

INTRODUCTION

Electrochemistry is a branch of chemistry which deals with the study of chemical reactions produced by passing electric current through an electrolyte or the production of electrical energy by chemical reactions.

Simply, Electrochemistry deals with inter conversion of electrical energy and chemical and vice versa.

The principle of electrochemistry is useful in various fields like electro analytical techniques for qualitative and quantitative analysis, corrosion prevention, batteries, electroplating, metallurgy, etc.,

Electrochemical Terms and Conventions

The following terms and conventions must be adopted for the electrode reaction, electrode potential and electrochemical cell.

i) Current

It is the flow of electrons through a conductor.

ii) Conductor

Conductor is a material that allows electric current to pass through it. Conductance is the ability of a material to conduct the electricity.

Examples : All metals, graphite, aqueous solution of acids and bases and fused salts.

The conductors are broadly classified into two types :

(a) Metallic conductors. (b) Electrolytic conductors.

a) Metallic Conductors or Electronic Conductors

Metallic conductors are the solid substances that conduct electricity without producing chemical reaction. In metallic conductor, the transfer of current from one end to another end is due to movement of electrons. *Examples* : All metals, graphite, etc.

b) Electrolytic Conductors

Electrolytic conductor is the solution that conduct electricity by producing chemical reaction. Here, conduction of electricity is only due to movement of ions from one electrode to another electrode. The chemical reactions take place at the electrode surface.

Examples : Acids, bases, salts, etc.

Difference between Metallic Conductors and Electrolytic Conductors

S.No	Metallic Conductors	Electrolytic Conductors
1	It involves the flow of electrons.	It involves the flow of ions.
2	Chemical reactions does not occur.	Chemical reactions occur at electrode surface.
3	It does not involve any transfer of matters.	It involves transfer of ions from one electrode to another.
4	Conduction decreases with increase in temperature.	Conduction increases with increase in temperature

Electrolytic conductors are further classified into three types. They are as follows:

1) Strong Electrolytes: Strong electrolytes are substances, which ionise completely almost at all dilution.

Examples : HCl, NaOH, NaCl, KCl, CH₃COONa, etc.

2) Weak Electrolytes : Weak electrolytes are substances which ionise to a very small extent even at high dilution.

Examples : CH₃COOH, NH₄OH, CaCO₃, BaSO₄, AgCl, etc.

3) Non Electrolytes : Non electrolytes are substances which do not ionize at any dilution.

Examples : Glucose, sugar, alcohol, benzene, petrol, etc.

iii) Non-conductor or Insulator

Non-conductor or insulator is the materials which do not allow electricity to pass through it.

Examples : Wood, plastics, non-metals, etc

iv) Electrolyte

Electrolyte is a water soluble substance forming ions in solution and conducts electricity.

v) Electrode

Electrode is a metallic rod/bar which conducts the electricity. In electrochemical cells, there are two electrodes:

- Anode where oxidation takes place.
- Cathode where reduction takes place.

vi) Anodic Compartment

It contains anode metal and its electrolytic solution where oxidation reaction occurs.

vii) Cathodic Compartment

It contains cathode metal and its electrolytic solution where reduction reaction occurs.

viii) Half Cell

It is a part of the cell. It containing electrode dipped in electrolytic solution. If oxidation occurs at the electrode then it is called oxidation half cell.

If reduction takes place at electrode then it is called reduction half cell.

ix) Cell

A cell is a single arrangement of two electrodes and an electrolytic solution capable of yielding electricity due to chemical reaction within the cell or producing chemical reaction by passing Electricity through the cell.

Types of Cells

There are two types of cells

1) Electrolytic Cells 2) Electrochemical Cells

ELECTROLYTIC CELLS

Electrolytic cells are the device which converts electrical energy into chemical energy.

Example : Electrolysis of an acid solution.

ELECTROCHEMICAL CELLS

Electrochemical cells or galvanic cells are the device which converts chemical energy into electrical energy.

REPRESENTATION OF CELL NOTATION

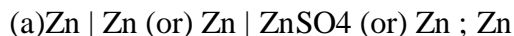
i) The anode is written on the left hand side and the cathode is written on the right hand side.

Daniel cell can be written as follows:



ii) The anode must be written by writing electrode metal first and then electrolyte. These two are separated by a single vertical line (|) or semicolon (;). The electrolyte may be written by the formula of the compound (or) by ionic species.

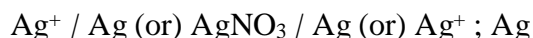
Examples :



(b) Standard hydrogen electrode, Pt, H₂ (1 atm) ; H⁺ (1 M)

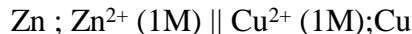
iii) The cathode must be written by writing electrolyte first and then electrode metal. These two are separated by a single vertical line or semicolon.

Examples :





iv) The two half cells are separated by a salt bridge, which is indicated by a double vertical lines (two). *Examples* : Daniel cell



EMF of the Cell

Electricity cannot flow from one point to another point unless there is a potential difference between two points. Hence, the flow of electricity from one electrode to another electrode in a Daniel cell indicates that the two electrodes have different potential.

