Cardamom Planters' Association College
(Re-accredited with 'B' Grade by NAAC)
Pankajam Nagar, Bodinayakanur - 625 582.

Electrochemistry

Electrochemistry Faradays law

Dr. B. Kavitha
Assistant Professor
PG and Research Department of Chemistry
C.P.A. College, Bodinayakanur

Electrochemistry

Electrochemistry is a branch of chemistry that studies the reactions which take place at the interface of an electric conductor (the electrode composed of a metal or a semiconductor, including graphite) and ionic conductor (the electrolyte).

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.

Non-electrolytes, 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.

An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution.

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).

The electrodes connected to the positive terminal of the battery attracts the negative ions (anions) and is called anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called cathode.

Mechanism of electrolysis

How the electrolysis takes place, is illustrated in Figure. 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 soln, HCl is ionised,

$$HCl \longrightarrow H^+ + Cl^-$$

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:

$$H^+ + e^- \longrightarrow H$$

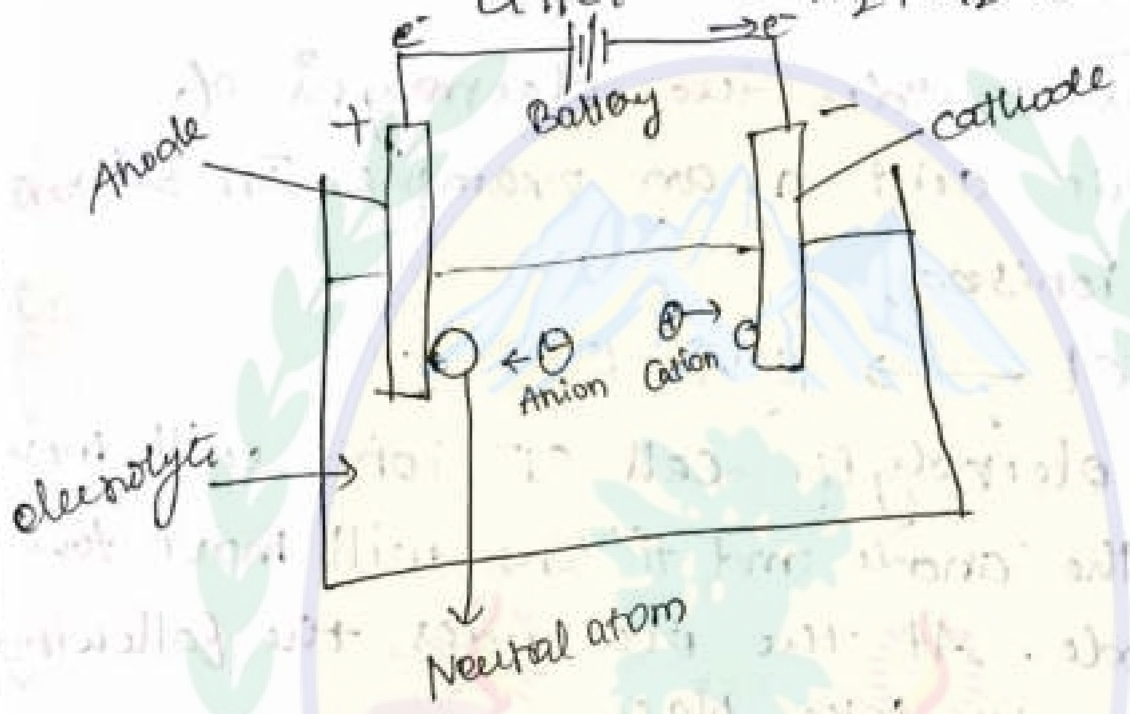
As you seen, each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H_2.

At anode: $Cl^- \longrightarrow Cl + e^-$

After the chloride ion loses its e^- to the anode, pair of chlorine atoms unite to form chlorine gas. Cl_2

The net effect of the process is the decomposition of HCl into hydrogen and Chlorine gases. The overall reaction is

$$2HCl \longrightarrow H_2 + Cl_2 \text{ (Decomposition)}$$



Faraday's law of Electrolysis

Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amount 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 law 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 solns of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalent.

Definition of Electrochemical equivalent in First Law

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

$$m \propto Q \quad \text{(First Law)}$$

we know that $Q = I \times t$

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

Therefore, $m \propto I \times t$

$$m = Z \times I \times t$$

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. (ie) one coulomb).

The Electrical unit Faraday

It has been found experimentally that the quantity of electricity required to liberate one-gram equivalent of a substance is 96,500 Coulombs. This quantity of electricity is known as Faraday and is denoted by the symbol F.

It is obvious that the quantity of electricity needed to deposit 1 mole of the substance is given by the expression.

$$\text{Quantity of electricity} = n \times F$$

where n is the valency of its ion. Thus, the quantity of electricity required to discharge:

One mole of $Ag^{+} = 1 \times F = 1F$

One mole of $Cu^{2+} = 2 \times F = 2F$

One mole of $Al^{3+} = 3 \times F = 3F$

We can represent the reactions on the cathode as:

$Ag^{+} + e = Ag$

$Cu^{2+} + 2e = Cu$

$Al^{3+} + 3e = Al$

It is clear that the moles of electrons required to discharge one mole of ions Ag^{+}, Cu^{2+} and Al^{3+} is one, two and three respectively. Therefore it means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say that,

$$1 \text{ Faraday} = 96,500 \text{ coulombs} = 1 \text{ Mole } e^{-}ns.$$

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:

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

Verification of the second law of Electrolysis

Acc. to this law, when the same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.

Pass the Same quantity of electricity through the three Coulometers (the term is now in practice replaced by the older name voltmeter) Containing the solutions of dilute H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively. These Coulometers are fitted with platinum, copper and silver electrodes. The masses of hydrogen, copper and silver liberated / deposited at the respective cathodes are in the ratio of their equivalent weights.

(ie) $\frac{\text{mass of hydrogen liberated}}{\text{mass of copper deposited}} = \frac{\text{Eq. wt. of hydrogen}}{\text{Eq. wt. of copper}}$

& $\frac{\text{mass of copper deposited}}{\text{mass of silver deposited}} = \frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of silver}}$

Importance of 2nd law of Electrolysis

The 2nd law of electrolysis helps to Calculate

(1) the equivalent weights of metals

(2) the unit of electric charge

(3) the Avagadro's number.