UNIT-I

ELECTROCHEMISTRY

Concept of electrochemistry

- The branch of science which deals with the relationship between electrical energy and chemical energy and their inter-conversion of one form to another is called electrochemistry.
- The chemical changes which involve the flow of electric current are called electro chemical changes. They are classified into two types:
  - *Electrolysis*: The changes in which electrical energy causes chemical reaction to occur.
  - *Electrochemical cells:* The changes in which electrical energy is produced as a result of chemical change.
- ***Conductors:*** The substances which allow the passage of electric current are called conductors.

  Eg. Metals like Cu, Ag, Sn etc.
- ***Insulators:*** The substances which do not allow the electric current to pass through them are called non-conductors or insulators.

  Eg. Rubber, wood, wax, wool, glass etc.
- ***Metallic conductors:*** These are the metallic substances which allow the electric current to pass through them without undergoing any chemical change. The flow of electric current in metallic conductors is due the flow of electrons in the metal atoms.

  Eg. Metals like Cu, Ag, Sn etc.
- ***Electrolytes:*** These are the substances which allow the electric current to pass through them in their molten states or in the form of there aqueous solutions and undergo chemical decomposition. The flow of electric current through an electrolytic solution is called electrolytic conduction in which charge is carried by ions. These substances do not conduct electricity in the solid state but conduct electricity in the molten state or aqueous solutions due to movement of ions.

  Eg. Acids, bases and salts
- ***Non-electrolytes:*** The substances which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes.

  Eg. Sugar, glucose, urea, ethyl alcohol etc.

- Differences between metallic and electrolytic conduction:

Sl.No.	Metallic conduction	Electrolytic conduction
1.	Metallic conduction is carried out by the movement of electrons.	Electrolytic conduction is carried out by the movement of ions.
2.	It involves no chemical change in the properties of the conductor.	It involves the decomposition of the electrolyte as a result of the chemical reaction.
3.	It does not involve the transfer of any matter.	It involves the transfer of matter as ions.
4.	Metallic conduction decreases with increase in temperature.	Electrolytic conduction increases with increase in temperature.

- **Strong electrolytes:** The electrolytes which are almost completely dissociated into ions in solution are called strong electrolytes.
  Eg. NaCl, KCl, HCl, NaOH, NH_4NO_3
- **Weak electrolytes:** The electrolytes which do not ionize completely in solution are called weak electrolytes. Equilibrium is established between unionized electrolyte and the ions formed in the solution.
- The extent of ionization of a weak electrolyte is expressed in terms of degree of dissociation or ionization (denoted by α). It is defined as the fraction of total number of molecules of the electrolyte which ionize in the solution. For strong electrolytes $\alpha = 1$ and for weak electrolytes $\alpha < 1$.
- When a voltage is applied to the electrodes dipped into an electrolytic solution, the movement of ions takes place and therefore electric current flows through the electrolytic solution. The power of electrolytes to conduct electric current is termed as conductance or conductivity. Like metallic conductors electrolytes also obey Ohms law.

Conductance

- **Ohms law:** This law states that the current flowing through a conductor is directly proportional to the potential difference across it.

$$I \alpha V \quad \text{or} \quad I = \frac{V}{R} \quad \text{or} \quad V = IR$$

where I is the current strength in amperes;
V is the potential difference applied across conductor in volts;
R is the resistance of conductor in ohms (Ω).

- **Resistance:** It measures the 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 (a) of the conductor.

$$R \ \alpha \ \frac{l}{a} \quad \text{or} \quad R = \rho\left(\frac{l}{a}\right)$$

Where ρ is the specific resistance or resistivity.

Units: ohms (Ω).

- **Specific resistance:** It is defined as the resistance of a conductor of 1cm length and having area of cross section equal to 1cm^2. Specific conductance is the resistance between opposite faces of one centimeter cube of the conductor.

$$R = \rho\left(\frac{l}{a}\right) \quad \text{or} \quad \rho = R\left(\frac{a}{l}\right)$$

$$\text{If} \ \ l = 1\text{cm and } a = 1\text{cm}^2 \ \text{ then } R = \rho$$

$$\rho = R\left(\frac{a}{l}\right) \quad \text{i.e} \ \ \rho = \text{ohm}\left(\frac{\text{cm}^2}{\text{cm}}\right) = \text{ohm cm}$$

Units: ohm cm (Ω cm)

- **Conductance:** It is the measure of the ease with which current flows through a conductor. It is the reciprocal of the resistance.

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

Units: ohms^{-1} (Ω^{-1}) or mho or Siemens.

Specific conductance: It is the reciprocal of specific resistance. It may be defined as the conductance of a solution of 1cm length and having 1cm^2 area of cross section.

$$\kappa = \frac{1}{\rho} = \frac{1}{\text{ohm cm}} = \text{ohm}^{-1}\ \text{cm}^{-1}$$

Where κ is the specific conductance.

Units: ohm^{-1} cm^{-1} (Ω^{-1} cm^{-1}) or S cm^{-1}.

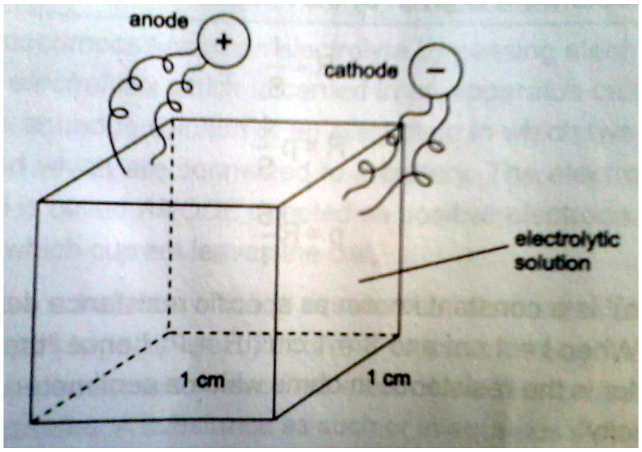


Figure 1. Specific conductance

- **Equivalent conductance:** It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. It is denoted by $\boldsymbol{\lambda_v}$.

$$\lambda_v = \frac{\kappa x1000}{\text{Normality}} = \frac{\text{ohm}^{-1}\text{cm}^{-1}\text{cm}^{3}}{\text{equiv}} = \text{ohm}^{-1}\text{cm}^{2}\text{equiv}^{-1}$$

Units: ohm^{-1} cm^{2} equiv^{-1}

- **Molar conductance:** It is defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte in the solution. It is expressed as $\boldsymbol{\lambda_m}$.

$$\lambda_M = \frac{\kappa x1000}{\text{Molarity}} = \frac{\text{ohm}^{-1}\text{cm}^{-1}\text{cm}^{3}}{\text{Molarity}} = \text{ohm}^{-1}\text{cm}^{2}\text{mole}^{-1}$$

Units: ohm^{-1} cm^{2} mole^{-1}

- ***Experimental determination of conductance and specific conductance***

1.*Measurement of conductance:* The conductance of a solution is reciprocal of the resistance; therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance. The resistance is commonly measured by Wheatstone bridge method as shown in the Figure 2. The solution whose resistance has to be measured is placed in a conductivity cell and is connected to the Wheatstone bridge. The cell is placed in thermostat to keep the temperature constant.

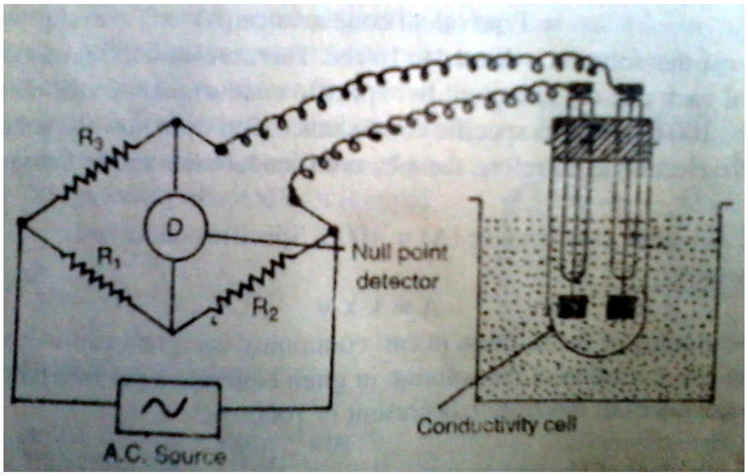


Figure 2. Determination of conductance & specific conductance by Wheatstone bridge

When the current flows through the circuit, the resistances R_1, R_2 and R_3 are so adjusted to get no current position. This is indicated by the null point detector. At this point,

$$\frac{R_{solution}}{R_3} = \frac{R_2}{R_1} \text{ or } R_{solution} = \frac{R_2R_3}{R_1}$$

Since the resistances R_1, R_2 and R_3 are known, the resistance of the solution is calculated. The

2. *Calculation of specific conductance:* Specific conductance is reciprocal of specific resistance. Reciprocal of the resistance gives the value of conductance of the solution.

$$\kappa = \frac{1}{\rho} \text{ and } \rho = R\left(\frac{a}{l}\right)$$

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right) \text{ or } \kappa = C\left(\frac{l}{a}\right)$$

Where C is the conductance;

l is the distance of separation of two electrodes;

a is cross-section area of the electrodes in cm^2.

