

Cambridge AS & A Level · Chemistry 9701 · Notes

Electrochemistry

A2

Read online at pastopic.com/cambridge/chemistry-9701/notes/electrochemistry-a-level

Last checked 30 September 2026

Read first: [Electrochemistry](#), [Equilibria](#)

© 2026 Pastopic. Free for personal study. Please share the link, not the file.

What you need to know

By the end of this topic you should be able to:

Electrolysis

1. **Predict what is released at each electrode** during electrolysis, from whether the electrolyte is molten or aqueous, where the ions sit in the redox series (their electrode potentials) and how concentrated the solution is.
2. **State and use** $F = Le$: the Faraday constant is the Avogadro constant times the charge on one electron.
3. **Calculate** the charge passed with $Q = It$, and from it the mass or gas volume of a product (or work backwards to a time or a current).
4. **Describe how electrolysis can measure the Avogadro constant**: pass a known charge, weigh the metal gained or lost, and compare the number of electrons with the number of moles.

Electrode potentials and cells

5. **Define standard electrode (reduction) potential and standard cell potential**, including the standard conditions.
6. **Describe the standard hydrogen electrode**.
7. **Describe how to measure standard electrode potentials** of a metal or non-metal in contact with its ions, and of two ions of the same element in different oxidation states.
8. **Calculate a standard cell potential** from two standard electrode potentials.
9. **Use** $E_{\text{cell}}^{\ominus}$ to find which electrode is positive, which way electrons flow in the wire, and whether a reaction is feasible.
10. **Rank oxidising and reducing agents** by their $E^{\ominus}$ values.
11. **Build redox equations** from two half-equations.
12. **Predict in words** how changing the concentration of an ion changes an electrode potential.
13. **Use the Nernst equation**, $E = E^{\ominus} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$, to calculate an electrode potential at other concentrations, for a metal/ion electrode such as Cu^{2+}/Cu and an ion/ion electrode such as $\text{Fe}^{3+}/\text{Fe}^{2+}$.
14. **Use** $\Delta G^{\ominus} = -nE_{\text{cell}}^{\ominus}F$ in both directions.

Oxidation numbers, half-equations and simple redox titrations come from the AS Electrochemistry topic (read it first). Batteries and fuel cells are not named in the syllabus, but Paper 4 uses them as settings for the skills above, so they are covered here.

Understand it

Electrolysis: which ions are discharged

Electrolysis uses electrical energy to force a redox reaction that would not happen by itself. The negative electrode (the **cathode**) pushes electrons onto positive ions, so **reduction** happens there. The positive electrode (the **anode**) pulls electrons off negative ions or water, so **oxidation** happens there.

Molten compounds contain only one kind of cation and one kind of anion, so the answer is simple: the metal at the cathode, the non-metal at the anode. Molten lithium bromide gives lithium and bromine:



In an **aqueous** solution, water competes, because it can be reduced to hydrogen or oxidised to oxygen:



- **At the cathode**, the species that is easiest to reduce wins: the one with the **more positive** $E^\ominus$. Ions of metals below hydrogen in the redox series (Cu^{2+} at +0.34 V, Ag^+ at +0.80 V) are reduced to the metal. Ions of reactive metals (Na^+ , K^+ , Mg^{2+} , Al^{3+} , all with very negative $E^\ominus$) stay in solution, and hydrogen is given off instead. In acid the half-equation is $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$.
- **At the anode**, the species that is easiest to oxidise wins. Sulfate and nitrate are never oxidised, so oxygen forms from water (in alkali, $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$). Iodide and bromide are oxidised to iodine and bromine. Chloride is the borderline case: **concentration** decides. Concentrated chloride solutions give chlorine; very dilute ones give mainly oxygen.

Electrolyte (inert electrodes)	Cathode	Anode
Molten LiBr	lithium	bromine
$\text{Na}_2\text{SO}_4(\text{aq})$	hydrogen	oxygen
$\text{KBr}(\text{aq})$	hydrogen	bromine
$\text{AgNO}_3(\text{aq})$	silver	oxygen
very dilute $\text{KCl}(\text{aq})$	hydrogen	mainly oxygen

If the anode is a **metal that is not inert**, such as copper, the anode itself is oxidised and dissolves ($\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$). That is why it loses mass, which is useful for measuring the Avogadro constant.

Charge, moles of electrons and the Faraday constant

Current is the rate at which charge flows. A current of I amps for t seconds passes a charge

$$Q = It \quad (\text{coulombs}).$$

One electron carries 1.60×10^{-19} C. A mole of electrons carries L times that, which is the **Faraday constant**:

$$F = Le = 6.022 \times 10^{23} \times 1.60 \times 10^{-19} = 9.64 \times 10^4 \text{ C mol}^{-1}$$

(the question paper gives $F = 9.65 \times 10^4 \text{ C mol}^{-1}$; use that). So

$$\text{moles of electrons} = \frac{Q}{F}.$$

The half-equation then tells you how many electrons each particle of product needs: 1 for silver ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$), 2 for copper or hydrogen ($\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$), 3 for aluminium ($\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$) and 4 for oxygen ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). At room conditions one mole of gas occupies 24.0 dm^3 .

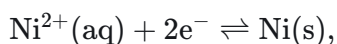
Measuring the Avogadro constant by electrolysis

Pass a steady, measured current through a solution between two electrodes of the same metal (for example copper electrodes in copper(II) sulfate solution) for a measured time. Weigh the cathode (or the anode) before and after, after rinsing and drying it.

- Charge passed: $Q = It$.
- Number of electrons: $Q \div e$.
- Number of atoms deposited: electrons $\div$ the charge on the ion (divide by 2 for Cu^{2+}).
- Moles of atoms: mass change $\div A_r$.
- $L = \text{number of atoms} \div \text{moles of atoms}$.

Electrode potentials

Put a strip of nickel into a solution of nickel(II) ions. A few atoms lose electrons and enter the solution, and a few ions pick up electrons from the metal. An equilibrium is set up,



and the metal ends up with a small charge compared with the solution. This arrangement is a **half-cell**. You can't measure the potential of one half-cell alone, because a voltmeter needs two connections. So every half-cell is measured against the same reference, the **standard hydrogen electrode**, which is defined as 0.00 V.

