

Electrochemistry (A Level)

A-Level Chemistry 9701 · Topic 24 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Electrolysis and the Faraday constant
2. Standard electrode potentials
3. Standard cell potentials and feasibility
4. The Nernst equation

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1 Electrolysis and the Faraday constant

Syllabus 24.1

In electrolysis the **cathode** (negative) reduces and the **anode** (positive) oxidises. In aqueous solution the ions compete with water: at the cathode the species with the **more positive** $E^\ominus$ is reduced (Cu^{2+} and Ag^+ before H_2O ; H_2 forms instead of Na or K), and at the anode the species with the **less positive** $E^\ominus$ is oxidised, unless a high **concentration** of Cl^- makes chlorine form instead of oxygen. The charge passed is **$Q = It$** , and one mole of electrons carries the **Faraday constant**, $F = Le = 96\,500 \text{ C mol}^{-1}$. So 2.00 A for 965 s passes $1930 \text{ C} = 0.0200 \text{ mol e}^-$, depositing 0.0100 mol (0.635 g) of copper. Measuring the charge and the mass deposited gives $L = F \div e$.

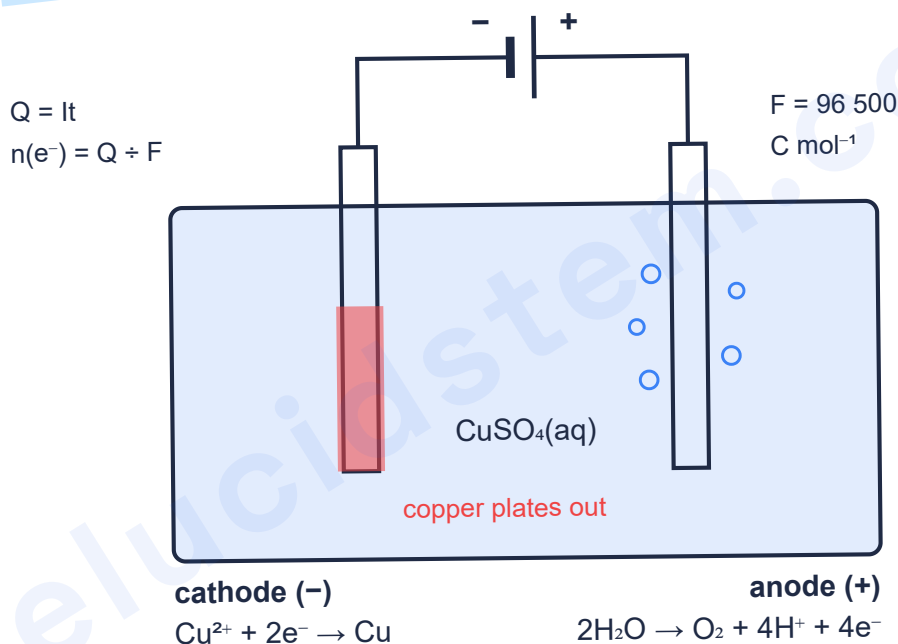


Fig. 1: electrolysis of copper(II) sulfate solution with inert electrodes

$Q = It$, then divide by F , then use the half-equation.

- ✓ $Q = It$ with t in seconds.
- ✓ $n(e^-) = Q \div F$, $F = 96\,500\text{ C mol}^{-1}$.
- ✓ **Half-equation** gives electrons per atom or molecule.
- ✓ **Cathode:** more positive $E^\ominus$ reduced;
anode: less positive $E^\ominus$ oxidised, unless concentration wins.

Watch out!

Time must be in **seconds** (minutes times 60). Use the **half-equation** to convert moles of electrons into moles of product: 2 e^- per Cu, 3 e^- per Al, 1 e^- per Ag, 4 e^- per O_2 . In aqueous solution, reactive metals such as Na and K are **never** deposited: hydrogen forms instead. Dilute chloride solutions give mainly **oxygen** at the anode, not chlorine.

2 Standard electrode potentials

Syllabus 24.2

The **standard electrode potential**, $E^\ominus$, of a half-cell is the potential difference between it and the **standard hydrogen electrode** (SHE), measured under **standard conditions**: 298 K, 1.00 mol dm^{-3} for every ion in solution and 100 kPa (Cambridge also accepts 101 kPa) for any gas. The SHE is H_2 gas bubbling over **platinum** (coated with platinum black) in $1.00 \text{ mol dm}^{-3} \text{H}^+$, and is defined as 0.00 V. A metal dips into its own ions; an ion/ion couple such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, or a non-metal such as Cl_2/Cl^- , needs an **inert platinum electrode**. Half-equations are written as reductions, so the **more positive** $E^\ominus$, the stronger the oxidising agent on the left; the **more negative**, the stronger the reducing agent on the right.