The quantity (l/a) is called cell constant and is expressed in cm^{-1}. The specific conductance can be calculated by knowing the value of cell constant and conductance of the solution.

$$\kappa = C \text{ x cell constant}$$

Specific conductance = conductance x cell constant

- Summary:

Sl.No.	Parameter	Notation	Formula	Units
1.	Resistance	R	$R = \rho\left(\frac{l}{a}\right)$	Ohms (Ω)
2.	Specific resistance	ρ	$\rho = R\left(\frac{a}{l}\right)$	Ohm cm
3.	Conductance	C	$C = \frac{1}{R}$	Ohm^{-1}
4.	Specific conductance	κ	$\kappa = \frac{1}{\rho}$	$\text{ohm}^{-1}\ \text{cm}^{-1}$ or S cm^{-1}
5.	Equivalent conductance	**λ_v**	$\lambda_v = \frac{\kappa \text{x} 1000}{Molarity}$	$\text{Ohm}^{-1}\ \text{cm}^{2}$ equiv^{-1}
6.	Molar conductance	**λ_m**	$\lambda_M = \frac{\kappa \text{x} 1000}{Molarity}$	$\text{Ohm}^{-1}\ \text{cm}^{2}$ mole^{-1}
7.	Cell constant	-	l/a	Cm^{-1}

Effect of dilution on conductance

- The increase in dilution further increases the ionization of electrolyte.

- The specific conductance decreases with increase in ionization because the specific conductance is the conductance of the ions present in one centimeter cube of the solution. On dilution, the number of charge carrying ions present in 1cm^3 of the solution becomes less. Hence specific conductance of an electrolyte decreases with dilution.

- Equivalent conductance/molar conductance of an electrolyte increases with dilution because both are the products of the specific conductance and volume of the solution. When volume increases by dilution, the number of ions in electrolyte solution also increases contributing to increase in conductance.

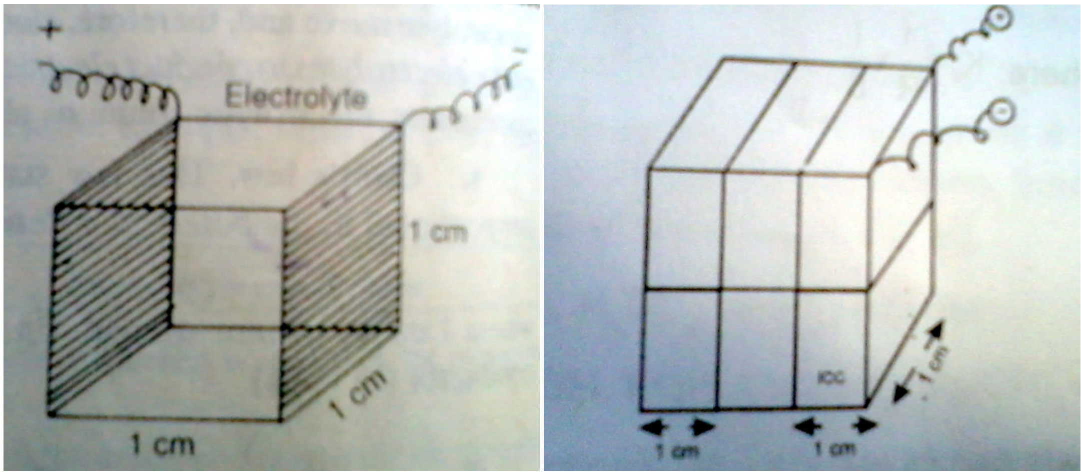


Figure 3. Effect of dilution on specific and equivalent conductances

Kohlrausch's law

- At infinite dilution when the dissociation is complete, each ion makes a definite contribution towards the equivalent conductance of an electrolyte irrespective of the nature of other ion with which it is associated. *i.e* the equivalent conductance at infinite dilution for a given salt can be expressed as the sum of the contributions from the ions of the electrolyte.

$$\lambda_v^{\infty} = \lambda^{\infty}_{cations} + \lambda^{\infty}_{anions}$$

where λ_v^{∞} is equivalent conductance of electrolyte at infinite dilution;

$\lambda^{\infty}_{cations}$ is contribution of cations towards equivalent conductance at infinite dilution;

$\lambda^{\infty}_{anions}$ is contribution of anions towards equivalent conductance at infinite dilution.

- *Examples:* NaCl: $\lambda_v^{\infty}(NaCl) = \lambda_v^{\infty}(Na^+) + \lambda_v^{\infty}(Cl^-)$
  KNO_3: $\lambda_v^{\infty}(KNO_3) = \lambda_v^{\infty}(K^+) + \lambda_v^{\infty}(NO_3^-)$
  $MgCl_2$: $\lambda_v^{\infty}(MgCl_2) = \lambda_v^{\infty}(Mg^{2+}) + 2\lambda_v^{\infty}(Cl^-)$
  $Al_2(SO_4)_3$: $\lambda_v^{\infty}(Al_2(SO_4)_3) = 2\lambda_v^{\infty}(Al^{3+}) + 3\lambda_v^{\infty}(SO_4^{2-})$

Applications of Kohlrausch's law

1. *Calculation of equivalent conductance at infinite dilution or weak electrolytes:* It is not possible to determine the equivalent conductance at infinite dilution for weak electrolytes experimentally.

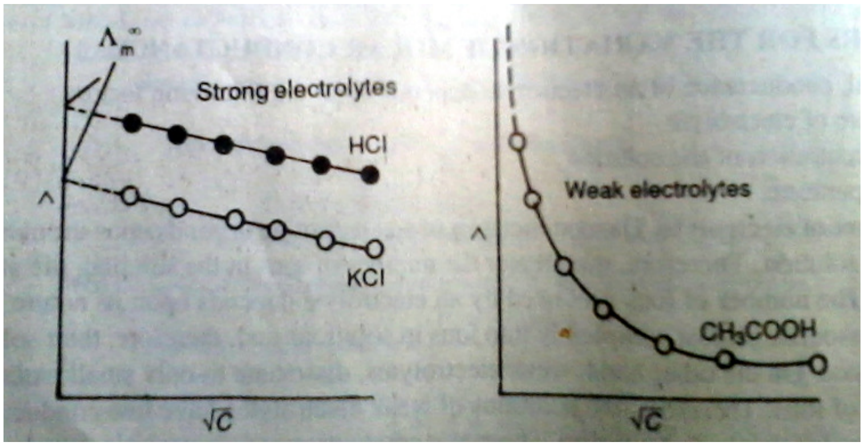


Figure 4. Plot of equivalent conductance Vs concentration for strong and weak electrolytes

However, this can be calculated by using Kohlrausch's law.

Eg. CH_3COOH: $\lambda_v^\infty(CH_3COOH) = \lambda_v^\infty(CH_3COO^-) + \lambda_v^\infty(H^+)$

This equation can be obtained by the knowledge of equivalent conductance at infinite dilution for some strong electrolytes like HCl, NaCl, CH_3COONa.

CH_3COONa: $\lambda_v^\infty(CH_3COONa) = \lambda_v^\infty(CH_3COO^-) + \lambda_v^\infty(Na^+)$

HCl: $\lambda_v^\infty(HCl) = \lambda_v^\infty(H^+) + \lambda_v^\infty(Cl^-)$

NaCl: $\lambda_v^\infty(NaCl) = \lambda_v^\infty(Na^+) + \lambda_v^\infty(Cl^-)$

It is clear that,

$\lambda_v^\infty(CH_3COO^-) + \lambda_v^\infty(H^+) = [\lambda_v^\infty(CH_3COO^-) + \lambda_v^\infty(Na^+)] + [\lambda_v^\infty(H^+) + \lambda_v^\infty(Cl^-)] -$
$[\lambda_v^\infty(Na^+) + \lambda_v^\infty(Cl^-)]$

Similarly we have,

$\lambda_v^\infty(NH_4OH) = \lambda_v^\infty(NH_4Cl) + \lambda_v^\infty(NaOH) - \lambda_v^\infty(NaCl)$

2. *Calculation of degree of dissociation of weak electrolytes:* Equivalent conductance of a weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, larger the equivalent conductance. With increase in dilution, the conductance increases and at infinite dilution, the electrolyte is completely dissociated so that degree of dissociation becomes one (at $C \longrightarrow 0$). The degree of dissociation at any concentration is given by

$$\alpha = \frac{\lambda_v^{\ c}}{\lambda_v^{\ \infty}}$$

Where, λ_v^{∞} is equivalent conductance at infinite dilution;

λ_v^{c} is equivalent conductance of electrolyte at any concentration.

The equilibrium constant (K) of weak electrolyte can be calculated by substituting the value of α in the equation given below:

$$K = \frac{C\alpha^2}{1-\alpha}$$

3. *Calculation of solubility product of sparingly soluble salt:* substances like AgCl or $PbSO_4$ are sparingly soluble and possess a definite value of solubility in water. Since a very small amount of solute present must be completely dissociated into ions even in the saturated solution so that the equivalent conductance (λ_v) is equal to the equivalent conductance at infinite dilution (λ_v^{∞}).

$$\lambda_v = \kappa \text{ x } V = \lambda_\infty = \lambda_a + \lambda_c$$

Knowing the value of κ and λ_∞ we can find out the volume in ml which contain one gram equivalent of electrolyte.