The **standard electrode potential**, $E^\ominus$, of a half-cell is the potential difference between it and a standard hydrogen electrode, measured under standard conditions:

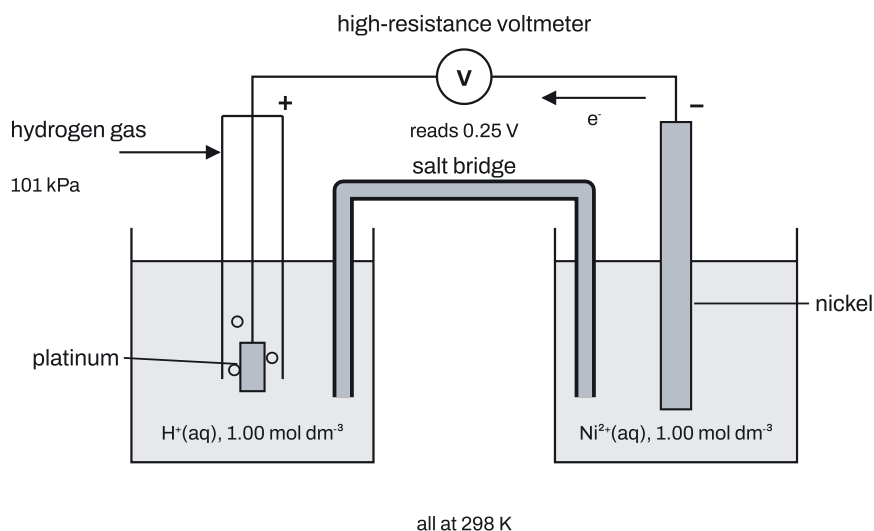
- every ion at 1.00 mol dm^{-3} ;
- every gas at 101 kPa (1 atm);
- 298 K;
- a platinum electrode wherever the half-cell has no solid metal of its own.

Every half-equation in a table of $E^\ominus$ values is written as a **reduction** (electrons on the left), which is why $E^\ominus$ is also called a standard reduction potential. A very positive value means the forward reaction (gaining electrons) happens readily; a very negative value means the backward reaction (losing electrons) happens readily.

The **standard cell potential**, $E_{\text{cell}}^\ominus$, is the potential difference between the two electrodes of a cell made from two half-cells, both under standard conditions.

The standard hydrogen electrode and measuring $E^\ominus$

The standard hydrogen electrode is hydrogen gas at 101 kPa bubbling over a platinum electrode (coated in finely divided platinum) that dips into a solution with $[\text{H}^+] = 1.00 \text{ mol dm}^{-3}$ (for example $1.00 \text{ mol dm}^{-3} \text{ HCl}$), at 298 K. The platinum is inert: it only carries electrons in and out.



To measure $E^\ominus$ of any half-cell, connect it to a standard hydrogen electrode:

- a **salt bridge** (filter paper soaked in saturated potassium nitrate solution) joins the two solutions. Its ions move to keep each solution electrically neutral, which completes the circuit **without** mixing the solutions;
- a **high-resistance voltmeter** joins the two electrodes, so that almost no current flows and the concentrations don't change while you measure.

In the circuit, **electrons** carry the current through the wires and **ions** carry it through the solutions and the salt bridge.

The half-cell you build depends on what is being measured:

- **A metal and its ions:** a strip of the metal in a 1.00 mol dm^{-3} solution of its ions, for example Ni in $\text{Ni}^{2+}(\text{aq})$.
- **A non-metal and its ions:** a platinum electrode. For a gas, the gas at 101 kPa bubbles over the platinum in a 1.00 mol dm^{-3} solution of its ions (like the hydrogen electrode). For bromine, platinum dips into a solution that is 1.00 mol dm^{-3} in both Br_2 and Br^- .

- **Two ions of the same element** (such as Sn^{4+} and Sn^{2+}): a platinum electrode in one solution containing **both** ions, each at 1.00 mol dm^{-3} . If H^+ appears in the half-equation (as for $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$), it must also be 1.00 mol dm^{-3} .

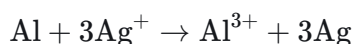
Iron, copper or any other metal must never be used as the electrode in an ion/ion half-cell: it would react with the ions.

Calculating $E_{\text{cell}}^\ominus$, polarity and electron flow

Two half-cells joined together make a cell. The half-cell with the **more positive** $E^\ominus$ is the **positive** electrode; reduction happens there. The other is the **negative** electrode; oxidation happens there. Electrons flow through the external wire **from the negative electrode to the positive electrode**.

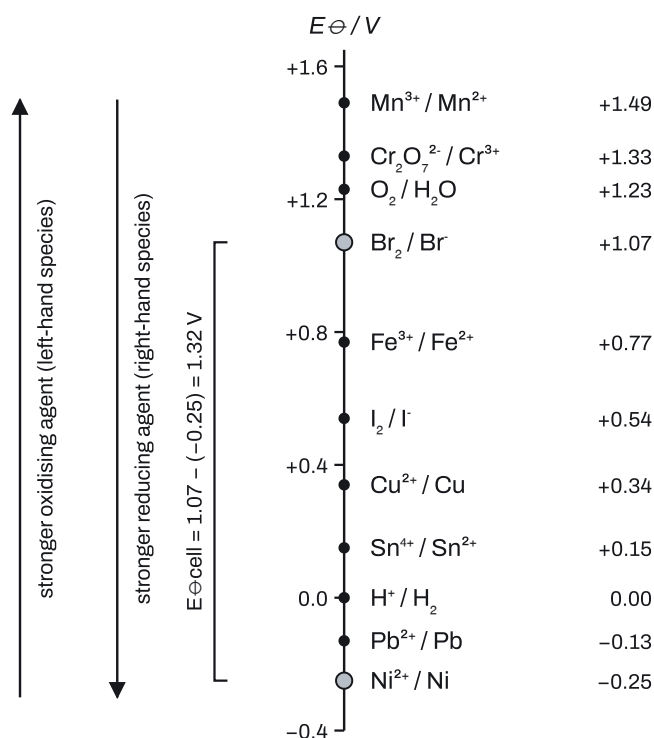
$$E_{\text{cell}}^\ominus = E^\ominus(\text{positive electrode}) - E^\ominus(\text{negative electrode})$$

For aluminium (Al^{3+}/Al , -1.66 V) with silver (Ag^+/Ag , $+0.80 \text{ V}$): silver is positive, and $E_{\text{cell}}^\ominus = 0.80 - (-1.66) = +2.46 \text{ V}$. The cell reaction is



The silver half-equation was multiplied by 3 to match the 3 electrons that aluminium loses, but $E^\ominus$ **is not multiplied**: it is a property of the half-cell, not of the amount reacting.

