Electrochemistry (A Level)

Electrolysis and the Faraday constant, standard electrode potentials and the standard hydrogen electrode, cell potentials and feasibility, the Nernst equation, and the link between ΔG and the cell potential.

24.1 Electrolysis

In **electrolysis** an electric current drives a non-spontaneous reaction. At the **cathode** (negative electrode) reduction occurs; at the **anode** (positive electrode) oxidation occurs.

Predicting the products

- **Molten electrolytes:** the cation is discharged at the cathode and the anion at the anode (molten $PbBr_2$ gives Pb and Br_2).
- **Aqueous solutions:** water can also be discharged. At the cathode the species with the **more positive** (less negative) $E^{\ominus}$ is reduced: **metals below hydrogen** in the series (Cu, Ag) are deposited; for reactive metals (Na, K, Ca, Mg, Al) hydrogen is released instead: $2H^+ + 2e^- \rightarrow H_2$. At the anode **halide ions** are oxidised in preference to water if concentrated (chlorine from concentrated NaCl); otherwise **oxygen** forms: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ or $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.
- **Concentration** matters: dilute NaCl solution gives oxygen at the anode, concentrated gives chlorine.
- The electrode material also matters; a **copper anode** dissolves ($Cu \rightarrow Cu^{2+} + 2e^-$), as in copper refining.

Quantitative electrolysis

$$Q = It \qquad F = Le$$

where Q is charge in coulombs, I is current in amps, t is time in seconds, F is the **Faraday constant** (96 500 C mol^{-1}), L is the Avogadro constant and e is the charge on the electron (1.60×10^{-19} C). The amount of electrons is $n_e = Q/F$.

> **TRY IT**
>
> A current of 2.00 A is passed through $CuSO_4(aq)$ for 30.0 minutes. What mass of copper is deposited? (A_r Cu = 63.5)

$Q = 2.00 \times 1800 = 3600$ C. Moles of electrons $= 3600/96\,500 = 0.0373$. $Cu^{2+} + 2e^- \rightarrow Cu$, so moles of Cu $= 0.0187$ and mass $= 1.18$ g.

Note Academy

Determining L experimentally: electrolyse for a measured time at a known current, find the mass of metal deposited at the cathode (the change in mass of a copper electrode), then calculate the amount of atoms deposited, the charge passed and $L = F/e$.

Charge carriers and electrode polarity

Electrons carry charge through wires and electrodes; ions carry charge through an electrolyte. Cations move towards the cathode and anions towards the anode, but migration alone does not prove which species is discharged. In water, hydrogen- or hydroxide-containing species may compete with the dissolved salt ions, and electrode material can participate.

Oxidation always occurs at the anode and reduction at the cathode. The **signs** differ between an electrolytic cell, where an external supply drives the process, and a galvanic cell, which supplies electrical energy spontaneously. In electrolysis the cathode is negative; in a working galvanic cell it is positive. Identify the cell type before attaching signs.

Worked example: electrolysing aqueous copper sulfate with inert electrodes deposits copper at the cathode, $Cu^{2+} + 2e^- \longrightarrow Cu$, and produces oxygen at the anode from water. With copper electrodes, oxidation of the copper anode can instead replace the ions removed at the cathode. State the electrode material when predicting products. Standard potentials guide predictions, but concentrations and kinetic effects such as overpotential can alter practical discharge behaviour.

Electrolysis calculations in both directions

The calculation chain is **current and time → charge → moles of electrons → moles of product**. The coefficient of electrons in the half-equation is the conversion factor, not the ion's subscript in a formula. Assume 100% current efficiency unless the question states otherwise.

Worked example: deposit 2.70 g Al from molten electrolyte using 5.00 A. $n(Al) = 2.70/27.0 = 0.100$ mol. Since $Al^{3+} + 3e^- \longrightarrow Al$, electrons required are 0.300 mol. Charge is $0.300(96500) = 28950$ C, giving $t = Q/I = 5790$ s, or **96.5 min**. For a gas, calculate its moles first, then apply the stated molar volume or $pV = nRT$.

For an experimental Faraday constant, weigh a clean dry electrode before and after electrolysis. If a divalent metal of molar mass M gains mass m, electron amount is $2m/M$, so $F = Q/(2m/M)$. Wet electrodes overestimate deposited mass; lost deposit underestimates it. Measure current throughout if it varies, rather than assuming an initial reading remains constant. Obtain L from F/e only after calculating the measured F.

> **TRY IT**
>
> How much silver ($M = 108$ g mol^{-1}) is deposited by 965 C if $Ag^+ + e^- \longrightarrow Ag$?

Note Academy

Answer: Electron amount is 0.0100 mol, equal to silver amount because one electron deposits one silver atom. Mass is **1.08 g**. The same charge would deposit half as many moles of a 2+ metal.