The potential difference which causes flow of current from higher potential electrode to lower potential electrode is called electromotive force. It is measured in volts.

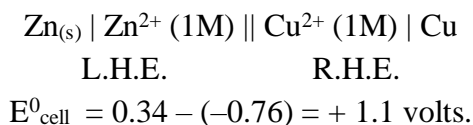
Thus, the emf of a cell can be calculated by using the following relationship. Standard reduction Standard reduction

$$\text{EMF} = (\text{Standard reduction potential of R.H.E}) - (\text{Standard reduction potential of L.H.E})$$

Where, R.H.E. and L.H.E. are right and side electrode and left and side electrode respectively. In otherwords,

$$\mathbf{E^0_{cell} = E^0_{right} - E^0_{left} \quad (or) \quad E^0_{cell} = E^0_R - E^0_L}$$

For Daniel cell, the notation is



The emf of a cell depends on the following factors:

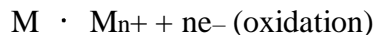
- a) Nature of the electrode and electrolyte.
- b) Concentration of the electrolyte.
- c) Temperature of the electrolytic solution.
- d) pH of the electrolytic solution.

ELECTRODE POTENTIAL

Origin of electrode potential - Nernst's solution pressure theory.

Nernst's theory of electrode potential explains how electrode potential develops. According to this theory, a metal (M) consists of metal ions (M_{n+}) with valence electrons. When the metal (M) is placed in its own salt solution, any one of the following reactions occurs.

(i) Metal passes into the solution as metal ion with the liberation of electrons.



(ii) Positive metal ion from the solution may deposit over the metal.



Examples:

1) When a zinc rod is dipped in a zinc sulphate solution, due to the solution pressure of the metal, zinc passes into the solution as Zn^{2+} ions. Now, the zinc electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative charge developed on the electrode attracts the positive ions from the solution. Due to this attraction, the positive ions remain close to the metal.

2) When a copper rod is dipped in a copper sulphate solution, due to the osmotic pressure of the solution, Cu^{2+} ions deposit over the metal. Now, the copper electrode attains a positive charge, due to the accumulation of Cu^{2+} ions on the metal. The positive charges developed on the electrode attract negative ions from the solution. Due to this attraction, the negative ions remain close to the metal. Thus, a sort of layer (positive or negative ions) is formed all around the metal. This layer is called the Helmholtz electrical double layer. This layer prevents further passing of positive ions from the metal or deposition of positive ions from the solution. A difference of potential is consequently set up between the metal and the solution. At equilibrium, the potential difference becomes a constant value, which is known as the electrode potential of a metal.

Thus, *the tendency of an electrode to lose electrons is called the oxidation potential and the tendency of an electrode to gain electrons is called the reduction potential.*

Single Electrode Potential (E)

It is the tendency of a metallic electrode to lose or gain electrons, when it is dipped in its own salt solution.

Standard Electrode Potential (E_0)

It is the tendency of a metallic electrode to lose or gain electrons, when it is dipped in its one molar own salt solution at 25°C .

Measurement of Single Electrode Potential

It is impossible to determine the absolute value of single electrode potential. But, we can measure the potential difference between two electrodes potentiometric ally by combining them to form a complete cell. For this purpose, reference electrode is used. Standard hydrogen electrode (SHE) is the commonly used reference electrode whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of single electrode.

NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following electrode reaction: aq



The emf of a reversible cell can be measured by free energy change (ΔG) of a reaction takes place in the reversible cell. If the reaction involves the transfer of 'n' electrons, 'F' Faradays of electricity will flow and E is the emf of the cell, then the total electrical energy produced by the cell is given by following equation

$$-\Delta G = n FE \quad \text{.....(1)}$$

Where, $-\Delta G$ is decrease in free energy change.

In other way,

$$-\Delta G^0 = n FE^0 \quad \text{.....(2)}$$

Where, $-\Delta G^0$ is standard free energy change and E^0 is the standard emf of a cell.

For a reversible reaction, the interrelationship of free energy change and equilibrium constant (K) is given by the following equation :

$$\Delta G = \Delta G^0 + RT \ln K \quad \text{.....(3)}$$

It can be written as,

$$\Delta G = \Delta G^0 + RT \ln [\text{Product}] / [\text{Reactant}] \quad \text{.....(4)}$$

The equation (4) is called as Van't Hoff isotherm.

Substituting the value of products and reactants in equation (4), we get

$$\Delta G = \Delta G^0 + RT \ln [M] / [M^{n+}] \quad \text{.....(5)}$$

Substituting the equation (1) and (2) in (5), we get

$$-nFE_{red} = -nFE^0_{red} + RT \ln [M] / [M^{n+}] \quad \text{.....(6)}$$

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

$$E_{red} = E^0_{red} - \frac{RT \ln [M]}{nF [M^{n+}]} \quad \text{.....(7)}$$

$$E_{\text{red}} = E^0_{\text{red}} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]} \quad \text{.....(8)}$$

$$T = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$F = 96500 \text{ coulombs}$$

$$[M] = 1$$

Substituting all the values in equation (8), we get

$$E_{\text{red}} = E^0_{\text{red}} - \frac{0.0591}{n} \log 1 \quad \text{.....(9)}$$

This equation is known as the Nernst equation

$$E_{\text{red}} = E^0_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{.....(10)}$$

Nernst equation for this equation is the reduction potential of single electrode
Consider the following oxidation reaction:



Then, the Nernst equation (10) becomes

$$E_{\text{oxi}} = E^0_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{.....(11)}$$

Equation (11) is Nernst equation for oxidation potential of single electrode.