Galvanic Cells

- An electrochemical cell is a device which converts chemical energy into electrical energy.
- The redox reaction is utilized for generation of electrical energy.
- The electrochemical cells are commonly referred as Voltaic or Galvanic cells.
- The electromotive force (EMF) of such cell is directly proportional to intensity of chemical reaction taking place in it.
- The electrochemical cell is divided into two half cells. The half cell electrode where oxidation (loss of electrons) occurs is called anode (negative electrode). The half cell electrode where reduction (gain of electrons) occurs is called cathode (positive electrode). An electrochemical cell is the coupling of these two half cells.

Daniel cell

- The Daniel cell is a typical example of Galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in $CuSO_4$ solution which is connected to another beaker containing zinc rod dipped in $ZnSO_4$ solution by a salt bridge.
- Salt bridge is an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO_3, NH_4NO_3 which does not undergo chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.
- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place. It completes the electrical circuit and maintains the electrical neutrality of two half cell solutions.

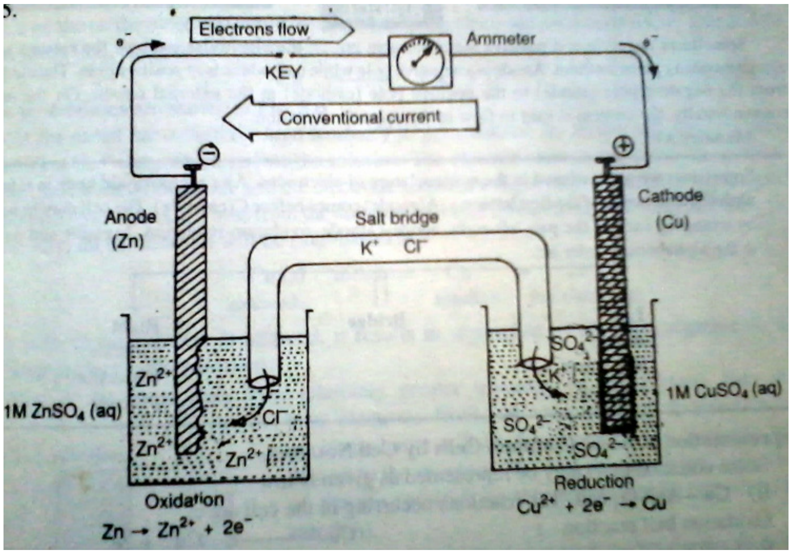


Figure 5. Daniel cell

- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter. The following observations are made:
  1. Zinc rod gradually loses its weight.
  2. The concentration of Zn^{+2}(*aq*) in the $ZnSO_4$ (*aq*) solution increases.
  3. Copper gets deposited on the electrode.
  4. The concentration of Cu^{+2}(*aq*) in $CuSO_4$ (*aq*) solution decreases.
  5. The flow of electrons is from Zn-electrode (anode) to Cu-electrode (cathode).
  6. The flow of electric current is from Cu-electrode (cathode) to Zn-electrode (anode).

The above observations can be explained as follows:

- Zn is oxidized to Zn^{+2} ions which goes in the solution and therefore Zn rod gradually loses its weight (oxidation half cell).

$$Zn \xrightarrow{\qquad\qquad} Zn^{+2} + 2e^- \quad \text{(At anode)}$$

- The electrons released at the Zn electrode move towards Cu electrode through external circuit.
- These electrons are accepted by the Cu^{+2} ions in the solution and gets reduced to copper which gets deposited on the Cu-electrode (reduction half cell).

$$Cu^{+2} + 2e^- \xrightarrow{\qquad\qquad} Cu \quad \text{(At cathode)}$$

- The oxidation of Zn occurs at anode (negative terminal) and reduction of Cu^{+2} occurs at cathode (positive terminal).
- The flow of electrons is from negative terminal (anode) to positive terminal (cathode).

$$\overset{\text{Flow of electrons}}{\longrightarrow}$$

$$\text{(-) Anode Zn} \mid ZnSO_4 \parallel CuSO_4 \mid \text{Cu Cathode (+)}$$

$$\underset{\text{Flow of electric current}}{\longleftarrow}$$

Cell reactions: *At Anode:* $Zn \xrightarrow{\qquad\qquad} Zn^{+2} + 2e^-$

At cathode: $Cu^{+2} + 2e^- \xrightarrow{\qquad\qquad} Cu$

Overall Reaction: $Zn + Cu^{+2} \xrightarrow{\qquad\qquad} Zn^{+2} + Cu$

Cell representation: $Zn_{(s)} \mid ZnSO_{4\,(aq)}\,(1M) \parallel CuSO_{4\,(aq)}\,(1M) \mid Cu_{(s)}$

EMF of galvanic cell

- The flow of electric current in Galvanic cell is due to potential difference between two electrodes which is known as electrode potential.
- Electrode potential is a measure of tendency of an electrode to gain or lose electrons. Each electrode has a different tendency to lose or gain electrons.

Electrode potential → Reduction potential
Electrode potential → Oxidation potential

- ➢ Reduction potential (conventionally used) is the measure of tendency of an electrode to lose electrons and oxidation potential is the measure of tendency of an electrode to lose electrons.
- ➢ Electrodes with high reduction potential readily gains electrons and gets reduced.
- ➢ Electrodes with low reduction potential (oxidation potential) readily looses electrons and gets oxidized.
- ➢ The difference between the electrode potentials of the two electrodes constituting a galvanic cell is known as EMF or cell potential (expressed in volts).

$$\text{EMF} = E_{\text{cell}} = E^{o}_{\text{cathode}} - E^{o}_{\text{anode}} = E^{o}_{\text{right}} - E^{o}_{\text{left}}$$

- ➢ The reduction potential of an electrode measured at 25°C, 1atm and 1M concentration of electrolyte is called standard reduction potential.
- ➢ The positive value of E_{cell} indicates that cell reaction is feasible.

Electrochemical series (Galvanic series)

- ➢ The arrangement of elements in increasing order of their standard electrode reduction potentials as compared to that of Standard Hydrogen Electrode (S.H.E) is called galvanic series.
- ➢ It is an arrangement of metals in the order of decreasing tendency of their atoms to lose electrons (Electro positive character) is known as galvanic series.

Li^{+}, K^{+}, Ba^{+2}, Ca^{+2}, Na^{+}, Mg^{+2}, Al^{+3}, Zn^{+2}, Cr^{+3}, Fe^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2}, Sn^{+2}, Pb^{+2}, **H**, Cu^{+2}, I_2, Fe^{+3}, Ag^{+}, Hg^{+2}, Pt^{+2}, Au^{+3}

$$\longrightarrow$$

* Increasing order of reduction potential
* Increasing power of oxidizing agent
* Decreasing order of oxidation potential
* Decreasing power of reducing agent

- ➢ Higher end of galvanic series acts as reducing agents (gets oxidized) and lower end of the series acts as oxidizing agents (gets reduced).
- ➢ Higher end of galvanic series can displace hydrogen gas from dilute acids.

$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$

- Metals with lower reduction potentials can displace the metal with higher reduction potential.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

- *Applications of galvanic series:* The galvanic series give more information on the following
  1. The relative corrosion tendencies of the metals.
  2. Relative ease of oxidation or reduction of metals.
  3. Replacement of tendency of metals.
  4. Calculating the equilibrium constant.

Nernst Equation

- Standard electrode potentials are measured at standard states i.e at1M concentration of electrolyte, temperature at 298 K and 1atm pressure.
- However the electrode potentials depend upon concentration of electrolyte solutions and temperature.
- Nernst equation gives the relationship between electrode potentials and concentration of electrolytic solutions.
- For the general reduction reaction occurring at an electrode,

$$M^{n+}{}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

$$E_{M^{n+}/M} = E^{\circ}{}_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{[M_{(s)}]}{[M^{n+}{}_{(aq)}]}$$

Where E° = Standard EMF of the cell for 1 M solution at 298 K;

R = Gas constant;

T = Kelvin temperature;

n = number of electrons involved in the cell reaction;

F = Faraday of electricity;

E = electrode potential of the metal;

[M] = activity of metal in the metal phase and is taken as unity;

$[M^{n+}]$ = activity of metal ions in the solution is taken equal to their molarities;

But at STP conditions, R = 8.314JK^{-1}mol^{-1}; T = 298K; F = 96500 coulomb charge. Then the Nernst equation becomes

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[M^{n+}_{(aq)}]} \qquad \text{considering } [M^{n+}_{(s)}] = 1$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{0.0592}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{0.0592}{n} \log[M^{n+}]$$

- *Applications*: Nernst equation enables us to calculate the following:
  1. Half cell potential or single electrode potential.
  2. Cell potential or EMF of the cell.
  3. Equilibrium constant for the cell reaction.

Types of electrodes

I. Reference Electrodes

- The single electrode potential is conveniently measured by combining the half cell with a standard electrode and measuring the total EMF of the cell.

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

$E_{cell} = E_{right} - E^{o}$ (if standard electrode is anode)

$E_{cell} = E^{o} - E_{left}$ (if standard electrode is cathode)

Where E^{o} is the standard electrode potential.