24.2 Standard electrode potentials, standard cell potentials and the Nernst equation

Standard electrode potential

The **standard electrode (reduction) potential**, $E^{\ominus}$, is the voltage of a half-cell, measured with a **standard hydrogen electrode** as the other half-cell, under standard conditions: **298 K, 1.00 mol dm^{-3}** for solutions of ions, and **101 kPa** for gases. The half-equation is written as a **reduction**.

The standard hydrogen electrode (SHE)

A platinum electrode coated with platinum black, in contact with H_2 **gas at 101 kPa** and a solution of H^+ **at 1.00 mol dm^{-3}**, at 298 K: $2H^+ + 2e^- \rightleftharpoons H_2$, with $E^{\ominus} = 0.00$ V by definition.

Measuring $E^{\ominus}$

- **A metal in contact with its ions** (for example Cu^{2+}/Cu): the metal in a 1.00 mol dm^{-3} solution of its ions, connected through a **salt bridge** and a high-resistance voltmeter to the SHE.
- **Ions of the same element in different oxidation states** (for example Fe^{3+}/Fe^{2+}): an **inert platinum electrode** in a solution containing both ions at 1.00 mol dm^{-3}.
- For a non-metal such as Cl_2/Cl^-: a gas bubbled around a platinum electrode in a solution of the ions.

Standard cell potential

$$E^{\ominus}_{cell} = E^{\ominus}(\text{positive electrode}) - E^{\ominus}(\text{negative electrode})$$

The **more positive** $E^{\ominus}$ is the **positive** electrode (reduction), and electrons flow in the external circuit **from the negative to the positive** electrode. The more negative half-cell is oxidised.

Note Academy

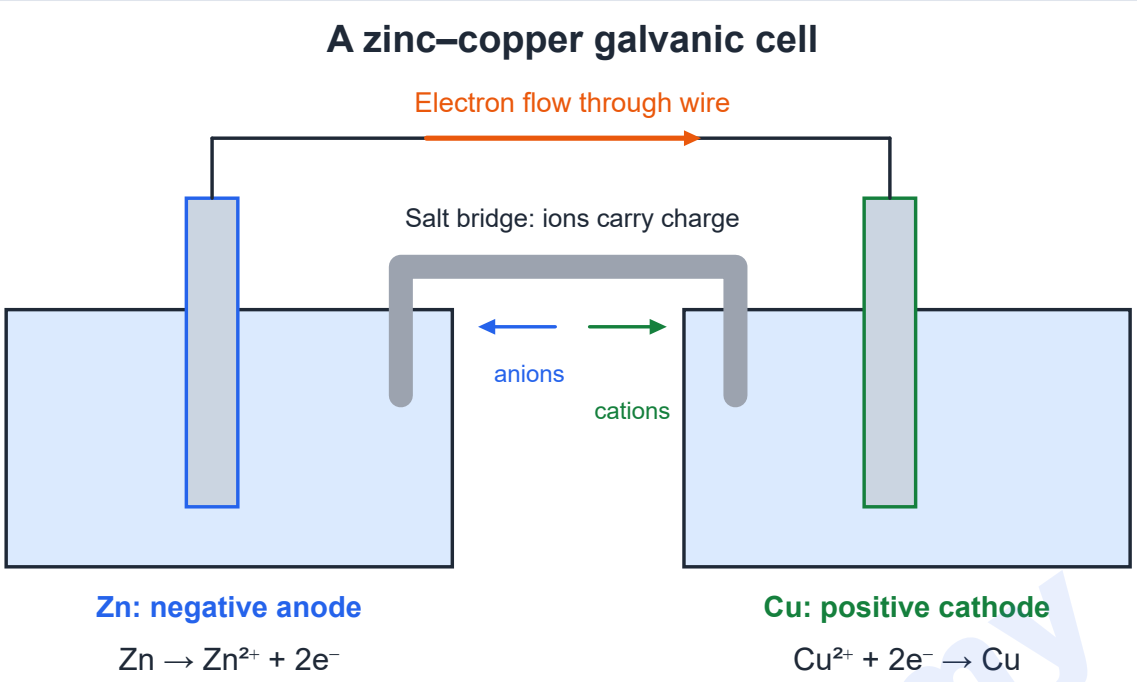
Half-equation	$E^{\ominus}$ / V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52

Using $E^{\ominus}$ values

- For half-equations written as reductions, the **strongest oxidising agents** are the species on the **left** of the most positive $E^{\ominus}$ equations; the strongest reducing agents are the species on the right of the most negative equations. Do not rely on the table's physical top/bottom order.
- A reaction is **feasible** if $E^{\ominus}_{cell} > 0$. To build the overall equation, reverse the half-equation with the lower (more negative) $E^{\ominus}$, balance the electrons and add. For $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$: $E^{\ominus}_{cell} = +0.34 - (-0.76) = +1.10$ V.
- Feasibility predicts the **thermodynamics**, not the rate; a reaction may be slow, and conditions may not be standard.