Oxidising agents, reducing agents and feasibility



Arrange the half-equations in order of $E^\ominus$:

- the **more positive** $E^\ominus$, the more strongly the species on the **left** (the oxidised form) takes electrons: it is a **stronger oxidising agent**. Of the ones in the diagram, Mn^{3+} is the strongest;
- the **more negative** $E^\ominus$, the more readily the species on the **right** (the reduced form) gives electrons away: it is a **stronger reducing agent**. Nickel metal is the strongest here.

A reaction between an oxidising agent from one half-equation and a reducing agent from another is **feasible** when

$$E_{\text{cell}}^\ominus = E^\ominus(\text{half-equation of the oxidising agent}) - E^\ominus(\text{half-equation of the reducing agent}) > 0$$

In words: the oxidising agent's half-equation must have the more positive $E^\ominus$. On the diagram, a species on the left of the equilibrium reacts with any species on the right that sits **lower down**.

Two cautions:

- "Feasible" says the reaction **can** happen, not that it is fast. A feasible reaction with a high activation energy may be too slow to see.
- $E^\ominus$ values are for standard conditions. If the concentrations are far from 1.00 mol dm^{-3} , the potentials shift, and when two $E^\ominus$ values are close the prediction can reverse.

Changing the ligands round a transition-metal ion changes $E^\ominus$ for its $\text{M}^{3+}/\text{M}^{2+}$ half-cell too, because the ligands stabilise the two oxidation states by different amounts. A less positive $E^\ominus$ means the M^{3+} complex is harder to reduce (a weaker oxidising agent) and the M^{2+} complex is easier to oxidise.

$\Delta G^\ominus$ and $E_{\text{cell}}^\ominus$

A positive $E_{\text{cell}}^\ominus$ and a negative $\Delta G^\ominus$ are two ways of saying the same thing: the reaction is feasible. They are linked by

$$\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$$

where n is the number of moles of electrons transferred in the equation as written, and $F = 96\,500 \text{ C mol}^{-1}$. The answer comes out in J mol^{-1} ; divide by 1000 for kJ mol^{-1} . For the aluminium–silver cell, $n = 3$:

$$\Delta G^\ominus = -3 \times 2.46 \times 96\,500 = -712\,170 \text{ J mol}^{-1} = -712 \text{ kJ mol}^{-1}$$

How concentration changes an electrode potential

Each half-cell is an equilibrium, so Le Chatelier's principle predicts what happens when a concentration changes. Take $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$:

- lower** $[\text{Cu}^{2+}]$ (the oxidised species): the equilibrium shifts **left**, releasing electrons onto the copper, so E becomes **more negative** (less positive);
- raise** $[\text{Cu}^{2+}]$: the equilibrium shifts right, so E becomes **more positive**.

The rule works for any half-cell: **more oxidised species or less reduced species makes E more positive**. Anything that removes an ion counts: diluting, adding an ion that forms a precipitate with it, or adding a common ion that makes a salt less soluble.

The Nernst equation

The Nernst equation puts numbers on this. At 298 K,

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

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

- **Metal/ion:** the reduced species is a solid metal, whose "concentration" is taken as 1. For Cu^{2+}/Cu with $[\text{Cu}^{2+}] = 0.050 \text{ mol dm}^{-3}$:

$$E = 0.34 + \frac{0.059}{2} \log(0.050) = 0.34 - 0.038 = +0.30 \text{ V}$$

- **Ion/ion:** both ions go in the ratio. For $\text{Sn}^{4+} + 2\text{e}^{-} \rightleftharpoons \text{Sn}^{2+}$ ($E^{\ominus} = +0.15 \text{ V}$) with $[\text{Sn}^{4+}] = 0.20$ and $[\text{Sn}^{2+}] = 0.020 \text{ mol dm}^{-3}$:

$$E = 0.15 + \frac{0.059}{2} \log \frac{0.20}{0.020} = 0.15 + 0.0295 = +0.18 \text{ V}$$

A tenfold change in the ratio shifts E by 0.059 V when $z = 1$, but by only 0.0295 V when $z = 2$. You may also see the equivalent form $E = E^{\ominus} + \frac{RT}{zF} \ln \frac{[\text{ox}]}{[\text{red}]}$, which gives the same answers at 298 K.

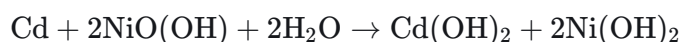
Batteries and fuel cells

A battery is one or more cells. When it **discharges**, the reaction at the negative electrode is an oxidation and the reaction at the positive electrode is a reduction, just as in any cell. A rechargeable cell is recharged by forcing a current the other way, which reverses both reactions.

In a nickel–cadmium cell (alkaline electrolyte), the half-equations during discharge are



Nickel goes from +3 to +2, so the nickel electrode is where reduction happens (positive). Doubling the second half-equation and adding gives the overall reaction:



A **fuel cell** is a cell whose reactants (a fuel and oxygen) are fed in continuously. Its overall reaction is the same as burning the fuel, but the energy is released as electricity. Oxygen is reduced at the positive electrode ($\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$ in acid, $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$ in alkali), and the fuel is oxidised at the negative electrode. Batteries and fuel cells are convenient, portable sources of electrical energy; fuel cells give only water (and CO_2 for carbon fuels) with no combustion.

