

Electrolysis

Electrolysis is using an electric current to break up an ionic compound to form elements.

Covalent compounds can't be split up by electrolysis.

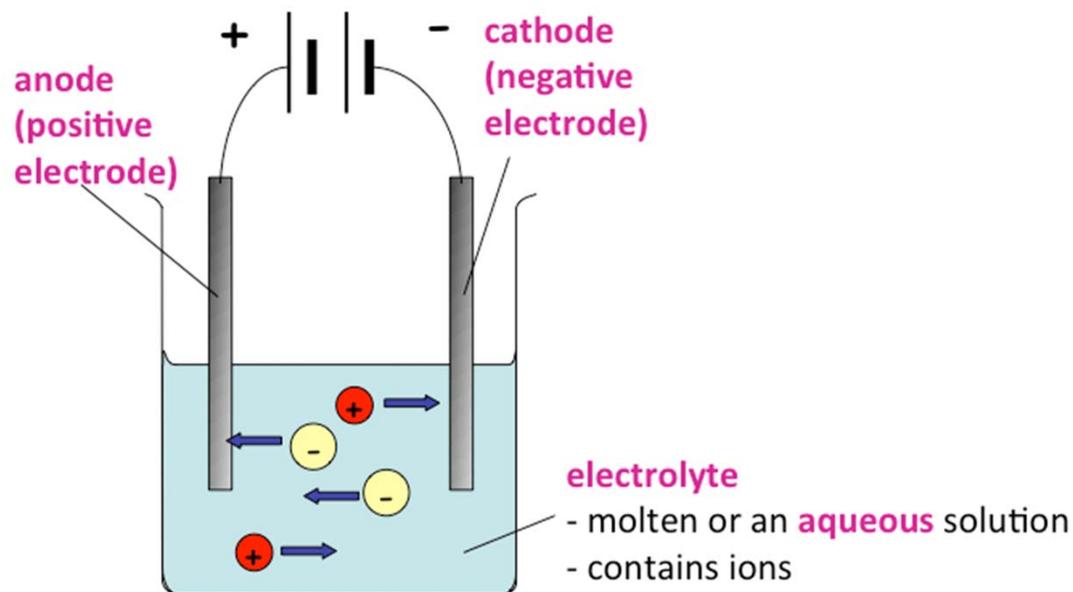
Terms used in electrolysis:

Electrolyte - the compound which is being broken down. Must contain ions, and the ions must be free to move (i.e. the substance must be a liquid/solution). Test: the solution or molten substance will conduct electricity if it is an electrolyte.

Anode – the positive electrode, to which negative ions, referred to as **anions** will be attracted.

Cathode – the negative electrode, to which positive ions, known as **cations** will be attracted

