

Electrochemistry

[TOPIC 1] Electrochemical Cells, Galvanic Cells and Nernst Equation

Electrochemistry It is the study of production of electricity from energy which is released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

A chemical reaction in which electrons are lost by one substance and gained by another is called **redox reaction**. In this, transfer of electrons is the reason for electric current.

There are two types of cells—**Electrochemical cells** and **electrolytic cells**.

1.1 Electrochemical Cell

An **electrochemical cell** is a device in which chemical energy of redox reaction is converted into electrical energy. It consists of two metallic electrodes dipping in electrolytic solutions. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCN or KNO_3 or NH_4NO_3 (inert electrolyte), etc. This tube is called **salt bridge**. The significance of salt bridge includes:

(i) It connects the solution of two half-cells, thus completes the cell circuit.

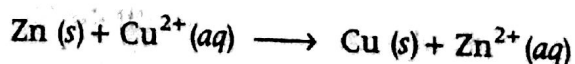
(ii) It prevents transference or diffusion of the solutions from one half-cell to other etc.

In galvanic cell, oxidation occurs at anode and it is a negative plate. While reduction occurs at cathode and it is a positive plate.

Daniell Cell

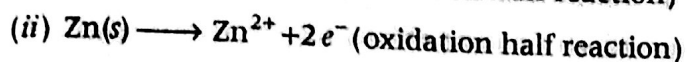
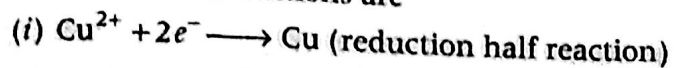
Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ion to produce an electric current, that cell is called Daniell cell.

In this cell, the following reaction occurs



Cell is represented as, $\text{Zn} | \text{Zn}^{2+}(\text{C}_1) || \text{Cu}^{2+}(\text{C}_2) | \text{Cu}$

The two half-cell reactions are



Standard Hydrogen Electrode

According to convention, a half-cell called standard hydrogen electrode (SHE) represented by $\text{Pt}(s) | \text{H}_2(g) | \text{atm} | \text{H}^+(aq)$ is assigned to zero potential at all temperatures corresponding to the reaction $\text{H}^+(aq) + e^{-} \longrightarrow \frac{1}{2}\text{H}_2(g)$

1.2 Electrode Potential

Potential difference between the metal and the metal ion in which electrode is dipped, is called **electrode potential** (E) in a given state. When the concentration of all the species involved in half-cell is unity then electrode potential is known as **standard electrode potential** [E°].

Electrode potential is dependent on *temperature* and *concentration* of the ion involved. For standard hydrogen electrode, $E_{\text{SHE}}^\circ = 0.00 \text{ V}$. SHE and calomel electrode are used as reference half-cells.

In electrochemical cell, the electrodes in different half-cells have different reduction potential. As the result of this, different flow of electrons is seen from the electrode with higher tendency to lose electrons to other electrode. This difference in electrode potential of electrodes is called **electromotive force or cell potential of a cell**. It is given by the following formula,

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \text{ OR } E_{\text{right}}^\circ - E_{\text{left}}^\circ$$

(no current is drawn through the cell).

Nernst Equation

It gives the relation between electrode potential, temperature and concentration of metal ions.

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

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

When $T = 298 \text{ K}$, $F = 96500 \text{ C mol}^{-1}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and concentration of solid M is taken as unity

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Relationship between equilibrium constant and standard potential of the cell

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log K_C$$

[where, K_C is equilibrium constant]

At equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}}^\circ = \frac{2.303RT}{nF} \log K_C$$

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

$$K_C = \text{Antilog} \left(\frac{nE_{\text{cell}}^\circ}{0.059} \right)$$

Electrochemical Series

The arrangement of metals in decreasing order of tendency to lose electrons is called electrochemical series.

The applications of electrochemical series include

- In comparing the reactivity of metals.
- In comparing the oxidising and reducing behaviour of elements.
- In calculation of emf of the cell.
- In predicting the feasibility of a reaction.
- In predicting the thermal stability of metallic oxides.
- In predicting the product of electrolysis.
- In protecting the metal from corrosion.

Concentration Cells

If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cell is known as **concentration cells**.