Eg. Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode

1. Standard Hydrogen Electrode (S.H.E)

- S.H.E is a primary reference electrode.
- S.H.E consists of a platinum electrode coated with Pt-black immersed in 1 Molar solution oh H^{+} ions maintained at 25°C.
- Hydrogen gas at 1atm pressure is constantly bubbled into the glass hood over the Pt-electrode.
- Hydrogen gets oxidized at the Pt-electrode and passes into the solution forming H^{+} ions and electrons.

- The standard electrode potential of Hydrogen electrode at these conditions is considered as zero.
- Depending upon the half cell to which it is combined, hydrogen electrode can act as either anode or cathode.

When S.H.E acts as anode: $H_{2(g)} \longrightarrow 2H^+ + 2e^-$

When S.H.E acts as cathode: $2H^+ + 2e^- \longrightarrow H_{2(g)}$

Therefore S.H.E is regarded as reversible electrode.

$$H_{2(g)} \longleftrightarrow 2H^+ + 2e^-$$

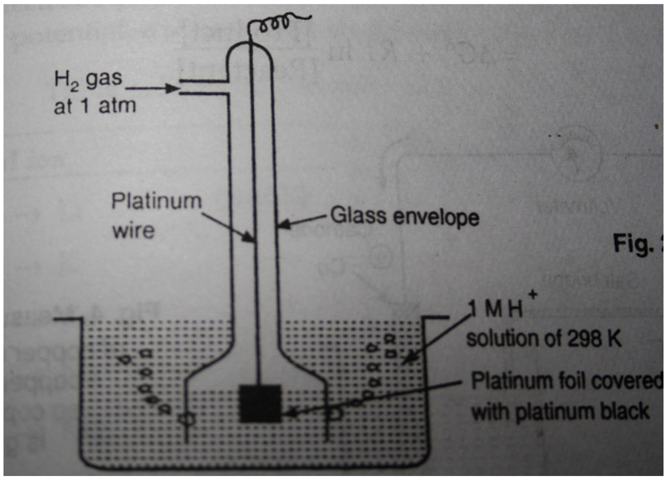


Figure 6. Standard Hydrogen Electrode

Applications of S.H.E

1. Determination of standard reduction potentials of the two half cells in Daniel cell using S.H.E:

- Daniel cell representation: $Zn \mid ZnSO_{4\,(aq)}\ (1M) \parallel CuSO_{4\,(aq)}\ (1M) \mid Cu$
- Each of the above half cells is connected to S.H.E to determine their standard electrode potentials respectively.
- *Zn-half cell:* Zinc half cell (anode) is connected to S.H.E (cathode).

Cell representation: $Zn \mid Zn^{+2}_{(aq)}\ (1M) \parallel H^+\ (1M) \mid H_2\ (1atm), Pt$

$$E_{cell} = E^o_{H^+/H_2} - E^o_{Zn/Zn^{+2}}$$

$$0.76 = 0 - E^o_{Zn/Zn^{+2}}$$

$$E^o_{Zn/Zn^{+2}} = -0.76 \text{ volts}$$

- *Cu-half cell:* Zinc half cell (cathode) is connected to S.H.E (anode).

Cell representation: Pt, H_2 (1atm) | H^+ (1M) ‖ $Cu^{+2}{}_{(aq)}$ (1M) | Cu

$$E_{cell} = E^o_{Cu^{+2}/Cu} - E^o_{H^+/H_2}$$

$$0.34 = E^o_{Cu^{+2}/Cu} - 0$$

$$E^o_{Cu^{+2}/Cu} = 0.34 \text{ volts}$$

$$E_{Daniel\ cell} = E_{right} - E_{left} = 0.34 - (-0.76) = 1.10V$$

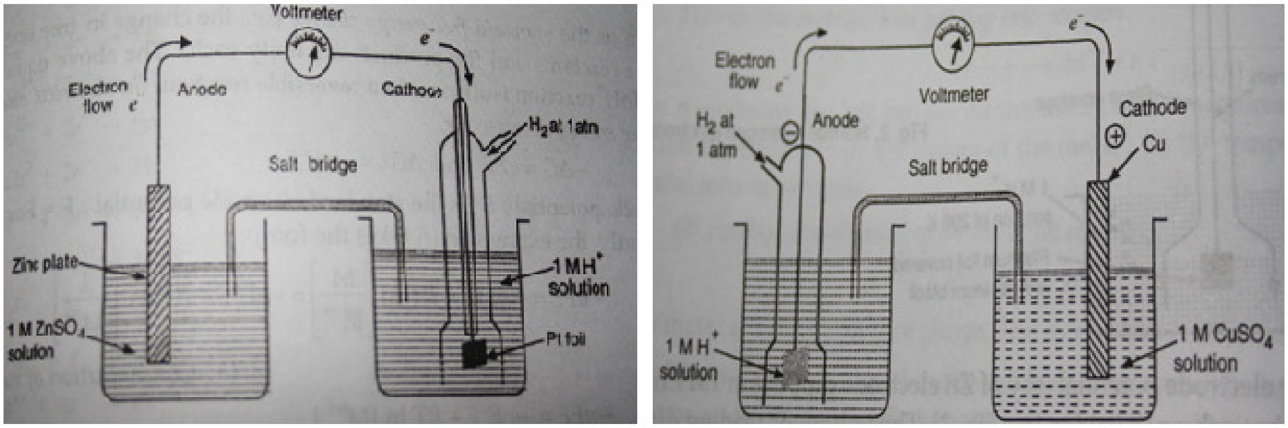


Figure 7. Determination of single electrode potential of Zn and Cu-half cells by S.H.E

2. Determination of pH for the unknown solution:

- For a Hydrogen electrode at 298K, the Nernst equation is given as follows:

$$2H^+{}_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

$$H^+{}_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$$

$$E_{Cell} = E^o - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$E_{Cell} = - \frac{0.0592}{nF} \log \frac{1}{[H^+]} (\because [H_2]^{1/2} = 1 \text{ and } E^o = 0)$$

$$E_{Cell} = - 0.0592 (-\log[H^+])$$

$$E_{Cell} = - 0.0592 \text{ pH}$$

- In order to determine the pH of anunknown solution, a Pt-electrode is immersed into the solution and connected to S.H.E.
- Cell representation: Pt, $H_{2(g)} \mid H^+_{(aq)} (?) \parallel H^+_{(aq)} (1M) \mid H_{2(g)}$ (1atm), Pt

$$E_{Cell} = E_{cathode} - E_{anode}$$
$$E_{Cell} = E_{S.H.E} - E_{H_2/H^+}$$
$$E_{Cell} = 0 - (-0.0592pH)$$
$$E_{Cell} = 0.0592pH$$
$$pH = \frac{E_{Cell}}{0.0592}$$

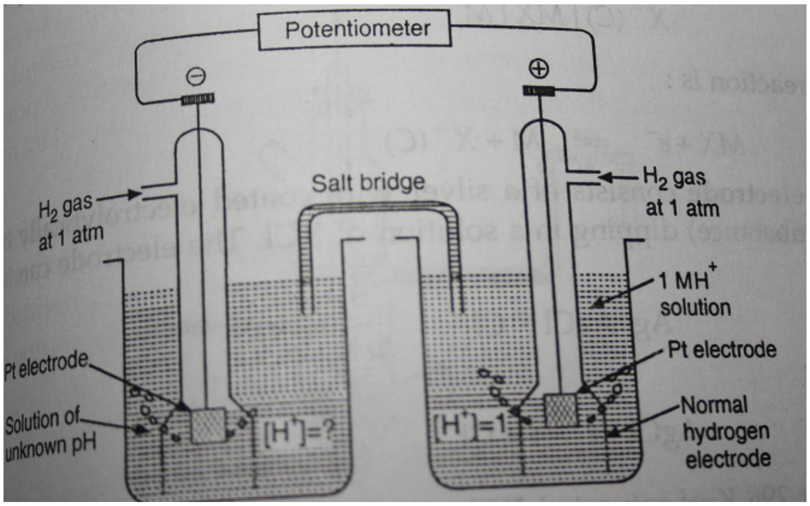


Figure 8. Determination of pH of unknown solution by S.H.E

2. Calomel Electrode

- It is a secondary reference electrode.
- It is a mercury-mercurous chloride (Hg-Hg_2Cl_2) electrode.
- The calomel electrode is used as only reducing electrode *i.e.* as cathode only.
- It consists of a glass tube having a side tube on each side. One side tube acts as salt bridge and other is used to fill KCl solution.
- The high purity mercury is placed at the tip of this tube and connected to the circuit by the means of Pt-wire, sealed in a glass tube.
- The surface of Hg is covered with a paste of mercurous chloride (calomel) and Hg in KCl solution.
- The electrolyte is the solution of KCl.
- The electrode is connected with the help of side tube on the left through salt bridge with the other electrode whose potential has to be determined.
- The potential of the calomel electrode depends upon the concentration of KCl.