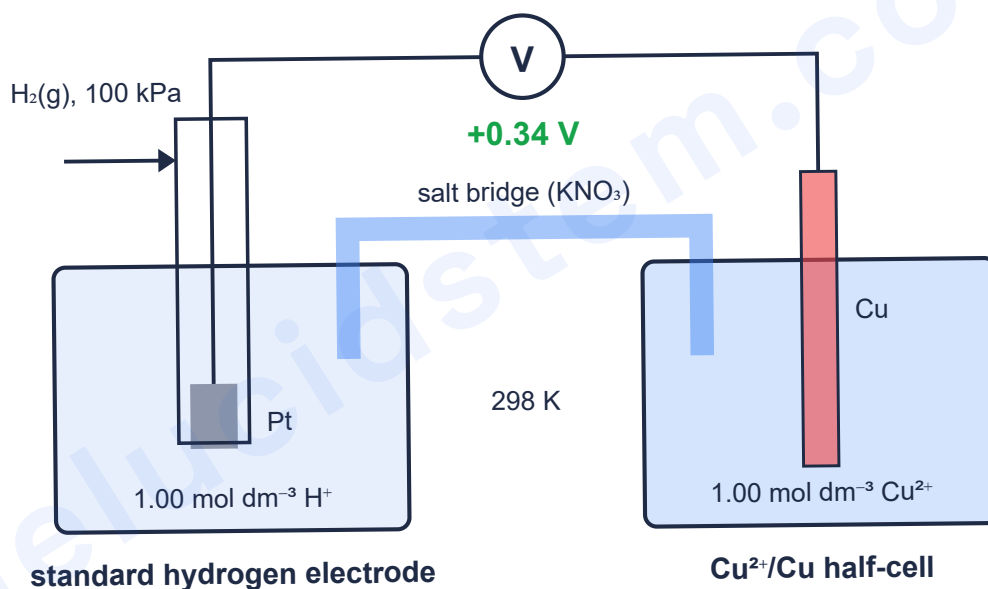


Fig. 1: measuring $E^\ominus (\text{Cu}^{2+}/\text{Cu})$ against the standard hydrogen electrode

Reduction, standard conditions, platinum.

- ✓ **SHE = 0.00 V:** Pt, H_2 100 kPa, $1.00 \text{ mol dm}^{-3} \text{ H}^+$, 298 K.
- ✓ **Pt electrode** for ion/ion and gas/ion couples.
- ✓ **More positive $E^\ominus$:** stronger oxidising agent (left).
- ✓ **More negative $E^\ominus$:** stronger reducing agent (right).

Watch out!

$E^\ominus$ values are **always quoted for the reduction**. Do **not** double $E^\ominus$ when a half-equation is multiplied up: it is a property of the couple, not of the amount. An ion/ion or gas/ion half-cell needs a **platinum** electrode and, for ion/ion, **equal 1.00 mol dm^{-3}** concentrations of both ions. A more positive $E^\ominus$ means the species on the **left** is a stronger oxidising agent, not that the species on the right is.

3 Standard cell potentials and feasibility

Syllabus 24.2

When two half-cells are joined, the one with the **more positive** $E^\ominus$ is the **positive electrode**; reduction happens there. The other is oxidised, and **electrons flow through the wire** from the negative to the positive electrode. The **standard cell potential** is $E^\ominus_{\text{cell}} = E^\ominus(\text{positive}) - E^\ominus(\text{negative})$, e.g. Zn/Cu: $+0.34 - (-0.76) = +1.10$ V. A reaction is **feasible** when $E^\ominus_{\text{cell}}$ for it, as written, is **positive**. E values say nothing about **rate** (a feasible reaction may have a high activation energy) and apply only under **standard conditions**. The cell potential links to free energy: $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$, so a positive E_{cell} gives a negative ΔG .

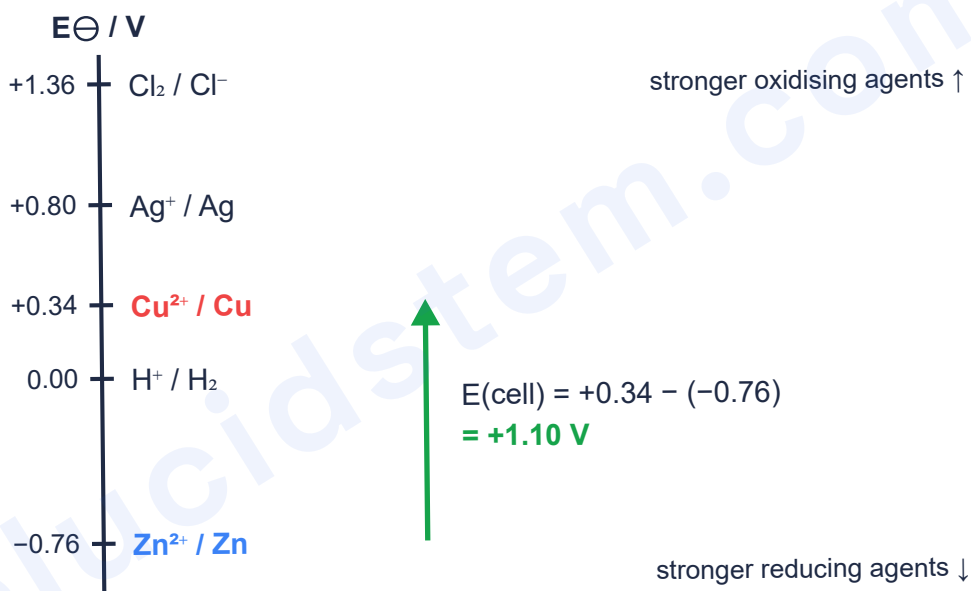


Fig. 1: reading $E^\ominus_{\text{cell}}$ for the zinc-copper cell from an $E^\ominus$ ladder

Positive minus negative, then check the sign.