Applications of Nernst Equation

- It is used to calculate the emf of a given cell.
- It is also used to calculate the electrode potential of a given
- Corrosion tendency of metals can be predicted.
- Spontaneity of a given cell reaction can be predicted.

Problem based on the application of EMF measurements

1) Predict the following cell reaction is spontaneous or not



Given that

o

Cu²⁺/Cu

E = 0.34 V

o

Zn²⁺/Zn

E = - 0.76 V

Solution :

Given data :

Cu²⁺/Cu E = 0.34 V

Zn²⁺/Zn E = 0.76V

T = 298 K

We know that,

$$\Delta G^\circ = -nFE^\circ$$

Where, n = number of electrons involved in the cell reaction

• n = 2 (obtained from the cell notation)

F = 96500 coulombs

o o o

$$E_{\text{cell}} = E_R - E_L$$

o cell E

•

•

0.34 -

(

•

0.76)

= 1.1 V.

Then, $\Delta G^\circ = -nFE^\circ = -(2 \times 96500 \times 1.1)$

= -212300 CV mol⁻¹ = - 212300 J mol⁻¹

• ΔG° is negative, therefore the cell reaction is spontaneous.

Note : 1 coulombs × Volt = 1 Joule

Reference Electrode

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose potential is already known or arbitrarily fixed as zero.

The important reference electrode is standard hydrogen electrode, whose standard electrode potential is taken as zero at all temperature. So, it is called *primary reference electrode*.

It is very difficult to set up a hydrogen electrode. So, other electrode called *secondary reference electrode* (like calomel electrode) is used.

Standard Hydrogen Electrode

Standard Hydrogen electrode is called a primary reference electrode because

- 1) The emf developed by the standard hydrogen electrode is arbitrarily fixed as zero at 1 atm pressure and the value of which is treated as constant at all temperature.
- 2) It is an only electrode with which the potential of all other electrodes are compared.

Construction of a Standard Hydrogen Electrode

The typical standard hydrogen electrode is shown in

It consists of rectangular platinum foil which is connected to a platinum wire and sealed in a glass tube. A glass jacket surrounds the tube carrying the platinum foil. The jacket is closed at the top and opened at the bottom. A side tube attached to the outer jacket is used for the injection of hydrogen gas into the cell. This electrode, when dipped in a 1 M HCl solution at 25 °C and hydrogen gas at 1 atm is passed, forms a standard hydrogen electrode.

When this electrode acts as anode, the electrode reaction is as follows :



When this electrode acts as cathode, the electrode reaction is as follows:



The standard hydrogen electrode is represented as,



Development of EMF of SHE

When hydrogen gas is bubbled through the solution, it is adsorbed by the platinum foil. Due to the adsorption of hydrogen gas, the equilibrium is established between hydrogen molecules and H⁺ ions. The electrode potential developed during this equilibrium is taken as zero and treated as constant at all temperature.

Limitation

- It requires H₂ gas and is difficult to set up and transport.
- It requires considerable volume of test solution.

- The solution may affect the surface of the platinum electrode.
- The potential of the electrode is altered by changing the pressure of H₂ gas.

Need for Secondary Reference Electrode

- It is very difficult to maintain the H⁺ ion concentration at 1 M and hydrogen gas pressure at 1 atm.
- Platinum electrode is poisoned by the presence of impurities in the solution or gas.

Calomel Electrode or Secondary Reference Electrode

To overcome the limitations of hydrogen electrode, the calomel electrode is developed. This is called the secondary reference electrode. It consists of a glass tube. Pure mercury is placed at the bottom of the tube and is covered with a paste of mercurous chloride. The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a platinum wire (Fig. 2.4).

If the electrode acts as anode, the reaction is



Net reaction :



Mercury undergoes oxidation to produce mercurous ion (Hg_2^{2+}) and combines with chloride ion to give mercurous chloride (Hg_2Cl_2). Hence, the concentration of chloride ions is decreased.

Calomel electrode the electrode acts as cathode, the reaction is



Net reaction :



The mercurous ion present in the mercurous chloride undergoes reduction to give mercury. Hence the concentration of chloride ions is increased. Calomel electrode is represented by $\text{Hg} | \text{Hg}_2\text{Cl}_2(s), \text{KCl} (\text{sat. solution})$.

Characteristics of Calomel Electrode

1) The electrode potential of calomel electrode depends on the activity of the chloride ions. When the concentration of chloride ion decreases, the electrode potential of calomel Electrode increases. The single electrode potential of calomel electrode with various concentration of KCl on the hydrogen scale at 298 K are given below

$$0.1 \text{ N KCl} = 0.3338 \text{ V}$$

$$1 \text{ N KCl} = 0.2800 \text{ V}$$

$$\text{Saturated KCl} = 0.2422 \text{ V}$$

2) The potential of calomel electrode is temperature dependent.

