Electrochemistry

Electrolysis of molten compounds and aqueous solutions, predicting the products and writing half-equations, electroplating, and hydrogen-oxygen fuel cells compared with petrol engines.

4.1 Electrolysis

Electrolysis is the decomposition of an ionic compound, when molten or in aqueous solution, by the passage of an electric current.

An ionic compound only conducts when its ions are **free to move**, which is when it is **molten** or **dissolved in water**. A solid ionic compound does not conduct.

Term	Meaning
electrolyte	the molten or aqueous substance that is electrolysed
electrode	a conductor that carries the current into and out of the electrolyte. **Inert** electrodes (platinum or carbon/graphite) do not react
anode	the **positive** electrode
cathode	the **negative** electrode

What happens during electrolysis

- **In the external circuit**, **electrons** flow through the wires from the negative terminal of the power supply to the cathode, and from the anode back to the positive terminal.
- **In the electrolyte**, **ions** carry the charge. **Positive ions (cations)** move to the **cathode** and **negative ions (anions)** move to the **anode**.
- **At the cathode**, positive ions **gain electrons**. This is **reduction**.
- **At the anode**, negative ions **lose electrons**. This is **oxidation**.

NOTE

A way to remember: **OIL RIG**: **O**xidation **I**s **L**oss of electrons, **R**eduction **I**s **G**ain. Also: the **a**node is where **o**xidation happens (both start with a vowel) and the **c**athode is where **r**eduction happens (both start with a consonant).

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Metals or hydrogen are formed at the **cathode**, and **non-metals other than hydrogen** are formed at the **anode**.

Predicting the products

Molten compounds (a binary compound, made of two elements). The metal forms at the cathode and the non-metal forms at the anode.

Aqueous solutions also contain H^+ and OH^- ions from the water, so there is a choice of ion at each electrode.

Electrode	Product
cathode	**hydrogen** is formed if the metal is more reactive than hydrogen. The **metal** is formed if it is less reactive than hydrogen, such as copper or silver
anode	a **halogen** is formed if a halide ion (Cl^-, Br^-, I^-) is present in **concentrated** solution. Otherwise **oxygen** is formed, from the hydroxide ions of the water

The cases to know

Electrolyte (inert electrodes)	At the cathode (−)	At the anode (+)
molten lead(II) bromide, $PbBr_2$	$Pb^{2+} + 2\,e^- \longrightarrow Pb$ **silvery molten lead**	$2\,Br^- \longrightarrow Br_2 + 2\,e^-$ **red-brown fumes** of bromine
concentrated aqueous sodium chloride	$2\,H^+ + 2\,e^- \longrightarrow H_2$ **hydrogen**, a colourless gas that burns with a squeaky pop	$2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$ **chlorine**, a pale yellow-green gas that bleaches damp litmus
dilute sulfuric acid	$2\,H^+ + 2\,e^- \longrightarrow H_2$ **hydrogen**	$4\,OH^- \longrightarrow 2\,H_2O + O_2 + 4\,e^-$ **oxygen**, which relights a glowing splint
aqueous copper(II) sulfate (carbon electrodes)	$Cu^{2+} + 2\,e^- \longrightarrow Cu$ a **pink-brown deposit** of copper	$4\,OH^- \longrightarrow 2\,H_2O + O_2 + 4\,e^-$ **oxygen** bubbles

Notes on these cases.

- In **concentrated sodium chloride**, sodium is more reactive than hydrogen, so hydrogen forms, not sodium. The solution left behind contains Na^+ and OH^- ions: it is **sodium hydroxide**, an alkali.
- In **dilute sulfuric acid**, the net effect is that **water** is decomposed. About **twice as much** hydrogen as oxygen is made, by volume (2 volumes of H_2 to 1 of O_2), and the acid becomes more concentrated.

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- In **copper(II) sulfate with carbon electrodes**, the **blue colour fades** as copper ions are removed from the solution, and the solution becomes acidic.

Copper(II) sulfate with copper electrodes. Copper is not inert, so the anode takes part:

- Anode: $\mathrm{Cu} \longrightarrow \mathrm{Cu^{2+}} + 2\,\mathrm{e^-}$. The copper anode **dissolves** and gets **smaller**.
- Cathode: $\mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}$. Copper is **deposited** and the cathode gets **bigger**.
- The solution stays **blue** because the concentration of $\mathrm{Cu^{2+}}$ does not change.

This is also how copper is **purified**: impure copper is the anode and pure copper builds up on the cathode.

> **TRY IT**
>
> Predict the products at each electrode when molten zinc chloride is electrolysed using carbon electrodes, and write the half-equations.

Zinc chloride is a binary compound. Zinc forms at the **cathode** and chlorine forms at the **anode**.

$\text{cathode: } \mathrm{Zn^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn} \qquad \text{anode: } 2\,\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2\,\mathrm{e^-}$

> **TRY IT**
>
> State the products at each electrode for the electrolysis of **dilute** aqueous sodium chloride.

At the cathode, hydrogen is formed. The solution is dilute, so no halogen forms at the anode, and **oxygen** is formed from the hydroxide ions.

Half-equations

A **half-equation** shows what happens at **one** electrode. It must balance in **atoms** and **charge**.

- At the cathode, electrons are on the **left** (they are gained): $\mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}$.
- At the anode, electrons are on the **right** (they are lost): $2\,\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2\,\mathrm{e^-}$.

The number of electrons lost at the anode equals the number gained at the cathode.

Electroplating

Electroplating coats a metal object with a thin layer of another metal. It is done to improve the **appearance** of the object, and to give **resistance to corrosion**, for example chromium plating on steel or tin plating on steel cans.

- The **object** to be plated is the **cathode** (the negative electrode).

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- The **anode** is a bar of the **plating metal**.
- The **electrolyte** is a solution containing ions of the plating metal.

For silver plating: the electrolyte is silver nitrate solution. At the cathode, $\mathrm{Ag^+ + e^- \longrightarrow Ag}$ (silver is deposited on the object). At the anode, $\mathrm{Ag \longrightarrow Ag^+ + e^-}$ (the silver dissolves, so the solution keeps its concentration).

4.2 Hydrogen–oxygen fuel cells

> **A hydrogen–oxygen fuel cell uses hydrogen and oxygen to produce electricity. The only chemical product is water.**

$$\mathrm{2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)}$$

The hydrogen is supplied continuously, and so is the oxygen (from the air). Unlike a battery, the cell does not run down while the fuel is supplied. The reaction directly makes electrical energy, which powers an electric motor in a vehicle.

Fuel cell compared with a petrol engine in a vehicle

Hydrogen fuel cell	Petrol engine
advantages	
the only product is **water**, so no carbon dioxide, carbon monoxide, oxides of nitrogen or particulates are released from the vehicle	burns a fossil fuel that releases **carbon dioxide** (a greenhouse gas) and pollutants such as CO, NO_x and particulates
quiet, and efficient as it makes electricity directly	noisy, and wastes much of the energy as heat
disadvantages	
hydrogen is **difficult to store** and transport (a flammable gas that must be compressed or liquefied)	petrol is a liquid that is easy to store and transport
hydrogen is often made from fossil fuels or with a lot of electricity	fuel is made from crude oil, and is cheap and widely available
few refuelling stations, and fuel cells are expensive	refuelling stations are everywhere, and the technology is cheaper

TRY IT

Note Academy

> Give one advantage and one disadvantage of using a hydrogen–oxygen fuel cell instead of a petrol engine in a car.

Advantage: the only product is water, so it does not produce carbon dioxide or other pollutants.
Disadvantage: hydrogen is flammable and difficult to store, and there are few places to refuel.

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