Key facts and formulas

"Given" means it is printed on the question paper ("Important values, constants and standards", or in the question itself). "Learn it" means you must remember it. Paper 4 prints the $E^{\ominus}$ values each question needs.

Formula	Status
$F = 9.65 \times 10^4 \text{ C mol}^{-1}$, $L = 6.022 \times 10^{23} \text{ mol}^{-1}$, $e = 1.60 \times 10^{-19} \text{ C}$	Given
Molar volume of gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions; $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$	Given
$E^\ominus$ values for the half-equations in a question	Given
$F = Le$	Learn it
$Q = It$ (Q in C, I in A, t in s)	Learn it
Moles of electrons = $\frac{Q}{F}$; moles of product = $\frac{\text{moles of electrons}}{\text{electrons per particle}}$	Learn it
$E_{\text{cell}}^\ominus = E^\ominus(\text{positive}) - E^\ominus(\text{negative})$; never multiply $E^\ominus$ by a coefficient	Learn it
Feasible when $E_{\text{cell}}^\ominus > 0$	Learn it
$E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$	Learn it
$\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$ (n = moles of electrons in the equation)	Learn it
Standard conditions: 1.00 mol dm^{-3} ions, 101 kPa gases, 298 K	Learn it
Standard hydrogen electrode: $E^\ominus = 0.00 \text{ V}$	Learn it

Sometimes a question prints the Nernst equation or the $E^\ominus$ values; often it does not print the Nernst equation, so learn it.

How to do it

In the Paper 4 questions we have tagged for this topic (58 questions, 2021–2025, of which 15 are repeats on another variant of the same paper), the types came up this often. 44 of the 58 questions mix several types, so the counts add up to more than 58.

Question type	Questions
Calculate a standard cell potential	25
Construct a redox or cell equation from half-equations	23
Predict feasibility or choose a reagent from $E^\ominus$ values	21
Electrolysis calculation with $Q = It$	15
Draw and label an electrochemical cell	14
Define standard electrode potential or standard cell potential	13
Polarity of the electrodes and direction of electron flow	12
Nernst equation calculation	11
$\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$	9
Effect of a concentration change on E , in words	9

Question type	Questions
Batteries and fuel cells	9
Redox titration calculation	7
Predict electrolysis products	4
Avogadro constant by electrolysis	2

1. Calculate a standard cell potential (25 questions)

1. Find the two half-equations involved and their $E^\ominus$ values.
2. The more positive one is the positive electrode.
3. $E_{\text{cell}}^\ominus = E^\ominus(\text{positive}) - E^\ominus(\text{negative})$. Give it with a + sign and the unit V.

Variations you will meet:

- **Work back to an unknown $E^\ominus$.** If you know $E_{\text{cell}}^\ominus$ and one electrode, rearrange: $E^\ominus(\text{positive}) = E_{\text{cell}}^\ominus + E^\ominus(\text{negative})$, or $E^\ominus(\text{negative}) = E^\ominus(\text{positive}) - E_{\text{cell}}^\ominus$.
- **One electrode is not standard.** Work out its E with the Nernst equation first, then use that value in place of $E^\ominus$. The electrode with the more positive value is still the positive one.
- **Alkaline half-equations** (with OH^-) are used in exactly the same way.

2. Construct a redox or cell equation from half-equations (23 questions)

1. Keep the half-equation with the **more positive** $E^\ominus$ as a reduction.
2. **Reverse** the other one, so it becomes an oxidation (electrons on the right).
3. Multiply one or both so the electrons match, then add.
4. Cancel electrons and anything that appears on both sides (H^+ , H_2O , OH^-).
5. Check both atoms and total charge balance.

Variations you will meet:

- **Alkaline conditions:** the half-equations already contain OH^- and H_2O ; just cancel them as usual.
- **A reaction "backwards"** because the concentrations are not standard: if a Nernst calculation makes the other electrode more positive, write the equation the other way round (Example 3).
- **Disproportionation:** one species appears in two half-equations, as the oxidising agent in one and the reducing agent in the other. Use one half-equation as a reduction and reverse the other.
- **Combining two steps** of a catalysed reaction into an overall equation: add them and cancel the catalyst, which appears on both sides.

3. Predict feasibility or choose a reagent from $E^\ominus$ values (21 questions)

1. Write the two half-equations as reductions with their $E^\ominus$ values.

- Decide which species must be the oxidising agent (it must be on the **left** of its half-equation) and which the reducing agent (on the **right** of its half-equation).
- $E_{\text{cell}}^{\ominus} = E^{\ominus}(\text{oxidising agent's half-equation}) - E^{\ominus}(\text{reducing agent's half-equation})$.
- Positive: feasible. Negative: not feasible under standard conditions. **Quote both $E^{\ominus}$ values** (or $E_{\text{cell}}^{\ominus}$) in your answer.

For example, zinc (Zn^{2+}/Zn , -0.76 V) with chromium(III) ions ($\text{Cr}^{3+}/\text{Cr}^{2+}$, -0.41 V ; Cr^{2+}/Cr , -0.91 V): zinc reduces Cr^{3+} to Cr^{2+} ($E_{\text{cell}}^{\ominus} = -0.41 - (-0.76) = +0.35\text{ V}$), but it cannot reduce Cr^{2+} to chromium metal ($-0.91 - (-0.76) = -0.15\text{ V}$). So with excess zinc the product stops at Cr^{2+} .

Variations you will meet:

- "Select a reagent from the list that can oxidise X"**: find X's half-equation (X is on the right). Any species on the left of a half-equation with a **more positive $E^{\ominus}$** will do. For "reduce X", pick a species on the right of a half-equation with a **more negative $E^{\ominus}$** .
- "Identify all the species that react with Y"**: Y may be oxidised or reduced. Check both: species that can oxidise Y and species that can reduce Y. A species in between on the scale reacts in neither direction.
- With an excess of oxidising (or reducing) agent**, keep going step by step down (or up) a series of oxidation states until the next step has a negative $E_{\text{cell}}^{\ominus}$.
- The same substance as oxidising and reducing agent** (such as hydrogen peroxide): look for one half-equation with it on the left and one with it on the right, and pair each with a suitable partner.
- Ligands change $E^{\ominus}$** . A complex with a less positive $E^{\ominus}$ for $\text{M}^{3+}/\text{M}^{2+}$ is harder to reduce, so it is a weaker oxidising agent, and its M^{2+} form is easier to oxidise (for example by air).
- Ordering $E^{\ominus}$ from cell readings**. If A is positive against B by 0.5 V , $E^{\ominus}(\text{A}) = E^{\ominus}(\text{B}) + 0.5$.