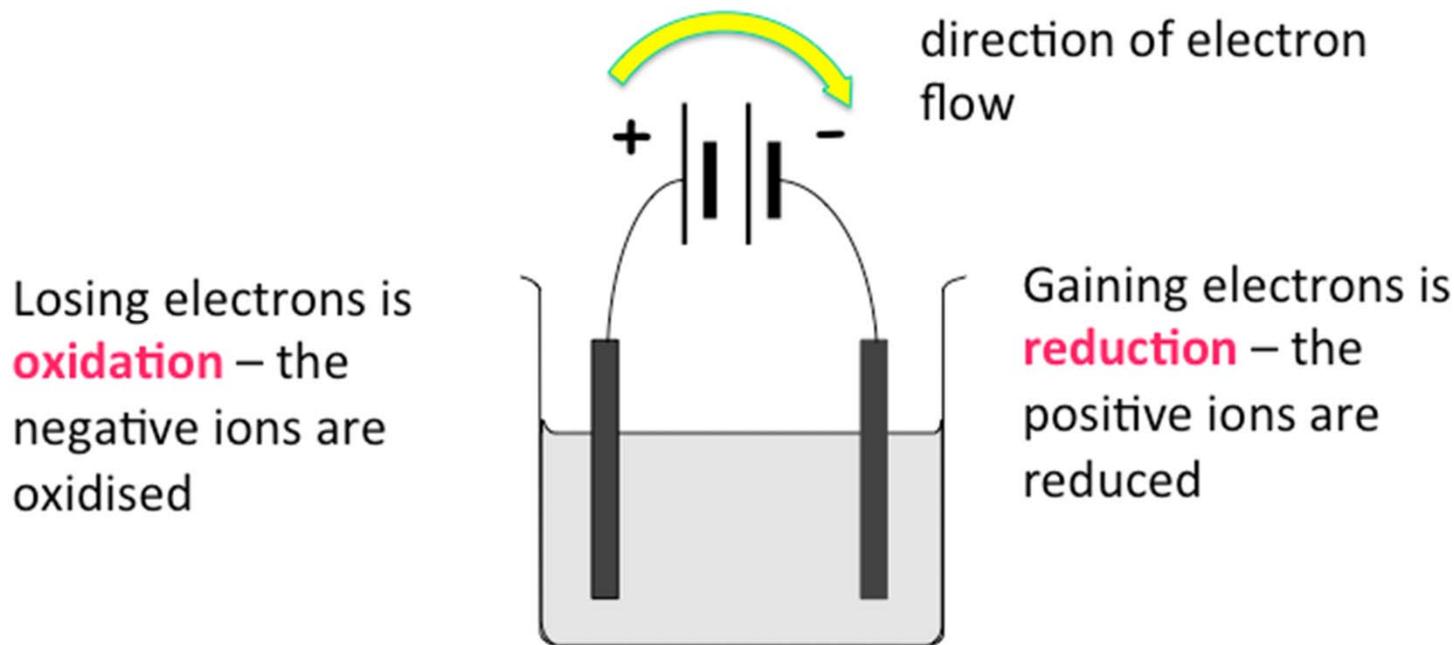
Electrolysis apparatus



Electrodes are normally made out of **inert** (unreactive) materials.

Graphite and **platinum** are common electrode materials.

During electrolysis, the positive ions travel to the negative electrode. Here they receive electrons which turns them from positive ions back into atoms. The negative ions travel to the positive electrode. Here they give up electrons to become atoms.



Because both reduction and oxidation take place at the same time, electrolysis is a **REDOX** reaction.

Oxidation Is **L**oss
Reduction Is **G**ain

} of electrons



Electrolysis of molten ionic compounds

e.g. molten copper(II) chloride, CuCl_2

1) What ions are present ?

Cu^{2+} and Cl^- ions

2) At the cathode:

- This negatively charged electrode attracts the Cu^{2+} ions
- The cathode gives 2 electrons to each Cu^{2+} ion
- The Cu^{2+} ions become **Cu** atoms and are deposited on the cathode



a half-equation

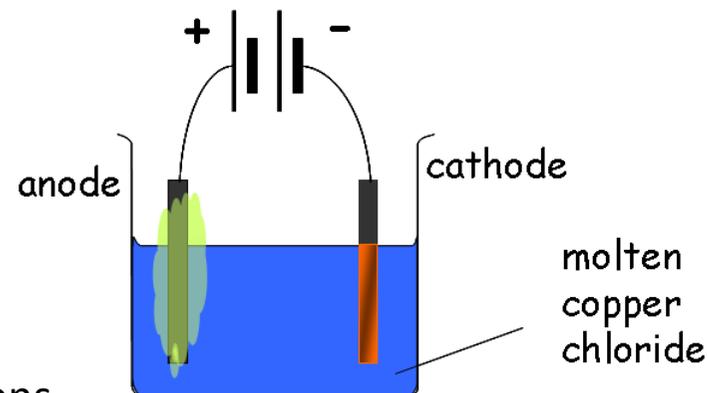
3) At the anode:

- This positively charged electrode attracts the Cl^- ions
- The anode takes 1 electron from each Cl^- ion
- The Cl^- ions become **Cl** atoms, which bond in pairs as Cl_2
- Bubbles of chlorine gas appear at the anode



the other half-equation

4) Overall:



Practice: *(answers at the end of the topic)*

What would the products be when aluminium chloride (which contains Al^{3+} and Cl^- ions) is melted and electrolysed? Write half equations to show what goes on at each electrode.

Explain the following observations: When lead(II) bromide is heated until it melts and an electric current passed through, a silvery coloured liquid is found under the negative electrode (cathode) and a brown gas appears at the positive electrode (anode). Use half equations to support your answer.

Electrolysis of solutions of ionic compounds

Ionic compounds will often dissolve in water, so the ions are free to move around in the solution.

