ELECTROLYSIS

Electrolysis is the process which the passage of an electric current through a substance causes it to decompose.

Electrical conductivity can be used to divide matter into distinct groups:

1. Electrical conductors – substances which conduct an electric current
2. Non-electrical conductors – substances which do not conduct an electric current (generally non-metals and non-polar covalent compounds)

Electrical Conductors

These can be divided into:

1. Metals and graphite – Conduction in these are due to the movement of electrons. These substances conduct electricity in the solid state even though metals can also conduct electricity in the liquid state.
2. Electrolytes – They conduct electric current when molten or dissolved in water (due to the movement of oppositely charged ions). Electrolytes are ionic compounds and polar covalent compounds such as water.

Types of Electrolytes

1. Strong electrolytes – These are substances which ionize completely when dissolved in water. E.g. Ionic compounds, strong acids (such as HCl and H_2SO_4) and strong alkalis (such as NaOH).
2. Weak electrolytes – These are substances which partially ionize in water. E.g. weak acids (such as ethanoic acid and methanoic acid) and weak alkalis (such as aqueous ammonia). Water is also a weak electrolyte.

The Electrolytic Cell

This is the apparatus in which electrolysis is carried out. It consists mainly of:

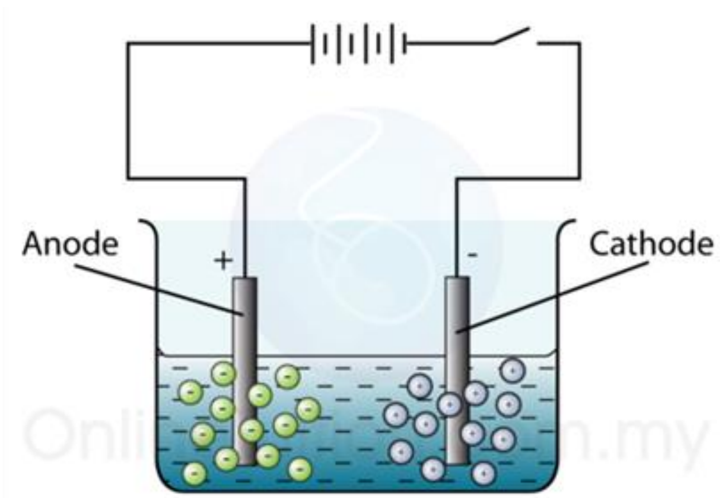
- Battery (Dry cell)
- Connecting wires for the flow of electrons
- Ammeter (to measure current flow)

- Electrodes – these are rods or poles of metal or graphite where the current enters and leaves the electrolyte. There are two types of electrodes: the anode and the cathode.
  - *Anode* – The anode is the positive electrode and is connected to the positive terminal of the battery. Electrons leave the electrolyte and enter the external circuit via the anode.
  - *Cathode* – The cathode is the negative electrode and is connected to the negative terminal of the battery. Electrons leave the external circuit and enter the electrolyte via the cathode.

  Electrodes may be active or inert.

  - Inert electrodes do not take part in the chemical changes occurring in electrolysis. E.g. Graphite electrodes and platinum electrodes.
  - Active electrodes take part in the chemical changes which occur during electrolysis. E.g. Copper electrode

- A suitable container with the electrolyte.



GENERAL PRINCIPLE OF ELECTROLYSIS

When an electrolytic cell is set up and an electric current starts flowing in the electrolyte, the cations will move towards the cathode and gain electrons from the cathode. The anions will move towards the anode and lose electrons to the anode. At both electrodes, atoms or molecules are formed.

Example: Electrolyte is molten NaCl

Ions Present: Na^{+} and Cl^{-}

At the cathode:

$Na^{+} + e^{-} \rightarrow Na$ (oxidation or reduction?)

At the anode:

$2Cl^{-} - 2e^{-} \rightarrow Cl_2$ (oxidation or reduction?)

