

Electrolysis

What happens at each electrode during electrolysis, and how much product does a current make?

●●○ Intermediate

Redox & Electrochemistry

Last reviewed 5 October 2026

Before you start: it helps to understand [Galvanic Cells and Electrode Potentials](#) and [Oxidation Numbers and Redox Reactions](#).

What is it?

Electrolysis uses electricity to drive a redox reaction that would **not** happen on its own. It is the reverse of a galvanic cell: there, a spontaneous reaction makes electricity; here, electricity forces a non-spontaneous reaction.

An **electrolytic cell** has:

- a **DC power supply**, which pumps electrons;
- two **electrodes**, often inert (graphite or platinum);
- an **electrolyte**: an ionic compound that is **molten** or **dissolved**, so that its ions can move.

The **anode** is connected to the **positive** terminal: negative ions (anions) move to it and are **oxidized**. The **cathode** is connected to the **negative** terminal: positive ions (cations) move to it and are **reduced**.

KEY IDEA

In every cell, **oxidation at the anode, reduction at the cathode**. In electrolysis the anode is **positive** and the cathode **negative**, the opposite signs to a galvanic cell, because the power supply decides the charges.

Why does it matter?

- **Metals.** All aluminium, and the most reactive metals (sodium, magnesium), are extracted by electrolysis because no chemical reducing agent is strong enough.
- **Chemicals.** Electrolysis of brine makes chlorine, hydrogen and sodium hydroxide, used in plastics (PVC), bleach, soap and water treatment.
- **Purity and protection.** Copper for electrical wiring is purified by electrolysis, and electroplating coats objects with chromium, nickel, silver or gold.

How does it work?

1. Molten electrolytes

A molten salt contains only its own ions, so the products are the elements:

- molten NaCl: cathode $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$; anode $2 \text{Cl}^- \longrightarrow \text{Cl}_2 + 2 \text{e}^-$.

2. Aqueous electrolytes: water competes

In solution, water molecules can also be reduced or oxidized, so the more easily discharged species wins:

Electrode	Product	Rule
Cathode (-)	the metal	if the metal is less reactive than hydrogen (Cu, Ag, Au)
Cathode (-)	hydrogen	if the metal is reactive (Na, K, Mg, Al): $2 \text{H}_2\text{O} + 2 \text{e}^- \longrightarrow \text{H}_2 + 2 \text{OH}^-$
Anode (+)	the halogen	for concentrated chloride, bromide or iodide
Anode (+)	oxygen	for sulfate, nitrate (and dilute chloride): $2 \text{H}_2\text{O} \longrightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$

3. Three important industrial processes

- Brine** (concentrated NaCl solution): chlorine at the anode, hydrogen at the cathode, and sodium hydroxide left in solution.
- Aluminium**: aluminium oxide is dissolved in molten cryolite at about 950 °C. Cathode: $\text{Al}^{3+} + 3 \text{e}^- \longrightarrow \text{Al}$. Oxygen forms at the carbon anodes, which burn away to CO_2 and must be replaced.
- Copper refining**: an impure copper **anode** dissolves ($\text{Cu} \longrightarrow \text{Cu}^{2+} + 2 \text{e}^-$), and pure copper deposits on the **cathode**; impurities such as silver and gold fall to the bottom as “anode sludge”.

4. Faraday's law

The amount of product depends only on the **charge** passed:

$$Q = It$$

$$n(\text{e}^-) = \frac{Q}{F}$$

$$F = 96\,485 \text{ C/mol}$$

Then use the half-equation to convert moles of electrons into moles of product: 1 mol Ag needs 1 mol e^- , 1 mol Cu needs 2 mol e^- , 1 mol Al needs 3 mol e^- , and 1 mol Cl_2 releases 2 mol e^- .

∞ THINK OF IT LIKE THIS

A galvanic cell is a ball rolling downhill and turning a wheel on the way. Electrolysis is pushing the ball back up the hill with a motor: it only goes as long as you keep supplying energy, and the amount moved depends on how hard and how long you push (current $\times$ time).

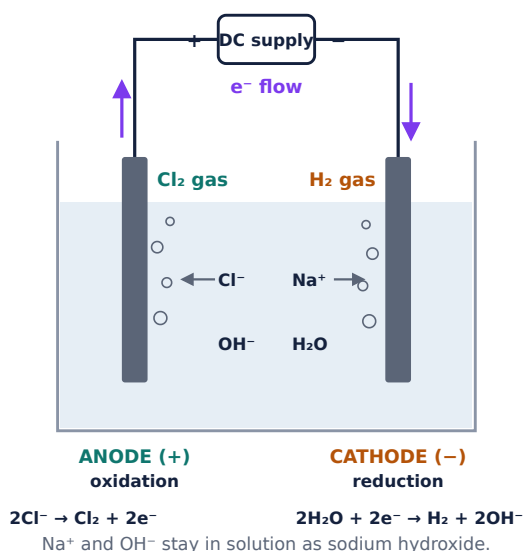
🔍 MORE PRECISELY

Which ion is discharged in solution depends on the electrode potentials, the concentrations and the electrode material. Concentrated chloride gives chlorine (not oxygen) even though oxygen has the less negative potential, because oxygen formation needs a large extra voltage (an **overpotential**) at most electrodes. The minimum voltage for electrolysis equals $-E^\circ_{\text{cell}}$ of the reverse, spontaneous reaction, but real cells need more, to overcome resistance and overpotentials.