$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

where $C_2 > C_1$ and $E^\circ_{\text{cell}} = 0$

Electrochemical Cell and Gibbs Energy of the Reaction

To obtain maximum work from a galvanic cell, charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, ΔG° gives the maximum work.

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$. If E°_{cell} is positive,

$\Delta G^\circ =$ negative, cell will work.

If E°_{cell} is negative, $\Delta G^\circ =$ positive, cell will not work.

A metal having negative reduction potential is stronger reducing agent than H_2 and a metal having positive reduction potential is weaker reducing agent than H_2 .

Note Hydrogen ions cannot oxidise Cu (or hydrogen gas can reduce copper ion) as it has positive value of standard electrode potential, that's the reason, Cu does not dissolve in HCl.

[TOPIC 2] Conductance of Electrolytic or Ionic Solutions and Its Measurement

2.1 Conductance

Every substance offers resistance to the flow of electricity to a small or large extent. Resistance, $R = \frac{V}{I}$ where, V is voltage and I is current. SI unit of resistance is ohm (Ω).

The **electrical resistance** (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A), i.e. $R \propto \frac{l}{A}$ or $R = \rho \frac{l}{A}$ where, ρ is called **resistivity** or

specific resistance. SI unit of ρ is ohm-metre (Ωm).

The ease with which current flows through a conductor is known as its **conductance**. It is inverse of resistance, i.e. conductance,

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

where, κ is the conductivity.

SI unit of conductance is Siemens (S) or ohm^{-1} .

The quantity l/A is called **cell constant** (G^*).

The cell constant is given by

$$G^* = l/A = R \times \kappa$$

SI unit of cell constant is m^{-1} .

The inverse of resistivity is called the **conductivity** (or specific conductance). Therefore, conductivity, $\kappa = 1/\rho$. SI unit of conductivity is Sm^{-1} but quite often, it is expressed in Scm^{-1} . It always decreases with decrease in concentration for weak and strong electrolytes.

Types of Conductors

Metallic or Electronic Conductors

In **metallic conductors**, the flow of electricity takes place due to the flow of electrons only. It depends on

- (i) the nature and structure of the metal.
- (ii) the number of valence electrons per atom.
- (iii) temperature (it decreases with increase of temperature).

Electrolytic Conductors

In **electrolytic conductors**, the flow of electricity takes place due to the flow of ions (charge). It depends on

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

NOTE Superconductors have zero resistivity or infinite conductivity.

Molar Conductivity

It is defined as the conductance of that volume of solution which contains one mole of the electrolyte such that, entire solution is in between the two electrodes kept one centimetre apart and have large cross-sectional area, so as to contain the electrolyte.

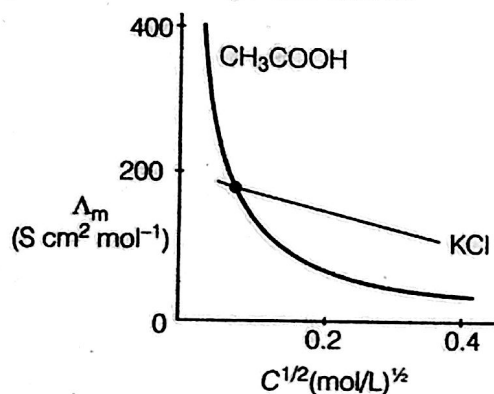
Thus, molar conductance

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

It increases with decrease in concentration (or increase on dilution). Its unit is $\text{Sm}^2\text{mol}^{-1}$ or $\text{Scm}^2\text{mol}^{-1}$.

When $C \rightarrow 0$, $\Lambda_m = \Lambda_m^\circ$, i.e. when concentration approaches zero, the molar conductivity reaches a limiting value known as **limiting molar conductivity** (Λ_m°).

The variation in Λ_m with concentration is different for **strong** and **weak electrolytes**. Such variation for KCl (strong electrolyte) and CH_3COOH (Weak electrolyte) has been depicted below:



For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the **Debye-Huckel-Onsager equation**,

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

2.2 Kohlrausch's Law of Independent Migration of Ions

This law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte.

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

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

where, λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and ν_+ and ν_- are the number of cations and anions respectively, at infinite dilution.