Measurement of Single Electrode Potential using Saturated Calomel Electrode

The saturated calomel electrode is coupled with another electrode whose potential is to be determined. If the reduction

potential of the unknown electrode (E_x) is less than the single : **Electrochemical Series** electrode potential of calomel electrode (+ 0.2422 V), calomel electrode will act as cathode. We know that,

$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{cal}} - E_x$$

E_{cell} can be determined experimentally by using potentiometer, then E_x can be calculated as follows :

$$E_x = E_{\text{cal}} - E_{\text{cell}}$$

ION SELECTIVE ELECTRODE (ISE)

These are the electrodes which have the ability to respond only to a particular ion and develop potential, ignoring the other ions in a mixture.

The potential developed by an ion selective electrode depends only on the concentration of particular ions.

GLASS ELECTRODE

Principle

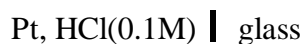
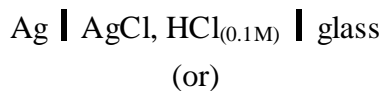
It has been found experimentally by F.Frietz that when two solutions of different pH values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in pH value.

The glass membrane functions as an ion exchange resin. Equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. This forms the basis of glass electrode.

CONSTRUCTION

Glass electrode consists of a thin walled glass bulb. The glass is of a special type of relatively low melting point and high electrical conductivity. The glass bulb may contain AgCl coated silver electrode or a platinum wire in 0.1M HCl.

Hence, the glass electrode may be represented as



Hydrochloric acid present in the glass bulb furnishes a constant H^+ ion concentration.

Thus, glass electrode is silver –silver chloride electrode, reversible with respect to chloride ion.

Glass electrode is usually employed as a internal reference electrode. The electrode potential varies with H^+ ion concentration and is given by $E_G = E^{\circ}_G + 0.0591\text{pH V}$

Hence glass electrode is mostly used to determine the pH of solutions, especially coloured solutions containing oxidising or reducing agent. Usually calomel electrode is used as the second electrode.

Determination of a pH of a solution using glass electrode

The glass electrode is placed in the solution under test and is coupled with saturated calomel electrode. The emf of the cell is measured, from which, pH of the solution is calculated.

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

$$E_{\text{cell}} = 0.2422\text{V} - [E^{\circ}_{\text{glass}} + 0.0591 \text{ V pH}]$$

$$E_{\text{cell}} = 0.2422\text{V} - E^{\circ}\text{G} - 0.0591 \text{ V pH}$$

$$\text{pH} = \frac{0.2422\text{V} - E^{\circ}\text{G} - E_{\text{cell}}}{0.0591}$$

ADVANTAGES OF GLASS ELECTRODE

- It can be easily constructed and readily used
- The results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.

LIMITATIONS

Since the resistance of glass membrane is quite high, special electronic potentiometers are employed for measurement.

The glass electrode can be used in the pH range of 0 to 10. Above pH 12 (high alkalinity), cations of the solution affect the glass and make the electrode useless.

APPLICATIONS OF ISE

- ISEs are used to determine the concentrations of cations like H^+ , Na^+ , K^+ , Ag^+ , and Li^+
- ISEs are used for the determination of hardness (Ca^{2+} Mg^{2+} ions)
- Concentrations of anions like NO_3^- , CN^- , S^{2-} and halides can also be determined.
- ISEs are used in the determination of concentration of a gas by using gas sensing electrodes.
- pH of the solution can be measured by using gas sensing electrodes.

ELECTROCHEMICAL SERIES OR EMF SERIES

The standard reduction potential of a number of electrodes is given in the table. These values are determined potentiometrically by combining the electrode with another standard electrode, whose electrode potential is zero.

Electrode	Electrode reaction	Potential E_0 (V)	Nature
Li ⁺ / Li	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	- 3.01	<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;">Anodic</div> <div style="flex-grow: 1; border-left: 1px solid black; border-right: 1px solid black; position: relative;"> <div style="position: absolute; top: -10px; left: 50%; transform: translate(-50%, -50%);">↑</div> <div style="position: absolute; bottom: -10px; left: 50%; transform: translate(-50%, -50%);">↓</div> </div> <div style="margin-left: 10px;">Reference Electrode</div> </div> <div style="margin-top: 10px; text-align: center;">Cathodic</div>
Ca ²⁺ / Ca	$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	- 2.93	
Na ⁺ / Na	$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	- 2.90	
Mg ²⁺ / Mg	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	- 2.71	
Al ³⁺ / Al	$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	- 2.37	
Pb ²⁺ / Pb	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	- 1.66	
Zn ²⁺ / Zn	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76	
Cr ³⁺ / Cr	$\text{Cr}^{3+} + 3e^- \rightleftharpoons \text{Cr}$	-0.74	
Fe ²⁺ / Fe	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44	
Co ²⁺ / Co	$\text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co}$	-0.28	
Ni ²⁺ / Ni	$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	-0.23	
Sn ²⁺ / Sn	$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0.14	
Fe ³⁺ / Fe	$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$	-0.04	
H ⁺ / H ₂	$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	+0.00	
Cu ²⁺ / Cu	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34	
Ag ⁺ / Ag	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0.80	
Pt ²⁺ / Pt	$\text{Pt}^{2+} + 2e^- \rightleftharpoons \text{Pt}$	+0.86	
Au ⁺ / Au	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	+1.69	
1/2 F ₂ / F ⁻	$1/2\text{F}_2 + e^- \rightleftharpoons \text{F}^-$	+2.87	

Definition :

“An increasing order of the standard reduction potentials is called electrochemical series”.

