

Electrochemistry

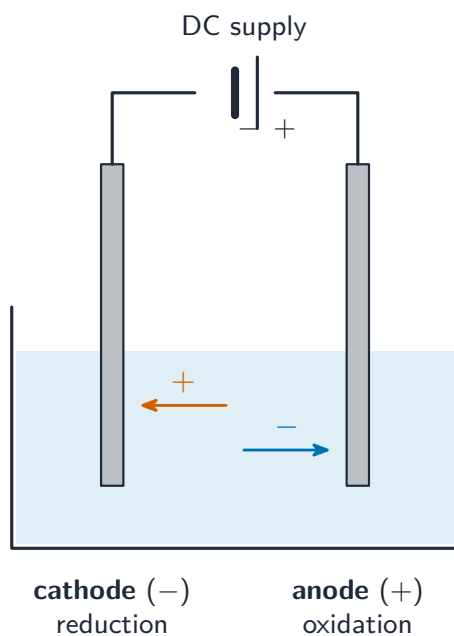
A-Level Chemistry

Electrolysis

Electrolysis uses electricity to break down a molten or aqueous **electrolyte**. Positive ions move to the negative electrode and negative ions move to the positive electrode.

At each **electrode** a half-reaction happens:

- at the **cathode** (negative): positive ions gain electrons (reduction).
- at the **anode** (positive): negative ions lose electrons (oxidation).



Electrolysis: the DC supply drives positive ions to the cathode (reduction) and negative ions to the anode (oxidation)



A Hofmann voltameter for the electrolysis of water: the power supply drives current through two electrodes, and the gas made at each one collects in its side tube

■ Predicting the products

- a **molten** electrolyte gives the metal at the cathode and the non-metal at the anode.
- an **aqueous** electrolyte also contains water. At the cathode, a less reactive metal is released, but for a reactive metal you get hydrogen instead. At the anode you usually get oxygen, but a concentrated halide solution gives the halogen.

molten
metal at cathode
non-metal at anode

aqueous
also contains water,
so H_2 or O_2 may form

A molten electrolyte gives the metal and non-metal; aqueous also has water

■ Calculations

The charge on one mole of electrons is the **Faraday constant**, linked to the **Avogadro constant** (L) and the charge on one electron (e) by $F = Le$.

The charge passed is $Q = It$ (current $\times$ time). Then:

1. moles of electrons = Q/F .
2. use the half-equation to find moles of product.
3. find the mass ($\times M_r$) or the gas volume.

Measuring the mass deposited for a known charge lets you work back to a value of the Avogadro constant.

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate solution, depositing copper at the cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$. Find the mass of copper deposited. ($F = 96\,500 \text{ C mol}^{-1}$, $A_r \text{ Cu} = 64$.)

Charge passed: $Q = It = 2.0 \times (30 \times 60) = 3600 \text{ C}$. Moles of electrons = $Q/F = 3600/96\,500 = 0.0373 \text{ mol}$. From the half-equation, 2 mol of electrons give 1 mol of Cu, so $n(\text{Cu}) = 0.0187 \text{ mol}$ and

$$m = nM = 0.0187 \times 64 \approx 1.2 \text{ g}.$$

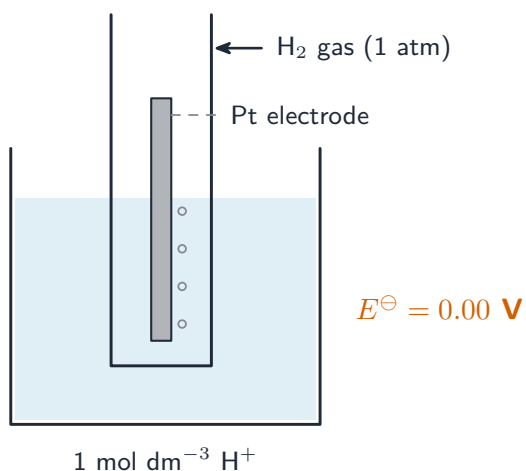


Electrolysis is used to electroplate an object with a thin, shiny layer of metal such as chromium

Standard electrode potentials and cell potentials

The **electrode potential** (E) of a half-cell shows how easily it is reduced. We measure it against a reference, under standard conditions, to get the **standard electrode potential** ($E^\ominus$), always written as a reduction.

The reference is the **standard hydrogen electrode** : hydrogen gas at 1 atm over platinum in $1 \text{ mol dm}^{-3} \text{ H}^+$, defined as exactly 0.00 V.



