductivity at a given concentration}}{\text{Molar conductivity at infinite dilution}}$

LIMITING MOLAR CONDUCTIVITY

The molar conductivity of a solution at infinite dilution is known as limiting molar conductivity. **OR**

When the concentration of the electrolyte approaches zero, the molar conductivity is known as limiting molar conductivity.

QUESTION

1. Explain how conductivity measurements help to determine the ionisation constant of a weak electrolyte like acetic acid.

For weak electrolytes, the degree of dissociation $\alpha = \frac{\lambda_m^c}{\lambda_m^0}$ where λ_m^c is the molar conductance at concentration 'C' and λ_m^0 is the limiting molar conductivity. Ionization constant of weak electrolyte,

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

$$K_a = C\left(\frac{\lambda_m^c}{\lambda_m^0}\right)^2$$

KOHLRAUSCH'S LAW

- Kohlrausch's law states that at infinite dilution, when the dissociation is complete, each ion makes a definite contribution towards the molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated. **OR**

- Kohlrausch's law states that the molar conductance at infinite dilution of an electrolyte is the sum of the molar conductance of the ions.
- Eg: λ_m^0 for NaCl and $MgCl_2$, $BaCl_2$ and $AlCl_3$ can be written as

$$\lambda^0_{M\,NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$$

$$\lambda^0_{M\,MgCl_2} = \lambda^0_{Mg^{2+}} + 2\lambda^0_{Cl^-}$$

$$\lambda^0_{M\,BaCl_2} = \lambda^0_{Ba^{2+}} + 2\lambda^0_{Cl^-}$$

$$\lambda^0_{M\,AlCl_3} = \lambda^0_{Al^{3+}} + 3\lambda^0_{Cl^-}$$

APPLICATIONS OF KOHLRAUSCH'S LAW

DETERMINATION OF λ_M^0 FOR WEAK ELECTROLYTES

- The molar conductance at infinite dilution for a weak electrolyte can be calculated by using Kohlrausch's law.
- For example, λ_M^0 values for acetic acid can be calculated from the λ_M^0 values of CH_3COONa, HCl, NaCl.

$$\lambda^0_{M\,CH_3COOH} = \lambda^0_{CH_3COO^-} + \lambda^0_{H^+} \quad \text{..............................} \ (1)$$

$$\lambda^0_{M\,CH_3COONa} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} \quad \text{..............................} \ (2)$$

$$\lambda^0_{M\,HCl} = \lambda^0_{H^+} + \lambda^0_{Cl^-} \quad \text{..............................} \ (3)$$

$$\lambda^0_{M\,NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \quad \text{..............................} \ (4)$$

Eqn (2) + (3) — (4)

$$\lambda^0_{M\,CH_3COONa} + \lambda^0_{M\,HCl} - \lambda^0_{M\,NaCl} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} + \lambda^0_{H^+} + \lambda^0_{Cl^-} - \left(\lambda^0_{Na^+} + \lambda^0_{Cl^-}\right)$$

$$\lambda^0_{M\,CH_3COONa} + \lambda^0_{M\,HCl} - \lambda^0_{M\,NaCl} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} + \lambda^0_{H^+} + \lambda^0_{Cl^-} - \lambda^0_{Na^+} - \lambda^0_{Cl^-}$$

$$= \lambda^0_{CH_3COO^-} + \lambda^0_{H^+} \quad \text{..............................} \ (5)$$

From equations (1) and (5)

$$\lambda^0_{M\,CH_3COOH} = \lambda^0_{M\,CH_3COONa} + \lambda^0_{M\,HCl} - \lambda^0_{M\,NaCl}$$

ELECTROLYSIS

- The phenomenon of decomposition of an electrolyte by the passage of electric current is called electrolysis.

ELECTROLYTIC CELL

- The device used to carry out electrolysis is called electrolytic cell.
- In an electrolytic cell, external source of voltage is used to bring about a chemical reaction.
- An electrolytic cell consists of an electrolyte and two metal electrodes connected to a battery.
- The electrode connected to the positive terminal of the battery is called **anode.**
- The electrode connected to the negative terminal of the battery is called **cathode**.
- During electrolysis +ve ions migrate the −ve electrode i.e., cathode
- The −ve ions migrate to the positive electrode i.e., anode.

