ENGINEERING CHEMISTRY FOR ELECTRICAL SCIENCES

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UNIT - I - ELECTROCHEMISTRY

Electrochemistry is a branch of chemistry, deals with the chemical applications of electricity. It deals with the chemical reaction produced by passing electric current through an electrolyte or the production of electric current through chemical reactions.

The Science of electrochemistry deals with the study of interconversion of electrical and chemical energy.

The principle of electrochemical cell deals with the conversion of energy from electrical to chemical and vice versa.

1) Current :

It is the flow of electrons through a conductor.

2) Conductors :

A substance that allows electric current to pass through it is called a conductor.

The ability of a material to conduct electric current is called conductance.

Eg. All metals, graphite, aqueous solution of acids, bases etc.

Non - Conductors :

Materials which do not conduct electric current are called non - conductors.

Eg. Plastics, wood etc.

Types of Conductors :

a) Metallic Conductors

b) Electrolytic Conductors.

Metallic Conductors:

Metallic Conductors are solid substance, which conduct electric current due to the movement of electrons from one to another end.

Eg - All metals. Graphite.

Electrolytic Conductors:

Electrolytic Conductors conduct electric current due to the movement of ions in solution or in fused state. The conduction increases with increase of temperature.

Eg - Acids, bases, Salts etc.

Difference between metallic Conduction and electrolytic Conductors.

S. NO	Metallic Conduction	Electrolytic Conduction
1.	It involves the flow of electrons in a Conductor.	It involves the movement of ions in a solution
2.	Conduction decreases with increases in temperature.	Conduction increases with increases in temperature.
3.	It does not involve any transfer of matter.	It involves transfer of electrolyte in the form of ions.
4.	No change in chemical properties of the conductor.	Chemical reactions occur at the two electrodes.

Types of Electrolytic Conductors:

The electrolytic Conductors are further sub-classified into three types of as follows.

a) Strong electrolytes:

Strong electrolytes are substances, which ionise completely almost at all dilutions.

Eg - HCl, NaOH, NaCl etc.

b) Weak electrolytes:

Weak electrolytes are substance, which ionise to a small extent even at high dilutions

Eg - $CaCO_3$, NH_4OH etc.

c) Non electrolytes :

Non electrolytes are substances which do not ionise at any dilutions.

Eg : Glucose, Sugar, alcohol etc.

Important cell Terminology :

Oxidation :

The tendency to lose electrons.

Reduction :

The tendency to gain electrons.

Electrode :

When a metal rod is dipped in its salt solution, it develops a positive or negative potential. This assembly is called as an electrode.

Anode :

Anode is the electrode at which oxidation occurs.

Cathode :

Cathode is the electrode at which reduction occurs.

Electrolytes :

Electrolytes is a water soluble substance forming ions in solution and conduct an electric current.

Half cell :

Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Cell :

Cell is a device consisting two half cell. The two half cells are connected through one wire.

Types of cells :

Based on the type of reaction, occuring in a cell, cells are classified into two types.

① Electrolytic cells.

Electrolytic cells are the cells in which electrical energy is used to bring about the chemical reaction.

Eg - electroplating etc.

② Electrochemical cells

Electrochemical cells are the cells in which chemical energy converted into electric energy.

Eg. Daniel cell.

Representation of a cell :

We will Consider that a cell Consists of two half cells. Each half is again made of a metal electrode in Contact with metal ion Solution.

① a Single vertical line (|) represents a phase boundary between metal electrode and ion Solution (electrolyte) Thus the two ha in a voltaic cell are indicated as

$Zn | Zn^{2+}$ — Anode half cell

$Cu^{2+} | Cu$ — Cathode half-cell (Phase Boundary)

The metal electrode in anode half cell is on the left, while in cathode half cell is on the right of the metal ion.

② In the Complete cell diagram, the two half cells are separated by a double vertical line in between. The Zinc-Copper cell can be written as

$Zn | Zn^{2+} \;||\; Cu^{2+} | Cu$

(Salt bridge)

Anode half cell — cathode half cell.

A double vertical line represents the Salt bridge.

③ The Symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket.

$Mg | Mg^{2+} \;||\; H^+ | H_2 (Pt)$

(Inert Electrode.)

Anode half-cell — Cathode Half-cell.