The standard hydrogen electrode: H_2 at 1 atm over platinum in $1 \text{ mol dm}^{-3} H^+$, the 0.00 V reference for every electrode potential

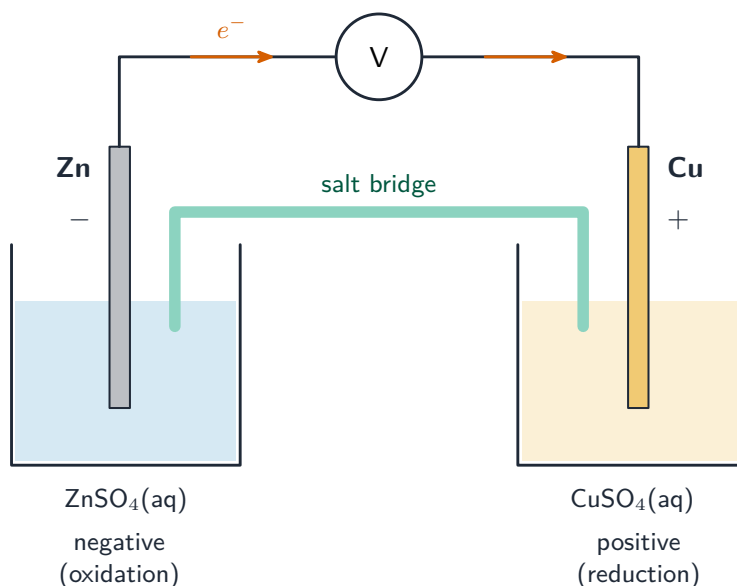
To measure an $E^\ominus$, connect the half-cell to the standard hydrogen electrode and read the voltage. A metal sits in a solution of its ions; for two ions of the same element (such as Fe^{3+}/Fe^{2+}), a platinum electrode dips into a solution containing both.

■ Combining half-cells

The **standard cell potential** is the difference between the two standard electrode potentials:

is the difference between the two stan-

$$E_{\text{cell}}^\ominus = E^\ominus(\text{more positive}) - E^\ominus(\text{less positive})$$



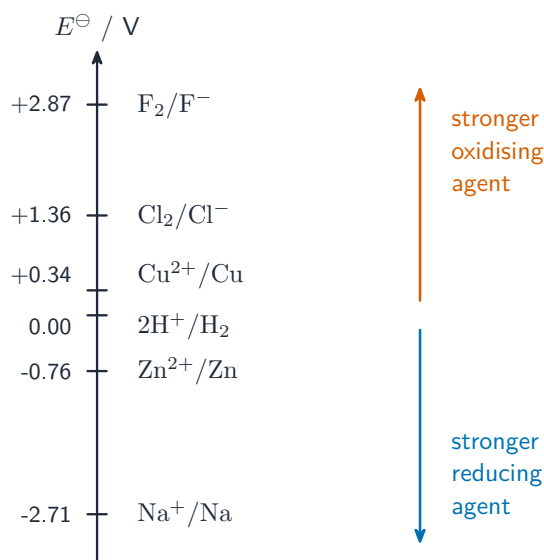
A simple cell: two half-cells joined by a salt bridge, with a voltmeter. Electrons flow from the negative (Zn) electrode to the positive (Cu)

Worked example. Find the standard cell potential of a cell built from the Zn^{2+}/Zn half-cell ($E^\ominus = -0.76 \text{ V}$) and the Cu^{2+}/Cu half-cell ($E^\ominus = +0.34 \text{ V}$).

$$E_{\text{cell}}^\ominus = E^\ominus(\text{more positive}) - E^\ominus(\text{less positive}) = (+0.34) - (-0.76) = 1.10 \text{ V}.$$

From $E^\ominus$ values you can:

- find the **polarity**: the more negative electrode is the negative terminal, and electrons flow from it through the external circuit to the positive electrode.
- judge **reactivity**: a more positive $E^\ominus$ means a better **oxidising agent** (easily reduced); a more negative $E^\ominus$ means a better **reducing agent**.



The electrochemical series: a more positive $E^\ominus$ (top) is a stronger oxidising agent; a more negative $E^\ominus$ (bottom) is a stronger reducing agent

■ Feasibility and redox equations

A reaction is feasible when $E_{\text{cell}}^\ominus$ is **positive**. To build the full equation, take the two **half-equations**, reverse the one that is oxidised, and add them so the electrons cancel. This $E^\ominus$ test tells you the **feasibility** of the reaction.

You can also link it to free energy: $\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$, where n is the moles of electrons.

■ The Nernst equation

If the concentrations are not standard, the electrode potential changes. Raising the concentration of the **oxidised** species makes E more positive. The **Nernst equation** gives the exact value:

$$E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons in the half-equation.

Exam tips

- $E_{\text{cell}}^\ominus = E^\ominus(\text{more positive}) - E^\ominus(\text{less positive})$; a **positive** $E_{\text{cell}}^\ominus$ means the reaction is feasible.
- Standard conditions for $E^\ominus$: **298 K**, **1 mol dm⁻³**, **100 kPa**, platinum electrode – state them if asked.
- A **more negative** electrode potential means a **stronger reducing agent**; use the series to predict the direction.

- For electrolysis quantities use $Q = It$ and moles of electrons = Q/F .