Water also contains **ions** - both H^+ and OH^- , as well as molecules of H_2O . These ions are also attracted to the electrodes.

e.g. When we make a solution of sodium chloride (NaCl), we get:

- Na^+ ions and Cl^- ions in the solution (from the NaCl)
- H^+ and OH^- ions in the solution (from the water)

The Na^+ and H^+ cations are both attracted to the cathode

The Cl^- and OH^- anions are both attracted to the anode

What happens at the electrodes during electrolysis of a solution:

At the cathode

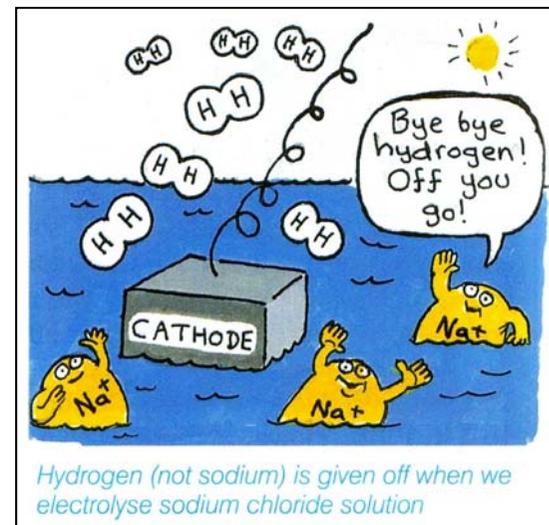
There is competition between the two positively charged ions.

RULE:

**The ion of the more reactive element stays in the solution.
The ion of the less reactive element is given electrons and reduced to atoms of that element.**

e.g.

- In a sodium chloride solution, **Na** is more reactive than **H**.
- The **Na⁺** cations stay in the solution
- The **H⁺** cations each gain an electron to become **H** atoms
- The **H** atoms bond in pairs to form molecules of **H_{2(g)}**



At the anode

In dilute solutions, oxygen is formed from the hydroxide ions. In more concentrated solutions of halides, the halogen can be produced in preference to oxygen:

RULE:

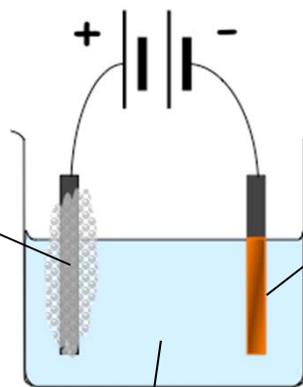
If Cl⁻, Br⁻ or I⁻ anions are present in sufficient concentration, they give up an electron and become Cl₂, Br₂ or I₂. e.g. $2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$

Otherwise, the **OH⁻** anions from water give up an electron, and oxygen gas is formed at the anode: $4\text{OH}^-_{(\text{aq})} - 4\text{e}^- \rightarrow \text{O}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$

Example: What would be seen during electrolysis of a copper(II) sulphate solution, $\text{CuSO}_{4(\text{aq})}$?

OH^- and SO_4^{2-} anions attracted

SO_4^{2-} remains in solution,
 O_2 given off



H^+ and Cu^{2+} cations attracted

Cu deposited and H^+ stays in solution

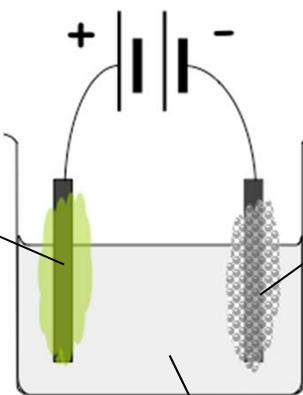


copper sulphate solution (electrolyte)

Example: What would be seen during electrolysis of a concentrated lithium chloride $\text{LiCl}_{(\text{aq})}$ solution?

Cl^- and OH^- anions attracted

OH^- remains in solution, Cl_2 given off



Li^+ and H^+ cations attracted

Li^+ remains in solution, H_2 given off

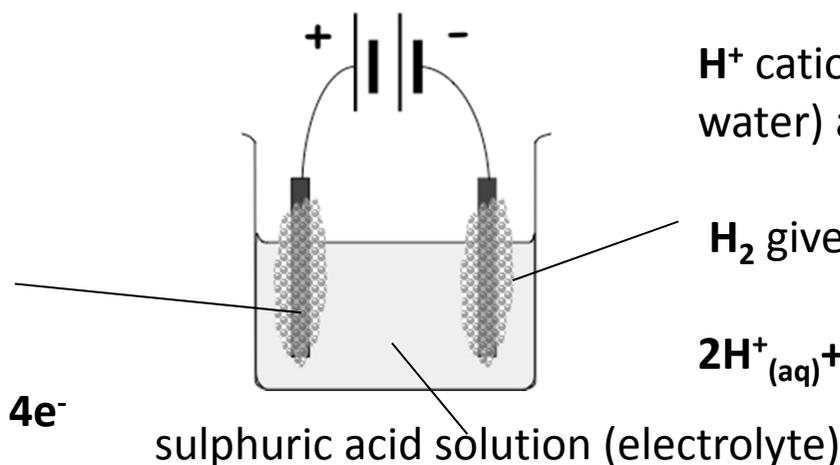
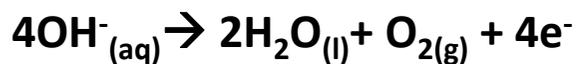


lithium chloride solution (electrolyte)

Example: What would be produced during electrolysis of a sulphuric acid $\text{H}_2\text{SO}_{4(\text{aq})}$ solution?