Significance of EMF series or Application of Electrochemical series or Importance of Electrode Potential

1) Calculation of standard emf of the cell

The standard emf of a cell (E°) can be calculated if the standard electrode potential values are known by using the following formula :

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R.H.E.}} - E^{\circ}_{\text{L.H.E.}}$$

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

The standard free energy change of a cell reaction can be calculated.

Where, n = number of electrons involved in cell reaction.

$F = 96500$ coulombs

E° = Standard emf of the cell.

2) The relative case of oxidation or reduction

By using the given formula :

$$\Delta G^{\circ} = nFE^{\circ}$$

A metal ion with higher reduction potential has a greater tendency to undergo reduction.

A metal ion with lower reduction potential has a greater tendency to undergo oxidation.

The elements present above the hydrogen in the series undergo oxidation whereas the elements present below hydrogen in the series undergo reduction.

From the series, the fluorine has higher positive value of standard reduction potential (+2.87 V) and shows higher tendency towards reduction.

Similarly, lithium has the highest negative value (−3.01 V) and shows higher tendency towards oxidation.

The reduction potential of Cu is 0.34 V while Zn is −0.76 V. Even though both of them are ready to undergo reduction reactions, Cu undergoes reduction reaction more readily than Zn because Cu has higher value of reduction potential than Zn.

3) The replacement or displacement tendency of one element by the other

Metals with a lower reduction potential have a greater tendency to replace another metal which has higher reduction potential.

In other words, the more electropositive metal is reduced and less electropositive metal is oxidised. The driving force for the displacement increases with increased separation of metals in the emf series.

Example: The reduction potential of zinc (−0.76 V) is lower than copper (0.34 V). Hence, zinc displaces copper from its salt solution.



4) *Displacement behavior of hydrogen*

Metals with negative reduction potential displaces the hydrogen from acid solution.



5) *Determination of equilibrium constant for the reaction*

Standard electrode potential can also be used to determine the equilibrium constant (K) for the reaction we know that

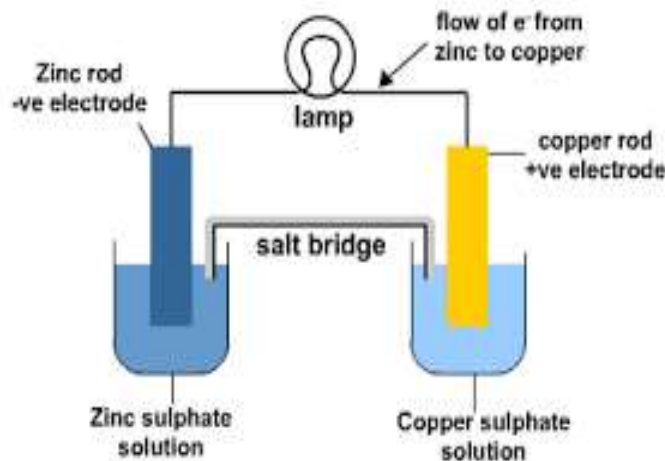
$$\begin{aligned} -\Delta G^0 &= RT \ln K = 2.303 RT \log K \\ \log K &= -\Delta G^0 / 2.303RT \\ &= nFE^0 / 2.303RT \end{aligned}$$

From the value of E^0 , the equilibrium constant for the cell reaction can be calculated.

ELECTROCHEMICAL CELLS

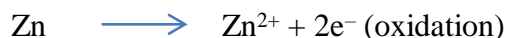
Electrochemical cells or galvanic cells are the device which converts chemical energy into electrical energy. Here, the electricity is produced by a spontaneous redox cell reaction.

Example : Daniel cell .



It consists of a zinc electrode dipped in 1 M zinc sulphate solution and a copper electrode dipped in 1 M copper sulphate solution. Each electrode is considered as a half cell. The two standard half cells are coupled by salt bridge and to form a cell. The electrode reactions are as follows:

At anode : Zinc passes into solution as zinc ion and liberates two electrons at the electrode. Here, oxidation reaction occurs at the zinc electrode.



At cathode: Copper ion gains two electrons, reduced to metallic copper and deposited at the copper electrode. Here, reduction reaction occurs at the copper electrode.



Now, both zinc and copper electrodes are connected through the external wire. The excess of electron liberated by the oxidation reaction flows along the wire in order to neutralize the positive charge on the copper electrode. This movement of electrons from Zn to Cu electrode produces current in the circuit (1.1 V).