4. Electrolysis calculation with $Q = It$ (15 questions)

- Convert the time to **seconds**. $Q = It$.
- Moles of electrons = $Q \div F$.
- Use the half-equation: moles of product = moles of electrons $\div$ electrons per particle.
- Mass = moles $\times A_r$ (or M_r); gas volume = moles $\times 24.0\text{ dm}^3$ at room conditions.
- To find t or I instead, run the chain backwards: moles of product $\rightarrow$ moles of electrons $\rightarrow Q \rightarrow t = Q \div I$ or $I = Q \div t$.

For example, the hydrogen from a current of 0.500 A for 30.0 min : $Q = 0.500 \times 1800 = 900\text{ C}$; moles of electrons = $900 \div 96\,500 = 9.33 \times 10^{-3}$; moles of $\text{H}_2 = 4.66 \times 10^{-3}$; volume = 112 cm^3 .

Variations you will meet:

- Counting particles**: number of electrons = $Q \div e$; number of molecules or atoms = electrons $\div$ electrons per particle; moles = number $\div L$.
- Two cells in series** carry the same charge. Moles of electrons are the same in both, so the moles of products are in the ratio of the charges on their ions.

- **Moles from a titration** (for example iodine formed at an anode, found with thiosulfate): convert back to moles of product first, then to charge.
- **A fuel cell or battery delivering a current**: the same chain gives the fuel or oxygen used.
- **A mixture of ions** discharged together (such as Fe^{2+} and Fe^{3+} in a fixed ratio): find the average number of electrons per atom first.

5. Draw and label an electrochemical cell (14 questions)

Draw two beakers, each with a liquid level, and include:

1. the correct **electrode** in each: the metal for a metal/ion half-cell; **platinum** for gas, halogen or ion/ion half-cells;
2. the correct **solution** in each, labelled with the ions (for example " $\text{Ni}^{2+}(\text{aq})$ "; " $\text{Sn}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$ " together in one beaker);
3. a **gas supply** for a gas electrode: a glass tube round the platinum with the gas going in, labelled (" H_2 at 101 kPa");
4. a **salt bridge** dipping into **both** solutions, labelled;
5. a **voltmeter** ("V", high-resistance) joined by wires to the tops of both electrodes, making a complete circuit.

The first diagram in "Understand it" has all of these. Conditions (1.00 mol dm^{-3} , 298 K, 101 kPa) are credited if you label them, but check whether the question says you need them.

Variations you will meet:

- **"State the function of the salt bridge"**: it lets ions move between the solutions to complete the circuit (keeping each solution neutral) without the solutions mixing.
- **"State the charge carriers"**: ions in the solutions and salt bridge; electrons in the wires.
- **Label the polarity** (+ and −) and the **electron flow** (an arrow on the wire from − to +).

6. Define standard electrode potential or standard cell potential (13 questions)

Learn the two definitions as pairs of marks:

- **Standard electrode potential**: the potential difference (voltage) between a half-cell and a standard hydrogen electrode, **plus** the conditions: all ions 1.00 mol dm^{-3} , gases at 101 kPa, 298 K.
- **Standard cell potential**: the potential difference between the two half-cells (electrodes) of a cell, **plus** the same standard conditions.

Variations you will meet: "describe the standard conditions for an ion/ion half-cell" needs both ions at 1.00 mol dm^{-3} (and H^+ if it is in the half-equation), a platinum electrode and 298 K.

7. Polarity of the electrodes and direction of electron flow (12 questions)

1. The electrode with the **more positive** E (or $E^\ominus$) is positive; the other is negative.
2. Electrons flow in the wire **from negative to positive**.
3. Name each electrode by its half-cell, for example "the nickel electrode" or "the Br_2/Br^- (platinum) electrode".

Variations you will meet: after a Nernst correction, compare the new E values, not the $E^\ominus$ values (Example 3). Against the standard hydrogen electrode, a half-cell with positive $E^\ominus$ is the positive electrode and electrons flow from the hydrogen electrode towards it.

8. Nernst equation calculation (11 questions)

1. Write the half-equation as a reduction and note z (the number of electrons).
2. Write $E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{ox}]}{[\text{red}]}$ with the numbers in.
3. For a metal/ion electrode, $[\text{red}]$ is the solid, taken as 1. For ion/ion, put **oxidised on top**.
4. Give E to 2 or 3 significant figures, with its sign.

Variations you will meet:

- **"Show that E is ..."**: write the equation with the numbers in and give the answer to one more significant figure than the printed value.
- **A ratio instead of concentrations** (" $[\text{Fe}^{3+}]$ is 100 times $[\text{Fe}^{2+}]$ "): the log term is just $\log 100$.
- **The question prints its own Nernst expression** (for example with $\log \frac{1}{[\text{Cl}^-]}$, or with $[\text{OH}^-]^2$): use exactly what is printed. Get a concentration first if needed, for example from grams per 100 cm^3 (multiply by 10 for per dm^3 , then divide by M_r), or $[\text{OH}^-] = K_w \div [\text{H}^+]$ from a pH.
- **Then use the new E** to find E_{cell} or to decide which way a reaction now goes.

9. $\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$ (9 questions)

1. Find $E_{\text{cell}}^\ominus$ (it may be given).
2. Find n : the electrons transferred in the balanced equation, or per mole of the species named in the question ("per mole of H_2O_2 " means $n = 2$ if each H_2O_2 gains 2 electrons).
3. $\Delta G^\ominus = -n \times E_{\text{cell}}^\ominus \times 96\,500 \text{ J mol}^{-1}$, then divide by 1000 for kJ mol^{-1} . Keep the minus sign.

