TOPIC 14 Electrolysis

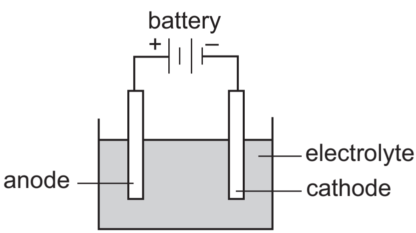
Objectives

Candidates should be able to:

(a) describe electrolysis as the conduction of electricity by an ionic compound (an electrolyte), when molten or dissolved in water, leading to the decomposition of the electrolyte
(b) describe electrolysis as evidence for the existence of ions which are held in a lattice when solid but which are free to move when molten or in solution
(c) describe, in terms of the mobility of ions present and the electrode products, the electrolysis of molten sodium chloride, using inert electrodes
(d) predict the likely products of the electrolysis of a molten binary compound
(e) apply the idea of selective discharge based on
  (i) cations: linked to the reactivity series
  (ii) anions: halides, hydroxides and sulfates
  (iii) concentration effects (In all cases above, inert electrodes are used.)
(f) predict the likely products of the electrolysis of an aqueous electrolyte, given relevant information
(g) construct ionic equations for the reactions occurring at the electrodes during the electrolysis, given relevant information
(h) describe the electrolysis of aqueous copper(II) sulfate with copper electrodes as a means of purifying copper
(i) describe the electroplating of metals
(j) describe the production of electrical energy from simple cells (i.e. two electrodes in an electrolyte) linked to the reactivity series and redox reactions (in terms of electron transfer)

1. Electrolytic Cell

Electrolysis is the use of electricity to break down a compound into its constituents. The process takes place in an electrolytic cell.



The battery provides a source of electricity for reactions to occur. During the process, electrons flow from the positive terminal to the negative terminal of the battery.

The electrodes used in electrolysis conduct electricity. Inert graphite or platinum electrodes are usually used.

The electrode connected to the positive terminal of the battery is the anode and the electrode connected to the negative terminal of the battery is the cathode. Reduction occurs at the cathode while oxidation occurs at the anode.

The electrolyte contains mobile ions which allow for electricity to flow through. It is usually an acid solution, or an ionic compound that is molten or dissolved in water. A solid ionic compound cannot be used as its ions are in fixed positions in the crystal lattice structure.

2. Electrolysis of Molten Ionic Compounds

When an ionic compound is molten, it splits up into positive ions (cations) and negative ions (anions) which are free to move to the cathode and the anode respectively.

At the cathode, electrons are taken in by cations, while at the anode, electrons are lost by anions. To maintain a complete electrical circuit, the number of electrons taken in at the cathode must be the same as the number of electrons lost at the anode.

Since cations take in electrons, they are reduced. Anions are oxidised as they lose electrons.

3. Electrolysis of Solutions of Ionic Compounds

When a solution of an ionic compound is used instead, the autoionisation of water has to be taken into consideration as well.

Water partially dissociates to form hydrogen and hydroxide ions.

water ⇌ hydrogen ion + hydroxide ion
$H_2O \rightleftharpoons H^+ + OH^-$

These ions will compete with those of the ionic compound to be discharged at each of the electrodes.

The ease of discharge of cations can be predicted based on the reactivity series. As reactive metals tend to form ions, their ions are not easily discharged. Ions of less reactive metals have a higher tendency of getting discharged as they accept electrons more easily.

OH^- I^- Br^- Cl^- NO_3^- SO_4^{2-} ⟶

Most likely to be discharged → Least likely to be discharged

Hydroxide ions are most readily discharged in dilute solutions. Nitrates and sulfates are usually not discharged and tend to stay in the solution.

However, when the solution is concentrated, halide ions are preferentially discharged rather than hydroxide ions.

5. **Purification of Copper**

Copper can be purified by electrolysing copper(II) sulfate solution using copper electrodes. Impure copper is used as the anode while pure copper acts as the cathode.

At the anode, OH^- ions are not discharged since the electrode is not inert. Instead, copper atoms are oxidised to form Cu^{2+} ions.

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The impure copper anode gradually dissolves as the atoms are oxidised. The impurities are left behind to sink to the bottom of the cell as the anode dissolves.

At the cathode, Cu^{2+} ions in the electrolyte are discharged and deposited on the pure copper.

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

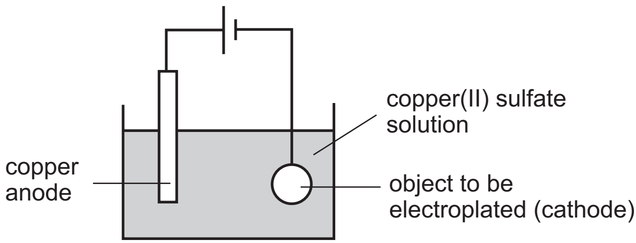
The pure copper cathode gains mass as a layer of pure copper is deposited.

6. **Electroplating**

Electroplating is done to coat a metal with another metal to improve its appearance or to improve its resistance to corrosion.

The metal used for plating is used as the anode and the object to be electroplated acts as the cathode. The electrolyte used is the salt solution of the metal used for plating.

The plating of an object with copper metal is shown below.



Copper metal acts as the anode as it is used to plate the object. The electrolyte used is a salt solution of its salt (copper(II) sulfate solution) and the object to be plated acts as the cathode.

At the anode, the copper atoms are oxidised into Cu^{2+} ions, which enter the electrolyte. At the cathode, Cu^{2+} ions are discharged and deposited on the object, plating it with copper metal.

7. **Simple Cells**

Simple cells convert chemical energy into electrical energy. The cell uses two different metals as electrodes and the voltage produced varies depending on the metals used.

In such a cell, the more reactive metal acts as the anode while the less reactive metal acts as the cathode.

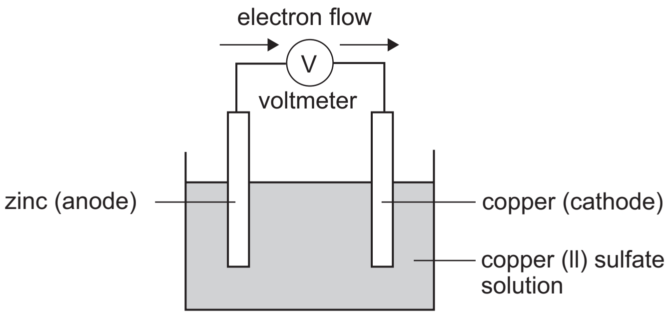
In a zinc-copper cell, zinc metal acts as the anode while copper acts as the cathode.

At the anode, zinc oxidises to form Zn^{2+} ions. In the process, electrons are released and they flow out of the anode through the wire.

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Electrons flow from the zinc anode to the copper cathode, where Cu^{2+} ions in the electrolyte are reduced and deposited as copper metal on the cathode.

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$



The zinc anode gradually loses mass as zinc atoms get oxidised while the copper cathode gains mass as Cu^{2+} ions are reduced and deposited. The overall equation of the reaction is obtained by adding the half-equations.

Overall equation: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

A greater voltage is produced when the two metals used are far apart in the reactivity series. A magnesium-copper cell generates a higher voltage than a zinc-copper cell since the difference in reactivity is greater in the magnesium-copper cell.