OH^- and SO_4^{2-}
anions attracted

SO_4^{2-} remains in solution,
 O_2 given off



H^+ cations (from acid and
water) attracted

H_2 given off



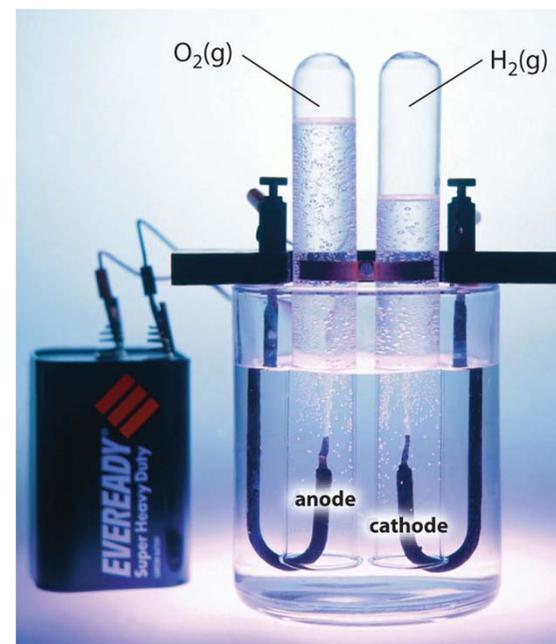
Practice: What would you observe during electrolysis of (i) silver nitrate solution; (ii) magnesium iodide solution? Give relevant half equations. *(answers at end of topic)*

In this reaction, water is being split up into hydrogen and oxygen.



We would observe that **twice the volume of hydrogen** is collected **compared to oxygen**. This proves that the chemical formula for water is H_2O .

Similar experiments can be used to determine the formula of other simple compounds that split up into gaseous elements during electrolysis.



Moles of electrons

One Faraday is the amount of electricity that corresponds to **one mole of electrons** flowing around an electrical circuit (such as an electrolysis cell)

In electrolysis we use half-equations to show what happens at each electrode. For example in electrolysis of brine:



“Two moles of chloride ions are oxidised to form one mole of chlorine molecules, and two Faradays of electrons flows from the anode around the circuit to the power supply”



“Two Faradays of electrons flows into the cathode from the power supply, allowing two moles of hydrogen ions to be reduced to form one mole of hydrogen molecules”

Calculations involving Faradays

e.g. 0.5 Faradays of electrons flow into the cathode during electrolysis of a copper sulphate solution. What mass of copper could be deposited on the cathode?



Ratio **1 : 2 : 1**

Moles of electrons = 0.5 (1 Faraday = 1 mole of electrons)

Mole ratio = 2 : 1 electrons : Cu

So moles of Cu = 0.25

Mass of Cu = moles of Cu x A_r of Cu = 0.25 x 64 = **16g**

Case Study – Electrolysis of Brine

Brine is a concentrated solution of sodium chloride in water, so it contains Na^+ , Cl^- , H^+ and OH^- ions.

At the cathode: H^+ is reduced to **hydrogen gas** $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

At the anode: Cl^- is oxidised to **chlorine gas** $2\text{Cl}^- - 2\text{e}^- \rightarrow \text{Cl}_2$

Overall: $2\text{NaCl}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{H}_{2(\text{g})} + \text{Cl}_{2(\text{g})} + 2\text{NaOH}_{(\text{aq})}$

The Na^+ and OH^- ions stay in the solution, so the brine solution gradually turns into a **sodium hydroxide** solution. All three products are very **important** in **industry**.