Variations you will meet: working backwards from $\Delta G^\ominus$. If $\Delta G^\ominus = -386 \text{ kJ mol}^{-1}$ for a reaction with $n = 4$, then $E_{\text{cell}}^\ominus = \frac{386\,000}{4 \times 96\,500} = 1.00 \text{ V}$; then subtract (or add) a known $E^\ominus$ to find the unknown one.

10. Effect of a concentration change on E , in words (9 questions)

1. Write the half-equation as a reduction.
2. Say which way the equilibrium shifts (Le Chatelier): less oxidised species, or more reduced species, shifts it **left**.

3. Left means E **more negative** (less positive); right means E **more positive**.
4. Then say what that does to E_{cell} : if the **positive** electrode's E falls, E_{cell} falls; if the **negative** electrode's E falls, E_{cell} rises.

Variations you will meet:

- **Dilution** lowers the concentration of every ion in that half-cell.
- **Common-ion effect or precipitation**: adding a salt that shares an ion with a sparingly soluble solid lowers the concentration of the solid's other ion; adding an ion that precipitates one of the half-cell's ions lowers that ion's concentration.
- **pH change**: if H^+ is on the left of the half-equation, raising the pH (less H^+) shifts it left and lowers E .
- **A precipitate can make an "unfeasible" reaction work**: if one product is removed as a solid, its half-cell potential shifts enough to change the sign of E_{cell} .

11. Batteries and fuel cells (9 questions)

1. **Overall reaction from half-equations**: as in type 2, reverse the one with the more negative $E^\ominus$ (the negative electrode), match electrons and add.
2. **Half-equations from an overall reaction**: find the species that is oxidised (its element's oxidation number rises; it is at the negative electrode) and the species reduced. Write each half-equation, balancing with OH^- and H_2O in alkali or H^+ and H_2O in acid.
3. **Fuel cell anode**: write the combustion equation, take away the oxygen half-equation, and what is left is the fuel's half-equation.
4. **Oxidation-state change** of a metal: work out its oxidation number in each compound (for example Ni in $\text{NiO}(\text{OH})$ is +3 and in $\text{Ni}(\text{OH})_2$ is +2).

12. Redox titration calculation (7 questions)

1. Build the ionic equation from the half-equations to get the mole ratio: MnO_4^- gains 5 electrons, $\text{Cr}_2\text{O}_7^{2-}$ gains 6, Fe^{2+} loses 1, $\text{C}_2\text{O}_4^{2-}$ loses 2, so $\text{MnO}_4^- : \text{Fe}^{2+} = 1 : 5$ and $\text{Cr}_2\text{O}_7^{2-} : \text{Fe}^{2+} = 1 : 6$.
2. Moles of titrant = concentration $\times$ volume in dm^3 .
3. Use the ratio to get moles of the other substance in the titrated portion.
4. Scale up to the whole sample (for example $\times 10$ for 25.0 cm^3 taken from 250 cm^3), then find mass, purity or concentration.

Variations you will meet: a **back titration** (excess reagent added, then the leftover titrated): moles reacted = moles added – moles left over. The end-point with manganate(VII) is the first permanent **pale pink**, since MnO_4^- is the only coloured species.

13. Predict electrolysis products (4 questions)

1. Molten: metal at the cathode, non-metal at the anode.

2. Aqueous, **cathode**: the metal if its ion has a more positive $E^\ominus$ than water's reduction (copper, silver); otherwise hydrogen.
3. Aqueous, **anode**: the halogen for iodide and bromide, and for chloride when concentrated; otherwise oxygen.
4. Write each half-equation, with state symbols if asked ($2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$).

14. Avogadro constant by electrolysis (2 questions)

1. State $F = Le$ if asked.
2. $Q = It$ (time in seconds).
3. Number of electrons = $Q \div (1.60 \times 10^{-19})$.
4. Number of atoms = electrons $\div$ charge on the ion (2 for Cu^{2+} or Fe^{2+}).
5. Moles of atoms = mass change $\div A_r$.
6. $L = \text{atoms} \div \text{moles}$.

For example, a silver cathode gains 0.672 g when 0.250 A flows for 40.0 min. $Q = 600 \text{ C}$, so $600 \div 1.60 \times 10^{-19} = 3.75 \times 10^{21}$ electrons, and as Ag^+ needs one electron, 3.75×10^{21} atoms. Moles of silver = $0.672 \div 107.9 = 6.23 \times 10^{-3}$. $L = 3.75 \times 10^{21} \div 6.23 \times 10^{-3} = 6.02 \times 10^{23} \text{ mol}^{-1}$.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

A cell is made from a Ni^{2+}/Ni half-cell and a Br_2/Br^- half-cell, both under standard conditions.

Half-equation	$E^\ominus / \text{V}$
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	−0.25
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.07

- (a) State the material of the electrode in the Br_2/Br^- half-cell. **[1]**
- (b) Calculate $E^\ominus_{\text{cell}}$ and identify the negative electrode. State the direction of electron flow in the external circuit. **[2]**

(c) Write the equation for the cell reaction. **[1]**

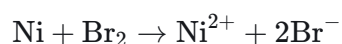
(d) Calculate $\Delta G^\ominus$, in kJ mol^{-1} , for the cell reaction. **[2]**

(a) Platinum. **B1**

(b) $E_{\text{cell}}^\ominus = 1.07 - (-0.25) = +1.32 \text{ V}$. **B1**

The nickel electrode is negative (more negative $E^\ominus$); electrons flow through the wire from the nickel electrode to the platinum electrode. **B1**

(c) Reverse the nickel half-equation ($\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$); both involve 2 electrons, so add:



B1

(d) $n = 2$. **M1** for $\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$ with $n = 2$:

$$\Delta G^\ominus = -2 \times 1.32 \times 96\,500 = -254\,760 \text{ J mol}^{-1} = -255 \text{ kJ mol}^{-1}$$

A1

Example 2

An aqueous solution of silver nitrate is electrolysed with inert electrodes. A current of 0.800 A is passed for 25.0 minutes.

