ELECTROCHEMISTRY

Concerned with the transformation of chemical reactions into electricity because energy is stored by chemical reagents.

ELECTROLYSIS:

When ionic compounds are in molten or aqueous state, they conduct electricity. This is because the electrostatic force of attraction between the ions while in solid form are overcome making the ions free and mobile to conduct an electric current.

The conductors which connect a molten substance or solution with the applied voltage are called **electrodes.**

In electrolysis, the negative electrode is called a cathode while the positive electrode is called the anode.

Chemical reactions occur at the electrodes and the elements are deposited as solids or liberated as gases

Definition:

Electrolysis is the process by which a compound in molten state or aqueous solution is decomposed by passing an electric current through it.

According to Faraday, substances or compounds which conduct electricity and are decomposed by it are called **electrolytes.**

The vessel in which an electrical change takes place is called a **cell**.

In aqueous or molten state, ions are produced which are responsible for the conduction of electricity. Most of the electrolysis products partially come from the electrolyte and some from the solvent.

During electrolysis **anions** are attracted to the anode where they give up electrons **(oxidation)** while cations are attracted to the **cathode** where they take up electrons **(Reduction).**

In cases where two or more ions of similar charge are present at a particular electrode, only one species will be selected for discharge.

Selective discharge:

The ion selected for discharge depends on the following factors;

- **Position of ion in the electrochemical series**

Keeping other factors constant an ion lower in the series or ion with lower electrode potential will be selected for discharge in preference to the one higher in the series or with higher electrode potential.

Consider the order of ions in the electrochemical series below;

Cations			Anions	
Ion	**Electrode potential**		**Ion**	**Electrode potential**
Li^+	-3.04		F^-	+2.85
K^+	-2.92		SO_4^{2-}	+2..01
Ca^{2+}	-2.87		Cl^-	+1.36
Na^+	-2.71		Br^-	+1.07
Mg^{2+}	-2.37		I^-	+0.54
Al^{3+}	-1.66		OH^-	+0.41
Zn	-0.76			
Fe^{2+}	-0.44			
Sn^{2+}	-0.14			
Pb^{2+}	-0.13			
H^+	0.00			
Cu^{2+}	+0.34			

- **Concentration of an ion in the electrolyte solution**

The greater the concentration of an ion in the greater is the chance of its discharge. For example the electrolysis of brine (concentrated sodium chloride), chloride ions are discharged at the anode in preference to the hydroxide ions irrespective of their positions in the series.

- **Nature of electrode used**

Regardless of other factors, in some cases the nature of electrode may affect the choice of ion selected for discharge. For example;

The electrolysis of brine using platinum cathode (hydrogen selected in preference to sodium) and also using the mercury cathode (sodium selected for discharge because of its solubility in the mercury cathode).

The electrolysis of copper (II) sulphate solution using carbon anode and copper anode; the reactions involved differ. Also that of silver nitrate solution using silver electrodes.

Faraday's laws of electrolysis:

These are the laws of electrolysis in general but were first stated by Faraday. They include:

1. *The mass of any substance liberated by a current at an electrode is proportional to the quantity of electricity which has passed.*
   Quantity of electricity (Q) is expressed in coulombs(C) and is obtained as a product of Current (in amperes) and time (in seconds)
   $$Q = current\ (I)\ X\ time\ (t)$$
2. *The quantity of electricity required to liberate 1 mole of any element is proportional to the charge number on the ion.*
   The charge number of an ion is the number of positive or negative charges which the ion possesses and is represented by *z.* for example;
   For H^+, OH^- and Ag^+, z = 1; for Zn^{2+} and Cu^{2+}, z = 2 for Al^{3+}, z = 3
   For instance, the quantity of electricity required to liberate Al^{3+}, Cu^{2+} and Ag^+ is in the ratio 3:2:1.
   The quantity of charge/electricity required to deposit I mole of a univalent ion is called the Faraday's constant, 1 F = 96500coulombs.
   1 mole of divalent ion would require 2 F = 2 X 96500 coulombs.
   1 mole of trivalent ion would require 3 F = 3 X 96500 coulombs.

Applications of electrolysis:

Electrolysis is of great importance in industry. Among the chief applications are the following;

- Extraction of elements. Both metals (e.g. Na, K, Mg, Ca, Al, Zn) and non – metals (e.g. H_2, F_2, Cl_2) are obtained by electrolysis of fused compounds or their aqueous solutions.
- Purification of metals. Copper and gold are refined electrolytically
- Electroplating. For example plating with silver, gold, chromium and nickel.
- Anodic oxidation of aluminium. Electrolysis of dilute sulphuric acid is used to grow a tough oxide layer/film on aluminium articles for some purposes.
- Preparation of important compounds for example sodium hydroxide and sodium chlorate(V)

Calculations on electrolysis:

1. A direct current of 0.1A flows for 4 hours through 3 cells in series which contain solutions of silver nitrate, copper (II) sulphate and Aluminium nitrate respectively. Calculate the mass of the metal deposited in each case. (Ag = 108, Cu = 63.5, Al = 27, 1F = 96500C)
   Hint: Ag = 1.61g; Cu = 0.474g; Al = 0.134g
2. A current of 3A was passed for 20 minutes through a cell containing sulphuric and the hydrogen produced at the cathode was collected. Calculate the volume in cm^3 of the hydrogen that was collected at 25^oC at 120KPa. Deduce the volume of oxygen liberated at the anode.
   Hint: hydrogen = 385cm^3; oxygen = 192.5cm^3
3. Two voltammeters are connected in series; one containing a solution of silver nitrate, the other a solution of copper (II) sulphate. A steady current I is passed through the two voltammeters for ten minutes and 0.54g of silver is deposited on the cathode of the first voltammeter. Calculate:
   i. The current I
   ii. The mass of copper deposited 0n the cathode of the second voltammeter (to 2 d.p.)

   (Ag = 108, Cu = 63.5, Take Faraday's constant to be 96000$Cmol^{-1}$)

   Hint: current = 0.8A; mass of Cu = 0.16g.

4. (a) State two conditions which must be fulfilled for an electrical current to pass through an electrolyte
   (b) State Faraday's laws of electrolysis
   (c) A current of 0.200A was passed for 20 minutes through two voltammeters in series. One voltammeter has copper electrodes and contains copper (II) sulphate solution while the other has platinum electrodes and contains dilute sulphuric acid. Calculate:
   i. The mass of copper deposited
   ii. The volume of oxygen gas in cm^3 at s.t.p. liberated at the anode of the second voltammeter. (Faraday's constant = 96500C, Cu = 63.5, O = 16)
   iii. The volume of oxygen liberated at 23^oC

   (d) State any two applications of electrolysis.