ELECTROLYSIS OF MOLTEN NaCl

- Molten NaCl contains free Na^+ and Cl^- ions.
- When it is electrolysed, sodium is deposited at the cathode and Cl_2 is liberated at anode.
- The reactions are
- At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$
- At cathode: $2Na^+ + 2e^- \longrightarrow 2Na$
- Overall cell reactions is $2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$

ELECTROLYSIS OF AQUEOUS NaCl

- Aqueous NaCl contains Na^+, Cl^-, H^+ and OH^- ions. During electrolysis, Cl_2 is liberated at the anode and H_2 at the cathode.
- NaOH is formed in the solution.
- The reactions are
- At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$
- At cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$
- Overall cell reactions is $2Cl^- + 2H_2O \longrightarrow 2OH^- + H_2$

FARADAY'S LAWS OF ELECTROLYSIS

1. FARADAY'S FIRST LAW

- The law states that the amount of substance liberated or deposited at the electrode is directly proportional to the quantity of electricity passed through the electrolyte.

$$m \ \alpha \ Q$$
$$m \ \alpha \ ct$$
$$m \ \alpha \ zct$$

2. FARADAY'S SECOND LAW

- The law states that when the same quantity of electricity is passed through different electrolyte solutions connected in series, the weights of different substances produced at the electrodes are proportional to their equivalents weights.

- 1 Faraday = 96, 500 C

ELECTROCHEMICAL EQUIVALENT

- Electrochemical equivalent of a substance is the mass of substance liberated or deposited at an electrode on passing 1 ampere current for 1 second.

QUESTIONS

1. How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b)1 mole of to Mn^{2+}?

(a) The reduction reaction is $Al^{3+} + 3e^{-} \rightarrow Al$

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}

$Q = 3 \times F = 3 \times 96500 = 289500$ coulomb

(b) The reduction is $Mn^{4-} + 8H + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$

$Q = 5 \times F = 5 \times 96500 = 48500$ coulomb

2. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ solution. How many gram of metal will be deposited assuming only cathodic reaction in each cell?

Ans:

The cathodic reactions in the cells are respectively.

$$Ag^{+} + e^{-} \longrightarrow Ag$$

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

$$Fe^{3+} + 3e^{-} \longrightarrow Fe$$

Hence, Amount of Ag deposited = $108 \times 0.4 = 43.2$ g

Amount of Cu deposited = $\frac{63.5}{2} \times 0.4 = 12.7$ g

Amount of Fe deposited = $\frac{56}{3} \times 0.4 = 7.47$ g

3. Calculate the quantity of electricity required to deposit 0.09 g of aluminium during the following electrode reaction $Al^{3+} + 3e^{-} \longrightarrow Al$

Quantity of electricity required to deposit 1 mol of Al = 3x 96, 500

Quantity of electricity required to deposit 0.09 g of Al = $\frac{3 \times 96500 \times 0.09}{27} = 965C$

BATTERIES

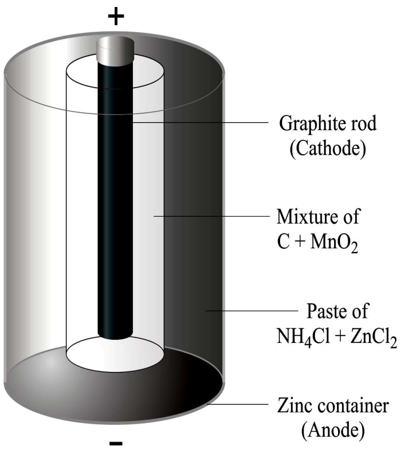
- A battery is an arrangement of two or more cells connected in series which is used as a source of energy.

TYPES OF BATTERIES

1. PRIMARY CELL

- In a primary cell, the reaction occurs only once and it becomes dead after a period of time and hence cannot be used again.
- Eg: Dry Cell, Mercury Cell etc.

A) DRY CELL



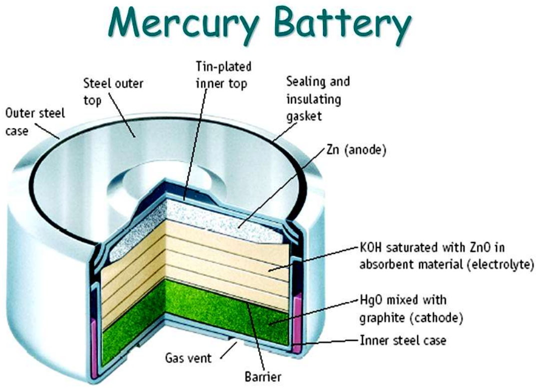
- A dry cell consists of a zinc container which acts as the anode.
- A carbon rod with a metal cap placed in the centre of the container acts as the cathode.
- It is surrounded by powdered MnO_2 and carbon.
- The space between the electrodes is filled with a paste of NH_4Cl and $ZnCl_2$ which acts as the electrolyte.
- A porous paper separates the zinc container from the paste.
- The potential of the cell is 1.5V.