(a) Identify the product at each electrode and write the half-equation for each. **[2]**

(b) Calculate the mass of the product formed at the cathode. **[3]**

(c) Calculate the volume of gas formed at the anode, measured at room conditions. **[1]**

(a) Cathode: silver, since Ag^+ ($E^\ominus = +0.80 \text{ V}$) is reduced more easily than water: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$. **B1**

Anode: oxygen, because nitrate is not oxidised: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. **B1**

(b) $Q = It = 0.800 \times 25.0 \times 60 = 1200 \text{ C}$. **M1**

Moles of electrons = $1200 \div 96\,500 = 0.012\,44 \text{ mol}$ = moles of Ag (one electron per ion). **M1**

Mass of silver = $0.012\,44 \times 107.9 = 1.34 \text{ g}$. **A1**

(c) Moles of $\text{O}_2 = 0.012\,44 \div 4 = 3.109 \times 10^{-3}$; volume = $3.109 \times 10^{-3} \times 24\,000 = 74.6 \text{ cm}^3$. **B1**

Example 3

The standard electrode potentials of lead and tin are very close.

Half-equation	$E^\ominus / \text{V}$
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$	-0.14

(a) A cell is made from standard Pb^{2+}/Pb and Sn^{2+}/Sn half-cells. Calculate $E_{\text{cell}}^\ominus$ and write the equation for the reaction when the cell produces a current. **[2]**

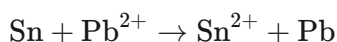
(b) The Pb^{2+}/Pb half-cell is replaced with one in which $[\text{Pb}^{2+}] = 0.0100 \text{ mol dm}^{-3}$. The tin half-cell stays standard.

(i) Use the Nernst equation to calculate the electrode potential of the new lead half-cell. **[2]**

(ii) Calculate E_{cell} and write the equation for the reaction that now occurs. **[2]**

(c) Explain, in terms of the equilibrium at the electrode, why lowering $[\text{Pb}^{2+}]$ changes the electrode potential in this direction. **[1]**

(a) Lead is positive: $E_{\text{cell}}^\ominus = -0.13 - (-0.14) = +0.01 \text{ V}$. **B1**



B1

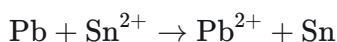
(b)(i) M1 for the Nernst equation with $z = 2$ and $[\text{red}] = 1$:

$$E = -0.13 + \frac{0.059}{2} \log(0.0100) = -0.13 - 0.059 = -0.189 \text{ V}$$

A1

(b)(ii) Now tin (-0.14 V) is the more positive electrode. $E_{\text{cell}} = -0.14 - (-0.189) = +0.049 \text{ V}$. **B1**

The reaction runs the other way:



B1

(c) Lowering $[\text{Pb}^{2+}]$ shifts $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$ to the left, so the lead releases more electrons and its potential becomes more negative. **B1**

Example 4

Hydrazine, N_2H_4 , has been tested as the fuel in a cell for spacecraft. In the cell, hydrazine is converted into nitrogen gas at one electrode, and oxygen is converted into hydroxide ions at the other. The electrolyte is aqueous potassium hydroxide, and $E_{\text{cell}}^\ominus = +1.56 \text{ V}$.



(a) Construct the half-equation for the reaction of hydrazine, and state the change in oxidation number of nitrogen. **[2]**

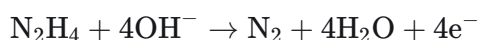
(b) Write the equation for the overall reaction in the cell. **[1]**

(c) Calculate the standard electrode potential of the hydrazine electrode, and state which electrode is negative. **[1]**

(d) Calculate $\Delta G^\ominus$, in kJ, per mole of hydrazine. **[2]**

(e) The cell supplies a current of 0.250 A for 5.00 hours. Calculate the volume of nitrogen produced, in cm^3 , at room conditions. **[3]**

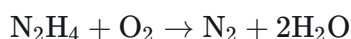
(a) Hydrazine loses electrons (it is the fuel). Balance N, then use OH^- and H_2O because the electrolyte is alkaline, then balance charge with electrons:



B1

Nitrogen goes from -2 to 0 (two N atoms, each losing 2 electrons: 4 in total, which matches). **B1**

(b) Both half-equations involve 4 electrons. Add them and cancel $2\text{H}_2\text{O}$ and 4OH^- :



B1

(c) The oxygen electrode is positive, so $E^\ominus(\text{hydrazine electrode}) = 0.40 - 1.56 = -1.16 \text{ V}$, and the hydrazine electrode is negative. **B1**

(d) Each mole of hydrazine transfers 4 moles of electrons, so $n = 4$. **M1**

$$\Delta G^\ominus = -4 \times 1.56 \times 96\,500 = -602\,160 \text{ J} = -602 \text{ kJ mol}^{-1}$$

A1

(e) $Q = 0.250 \times 5.00 \times 3600 = 4500 \text{ C}$. **M1**

Moles of electrons = $4500 \div 96\,500 = 0.046\,63$; moles of $\text{N}_2 = 0.046\,63 \div 4 = 0.011\,66$. **M1**

Volume = $0.011\,66 \times 24\,000 = 280 \text{ cm}^3$. **A1**

Common mistakes

- **Giving the wrong definition.** Examiners regularly see the definition of standard electrode potential when the question asks for standard cell potential, or either definition without the standard conditions. Learn both, and always add 1.00 mol dm^{-3} , 101 kPa and 298 K .
- **Cell diagrams that can't work.** Common faults: a cell (battery) symbol instead of a voltmeter, a salt bridge or electrode that doesn't reach the liquid, no liquid level drawn, no platinum label, no hydrogen supply for the hydrogen electrode, and an iron (or other metal) electrode in an $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell. Draw the liquid level and make it touch both the electrode and the salt bridge.