Note Academy

Building a cell and an overall equation



A single electrode potential cannot be measured in isolation; measure the potential difference against a reference half-cell. The standard hydrogen electrode defines zero, so a negative value means a half-cell is less favourable for reduction relative to that reference. The high-resistance voltmeter draws negligible current, helping preserve the conditions being measured. A salt bridge completes the internal ionic circuit without directly mixing the two solutions.

Worked example: combine $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, +0.77 V, with $I_2 + 2e^- \rightleftharpoons 2I^-$, +0.54 V. Iron(III) is reduced and iodide is oxidised. Multiply the iron half-equation by two to cancel electrons:

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$E^{\ominus}_{cell} = 0.77 - 0.54 = +0.23$ V. **Do not multiply an electrode potential** when multiplying a half-equation: potential is an intensive quantity. In contrast, the electron count used later in ΔG must match the balanced overall equation.

> **TRY IT**
>
> Which is the stronger oxidising agent, Cu^{2+} in a +0.34 V half-equation or Fe^{3+} in a +0.77 V half-equation?

Answer: Fe^{3+}, because its reduction potential is more positive under the stated standard conditions. Compare the species accepting electrons, not the metals/ions appearing on the product side.

The Nernst equation

When concentrations are not 1.00 mol dm^{-3} the electrode potential changes. At 298 K:

Note Academy

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

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

- For $Cu^{2+} + 2e^- \rightleftharpoons Cu$: $E = +0.34 + \dfrac{0.059}{2} \log[Cu^{2+}]$. Diluting the solution makes E **less positive**.
- For $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$: $E = +0.77 + 0.059 \log \dfrac{[Fe^{3+}]}{[Fe^{2+}]}$.

Qualitatively, increasing the concentration of the oxidised species makes E more positive, since the equilibrium moves towards the reduced form (the opposite for the reduced species).

> **TRY IT**
>
> Find E for the Cu^{2+}/Cu half-cell with $[Cu^{2+}] = 0.0100$ mol dm⁻³.

$E = 0.34 + 0.0295 \times \log(0.0100) = 0.34 - 0.059 = +0.28$ V.

Applying Nernst with the correct ratio

The reduced form may be a pure solid, whose concentration is omitted. For a pair of aqueous ions, include both concentrations. A tenfold change in their ratio changes E by $0.059/z$ V at 298 K. Use base-10 logarithms with the given 0.059 coefficient and do not substitute the number of electrons in an unrelated overall cell reaction for the half-equation's z.

Worked example: for Fe^{3+}/Fe^{2+} with $[Fe^{3+}] = 0.200$ and $[Fe^{2+}] = 0.0200$ mol dm⁻³, $E = 0.770 + 0.059 \log(10.0) = \mathbf{0.829}$ V. The increased oxidised-to-reduced ratio makes reduction more favourable. If both concentrations are diluted by the same factor, their ratio is unchanged in this simple expression.

For equations containing several ions or gas-pressure terms, use the appropriately stated form of the equation; the simple single-ratio examples are not permission to ignore coefficients or additional species. Qualitative concentration reasoning and numerical substitution should agree about the direction of the potential change.

> **TRY IT**
>
> Using $E^{\ominus} = 0.770$ V, find E when $[Fe^{3+}]/[Fe^{2+}] = 0.100$ at 298 K.

Answer: $E = 0.770 + 0.059 \log(0.100) = \mathbf{0.711}$ V. The negative logarithm reduces the potential.

ΔG and the cell potential

$$\Delta G^{\ominus} = -nE^{\ominus}_{cell}F$$

Note Academy

where n is the number of moles of electrons transferred in the balanced equation and $F = 96\,500$ C mol^{-1}. A positive $E^{\ominus}_{cell}$ gives a negative $\Delta G^{\ominus}$ (feasible). The result is in J mol^{-1}; divide by 1000 for kJ mol^{-1}.

> **TRY IT**
>
> Find $\Delta G^{\ominus}$ for $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.

$n = 2$ and $E^{\ominus}_{cell} = 1.10$ V, so $\Delta G^{\ominus} = -2 \times 1.10 \times 96\,500 = -212\,300$ J mol^{-1}, or −212 kJ mol^{-1}.

Interpreting feasibility and its limits

For the iron(III)/iodide example above, two moles of electrons are transferred, so $\Delta G^{\ominus} = -2(96500)(0.23) = -44.4$ kJ mol^{-1} for the balanced reaction. Reversing the reaction changes the signs of both cell potential and free energy. Doubling the equation doubles n and ΔG, but leaves the potential unchanged.

A positive cell potential predicts a thermodynamic driving force under the stated conditions. It does not specify the rate, the time needed for completion or the extent to which competing reactions occur. Non-standard concentrations, surface films and slow electron-transfer kinetics help explain why a predicted reaction may not be observed immediately.

Chapter check: identify cell type, label electron flow through the wire and ionic movement through the bridge, balance electrons, then use the appropriate potential expression. Link sign and feasibility reasoning to **Gibbs free energy**.

References and further reading

Scope follows section 24 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy