

Galvanic cells, electrode potentials and electrolysis

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: A galvanic cell turns a spontaneous redox reaction into electricity: oxidation at the anode, reduction at the cathode. Cell emf is $E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$, and a positive value means the reaction is feasible. Electrolysis reverses this, with $Q = It$ and 96 500 C per mole of electrons.

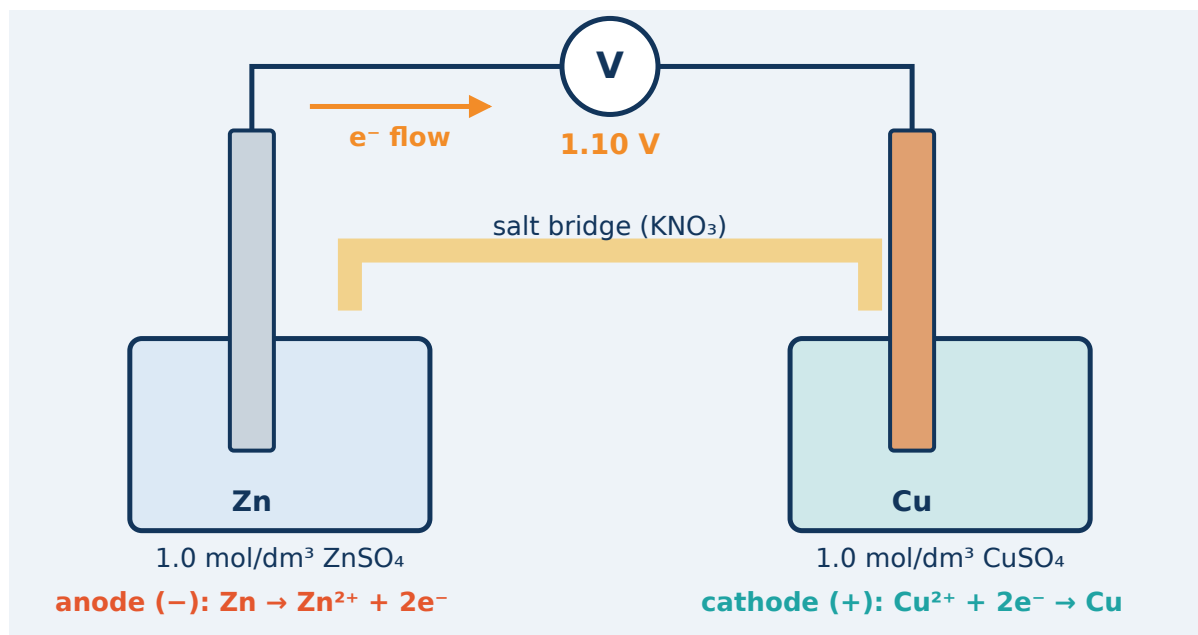
Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R3.2

How does an electrochemical cell produce a voltage?

An electrochemical cell links two half-cells so that electrons are forced to travel through an external circuit. Each half-cell holds a metal electrode in a solution of its own ions. Oxidation happens in one half-cell and reduction in the other.

Definition

In a galvanic (voltaic) cell a spontaneous redox reaction produces electrical energy. The **anode** is the electrode where oxidation occurs and is negative; the **cathode** is where reduction occurs and is positive. Electrons flow in the external wire from anode to cathode.



The salt bridge contains an inert electrolyte such as KNO_3 . It completes the circuit by letting ions move, so charge does not build up in either half-cell. Cell notation lists the anode on the left: $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$, where a single bar is a phase boundary and a double

bar is the salt bridge.