Concentration of KCl	0.1N	1.0N	Saturated
Electrode potential (V)	0.3335	0.2810	0.2422

Representation of calomel electrode: Hg, $Hg_2Cl_{2(s)}$ │ KCl (saturated solution)

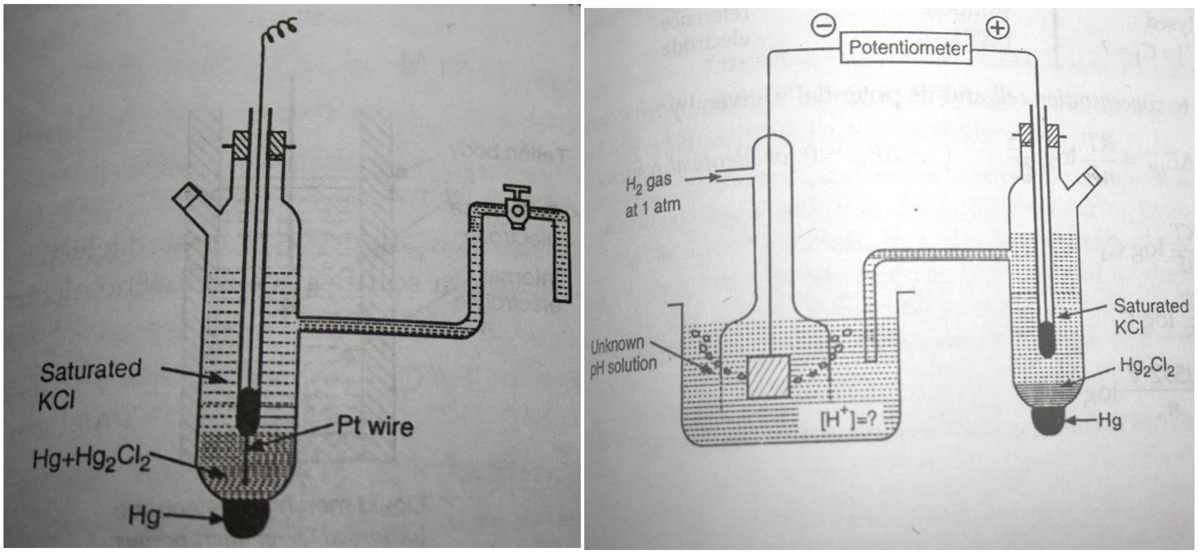


Figure 9. Calomel Electrode and determination of pH by calomel electrode

Determination of pH of unknown solution by Saturated Calomel electrode:

- Cell representation: Pt, H_2 (1atm) │ H^+ (?) ‖ KCl (*saturated*) Hg_2Cl_2 │ Hg

$$E_{Cell} = E_{Calomel} - E_{H_2/H^+}$$

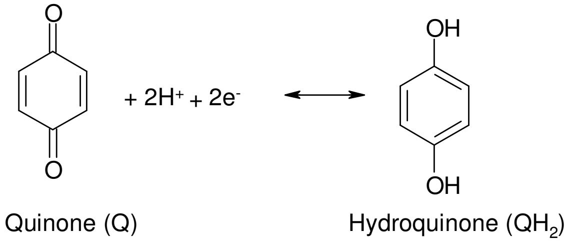
$$E_{Cell} = 0.2422 - (-0.0592pH)$$

$$E_{Cell} = 0.2422 + 0.0592pH$$

$$pH = \frac{E_{Cell} - 0.2422}{0.0592}$$

3. Quinhydrone electrode

- It is a Quinone-hydroquinone system which forms a reversible redox system.



- When a Pt-electrode is immersed in this system, the potential E developed is given by

$$E_Q = E^o_Q - \frac{2.303RT}{nF}\log_{10}\frac{[QH_2]}{[Q][H^+]^2}$$

When Quinone and Hydroquinone are maintained at equimolar ratios, then

$$E_Q = E^o_Q - \frac{2.303RT}{2F}\log_{10}\frac{1}{[H^+]^2} = E^o_Q - \frac{2.303RT}{F}\{-\log_{10}[H^+]\}$$

$$E_Q = E^o_Q - 0.0592pH \quad \text{(when T = 298K)}$$

$$E_Q = 0.6994 - 0.0592pH \quad (\because E^o_Q = 0.6994V)$$

- pH of an unknown solution can be determined using this electrode.
- The electrode potential of Quinhydrone electrode depends upon concentration of H^+ ions which can be used for the determination of pH of unknown solution.
- A pinch of quinhydrone powder which is sparingly soluble solid is added to the experimental solution with stirring until the solution is saturated.

Determination of pH of unknown solution by Quinhydrone electrode:

- Cell representation: Pt, $QH_2 \,|\, Q, H^+ (?) \,\|\,$ KCl (*saturated*) $Hg_2Cl_2 \,|\,$ Hg
- A Pt-electrode is inserted into the solution and a pinch of quinhydrone is added.
- This half cell is connected to a saturated electrode calomel electrode and the EMF of the solution is determined potentiometrically.

$$E_{Cell} = E_{Calomel} - E_{Quinhydrone}$$

$$E_{Cell} = 0.2422 - (0.6994 - 0.0592pH)$$

$$pH = \frac{E_{Cell} - 0.4572}{0.0592}$$

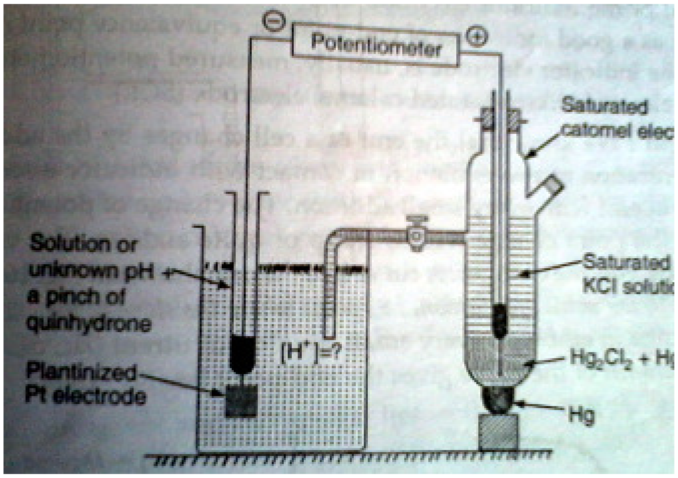


Figure 10. Quinhydrone electrode

Advantages:

1. It is useful in acid-base titrations.
2. Equilibrium is rapidly attained.
3. It can be used for many metal ions which usually effect hydrogen electrode.

II. Ion Selective Electrodes

- They possess an ability to respond to only certain specific ions thereby developing a potential with respect to that species only in a given mixture and ignore all the other ions totally.
- The potential developed by ion selective electrode depends on the concentration of specific ion of interest.
- Eg. Glass electrode specific for H^+ ions

  Pressed pallet of Ag_2S + AgCl specific for Cl^- ions.

Glass electrode

- When two solutions of different pH values are separated by a thin glass membrane, a potential difference develops between the two surfaces of the membrane.
- This potential difference developed is proportional to the difference in pH value.
- The glass membrane functions as ion-exchange resin.
- An equilibrium is established between Na^+ ions of the glass and H^+ ions in the solution.
- The potential of the glass electrode is given by,

$$E_G = E^o_G + 0.0592\ pH$$

Where pH range of the test solution is between 1-10.

- The glass electrode consists of a thin walled glass tube containing AgCl coated Ag-electrode or simply Pt-electrode in 0.1M HCl.

- Cell representation of glass electrode is given by

$$\mathrm{Ag} \,\big|\, \mathrm{AgCl_{(s)}}\ \mathrm{H^+}\,(0.1\mathrm{M}) \,\big|\, \mathrm{Glass} \quad \textbf{or} \quad \mathrm{Pt,\ HCl}\,(0.1\mathrm{M}) \,\big|\, \mathrm{Glass}$$

- HCl in the bulb furnishes constant H^+ ion concentration. Thus it is Ag-AgCl electrode reversible with respect to Cl^- ions.
- It is used as internal reference electrode for determining the pH of the solution especially the colored solution containing oxidizing or reducing agents.

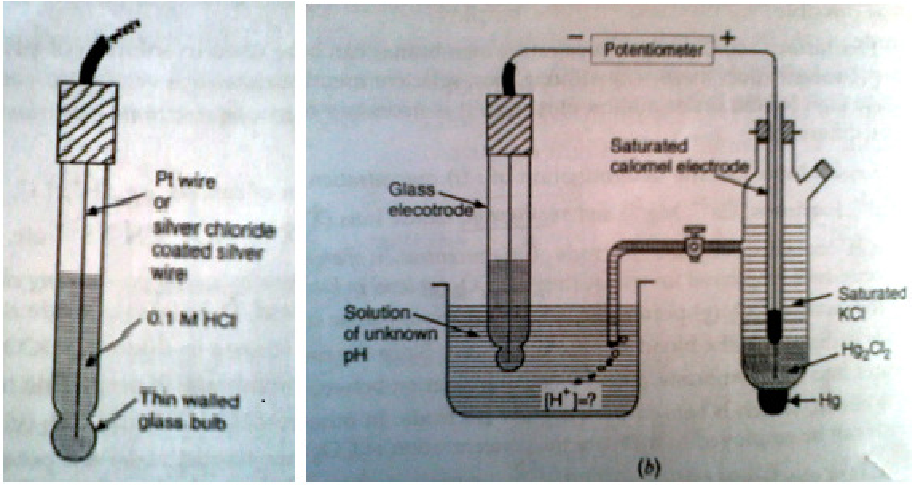


Figure 11. Glass electrode & determination of pH by glass electrode

Determination of pH of unknown solution by Quinhydrone electrode:

- In order to determine the pH of the solution, the glass electrode is placed in the test solution. This half cell is coupled with saturated calomel electrode and the EMF of the cell is measured.
- Cell representation: $\mathrm{Pt,\ H_2Q}\,\big|\,\mathrm{Q,\ H^+}\,\big\|\,\mathrm{KCl\ (sat)\ Hg_2Cl_{2(s)}}\,\big|\,\mathrm{Hg}$

$$E_{Cell} = E^{o}_{Calomel} - E^{o}_{Glass}$$

$$E_{Cell} = 0.2422 - [E^{o}_{Glass} + 0.0592\mathrm{pH}]$$

$$E_{Cell} = \frac{0.2422 - E_{Cell} - E^{o}_{Glass}}{0.0592}$$

- Since the resistance is very high, a special electron tube voltmeter is used to measure the EMF of the above cell.