Uses of products from electrolysis of brine

CHLORINE is used:

- for making **bleach** and **hydrochloric acid**
- for sterilising (killing bacteria) in **drinking water**
- for killing micro-organisms in **swimming pool** water

HYDROGEN is used:

- in the **Haber process** for making ammonia
- for **hydrogenation of vegetable oils** to make spreads etc.
- as a **fuel**

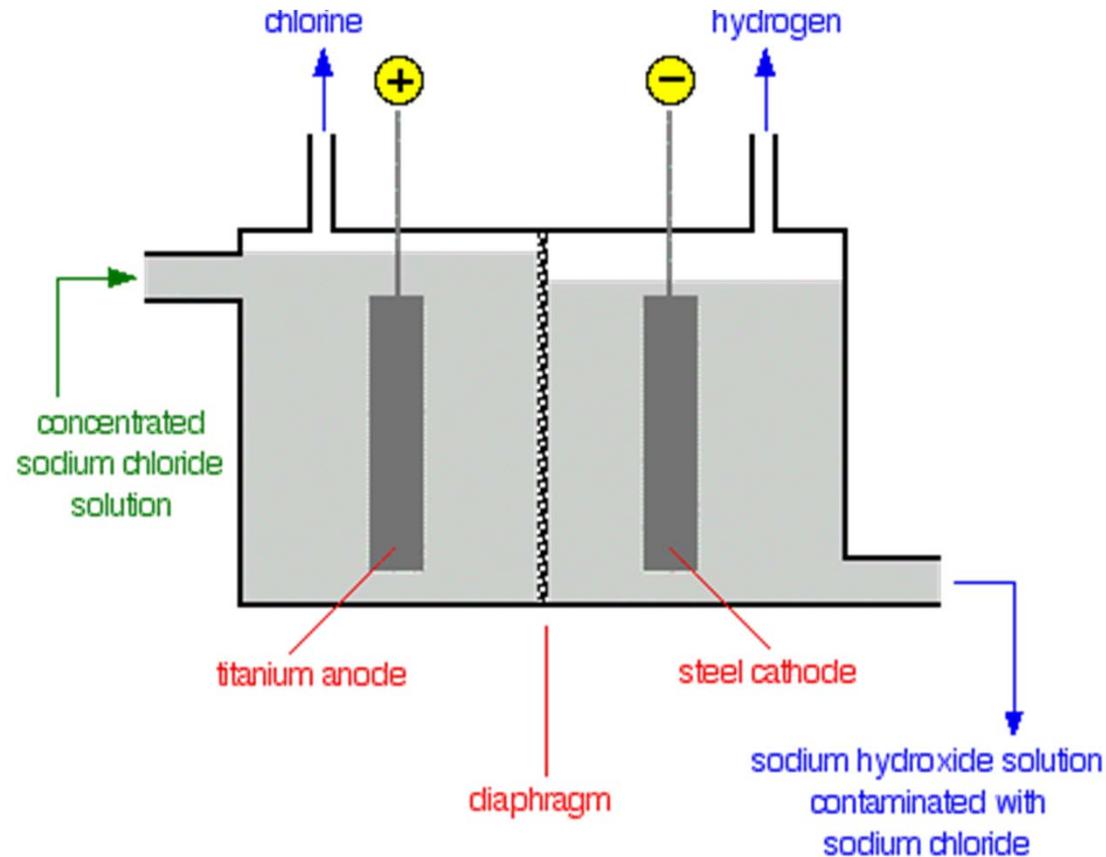
SODIUM HYDROXIDE is used:

- in **soap** and **paper** manufacturing
- for making **bleach**

Environmental:

Lots of electrical energy is needed to do electrolysis. This has to be produced by burning fossil fuels, so CO_2 is released into the environment (global warming) and finite reserves of crude oil are used up.

Electrolysis of brine is carried out in a **diaphragm cell** (or sometimes in a membrane cell).



The diaphragm cell is designed so that all the products are kept separate:

If chlorine mixes with hydrogen, it produces a mixture which will **explode violently** on exposure to sunlight or heat, so the **hydrogen and chlorine gases need to be kept apart**.

Chlorine also reacts with sodium hydroxide solution. Therefore, if we are trying to manufacture **chlorine and sodium hydroxide these must be kept apart** as well.

Answers

- 1) What would the products be when aluminium chloride (which contains Al^{3+} and Cl^- ions) is melted and electrolysed? Write half equations to show what goes on at each electrode.

Aluminium would be produced at the cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

Chlorine would be produced at the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

- 2) Explain the following observations: When lead(II) bromide is heated until it melts and an electric current passed through, a silvery coloured liquid is found under the negative electrode (cathode) and a brown gas appears at the positive electrode (anode). Use half equations to support your answer.

Molten lead forms under the cathode: $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

Bromine is given off at the anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$

- 3) What would you observe during electrolysis of (i) silver nitrate solution; (ii) magnesium iodide solution? Give relevant half equations.

Silver would be deposited on the cathode: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

Oxygen would be given off at the anode: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^-$

Hydrogen would be produced at the cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Iodine would be formed at the anode: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$