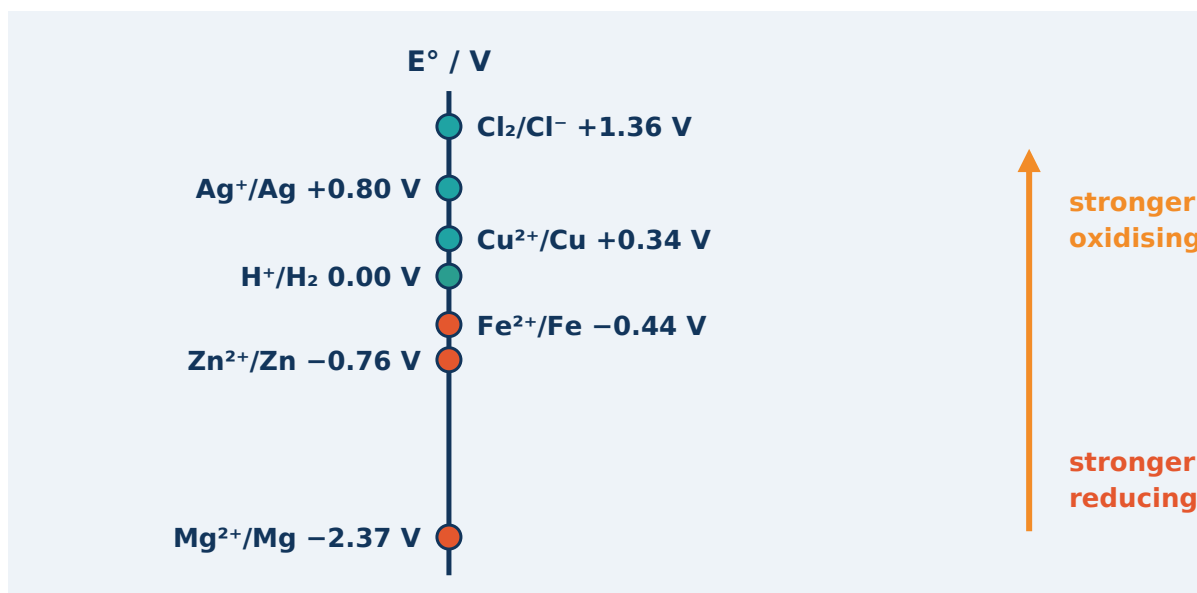
What is a standard electrode potential?

The voltage of a half-cell cannot be measured alone, so every half-cell is compared with the standard hydrogen electrode (SHE), which is given exactly 0.00 V.

Definition

The standard electrode potential E° of a half-cell is its emf measured against the standard hydrogen electrode under standard conditions: 298 K, ion concentration 1.00 mol/dm³ and gas pressure 100 kPa. Half-equations are always written as reductions.

Half-equation (reduction)	E° / V
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.37
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36



A higher E° means the oxidised form is a stronger oxidising agent; a lower E° means the metal is a stronger reducing agent.

How do you calculate cell emf and predict reactions?

Formula

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$$

E°_{cell} is the standard cell emf in volts (V). The half-cell with the more positive E° is the cathode, where reduction happens.

Worked example 1

Find E°_{cell} for the cell $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$.

Cu^{2+}/Cu is more positive (+0.34 V), so copper is the cathode and zinc the anode.

$$E^{\circ}_{\text{cell}} = +0.34 - (-0.76) = \mathbf{+1.10 \text{ V}}$$

A positive E°_{cell} means the reaction is feasible under standard conditions. A negative value means the reverse reaction is the spontaneous one. Feasibility says nothing about speed: a reaction with a large positive E°_{cell} can still be extremely slow.

Worked example 2

Will Fe^{3+} oxidise copper metal?

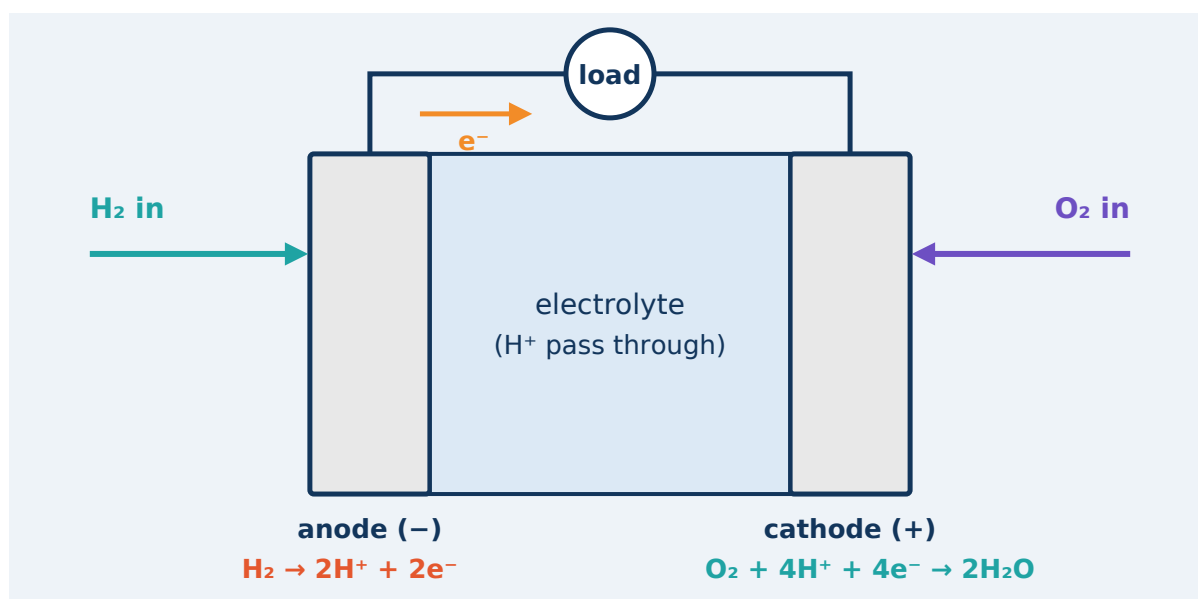
Reduction: $\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$ (+0.77 V). Oxidation: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^{-}$ (+0.34 V).

$$E^{\circ}_{\text{cell}} = 0.77 - 0.34 = \mathbf{+0.43 \text{ V}}, \text{ so yes: } 2\text{Fe}^{3+} + \text{Cu} \rightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}.$$

How do fuel cells work?

A fuel cell is a galvanic cell supplied continuously with fuel and oxidant, so it never runs flat as long as they are fed in. In a hydrogen-oxygen cell with an acidic electrolyte the half-equations are:

- Anode: $\text{H}_2 \rightarrow 2\text{H}^{+} + 2\text{e}^{-}$ ($E^{\circ} = 0.00 \text{ V}$ as the reverse of the SHE reaction)
- Cathode: $\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$ ($E^{\circ} = +1.23 \text{ V}$)
- Overall: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, $E^{\circ}_{\text{cell}} = 1.23 - 0.00 = \mathbf{+1.23 \text{ V}}$