- *Advantages:*
  1. It is simple and can be easily used.
  2. The results are accurate.
  3. Equilibrium is rapidly reached.
- *Limitations:*
  1. The range of solution pH is between 1 to 10.
  2. The resistance of the membrane is very high.

Concentration cell

- The electrical energy in a concentration cell is due to transfer of substance from the solution of high concentration to the solution of low concentration.
- The concentration cell is made up of two half cells having identical electrodes and electrolytes.
- However the concentrations of the reactive ions at the two electrodes are different.
- General cell representation for a concentration cell: $M \mid M^{n+}_{(aq)}\ (C_1) \parallel M^{n+}_{(aq)}\ (C_2) \mid M$

  where C_1 and C_2 are the concentrations of the active metal ions in contact with the two electrodes respectively.

  Eg. Silver concentration cell

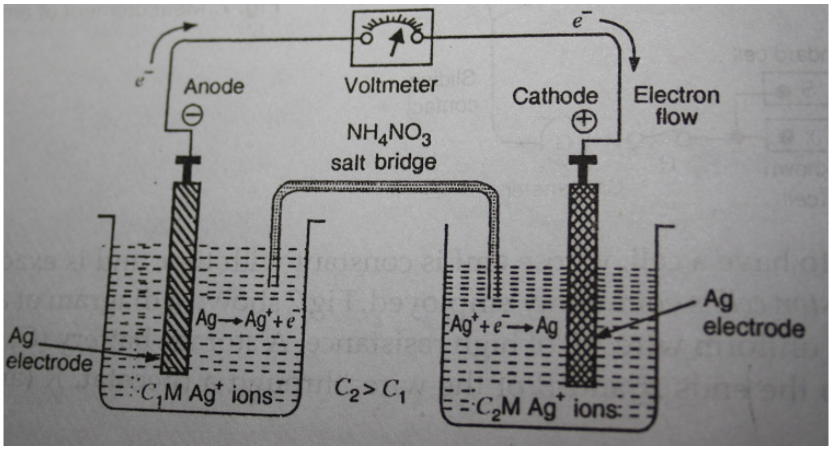


Figure 12. Silver concentration cell

- When a metal electrode is dipped in solution containing M^{n+} ions, then a potential E is developed at the electrode.
- The value of E varies with the concentration (C) of the ions in accordance with Nernst equation.

$$E_{Cell} = E^o + \frac{2.303RT}{nF} \log C$$

- For a general concentration cell: M │ $M^{n+}_{(aq)}$ (C_1) ‖ $M^{n+}_{(aq)}$ (C_2) │ M

$$E_{Cell} = E_{Cathode} - E_{Anode}$$

$$E_{Cell} = E^o_{M^{n+}/M} + \frac{2.303RT}{nF} \log C_2 - [E^o_{M^{n+}/M} + \frac{2.303RT}{nF} \log C_1]$$

$$E_{Cell} = \frac{2.303RT}{nF} \log C_2 - \frac{2.303RT}{nF} \log C_1$$

$$E_{Cell} = \frac{2.303RT}{nF} [\log C_2 - \log C_1]$$

$$E_{Cell} = \frac{2.303RT}{nF} \log\left(\frac{C_2}{C_1}\right)$$

$$E_{Cell} = \frac{0.0592}{n} \log\left(\frac{C_2}{C_1}\right) \quad \text{(At 298K)}$$

If $C_1 = C_2$, then $E_{cell} = 0$.

Types of concentration cells:

1. *Electrode concentration cells*: In this cell, the electrodes themselves have different concentrations. The EMF arises as a result of two like electrodes at different concentration which are dipped in the same solution of the electrolyte.

Eg.1. Two hydrogen electrodes at unequal gas pressure P_1 and P_2 immersed in the same solution of H^+ ions. The following cell reaction takes place:

Oxidation reaction: $H_2 (P_1) \rightarrow H^+ + 2e^-$

Reduction reaction: $2H^+ + 2e^- \rightarrow H_2 (P_2)$

Overall reaction: $H_2 (P_1) \rightarrow H_2 (P_2)$

- Cell representation: Pt, H_2 (P_1) │ H^+ ‖ H^+ │ H_2 (P_2), Pt
  Where P_1 and P_2 are the pressures at the two electrodes respectively.
- The EMF depends only on two pressures and independent of the concentration of electrolyte solutions hydrogen ions, in which the electrodes are dipped.

$$E_{cell} = \frac{2.303RT}{nF}\log_{10}\left(\frac{P_1}{P_2}\right)$$

2. *Electrolytic concentration cells:* These cells consist of two identical electrodes immersed in two solutions of the same electrolyte at different concentrations. The electrodes of such cells are reversible to one of the ions of the electrolyte.

Eg. Zinc concentration cell: $Zn \mid Zn^{+2}_{(aq)}\ (C_1) \parallel Zn^{+2}_{(aq)}\ (C_2) \mid Zn$

where C_1 and C_2 are the concentration of Zn^{+2} at anode and cathode respectively ($C_2 \geq C_1$).

$$E_{cell} = \frac{2.303RT}{nF}\log_{10}\left(\frac{C_2}{C_1}\right)$$

- Thus EMF so developed is due to the transference of metal ions from the solution of higher concentration (C_2) to the solution of lower concentration (C_1)

Applications of concentration cells:

1. To determine the solubility of a sparingly soluble salts.
2. To calculate the valency of cations.
3. To calculate the extent of corrosion in metals.
4. To determine the transition point.

Potentiometric titrations

The titration in which the equivalent or end point of a reaction is determined with the help of measurement of the potentials of the reaction mixture is known as potentiometric titration.

1. *Acid-Base Titrations:* The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes are connected to the potentiometer and the EMF is measured. A known volume of standard alkali solution is added from a burette, stirred thoroughly and the EMF of the cell is recorded. Like this 10-15 readings are recorded by repeating the procedure of the addition of alkali. The volume of alkali added is plotted against EMF observed. The steepest portion of the curve indicates the equivalent point of the titration.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

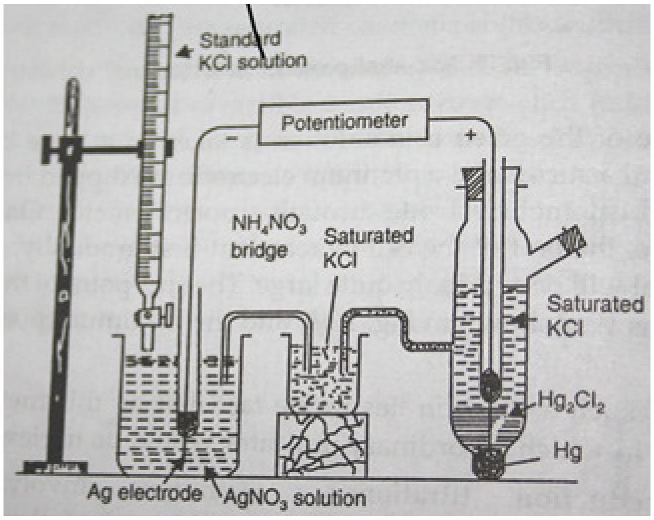


Figure 13. Potentiometric titration of HCl Vs NaOH

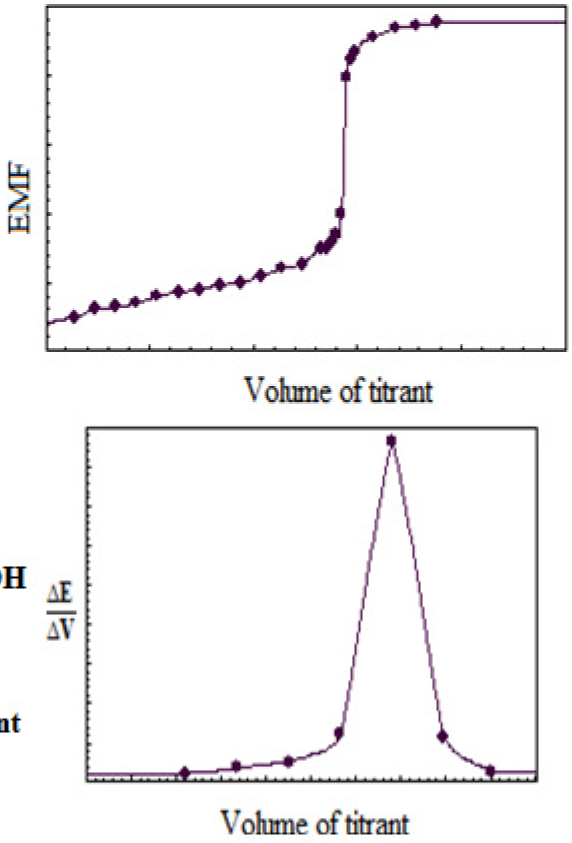


Figure 14. Plot of EMF Vs Vol. of titrant

2**.** *Redox titrations:* The EMF of the electrode is determined by the activity of ratio of the substance being oxidized or reduced. For example Fe^{+2} titrated against $K_2Cr_2O_7$. Ferrous iron solution is taken in the beaker and treated with dil. H_2SO_4. Platinum electrode and calomel electrode are dipped into the solution and they are connected to the potentiometer. The EMF of the solution after the addition of $K_2Cr_2O_7$ from burette is recorded. A graph is plotted with EMF and volume of $K_2Cr_2O_7$. The steep rise is the end point of the titration.