Visualise it

Electrolysis of concentrated brine

A power supply forces a non-spontaneous reaction.



Brine gives three products: chlorine, hydrogen and sodium hydroxide.

Worked example

WORKED EXAMPLE: Predicting the products

Question: Give the products at each electrode (inert electrodes) for: (a) molten PbBr_2 (b) aqueous CuSO_4 (c) dilute H_2SO_4 .

Step 1 (a) Molten: cathode **lead** ($\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$), anode **bromine** ($2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{e}^-$).

Step 2 (b) Cathode **copper** (less reactive than hydrogen); anode **oxygen** (sulfate is not discharged). The blue colour fades as Cu^{2+} is used up, and the solution becomes acidic.

Step 3 (c) Cathode **hydrogen**, anode **oxygen**, in a 2 : 1 volume ratio: overall, water is split, $2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$.

WORKED EXAMPLE: Aluminium from a cell

Question: What mass of aluminium is produced by a cell running at $1.00 \times 10^5 \text{ A}$ for 24.0 h? ($\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$; $\text{Al} = 26.98 \text{ g/mol}$)

Step 1 $t = 24.0 \text{ h} \times 3600 \text{ s/h} = 8.64 \times 10^4 \text{ s}$

Step 2 $Q = It = (1.00 \times 10^5 \text{ C/s})(8.64 \times 10^4 \text{ s}) = 8.64 \times 10^9 \text{ C}$

Step 3 $n(\text{e}^-) = \frac{8.64 \times 10^9 \text{ C}}{96\,485 \text{ C/mol}} = 8.955 \times 10^4 \text{ mol}$

Step 4 $n(\text{Al}) = 8.955 \times 10^4 \text{ mol e}^- \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} = 2.985 \times 10^4 \text{ mol}$

Step 5 $m = 2.985 \times 10^4 \text{ mol} \times 26.98 \text{ g/mol} = 8.05 \times 10^5 \text{ g} = \mathbf{805 \text{ kg}}$

 WORKED EXAMPLE: Volume of chlorine from brine

Question: A current of 2.00 A passes through brine for 1.00 h. What volume of Cl_2 forms at 25.0 °C and 1.00 atm?

Step 1 $Q = (2.00 \text{ C/s})(3600 \text{ s}) = 7200 \text{ C}; n(e^-) = \frac{7200 \text{ C}}{96485 \text{ C/mol}} = 0.07462 \text{ mol}$

Step 2 $2 \text{Cl}^- \longrightarrow \text{Cl}_2 + 2 e^-; n(\text{Cl}_2) = \frac{0.07462 \text{ mol}}{2} = 0.03731 \text{ mol}$

Step 3 Ideal gas law:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= (0.03731 \text{ mol}) \\ &\quad \times \left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right) \\ &\quad \times (298.15 \text{ K}) \\ &\quad \div (1.00 \text{ atm}) \\ &= \mathbf{0.913 \text{ L}} \end{aligned}$$

Common mistake

 COMMON MISTAKE: Using galvanic-cell signs

In electrolysis the anode is **positive**; in a galvanic cell it is negative. What never changes is that oxidation happens at the anode.

 COMMON MISTAKE: Expecting a reactive metal from its solution

Electrolysis of aqueous NaCl does not give sodium: water is reduced instead, giving hydrogen. Sodium is made only from **molten** sodium chloride.

 COMMON MISTAKE: Forgetting the electron ratio

After finding moles of electrons, divide by the number of electrons in the half-equation: 3 for Al^{3+} , 2 for Cu^{2+} and Cl_2 . Skipping this step makes the answer two or three times too large.

NOTATION NOTE

- $1\text{ A} = 1\text{ C/s}$; 1 faraday = 96 485 C, the charge on one mole of electrons.
- “Inert” electrodes (graphite, platinum) conduct electricity but do not react.
- “Discharged” means an ion gains or loses electrons at an electrode and becomes a neutral atom or molecule.

Remember this

REMEMBER THIS

- **Electrolysis:** electricity forces a non-spontaneous redox reaction. Anode (+): oxidation; cathode (-): reduction.
- Molten salts give the elements. In water: cathode gives the metal (if below hydrogen) or H_2 ; anode gives the halogen (concentrated halide) or O_2 .
- Brine $\rightarrow \text{Cl}_2, \text{H}_2, \text{NaOH}$. Aluminium from molten Al_2O_3 in cryolite. Copper refined with an impure copper anode.
- $Q = It, n(e^-) = Q/F$, then the half-equation ratio.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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