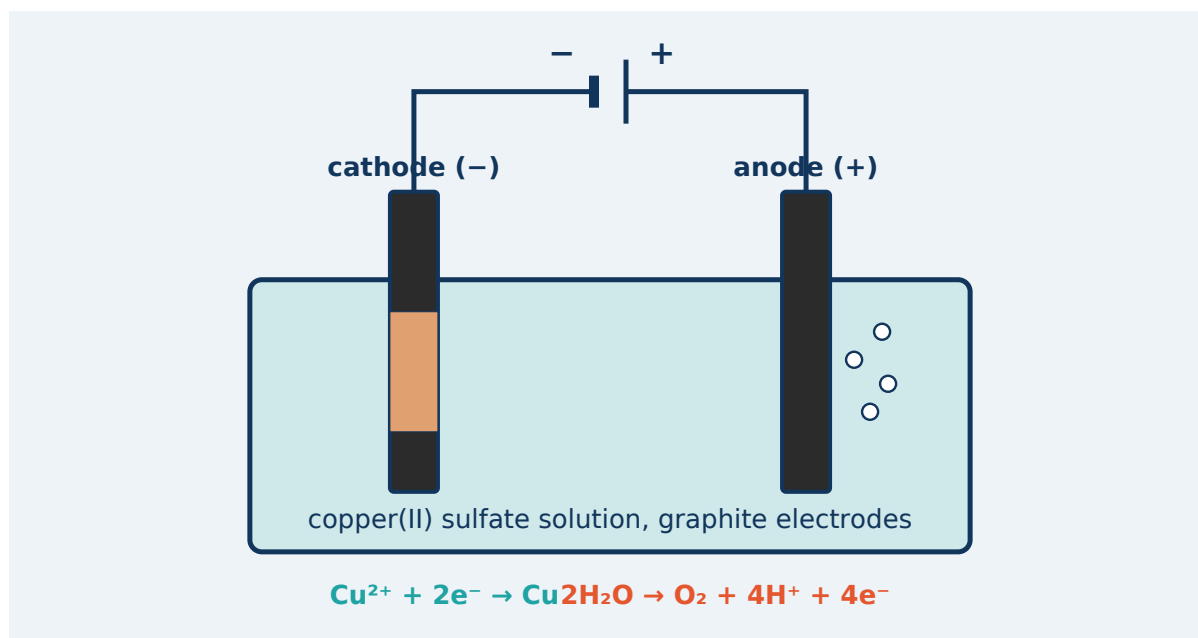


A hydrogen fuel cell with an acid electrolyte; water forms at the cathode.

The only product is water, which is why hydrogen fuel cells are used in buses and spacecraft.

What happens in electrolysis, and how much product forms?

Electrolysis uses electrical energy to drive a non-spontaneous reaction. The anode is now the positive electrode and the cathode the negative one. The ion with the higher E° is reduced at the cathode; at the anode, halide ions are oxidised in concentrated solution, otherwise water is oxidised to oxygen.



Copper forms at the cathode and oxygen at the anode.

Faraday's law

$$Q = I \times t \text{ and } n(\text{e}^-) = Q / F$$

Q = charge in coulombs (C), I = current in amperes (A), t = time in seconds (s), $F = 96\,500$ C/mol of electrons.

Worked example 3

Copper is plated using 2.00 A for 30.0 minutes.

$$Q = 2.00 \text{ A} \times 1800 \text{ s} = 3600 \text{ C}; n(\text{e}^-) = 3600 \div 96\,500 = 0.0373 \text{ mol.}$$

$$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}, \text{ so } n(\text{Cu}) = 0.0373 \div 2 = 0.01865 \text{ mol and } m = 0.01865 \times 63.5 = \mathbf{1.18 \text{ g}}$$

Common mistake

Do not multiply E° by the number of electrons when combining half-cells: E° is an intensive property. Doubling a half-equation does not double its potential, so Zn/Cu is still 1.10 V whether you write one or two electrons.

Lina's tip

Write the two half-reactions as reductions, circle the larger E° as the cathode, subtract, and check the answer is positive for a working cell. If it is negative you swapped the electrodes.

Key points to remember

- $E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$; standard conditions are 298 K, 1.00 mol/dm³ and 100 kPa.
- Anode: oxidation; cathode: reduction; electrons flow anode to cathode in the wire.
- The salt bridge completes the circuit and keeps each half-cell electrically neutral.
- Hydrogen fuel cell (acid): $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ at the anode, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ at the cathode, $E^{\circ}_{\text{cell}} = +1.23 \text{ V}$.
- Electrolysis: $Q = It$, $n(\text{e}^-) = Q/F$ with $F = 96\,500 \text{ C/mol}$.

Galvanic cells, electrode potentials and electrolysis: frequently asked questions

What is the standard hydrogen electrode?

It is a platinum electrode in 1.00 mol/dm³ H⁺ with hydrogen gas at 100 kPa and 298 K. Its potential is defined as exactly 0.00 V, and all other electrode potentials are measured against it.

How do you know which electrode is the anode?

The anode is where oxidation occurs. In a galvanic cell it is the half-cell with the more negative E° . In electrolysis the anode is connected to the positive terminal of the supply but oxidation still happens there.

What does a positive E°_{cell} tell you?

It tells you the reaction is thermodynamically feasible under standard conditions. It does not say how fast the reaction is, and non-standard concentrations or temperatures can change the emf.

Why do fuel cells not run flat?

Fuel and oxidant are fed in continuously and the products leave, so the reactants are never used up. A battery, in contrast, has a fixed amount of chemicals stored inside.

How do you calculate the mass deposited in electrolysis?

Find the charge $Q = It$, divide by 96 500 C/mol for the moles of electrons, use the half-equation ratio to get moles of metal, then multiply by the molar mass.