Example: Electrolysis of Fused Potassium Iodide ($KI_{(l)}$)

Ions present: K^{+}, I^{-}

At the Cathode:

$2K^{+} + 2e^{-} \rightarrow 2K_{(s)}$

At the Anode:

$2I^{-} - 2e^{-} \rightarrow I_2(s)$

Factors Affecting Discharge of Ions During Electrolysis

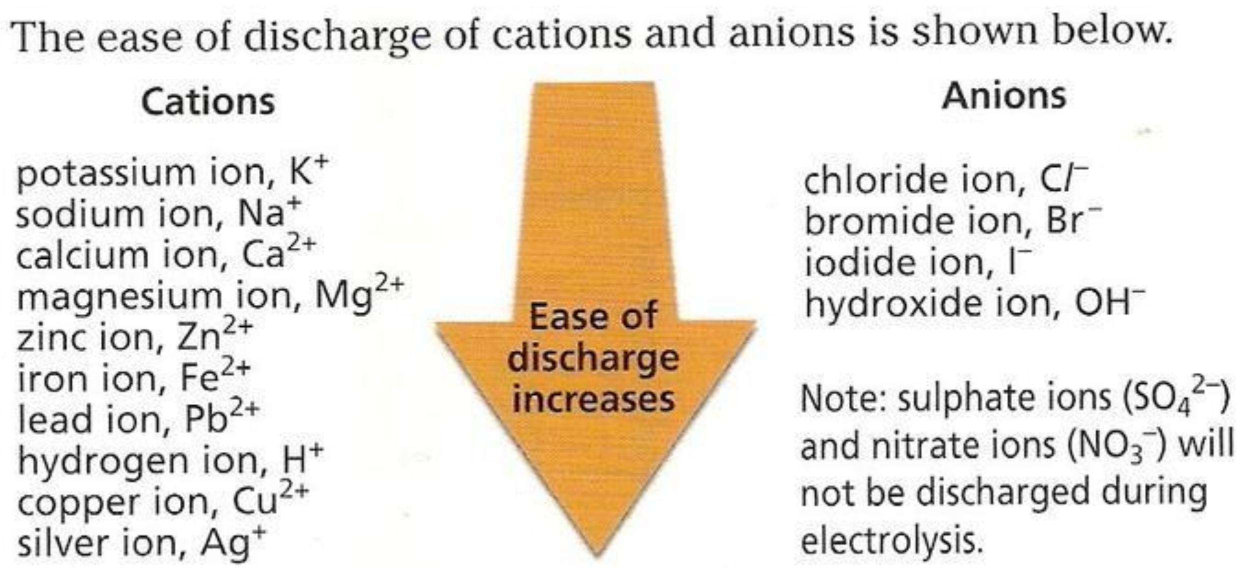
The main factors are:

1. The type of electrodes used, whether they are inert or active.
2. The concentration of the electrolyte. If the electrolyte is concentrated, it tends to promote the concentrated ion.
3. The position of the ions in the electrochemical or reactivity series.

Preferential Discharge of Ions

When a molten salt is electrolysed, no competition for discharge occurs at the electrodes as a single type of cation and a single type of anion are present in the melt. However, when an aqueous solution is electrolysed, hydrogen ions and hydroxide ions from the partial ionisation of water are also present, in addition to the ions from the electrolyte.

When the current is passed through this aqueous solution, more than one type of ion moves towards each electrode. When this happens, one type of ion is discharged in preference to the other. For example, when a current is passed through aqueous sodium sulphate, hydrogen ions and sodium ions move to the cathode, while hydroxide ions and sulphate ions move to the anode. The ion that is preferentially discharged is determined mainly by its position in the electrochemical or reactivity series.


The ease of discharge of cations and anions is shown below.

Example: Electrolysis of concentrated $HCl_{(aq)}$ using graphite electrodes

Ions present:

From HCl: H^+ and Cl^-

From H_2O – H^+ and OH^-

At the Cathode:

Hydrogen ions are discharged

$2H^+ + 2e^- \rightarrow H_{2(g)}$

At the Anode:

Cl^- ions are discharged in preference to the OH^- ions because the Cl^- ions are of a greater concentration

$2Cl^- - 2e^- \rightarrow Cl_{2\,(g)}$

Changes in the Electrolyte

The acid becomes dilute. This is because Cl^- ions and H^+ ions are being removed, leaving behind OH^- ions and H^+ ions, making up additional H_2O.