Salt Bridge

It bridges the two half cells and hence the name. A saturated solution of KCl or NH_4NO_3 in agar-agar gel is taken in U-tube and used as a salt bridge.

Function of Salt Bridge

- 1) It prevents the physical contact of electrolytic solution in two half cells.
- 2) It maintains the internal electrical continuity between two half cells.
- 3) It eliminates the liquid junction potential.

Table : Difference between Electrolytic Cell and Electrochemical Cell

S.No	Electrolytic Cell	Electrochemical Cell
1	In this cell, chemical reactions are carried out by passing electric current.	In this cell, electric current is produced by chemical Reaction.
2	In this cell, negative electrode is cathode and positive electrode is anode.	In this cell, negative electrode is anode and positive electrode is cathode.
3	Example: Electrolysis of aqueous hydrochloric acid.	Example: Daniel cell, Lead-acid cell, etc
4	In this cell, the electrodes may be same or different material.	In this cell, the electrodes are Different materials.
5	No salt bridge is required.	Salt bridge is required.
6	Amount of electricity required to carried out the electrolysis is measured by Calorimeter.	Electricity produced by this cell is measured by potentiometer.

Measurement of EMF of a cell

EMF of a cell can be determined by connecting a voltmeter between the electrodes. The voltage is read directly from the instrument. But the drawbacks of using this method are:

- (1) The instrument draws current from the cell, causing a change in the emf due to formation of reaction products at the electrodes and changes in the concentration of the electrolyte around the electrodes.
- (2) An internal resistance of the cell is developed due to concentration polarization. Hence potentiometers are used which require extremely small current at balance.

Potentiometers are used for accurate measurement of emf of electrochemical cells. They operate on the Poggendorff's compensation principle. In this method an unknown emf is opposed by another known emf until the two are equal as shown by no deflection on a galvanometer present in the circuit.

The potentiometer, as shown in fig. consists of a uniform wire AB. A storage battery (K) is connected to the ends A and B of the wire through a rheostat @. The cell of unknown emf (X) is connected in the circuit by connecting its positive pole to A and the negative pole to a sliding contact (D) through a galvanometer (G). The sliding contact (D) is freely moved along the wire AB till no current flows through the galvanometer, Then the distance AD is measured. The emf of unknown cell is directly proportional to the distance AD.

$$E_x \propto AD$$

Then the unknown cell (X) is replaced by a standard cell (S) in the circuit. The sliding contact is again moved till there is null deflection in the galvanometer. Then the distance AD' is measured.

The emf of standard cell E_s is directly proportional to the distance AD'

$$E_s \propto AD'$$

Then, the emf of the unknown cell can be calculated from the following equation,

$$\frac{\text{Emf of the unknown cell (X)}}{\text{Emf of the standard cell (S)}} = \frac{\text{Length AD}}{\text{Length AD'}}$$

$$\frac{E_x}{E_s} = \frac{AD}{AD'}$$

$$\text{Emf of the unknown cell } E_x = \frac{AD}{AD'} \times E_s$$

Energy storage devices

BATTERIES

Battery is an arrangement of one or more electrochemical cells connected in series or parallel that can be used as a source of direct electric current at constant voltage.

A good batteries possess the following characteristics:

1. It should be cheap and easy for construction.
2. It should be light and compact.
3. It should have long life without change in voltage.
4. It should be reusable.
5. It should be easily transported.

Classification of batteries

Based on nature of the batteries, they are classified into three types which are described below:

Primary Battery (or) Primary Cell

In these cells, the electrode reaction cannot be reversed by passing an external electrical energy through them. The cell reaction occurs only once and after use they become dead. Therefore, they are not rechargeable. These batteries are simply called as use and throw batteries.

Examples: Dry cell and Mercury cell.

They are used in Torches, Flashlights, Calculators, Transistors, etc.

Secondary Battery (or) Secondary Cell

In these cells, the electrode reaction can be reversed by passing an external electrical energy. Hence, they can be recharged by passing electric current through them and can be used again and again. They are also called as storage cells or accumulators.

Examples: Lead acid storage cell, Nickel – Cadmium cell, etc.

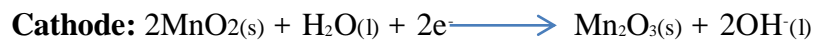
Flow battery (or) Fuel cell

In these cells, the reactants and electrolyte are continuously passing through the cell. Here, chemical energy is directly converted into electrical energy. The efficiency of this cell is higher than all the other conventional batteries.

Example : Hydrogen - Oxygen fuel cell.

Alkaline batteries

It is the improved form of dry cell. It consists of a zinc cylinder which acts as anode and a graphite rod (carbon rod) at the center of the container which acts as the cathode. The zinc cylinder is filled with an electrolyte consisting of powdered zinc, KOH and MnO₂ in the form of paste. The zinc cylinder has an outer insulation of card board case (Fig. 3.15). The cell reaction is as follows:



Net Reaction:



Advantages of alkaline battery over dry battery

Zinc does not dissolve in a basic medium.

The life time of alkaline battery is longer than the dry battery because zinc cylinder is not involved in cell reaction. Zinc powder present in the electrolyte is only involved in reaction. So, there is no corrosion of zinc cylinder.