✓ $E_{\text{cell}} = E(\text{positive}) - E(\text{negative}) = E_{\text{right}} - E_{\text{left}}$

✓ **Electrons** flow in the wire from negative to positive.

✓ **Feasible** if $E_{\text{cell}} > 0$, but rate and conditions can intervene.

✓ $\Delta G = -nFE$, then $\div 1000$ for kJ.

Watch out!

$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{positive}) - E^{\ominus}(\text{negative})$: never add them, and never multiply $E^{\ominus}$ by the coefficients used to balance electrons. Electrons flow in the **external wire**, from negative to positive; ions, not electrons, carry the current through the salt bridge. In $\Delta G = -nFE$, n is moles of **electrons**, and the answer in J must be converted to kJ. A feasible reaction may still be too **slow** to see.

4 The Nernst equation

Syllabus 24.2

For any half-cell written as a reduction, **raising the concentration of the oxidised form** pushes the equilibrium to the right, so E becomes **more positive**; raising the reduced form makes it **less positive**. The **Nernst equation** puts a number on this at 298 K: $E = E^\ominus + (0.059 \div z) \log ([\text{oxidised}] \div [\text{reduced}])$, where z is the number of electrons in the half-equation. Solids are left out, so for a metal $E = E^\ominus + (0.059 \div z) \log [M^{z+}]$. For Cu^{2+} at $0.010 \text{ mol dm}^{-3}$: $E = 0.34 + 0.0295 \times \log 0.010 = 0.34 - 0.059 = \textbf{+0.281 V}$. A **tenfold** dilution changes E by only $0.059 \div z$ volts, which is why $E^\ominus$ predictions are reliable unless $E^\ominus_{\text{cell}}$ is small.

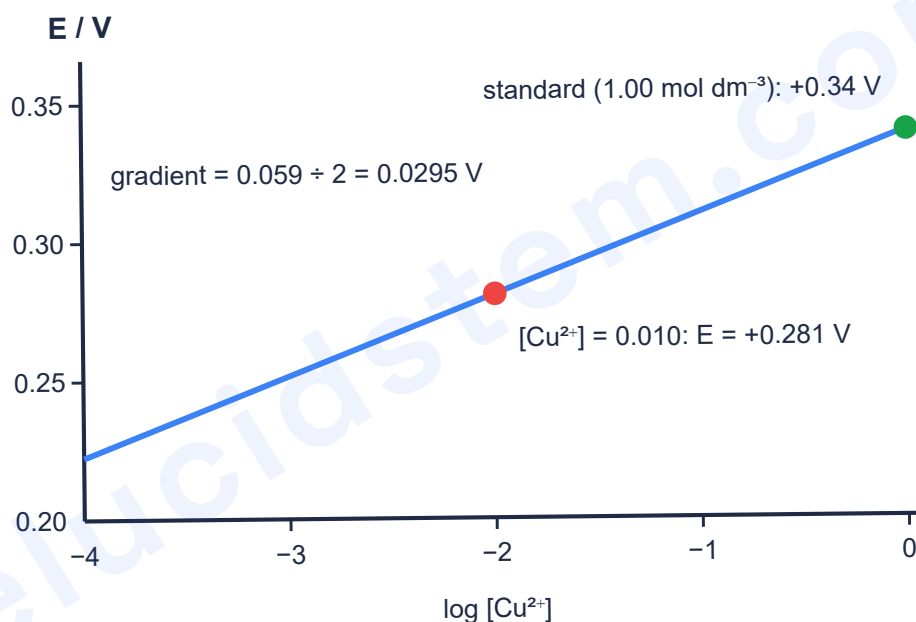


Fig. 1: E for the Cu^{2+}/Cu half-cell falls by 0.0295 V for every tenfold dilution

Oxidised on top, divide by z, base-10 log.

- ✓ $E = E^\ominus + (0.059 \div z) \log ([\text{ox}] \div [\text{red}])$ at 298 K.
- ✓ **Solids** (metals) are left out of the fraction.
- ✓ **More oxidised form:** E more positive.
- ✓ **Tenfold change:** $0.059 \div z$ volts.

Watch out!

Use **log to base 10**, not $\ln$, with the 0.059 V form. Divide 0.059 by **z**, the electrons in the half-equation (2 for Cu^{2+} , 1 for Ag^+ and Fe^{3+}). Put the **oxidised** species on the top of the fraction, and raise concentrations to their coefficients (2Cl^- gives $[\text{Cl}^-]^2$). Diluting the oxidised form makes E **less positive**, never more.

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