- **Electrons flowing the wrong way.** They go through the wire from the negative electrode (more negative E) to the positive one, never through the salt bridge.
- **Multiplying $E^\ominus$ by the coefficients** in the balanced equation. $E^\ominus$ never changes when a half-equation is doubled.
- **Nernst ratio upside down.** Oxidised species go on **top**. Swapping them gives a change of the right size in the wrong direction, a common wrong answer in examiner reports. Also check z : it is the number of electrons in the half-equation.
- **Using the old $E^\ominus$ after a Nernst calculation**, or keeping the reaction the "standard" way round when the new E values have swapped order.
- **$\Delta G^\ominus$ slips:** forgetting n , using the wrong n for "per mole of X", leaving the answer in J when kJ is asked, or losing the minus sign.
- **Minutes and hours in $Q = It$.** Time must be in seconds.
- **Missing the "electrons per particle" factor.** Dividing by 2 for Cu^{2+} , 3 for Al^{3+} and 4 for O_2 is the step most often left out, especially when counting atoms for the Avogadro constant.
- **Explaining a concentration effect without the equilibrium.** "The concentration decreases so E decreases" is not enough: say which way the equilibrium shifts and why that changes E .
- **Saying a reaction is feasible without evidence.** Quote the two $E^\ominus$ values or $E_{\text{cell}}^\ominus$ and its sign.

How to get the marks

- **Cell potentials:** one mark, for the value with its sign and unit. Show the subtraction; it earns method credit if a value is misread.
- **Equations:** any correct multiple is accepted, but electrons must not appear in a full equation, and atoms and charges must balance. State symbols only when asked (they are required in some half-equations).
- **Feasibility and "explain":** name the relevant $E^\ominus$ values, compare them (or give $E_{\text{cell}}^\ominus$ as positive or negative) and then conclude. The conclusion alone scores nothing.
- **Diagrams:** marks are typically for (1) salt bridge, voltmeter and a complete circuit, and (2) correct electrode and solution in each half-cell. Label every substance.
- **Nernst:** one mark for the expression with the numbers in (correct z , oxidised over reduced), one for the answer, usually to at least 2 significant figures. For "show that", give one more figure than the printed value.
- **$\Delta G^\ominus$:** one mark for $-nE_{\text{cell}}^\ominus F$ with the right n , one for the value in the unit asked.
- **Electrolysis calculations:** marks go to each link of the chain (charge, moles of electrons, moles of product, answer), so set them out on separate lines. Wrong earlier numbers still earn later marks if used correctly. Give the answer to the number of significant figures asked, often 3.
- **"Suggest"** means apply the ideas to an unfamiliar case (a new battery or a new complex). **"Deduce"** means work it out from the data given, so use that data.
- **Concentration effects:** state the direction of change **and** the reason (the equilibrium shift).

Quick check

1. Describe the half-cell you would connect to a standard hydrogen electrode to measure $E^\ominus$ for $\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$.
2. Use $E^\ominus$ values to decide whether acidified dichromate(VI) can oxidise (a) bromide ions and (b) chloride ions under standard conditions. Write an equation for any reaction. $E^\ominus$: $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} +1.33\text{ V}$; $\text{Br}_2/\text{Br}^- +1.07\text{ V}$; $\text{Cl}_2/\text{Cl}^- +1.36\text{ V}$.
3. For $\text{Mn}^{3+} + \text{e}^- \rightleftharpoons \text{Mn}^{2+}$, $E^\ominus = +1.49\text{ V}$. Calculate E when $[\text{Mn}^{3+}] = 0.0050\text{ mol dm}^{-3}$ and $[\text{Mn}^{2+}] = 0.50\text{ mol dm}^{-3}$.
4. A steel object is plated with chromium from a solution of Cr^{3+} ions using a current of 1.20 A . How long, in minutes, does it take to deposit 0.260 g of chromium? (A_r : Cr 52.0)
5. 25.0 cm^3 of a solution of iron(II) ions reacts with 21.60 cm^3 of $0.0200\text{ mol dm}^{-3}$ acidified potassium dichromate(VI). Calculate $[\text{Fe}^{2+}]$.

Answers

1. A platinum electrode dipping into an aqueous solution that is 1.00 mol dm^{-3} in both bromine and bromide ions (for example from KBr), at 298 K, joined to the hydrogen electrode by a salt bridge and a high-resistance voltmeter.
2. (a) $E_{\text{cell}}^{\ominus} = 1.33 - 1.07 = +0.26 \text{ V}$, so yes: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Br}^- \rightarrow 2\text{Cr}^{3+} + 3\text{Br}_2 + 7\text{H}_2\text{O}$. (b) $E_{\text{cell}}^{\ominus} = 1.33 - 1.36 = -0.03 \text{ V}$, so no reaction under standard conditions.
3. $z = 1$: $E = 1.49 + 0.059 \log \frac{0.0050}{0.50} = 1.49 + 0.059 \times (-2) = +1.37 \text{ V}$.
4. Moles of Cr = $0.260 \div 52.0 = 0.00500$; moles of electrons = $3 \times 0.00500 = 0.0150$; $Q = 0.0150 \times 96500 = 1447.5 \text{ C}$; $t = 1447.5 \div 1.20 = 1206 \text{ s} = 20.1 \text{ minutes}$.
5. Moles of $\text{Cr}_2\text{O}_7^{2-} = 0.0200 \times 0.02160 = 4.32 \times 10^{-4}$. Ratio 1 : 6, so moles of $\text{Fe}^{2+} = 2.592 \times 10^{-3}$. $[\text{Fe}^{2+}] = 2.592 \times 10^{-3} \div 0.0250 = 0.104 \text{ mol dm}^{-3}$.

Past questions to try

- **9701/43/M/J/24 Q4**: define $E^{\ominus}$, draw the cell to measure it, and a concentration change in words.
- **9701/42/O/N/22 Q3**: a cell diagram, polarity, $E_{\text{cell}}^{\ominus}$, the cell equation and an electrolysis calculation.
- **9701/43/O/N/23 Q3**: $E_{\text{cell}}^{\ominus}$, $\Delta G^{\ominus}$ per mole, and a Nernst calculation that reverses a reaction.
- **9701/42/M/J/22 Q5**: electrolysis products and measuring the Avogadro constant.