Electrolysis of aqueous solutions

Aqueous solutions are dissolved in water. So in addition to the ions from the salt, the ions from the water molecules also have to be considered.

Water molecules ionise (or split) to form hydrogen ions (H^+) and hydroxide ions (OH^-).

$$H_2O \rightleftharpoons H^+ + OH^-$$

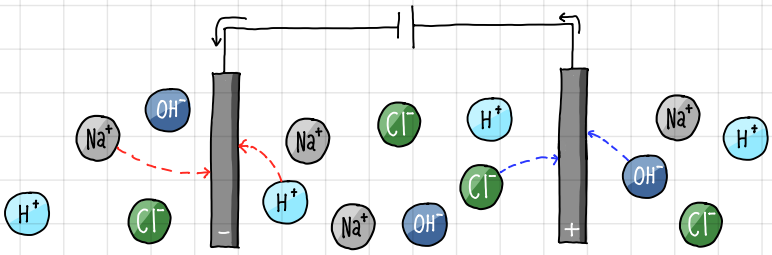
During the electrolysis of aqueous solutions the fate of these ions also needs to be considered.

Electrolysis of sodium chloride solution

Sodium chloride ionises in water to form positive sodium ions (Na^+) and negative chloride ions (Cl^-).

$$NaCl_{(aq)} \longrightarrow Na^+ + Cl^-$$

There are four ions in the aqueous solution. The two positive ions will be attracted to the negative electrode (cathode). These are H^+ and Na^+. The two negative ions will be attracted to the positive electrode (anode). These are OH^- and Cl^-.



The reactivity series is used to work out which ion will react at the electrode.

sodium
magnesium
carbon
zinc
iron
hydrogen
copper

Hydrogen will be produced at the negative electrode (cathode) if the metal is more reactive than hydrogen.

Sodium is more reactive than hydrogen, so hydrogen will be produced at the negative electrode (cathode).

If the aqueous solution contains halide ions (e.g. F^-, Cl^-, Br^- or I^-), then the halogen will be produced at the positive electrode (anode). As a result, chlorine will be produced at the positive electrode.

Electrolysis of aqueous solutions...

Half equations for electrolysis of sodium chloride

H^+ At the negative electrode (cathode): $2H^+ + 2e^- \xrightarrow{\text{reduction}} H_2$

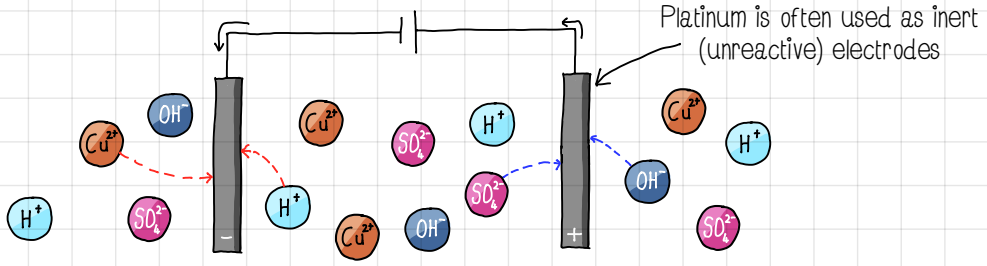
OH^- At the positive electrode (anode): $2Cl^- - 2e^- \xrightarrow{\text{oxidation}} Cl_2$

Electrolysis of copper sulfate solution

OH^- Copper sulfate ionises in water to form positive copper ions (Cu^{2+}) and negative sulfate ions (SO_4^{2-}).

$$CuSO_{4(aq)} \longrightarrow Cu^{2+} + SO_4^{2-}$$

H^+ There are four ions in the aqueous solution. The two positive ions will be attracted to the negative electrode (cathode). These are H^+ and Cu^{2+}. The two negative ions will be attracted to the positive electrode (anode). These are OH^- and SO_4^{2-}.



OH^- The reactivity series is used to work out which ion will react at the electrode.

sodium
magnesium
carbon
zinc
iron
hydrogen
copper

H^+ Hydrogen will be produced at the negative electrode (cathode) if the metal is more reactive than hydrogen.

OH^- Copper is less reactive than hydrogen, so copper will be produced at the negative electrode (cathode).

H^+ If the aqueous solution does not contain halide ions then oxygen will be produced at the positive electrode by the OH^- ions.

Half equations for electrolysis of copper sulfate

H^+ At the negative electrode: $Cu^{2+} + 2e^- \xrightarrow{\text{reduction}} Cu$

OH^- At the positive electrode: $4OH^- - 4e^- \xrightarrow{\text{oxidation}} O_2 + 2H_2O$

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