**ELECTROLYSIS**

Electrolytes are electrovalent substances that form ions in solution which conduct an electric current. Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

Nonelectrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution. Their water-solutions do not conduct an electric current. Sugar, alcohol and glycerol are typical nonelectrolytes.

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed Electrolysis (lyo = breaking).

The process of electrolysis is carried in an apparatus called the Electrolytic cell. The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped. These rods are connected to the two terminals of a battery (source of electricity).

**MECHANISM OF ELECTROLYSIS**

The cations migrate to the cathode and form a neutral atom by accepting electrons from it. The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes chemical reaction takes place.

**Example.** Let us consider the electrolysis of hydrochloric acid as an example. In solution, HCl is ionized,

HCl ⎯⎯→ H+ + Cl−

In the electrolytic cell Cl– ions will move toward the anode and H+ ions will move toward the cathode. At the electrodes, the following reactions will take place.

**At cathode :**

H+ + e– ⎯⎯→ H (Reduction)

Here, each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H2.

**At Anode :**

Cl– ⎯⎯→ Cl + e− (Oxidation)

After the chloride ion loses its electron to the anode, pair of chlorine atoms unite to form chlorine gas, Cl2.

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is : 2HCl ⎯⎯→ H2 + Cl2 (Decomposition)

**ELECTRICAL UNITS**

There are a few electrical units which we should understand before taking up the study of quantitative aspects of electrolysis. These are :

**Coulomb**

A coulomb is a unit quantity of electricity. It is the amount of electricity which will deposit 0.001118 gram of silver from a 15 per cent solution of silver nitrate in a coulometer.

**Ampere**

An ampere is a unit rate of flow of electricity. It is that current which will deposit 0.001118 gram of silver in one second. In other words, an ampere is a current of one coulomb per second.

**Ohm**

An ohm is a unit of electrical resistance. It is the resistance offered at 0ºC to a current by a column of mercury 106.3 cm long of about 1 sq mm cross-sectional area and weighing 14.4521 grams.

**Volt**

A volt is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

**FARADAY’S LAWS OF ELECTROLYSIS**

Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. In 1834, he formulated two laws which are known as Faraday’s

Laws of Electrolysis. These are :

**First Law**

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.

**Second Law**

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

**Definition of Electrochemical equivalent in light of First Law**

If m is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

m ∝ Q (First Law)

We know that Q = I × t

where I is the strength of current in amperes and t is the time in second for which the current has been passed.

Therefore, m ∝ I × t

or m = Z × I × t

where Z is the constant known as the Electrochemical equivalent of the substance (electrolyte).

If I = 1 ampere and t = 1 second, then

m = Z

Thus, the **electrochemical equivalent** is the amount of a substance deposited by 1 ampere current passing for 1 second (i.e., one coulomb).

**Importance of the First law of Electrolysis**

With the help of the first law of electrolysis we are able to calculate :

(1) the value of electrochemical equivalents of different substances; and

(2) the masses of different substances produced by passing a known quantity of electricity through their solutions.

**Importance of the Second law of Electrolysis**

The second law of electrolysis helps to calculate :

(1) the equivalent weights of metals

(2) the unit of electric charge

(3) the Avogadro’s number

**STRONG AND WEAK ELECTROLYTES**

Electrolytes may be divided into two classes :

(a) Strong electrolytes

(b) Weak electrolytes

**Strong Electrolytes**

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionised. The solution itself is called a strong electrolytic solution. Such solutions are good conductors of electricity and have a high value of equivalent conductance even at low concentrations. The

Strong electrolytes are :

(1) The strong acids e.g., HCl, H2SO4, HNO3, HClO4, HBr and HI.

(2) The strong bases e.g., NaOH, KOH, Ca (OH)2, Mg (OH)2, etc.

(3) The salts. Practically all salts (NaCl, KCl, etc) are strong electrolytes.

**Weak Electrolytes**

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionised. Such a solution is called a weak electrolytic solution, that has low value of equivalent conductance. The weak electrolytes are :

(1) The weak acids : All organic acids such as acetic acid, oxalic acid, sulphurous acid

(H2SO3) are examples of weak electrolytes.

(2) The weak bases : Most organic bases e.g., alkyl amines (C2H5NH2) are weak electrolytes.

(3) Salts. A few salts such as mercury (II) chloride and lead (II) acetate are weak electrolytes.

**Extraction and purification of copper from Cu-ore by Electrolysis:**

Copper is purified by**electrolysis**, when a current is applied, positively-charged copper ions (called cations) leave the anode (positive electrode) and move toward the cathode (negative electrode).

**Copper can be extracted from its ore by heating it with carbon. Impure copper is purified by electrolysis in which the anode is impure copper, the cathode is pure copper and the electrolyte is copper sulphate solution.**

Copper is less reactive than carbon, so it can be extracted from its ores by heating it with carbon. For example, copper is formed if copper oxide is heated strongly with charcoal, which is mostly carbon:

**copper(II) oxide + carbon    →    copper + carbon dioxide**

**2CuO + C → 2Cu + CO2**

Removing oxygen from a substance is called reduction. The copper oxide is reduced to copper in the reaction above.

The simulation below shows what happens during the purification of copper by electrolysis.

A half-equation shows what happens at one of the electrodes during electrolysis. Electrons are shown as e–. These are the half-equations:

* **anode: Cu – 2e¯ → Cu²+ (oxidation)**
* **cathode: Cu²+ + 2e¯ → Cu (reduction).**

Oxidation happens at the anode because electrons are lost. Reduction happens at the cathode because electrons are gained.

Pure copper forms on the negative electrode. Important for the purification of copper is:

* the anode (positive electrode) is made from impure copper
* the cathode (negative electrode) is made from pure copper
* the electrolyte (the solution that conducts electricity) is copper(II) sulfate solution.

During electrolysis, the anode loses mass as copper dissolves, and the cathode gains mass as copper is deposited.

**Conductor & Insulator:**

All substances do not conduct electrical current. The substances, which allow the passage of electric current, are called **conductors**. The best metal conductors are such as copper, silver, tin, etc. Non-metals like graphite.

On the other hand, the substances, which do not allow the passage of electric current through them, are called non-conductors or **insulators**. Some common examples of insulators are rubber, wood, wax, etc.

The conductors are broadly classified into two types, Metallic and electrolytic conductors.

**Difference between metallic & electrolytic conductor:**

|  |  |
| --- | --- |
| **Metallic conduction** | **Electrolytic conduction** |
| (i) It is due to the flow of electrons. | (i) It is due to the flow of ions. |
| (ii) It is not accompanied by decomposition of the substance.(Only physical changes occurs) | (ii) It is accompanied by decomposition of the substance. (Physical as well as chemical change occur) |
| (iii) It does not involve transfer of matter. | (iii) It involves transfer of matter in the form of ions. |
| (iv) Conductivity decreases with increase in temperature. | (iv) Conductivity increases with increases in temperature and degree of hydration due to decreases in viscosity of medium. |