A weak electrolyte is not completely dissociated at all concentrations. With dilution, the degree of dissociation increases, resulting in increase in the number of ions.

In case of weak electrolytes, the Λ_m value increases steeply with dilution, especially in the low concentration region.

The ratio of molar conductivity at a specific concentration to the molar conductivity at infinite dilution (limiting molar conductivity) is known as **degree of dissociation** (α), i.e.

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

where Λ_m^C is molar conductance at concentration C and Λ_m° is molar conductance at infinite dilution.

For a weak electrolyte, if K_a is dissociation constant, then

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

For sparingly soluble salts,

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Solubility (in mol L}^{-1}\text{)}}$$

Applications of Kohlrausch's Law

- (i) The molar conductivity of weak electrolytes at infinite dilution can be calculated by using Kohlrausch's law.
- (ii) Degree of dissociation of weak electrolyte (like acetic acid) at a given concentration can be calculated.
- (iii) Knowing the degree of dissociation (α), the dissociation constant (K) of the weak electrolyte at a given concentration of the solution, can be calculated.

[TOPIC 3] Electrolysis, Batteries, Fuel Cells and Corrosion

3.1 Electrolysis

The cell which converts electrical energy to chemical energy are called **electrolytic cells**. In this oxidation occurs at anode and it is a positive plate while reduction occurs at cathode and it is a negative plate. In electrolytic cells, **electrical energy** is used to carry out non-spontaneous chemical reactions and the **process** which takes place in an electrolytic cell is called **electrolysis**.

Many metals, e.g. Na, Mg, Al, etc., are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Faraday's First Law of Electrolysis

The amount of chemical reaction which occurs at any electrode during electrolysis by passing current is proportional to the quantity of electricity passing through the electrolyte (in solution or in molten state).

Thus, w g of the substance gets deposit on passing Q coulomb of electricity

$$w \propto Q \quad \text{or} \quad w = ZQ$$

or $w = Zit$

where, Q = quantity of electricity, i = current (in A) t = time (in s), Z = constant of proportionality called electrochemical equivalent.

Faraday's Second Law of Electrolysis

The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights,

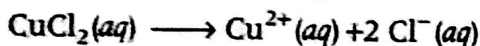
$$\text{i.e.} \quad \frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3} \dots\dots\dots$$

where, w_1 is the mass of substance deposited and E_1 is its equivalent weight and so on.

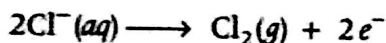
Products of Electrolysis

The products of electrolysis depend upon the nature of electrolyte being electrolysed and the nature of the electrodes. If electrodes are inert like Pt or Au, they do not take part in chemical reaction. The products of electrolysis are also depend upon the electrode potentials of oxidising and reducing species.

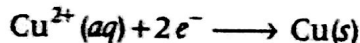
(i) Electrolysis of $\text{CuCl}_2(aq)$ using Pt electrode,



At anode



At cathode

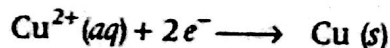


(ii) Electrolysis of CuCl_2 using Cu electrode,

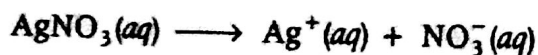
At anode



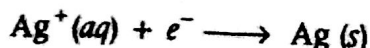
At cathode



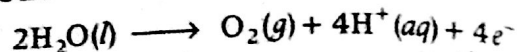
(iii) Electrolysis of $\text{AgNO}_3(aq)$ using Pt electrode,



At cathode

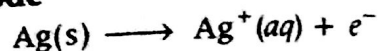


At anode

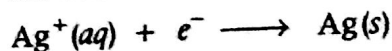


(iv) Electrolysis of AgNO_3 using Ag electrode,

At anode



At cathode



3.2 Primary Cell

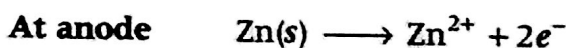
The device which provide electrical energy are called the cell. It can be **primary** or **secondary**.

The cell in which products cannot be changed back into reactants is called **primary cell**, e.g. Daniell cell, mercury cell, dry cell.