It gives constant voltage when the current is drawn from it.

Even in hot weather, it performs better than other type of batteries.

Uses

It is used in cameras, calculators, radios and watches.

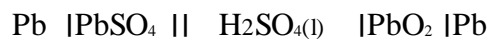
Lead acid battery (or) Lead storage cell (or) Lead accumulator (or) Acid storage cell

Lead acid battery can be operated both as a voltaic and electrolytic cell. When it acts as a voltaic cell, it supplies electrical energy and run down. When it is recharged, it acts as an electrolytic cell. Thus, it is rechargeable.

Construction

A lead storage battery consists of 3 to 6 voltaic cells connected in series. In each cell, lead acts as anode and lead dioxide (PbO_2) acts as cathode .

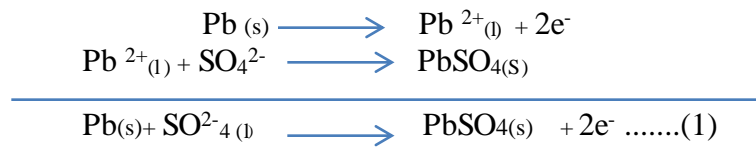
Various plates are separated from the adjacent one by insulator like rubber. Anodes and cathodes are immersed in 20 to 21 % dil. H_2SO_4 having a density of 1.3 gm/ml. The cell representation is given below.



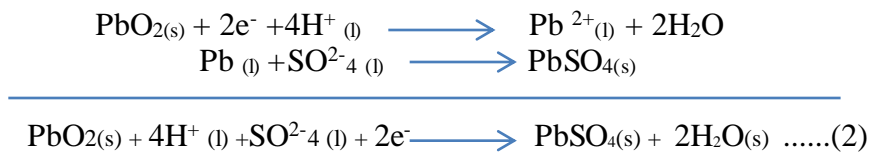
Working (Discharging)

When the storage cell is supplying electricity, lead is oxidized to Pb^{2+} ions and PbSO_4 is formed at anode. At cathode, PbO_2 gains the liberated electrons and gets reduced to Pb^{2+} and PbSO_4 is formed.

At anode:



At cathode:



Overall cell reaction during (discharging) use (1) + (2)



At the time of discharging process, PbSO_4 is deposited at both the electrodes and H_2SO_4 is consumed. As a result, the concentration of H_2SO_4 decreases gradually.

Recharging

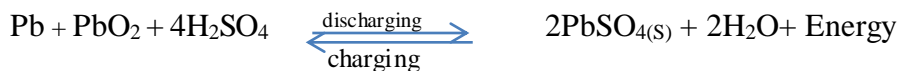
The cell is recharged when the density of H_2SO_4 becomes below 1.2 gm/ml. It can be done by applying an external electricity across the electrodes. The following reaction will take place during recharging process :



Overall Reaction



Net Reaction :



Hence, the recharging involves exactly the reverse process of the normal cell reaction.

Note:

Decrease in density of dil. H_2SO_4 can be measured with the help of hydrometer.

Uses

It is used in automobiles such as cars, buses, etc.

It is also used in gas engine ignition, telephone exchanger, hospitals, power stations, etc.

Advantages of lead acid battery

It can be constructed easily.

It produces high voltage.

It acts as effectively even at low temperature.

Self-discharge is very low when compared to all other batteries.

Disadvantages

Recycling of this battery causes environmental pollution.

Mechanical strain and normal pumping reduces battery capacity.

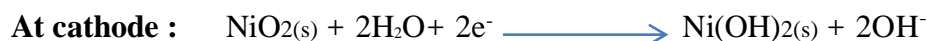
Nickel-Cadmium cell (or) NiCad battery

It is also a rechargeable battery. It consists of a cadmium anode and a NiO₂ cathode. Both electrodes are immersed in a solution of KOH electrolyte. The cell notation of the Nickel - cadmium battery is as follows.

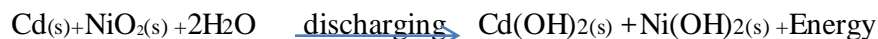


Working : (Discharging)

During the discharge process, the cadmium is oxidized to Cd²⁺ ions and insoluble Cd(OH)₂ precipitate is formed. NiO₂ is reduced to Ni²⁺ ions which combined with OH⁻ ions to form Ni(OH)₂. It gives a constant voltage of 1.4 V.



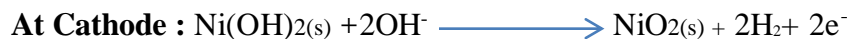
Overall reaction



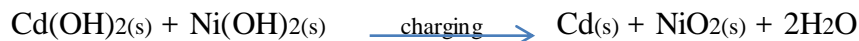
Both the insoluble products are deposited at their respective electrodes. Hence, the cell can be recharged.

Recharging : When the current is passed in opposite direction, the electrode reaction gets reversed. Cd gets deposited on the anode and NiO₂ gets deposited on the cathode.