Cell Reactions

- At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$
- At cathode: $2NH_4^+ + 2MnO_2 + e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$
- Overall cell reactions is $Zn + 2NH_4^+ + 2MnO_2 \longrightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$

B) MERCURY CELL

- It is a miniature form of a primary cell used in watches, hearing aids, calculators and other compact devices.
- A Zinc-Mercury amalgam is the anode.
- A paste of mercury oxide is the anode.
- A paste of mercury oxide (HgO) and carbon acts as the cathode.
- The electrolyte is a moist paste of KOH and ZnO.



Cell Reactions

- At anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$
- At cathode: $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$
- Overall cell reactions is $Zn + HgO \longrightarrow ZnO + Hg$
- The potential of the cell is approximately 1.35 V.
- Its potential remains almost constant throughout its life.
- Because the overall reaction does not involve any ions in solution.

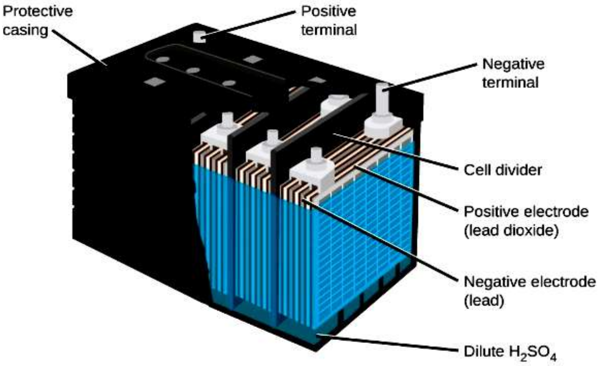
2. SECONDARY CELLS

- In a secondary cell, the electrode reaction can be reversed by passing electricity.

- These cells can be recharged by passing electric current and can be used again and again.

A) LEAD STORAGE CELL

- In this cell, lead acts as the anode.
- A grid of lead packed with lead dioxide acts as the cathode.
- A 38% solution of sulphuric acid is used as the electrolyte.
- The following reactions take place in the lead storage cell.



At anode:

$$\begin{array}{l} Pb \longrightarrow Pb^{2+} + 2e^- \\ Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \\ \hline Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \end{array}$$

At cathode:

$$\begin{array}{l} PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O \\ Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \\ \hline PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O \end{array}$$

Overall Cell Reaction

When the battery is in use, the following cell reactions take place.

At anode: $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

Overall Cell Reaction : $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

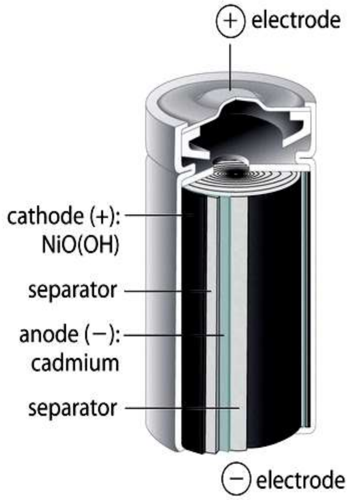
- During the working of the cell, the concentration of sulphuric acid is decreased as sulphate ions are consumed to form $PbSO_4$.
- With the decrease in the concentration of H_2SO_4, the density of the electrolyte decreases.

RECHARGING THE BATTERY

- The battery can be recharged by connecting it to an external source of direct current.
- It reverses the flow of electrons resulting in the deposition of lead on anode and PbO_2 on cathode.

$$\begin{array}{l} PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-} \\ PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \\ \hline 2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ 2e^- \end{array}$$

B) NICKEL CADMIUM CELL



- It consists of cadmium anode.
- Cathode is made up of a metal grid containing nickel (IV) Oxide.
- These are immersed in KOH solution which acts as the electrolyte.
- The reactions occurring in the cell are
- **At anode:**