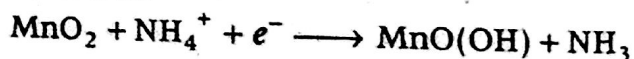
Dry Cell (Leclanche cell)

It consists of a zinc container which acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 .

The reactions are



At cathode



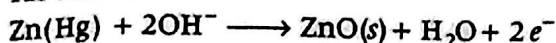
At cathode, manganese is reduced from the + 4 oxidation state to the + 3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V, it decreases with time.

Mercury Cell

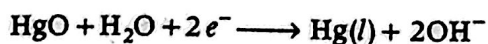
It consists of Zn - Hg amalgam as anode. The cathode is a paste of mercuric oxide (HgO) and carbon powder. The electrolyte is a paste of KOH and ZnO .

The electrode reactions are given as:

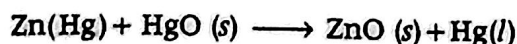
At anode



At cathode



The overall reaction is



The cell potential is approximately 1.35 V and remains constant during its life.

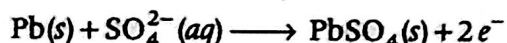
3.3 Secondary Cell

A secondary cell is capable of being charged after discharging again and again, e.g. lead storage battery, nickel-cadmium battery.

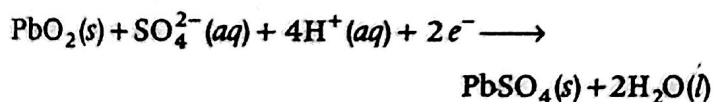
Lead Storage Battery

It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of sulphuric acid acts as the electrolyte. When the battery is in use (discharging), the cell reactions are

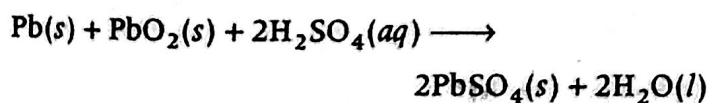
At anode



At cathode



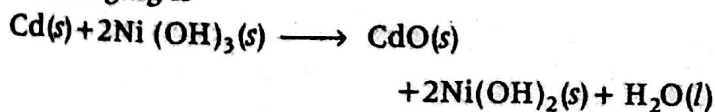
The overall reaction is



During charging, the reactions are reversed.

Nickel-Cadmium cell

The overall cell reaction of Ni-Cd cell during discharging is



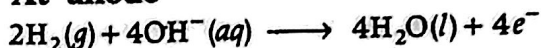
It is another important secondary cell.

3.4 Fuel Cells

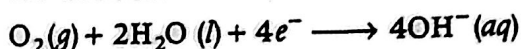
They are galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol directly into electrical energy, e.g. hydrogen-oxygen fuel cell, in which hydrogen and oxygen are bubbled through porous carbon electrodes into conc. KOH solution.

The electrode reactions of H_2 — O_2 fuel cell are

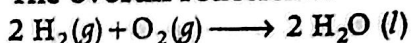
At anode



At cathode



The overall reaction is

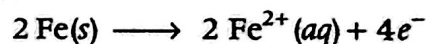


$$\text{Efficiency of a cell} = \frac{\Delta G}{\Delta H} = \frac{\text{Useful work}}{\text{Total work}}$$

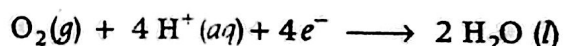
3.5 Corrosion

It is basically an electrochemical phenomenon in which a metal oxide or other salt of the metal forms a coating on the metal surface, e.g. rusting of iron, in which the following reactions take place:

Oxidation, at anode



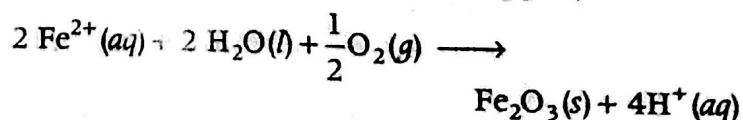
Reduction, at cathode



The overall reaction is



Atmospheric oxidation (when Fe^{2+} ions are further oxidised by atmospheric oxygen).



Methods Used for Prevention of Corrosion

There is an electrochemical method which provides a sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes itself but saves the object. Barrier protection, anti rust solutions are some other methods.