EMF of a cell:

Electromotive force is defined as "the difference of potential which cause flow of current from one electrode of higher potential to the other electrode of lower potential.

Thus, the emf of a galvanic cell can be calculated using the following relationship.

$$EMF = \{\text{Standard reduction potential of right hand side electrode}\} - \{\text{Standard reduction potential of left hand side electrode}\}$$

$$E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left}$$

Factors affecting emf of a cell:

1) nature of the electrolytes and electrodes.
2) Concentration and composition of the electrolytes
3) pH and temperature of the solution.

Electrode potential

Origin of Electrode potential:

A metal (M) consists of metal ions (M^{n+}) with valance electrons when the metal (M) is placed in a solution of its own salt, any one of the following reactions will occur.

i) positive metal ions may pass into the solutions.

$$M \longrightarrow M^{n+} + ne^- \text{ (oxidation)}$$

ii) positive metal ions from the solution may deposit over the metal

$$M^{n+} + ne^- \longrightarrow M \text{ (reduction)}$$

Example 1) Zn electrode dipped in $ZnSO_4$ solution.

when Zn electrode is dipped in $ZnSO_4$ solution, Zn goes into the solution as Zn^{2+} ions due to oxidation.

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

Now, the Zn electrode attains a negative charge, due to the accumulation of valance electrons on the metal. The negative charges developed on the electrode attract the positive ions from

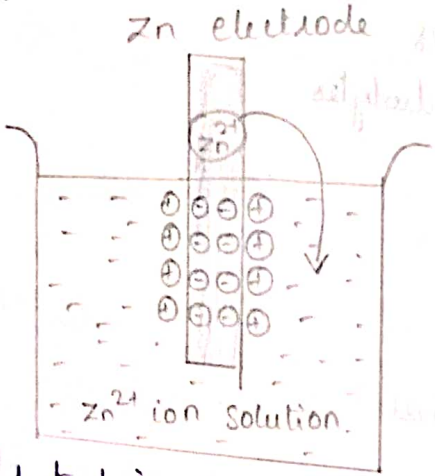
Solution. Due to this attraction the positive ions remain cl to the metal.

2) Cu electrode dipped in $CuSO_4$ solution

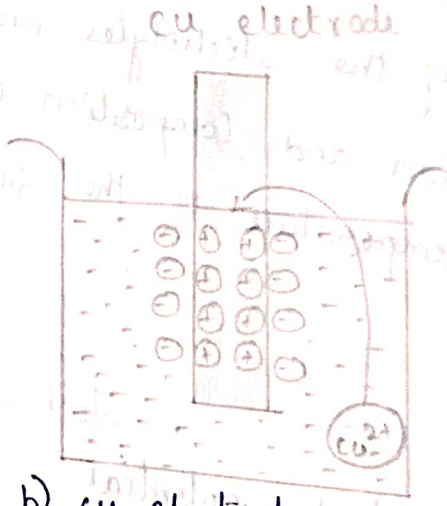
When Cu electrode is dipped in $CuSO_4$ solution, Cu^{2+} ions from the solution deposit over the metal due to reduction.

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

Now, the Cu electrode attains a positive charge, due to th accumulation of Cu^{2+} ions on the metal. The positive charge developed on the electrode attract the negative ions from solution. Due to this attraction, the negative ions remain close to the metal.



a) Zn electrode in $ZnSO_4$ solution



b) Cu electrode in $CuSO_4$ solutio

Thus, a sort of layer ((+) or (-)) ions is formed all around metal. This layer is called Helmholtz electrical double layer. thi layer prevents passing of the positive ions from or to the meta A difference of potential is consequently set up between the meta and the solution. At equilibrium, the potential difference betwee constant value. which is known as the electrode potential of a m

Oxidation potential: If oxidation occurs at the electrode, at equilibrium, the potential of the electrode is oxidation potenti The tendency of an electrode to lose electrons is oxidation Potential.

Reduction potential: The tendency of an electrode to gain electron is called reduction potential

Single Electrode potential : (E)

It is a measure of tendency of a metallic electrodes to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard Electrode potential (E°)

The tendency of a metallic electrodes to lose or gain electron when it is in contact with a solution of its own salt of 1 Molar concentration at 25°C