3. *Precipitation reactions:* The EMF of the electrode is determined by the precipitation of product. For example, titration of $AgNO_3$ with AgCl where the later precipitates out. AgCl is used along with calomel electrode. $AgNO_3$ is taken in the burette and AgCl is taken in the beaker containing electrodes. The EMF of the cell is measured and plotted against volume of silver nitrate added. The steep rise in the curve shows the end point of the titration.

$$AgNO_3 + Cl^- \longrightarrow AgCl\ (ppt) + NO_3^-$$

4. *Determination of pH*: The EMF of a solution depends on the concentration of H^+ ions or pH of the solution. A hydrogen electrode containing solution of unknown pH is paired with a standard calomel electrode.

$$Pt, H_2 \text{ (1 atm)} / H^+ \text{ (unknown)} // KCl \text{ (saturated)} / Hg_2Cl_2, Hg$$

The EMF of this cell is measured by potentiometer and the pH of the unknown solution can be determined.

$$E_{cell} = E_{right} - E_{left} \quad \text{or} \quad E_{cell} = 0.2415 – (-0.0591 \text{ x pH})$$

$$E_{cell} = 0.2415 + 0.0591 \text{ x pH}$$

Advantages:

1. Colored solutions where the use of indicator is impossible are estimated by potentiometric titrations.
2. Solutions more than one halide can be analyzed in a single titration against silver nitrate.

Batteries

- The term battery is generally used for two or more galvanic cells connected in series. Thus a battery is a series of portable electrochemical cells which are capable of generating electrical energy.
- Batteries are of three types: (1) Primary cell (2) Secondary cell (3) Fuel cell.
- Applications of batteries
- The portability of electronic equipments in the form of handsets has been made possible by batteries.
- A variety of electronic gadgets with more reliability and service have been made more useful with the introduction of rechargeable storage batteries.

Comparison between primary, secondary and fuel cells:

Sl. No.	Primary cells	Secondary cells	Fuel cells
1.	Cell reaction is irreversible	Cell reaction is reversible.	Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained.
2.	Must be discarded after use.	May be recharged.	Cannot be reused.
3.	Have relatively short shelf life	Have long shelf life.	Have life as long as the fuel is supplied.
4.	Function only as galvanic cells.	Functions both galvanic Cell & as electrolytic cell.	Functions as only galvanic cell.
5.	They cannot be used as storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)	Do not store energy.
6.	They cannot be recharged	They can be recharged.	They cannot be recharged.
7.	Eg. Dry cell and $Li\text{-}MnO_2$ battery.	Eg. Lead acid storage cell, Ni-Cd battery.	Eg: Hydrogen-oxygen fuel cell.

Primary batteries

- The cell reaction is not reversible.
- No electricity is produced after complete conversion of the reactants to products and the cell becomes dead.
- These batteries are used as source of DC power.
- Eg. Leclanche cell and Lithium cells

Leclanche cell (Dry cell)

- This is a primary cell without fluid component.
- The anode of the cell is a Zn-container containing an electrolytic mixture of NH_4Cl, $ZnCl_2$ and MnO_2 to which starch is added to make a thick paste.
- The graphite rod which is immersed in the centre of the cell acts as cathode.

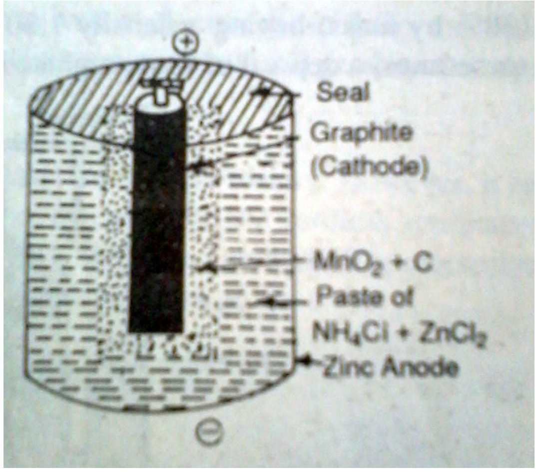


Figure 13. Dry cell

Cell representation: $Zn_{(s)} \mid ZnCl_{2\,(aq)}, NH_4Cl \parallel MnO_2 \mid C$

$$\begin{aligned} &\text{Cell reactions:}\quad \text{Anode:}\quad Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^- \\ &\underline{\text{Cathode:}\quad 2MnO_{2(s)} + H_2O_{(l)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2OH^-{}_{(aq)}} \\ &\text{Net Reaction: } Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}{}_{(aq)} + Mn_2O_{3(s)} + 2OH^-{}_{(aq)} \end{aligned}$$

- Reaction between NH_4^+ (from NH_4Cl) and OH^- formed at cathode evolves NH_3 gas which disrupts the current flow. This is prevented by the reaction of NH_3 with Zn^{2+} (from $ZnCl_2$) to form complex $[Zn(NH_3)_2Cl_2]$.

  Secondary reactions: $NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$

  $Zn^{2+}{}_{(aq)} + 2NH_{3(s)} + 2Cl^- \longrightarrow [Zn(NH_3)_2]\,Cl_2$

- The reactions involved in the dry cell cannot be reversed by passing electricity back through the cell. Hence dry cell is a primary cell.
- *Advantages:* Low price; gives voltage of about 1.5 V; normally works without leaking (leak proof cells); possess high energy density; non- toxic; contains no liquid electrolytes.
- *Applications:* Dry cell is used in consumer electronic devices like calculators, transistor radios, flash lights, quartz wall clocks, walkman etc. and in small portable appliances where small amount of current is needed.

Lithium cells

- Lithium metal batteries are primary cells in which Li acts as anode. They are of two types: (1) Solid cathode lithium cells (2) Liquid cathode lithium cells.

1. Solid cathode lithium cells

- They may have solid or liquid electrolyte.
- Most widely used Li-batteries are made up of Li-MnO_2.
- MnO_2 acts as cathode which is heated up to 300°C to remove water before incorporating it in the cathode. This improves the efficiency of the cells.
- Propylene carbonate and 1,2-dimethoxyethane acts as electrolyte.

Cell reactions: Anode: $Li \longrightarrow Li^+ + e^-$

Cathode: $Li^+ + MnO_2 + e^- \longrightarrow LiMnO_2$

Net reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

- *Applications*: Cylindrical Li-batteries are used in automatic cameras and coin type cells are used in electronic devices such as calculators and watches.

2. Liquid cathode lithium cells

- This cell contains a liquid cathode i.e $SOCl_2$ (Thionyl chloride). It also acts as electrolyte.
- Acrylonitrile and propylene carbonate are used as co-solvents.

Cell reactions: Anode: $Li \longrightarrow Li^+ + e^-$

Cathode: $4Li^+ + 4e^- + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$

Net reaction: $4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$

- *Applications:* Owing to the excellent voltage control they are used in electronic circuit boards, military and space applications, medical devices such as neuro-simulators, drug delivery systems etc.

Secondary cells

- The cells in which the cell reaction is reversed by passing direct current in opposite direction i.e. it can operate both as a voltaic cell and as an electolytic cell.
- The secondary batteries can be used through a large number of cycles of discharging and

charging. They are used as a source of DC power.

Eg. Lead –acid storage cell, Ni-Cd battery etc.

Lead acid storage cell

- It consists of lead –antimony alloy coated with lead dioxide (PbO_2) as cathode and spongy lead as anode. The electrolyte is a 20% solution of H_2SO_4.
- The storage cell can operate both as voltaic cell and electrolytic cell.
- It acts as voltaic cell when supplying energy and as a result eventually becomes rundown.
- The cell operates as electrolytic cell when being recharged.
- The cell consists of a series of Pb-plates (negative plates) and PbO_2 plates (positive plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fiber.
- Cell reactions during discharging (voltaic cell):

$$\text{Anode: } Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^-$$

$$\text{Cathode: } PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$$

$$\text{Net reaction: } Pb + PbO_2 + 4H^+ \longrightarrow 2Pb^{+2} + 2H_2O$$

- The Pb^{+2} ions produced at anode and cathode then combine with SO_4^{2-} ions to form $PbSO_4$ which is precipitated at both the electrodes.
- When $PbSO_4$ covers completely both anode and cathode, the cell stops functioning as a voltaic cell. For further use, it needs to be recharged.