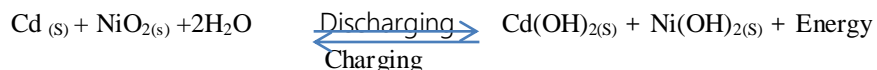
The electrode reaction during the recharging process are given below:



Overall Reaction



Net Reaction :



Advantages

- It gives a constant voltage of 1.4 V.
- It is very small and compact.
- It has longer life than lead acid storage battery.
- It can be packed in a sealed container like dry cells.

Disadvantage

- It is more expensive than lead storage battery.

Uses

It is used in calculators, electronic camera flashes, transistors, rechargeable flash light and cordless appliances.

Lithium battery

Lithium battery is the cell of the future. It is a solid state battery because instead of liquid or a paste electrolyte solid electrolyte is used.

Advantages of Lithium battery

- Lithium is a light weight metal, only 7 g (1 mole) lithium is sufficient to produce 1 mole of electrons.
- Its cell voltage is high '3 V'.
- It generates a higher voltage than all other types of cells.
- All the constituents of the battery are solids and hence there is no risk of leakage from the battery.
- It can be made into convenient size and shape.

Example : i) Li/TiS₂ ii) Li/S

Disadvantage

It is more expensive than all other batteries.

(i) Solid state Lithium battery

It consists of a lithium anode, TiS₂ cathode and a solid electrolyte (polymer). The solid electrolyte is packed in between the electrodes. The electrolyte (polymer) permits only the passage of ions and not electrons. Hence, the electrons are transferred from anode to cathode through external circuit. The various electrode reactions during the discharging process are given below.



When the anode is connected to cathode, electrons and lithium ions are transferred from anode to cathode through external circuit and solid electrolyte respectively. This cell is rechargeable and produces a cell voltage of 3 V.

Recharging Process

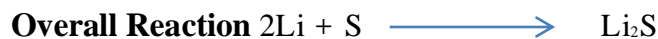
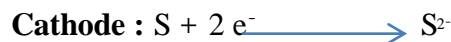
The lithium battery is recharged by supplying external current which leads to the deposition of lithium and TiS₂ at the anode and cathode respectively. The reverse electrode reaction in the cell during the recharging process is given below:



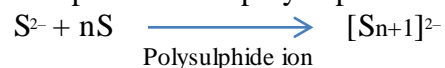
Lithium sulphur battery

It is a rechargeable battery. It is operated at higher temperature. So, lithium and sulphur is in the molten state. In this battery, lithium is used as anode and S as the cathode. Both of them are present in molten state. The electrons from lithium are conducted to sulphur by a graphite rod. Two graphite rods are used in this cell which are partially immersed in the molten materials. β -alumina ($\text{NaAl}_{11}\text{O}_{17}$) is used as solid electrolyte. It is placed between molten lithium and sulphur.

The various electrode reactions during the discharging process are given below:



The S^{2-} ion reacts with elemental sulphur to form polysulphide ion.



In order to neutralize the negative charge, lithium ion migrates through the solid electrolyte which does not allow big polysulphide ion.

Other types of secondary Lithium batteries

- i) Li/MoO₃ ii) Li/MnO₂
- iii) Li/V₂O₅ iv) Li/Cr₃O₈

Uses of Lithium battery

It is light in weight and has high energy density and used in electric cars, computers, communication devices, etc.

It is used in clinical devices and electronic medical devices.

A small size of lithium battery is used in cellphone.

Advantages of Lithium sulphide battery

It is rechargeable.

It is light in weight and much smaller than lead acid battery.

It has high energy density.

ZINC – AIR BATTERIES

Zinc air batteries are the batteries which breathe air, that is, they use oxygen directly from the air to bring about the electrochemical reaction. These are basically alkaline batteries in which the cathodic active material is not stored in the cell. Of the several types available, Zinc – air batteries are more popular. They were commercialized in 1977.

Construction:

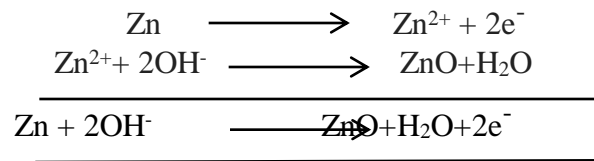
1. Anode is composed of granulated zinc powder mixed with an aqueous solution 30% KOH and a gelling agent to immobilize the material.
2. Cathode is composed of mixture of carbon and the catalyst and a gelling agent held on a nickel coated steel matrix. Several hydrophobic, gas permeable, thin layers of Teflon are provided to steady the air entry.
3. Electrolyte contains 30% KOH.
4. There is also vent for the entry of air or O₂ into the cell.
5. The container is made of glass and has a separator made of nylon.

The cell is represented as:

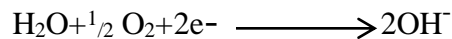


The reactions involved in the cell are:

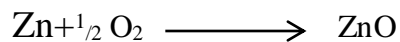
At the anode:



At the cathode:



The overall cell reaction :



The battery offers an EMF of 1.25-1.35V.

Characteristics of Zinc – air batteries are as follows:

- These are light and have high energy density.
- These are relatively eco-friendly and have unlimited capacity.
- These suffer from low shelf life. still, they are known for low energy cost.