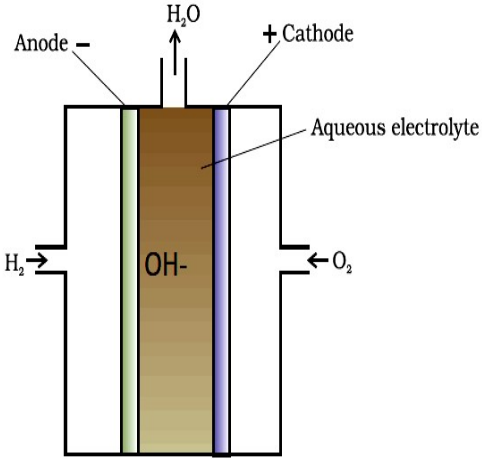
  $Cd+2OH^{-}\longrightarrow Cd(OH)_2+2e^{-}$

- **At cathode:**

  $NiO_2+2H_2O+2e^{-}\longrightarrow Ni(OH)_2+2OH^{-}$

- **Overall cell reactions:**
- $Cd+NiO_2+2H_2O\longrightarrow Cd(OH)_2+Ni(OH)_2$

FUEL CELLS



- A fuel cell is a device used to convert the energy of combustion of a fuel directly into electrical energy.
- Eg: H_2—O_2 fuel cell
- In a fuel cell, the reactants are continuously supplied to the electrodes.
- The common example is H_2—O_2 fuel cell.
- Fuels H_2 and O_2 are bubbled through porous carbon electrodes into a concentrated solution of NaOH or KOH.
- H_2 is fed into anode compartment where it is oxidised.
- At the same time, O_2 is fed into the cathode compartment where it is reduced.
- EMF of the cell is 0.9 V.

Cell Reactions

- At anode: $2H_2+4OH^{-}\longrightarrow 4H_2O+4e^{-}$
- At cathode: $O_2+2H_2O+4e^{-}\longrightarrow 4OH^{-}$
- Overall cell reactions is $2H_2+O_2\longrightarrow 2H_2O$
- The fuel cells run continuously as the reactants are fed.
- These fuel cells are more efficient than other methods.

QUESTION

1. Fuel cells are special types of Galvanic cells. Write any two advantages of fuel cells.

a) Fuel cells are pollution free.

b) Fuel cell produces continuous electricity.

c) More efficient than conventional methods.

CORROSION

- When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds, usually oxides.
- This process is called corrosion.
- In the case of iron, corrosion is called rusting.
- Chemically rust is hydrated form of ferric oxide, $Fe_2O_3.xH_2O$.

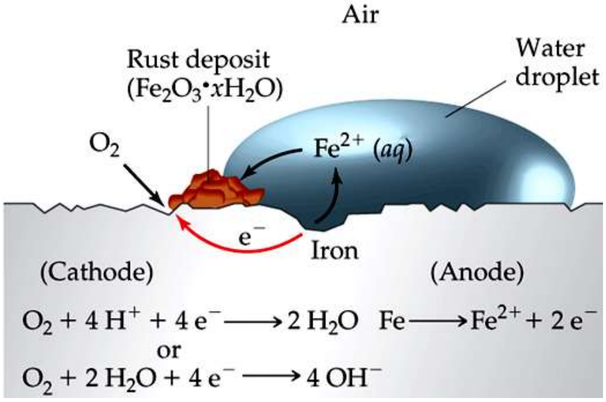
EXAMPLS OF CORROSION

- Rusting of Iron
- Green Coating on Copper and Bronze
- Tarnishing of Silver.

MECHANISM OF RUSTING

ELECTROCHEMICAL THEORY OF RUSTING

- The non-uniform surface of metal or impurities present in iron behave like small electric cells in the presence of water containing dissolved O_2 or CO_2.
- Pure iron acts as anode.
- The impurities act as cathode.
- Water containing dissolved CO_2 acts as electrolyte.



Cell Reactions

- **Anode Reaction** $2Fe \longrightarrow 2Fe^{2+} + 4e^-$
- **Cathode Reaction** $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
- **Overall Cell Reaction** $2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$
- The ferrous ions are further oxidized by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide $Fe_2O_3.xH_2O$.

PREVENTION OF CORROSION

- Covering the surface with paint or by some chemicals like bisphenol.
- Covering the surface with a layer of other metals like Sn, Zn etc which are more active than Iron.
- Electrical protection is done by connecting the Iron article with more active metals like Mg or Zn.
- By using anti rust solutions like alkaline phosphates and alkaline chromates.