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(aq)} + 2e^-$$

- Cell reactions during recharging (electrolytic cell):

During recharging of the battery an external EMF greater than two volts is passed so that the cell reactions are reversed.

Cathode: $PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e-$

Anode: $PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$

Net reaction: $2PbSO_4 + 2H_2O + \text{energy} \longrightarrow Pb + PbO_2 + H_2SO_4 + 2H^+$

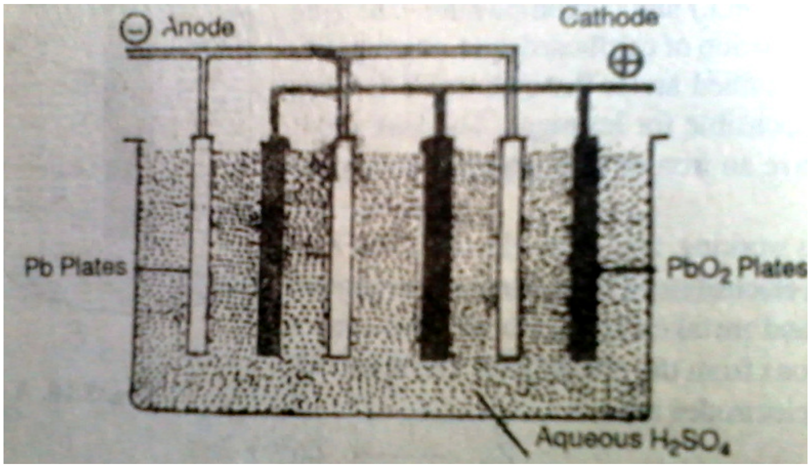


Figure 14. Lead-acid storage cell

Applications: The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, automobiles and power station.

Nickel-Cadmium cell

- This battery consists of Cd anode and cathode is composed of a paste of nickeloxyhydroxy [NiO(OH)].
- These cells are rechargeable and give a voltage of 1.4V each. They can be connected in series to give Ni-Cd battery.
- Electrolyte is 20-28% aqueous KOH jelled with a jelling agent.

Cell Representation*:* $Cd/Cd(OH)_2,KOH//Ni(OH)_2, Ni(OH)_3/Ni$

Cell reactions during discharging (voltaic cell):

$$\text{Anode: } Cd_{(s)} + 2OH^-_{(aq)} \xrightarrow{\qquad} Cd(OH)_{2(s)} + 2e^-$$

$$\text{Cathode: } 2NiO(OH)_{(s)} + 2e^- \xrightarrow{\qquad} 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$$

$$\text{Net Reaction: } Cd_{(s)} + 2NiO(OH)_{(s)} \xrightarrow{\qquad} 2Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$$

Cell reactions during charging (electrolytic cell):

$$\text{Anode: } Cd(OH)_{2(s)} + 2e^- \xrightarrow{\qquad} Cd_{(s)} + 2OH^-_{(aq)}$$

$$\text{Cathode: } 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \xrightarrow{\qquad} 2NiO(OH)_{(s)} + 2e^-$$

$$\text{Net reaction: } 2Ni(OH)_{2(s)} + Cd(OH)_{2(s)} \xrightarrow{\qquad} 2NiO(OH)_{3(s)} + Cd_{(s)}$$

Applications

1. It is used - in flash lights, photoflash units and portable electronic equipments.
2. In emergency lighting systems, alarm systems
3. In aircrafts and space satellite power systems.
4. For starting large diesel engines and gas turbines etc.

Fuel Cells

- A fuel cell is a galvanic cell in which chemical energy of a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process.
- The chemical energy provided by the fuel cell is stored outside the cell.
- The fuel and oxidants are continuously and separately supplied to the electrodes of the cell where they undergo reactions.
- Fuel cells are capable of supplying current as long as reactants are supplied.
- Eg. Hydrogen - oxygen fuel cell.

Hydrogen – Oxygen Fuel Cell

- Both anode and cathode consists porous graphite electrodes impregnated with finely divided Pt/Pd.
- The electrolyte is 2.5% KOH held in asbestos matrix.
- The reactants (fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.
- The product discharged is water and the standard EMF of the cell is 1.23V.

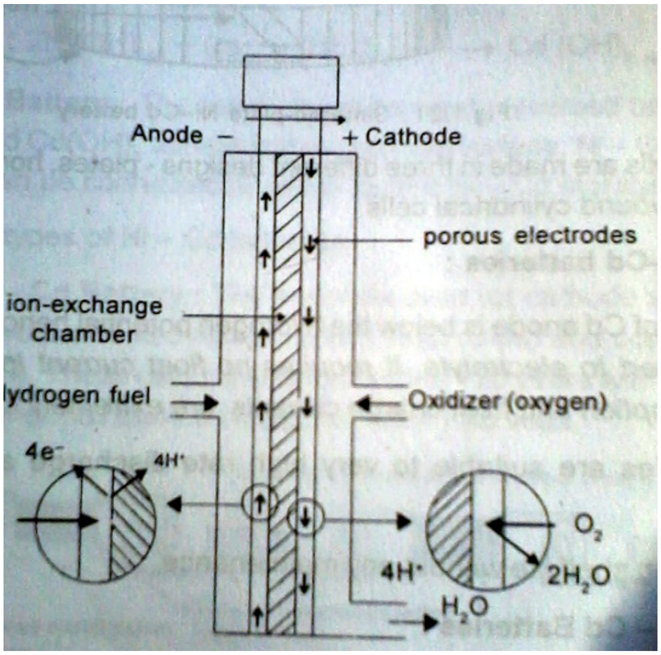


Figure 15. Fuel Cell

- Cell reactions: Anode : $2H_{2(g)} + 40H^{-}_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^{-}$

  Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \longrightarrow 4OH_{(aq)}$

  Net Reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$.

Applications

1. It is used as energy source in space shuttles e.g. Apollo spacecraft.
2. Used in small- scale applications in submarines and other military vehicles.
3. Suitable in places where environmental pollution and noise are objectionable
4. Drinking water source in space crafts, submarines and other military applications.

Advantages of fuel cell

1. High efficiency in energy conversion.
2. The product H_2O is a drinking water source for astronauts.
3. Noise and thermal pollution are low.
4. Low maintenance cost.
5. It is an energy storage system for space applications.

Previous Exam Questions

1. (a) What is a reference electrode? Explain the functioning of a standard calomel electrode and Quinhydrone electrode with Nernst equation?
   (b) At 18°C the conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 mhos respectively. Calculate the equivalent conductivity at infinite dilution of NH_4OH?
   (c) Differentiate primary, secondary cells with suitable examples? **[June-2012]**

2. (a) What is a single electrode potential? Describe a method for its determination?
   (b) Write the cell reactions of a Daniel cell?
   (c) Write a brief account of concentration cells? **[June-2011]**

3. (a) What is an electro chemical cell? Explain the construction and reactions of any electrochemical cell?
   (b) Explain how Nernst equation is useful in calculating the electrode potential? **[June-2011]**

4. (a) Explain the principle of the hydrogen-oxygen fuel cells? **[June-2011]**
   (b) Di_erentiate between electrolytic cells and concentration cells with suitable examples?

5. (a) Define the terms: (i.) Specific conductance (ii.) Equivalent conductance of an electrolyte. How do they vary on dilution?
   (b)Describe how the equivalent conductance of a 0.01M solution of $NaNO_3$ is determined experimentally? **[June-2011]**

6. (a) What are concentration cells? How can the EMF of a concentration cell be evaluated?
   (b) Write short notes on single electrode potential and its significance? **[June-2010]**

7. (a) What do you understand by electrochemical series? How is this series useful in the determination of corrosion of metals? **[June-2010]**
   (b) The resistance of a 0.1N solution of an electrolyte of 40 ohms. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm^2. Calculate equivalent conductivity?

8. (a) Give reasons for the following statements: **[June-2010]**
   i. When a zinc rod is dipped in a solution of aq. copper sulphate, copper is precipitated out.
   ii. Nernst equation is applicable for the determination of EMF of a concentration cell.
   (b) State and explain the Kohlrausch’s law and its applications?

9. (a) Define the terms specific, equivalent and molar conductivities. How do they vary with dilution? **[June-2010]**
   (b) Calculate the cell constant of a cell having a solution of concentration N/30 gm. equiv/litre of an electrolyte which showed the equivalent conductance of 120 mho cm^2 gm $equiv^{-1}$?

10. (a) Give an account on Arrhenius theory of ionization? **[Dec-2011]**
    (b) What are potentiometric titrations? Explain their applications?

11. (a) Write a note on single electrode potential and ion selective electrodes? **[Dec-2011]**
    (b) Differentiate between reversible and irreversible cells?
    (c) Define the term Transport number and explain how is it determined experimentally?

12. (a) Describe the experimental method for the determination of the pH of a solution, using quinhydrone electrode?
    (b) What are conductometric titrations? Explain their applications? **[Dec-2011]**

13. (a) The specific conductivity of a N/50 solution of NaCl at300c is 0.003686 $ohm^{-1}cm^{-1}$. If the resistance offered by the solution when placed in a cell is 1,500 Ohms, calculate Cell constant and Equivalent conductance of solution?
    (b) Write a note on hydrogen-oxygen fuel cells? **[Dec-2011]**

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