

Redox reactions and electrolysis: AS Chemistry notes

These notes cover redox and electrolysis for Cambridge International AS and A Level Chemistry (9701). They start with oxidation numbers, the tool that makes every other part of the topic easier, then move on to describing redox reactions, balancing equations, disproportionation and finally electrolysis, including the three big industrial examples and Faraday calculations. Learn the boxed definitions word for word.

1. Oxidation numbers

1.1 What an oxidation number is

An oxidation number is a number given to each atom in a substance to show how many electrons it has lost or gained (or shares unequally) compared with the uncombined element. In an ionic compound it equals the charge on the ion. In a covalent compound we pretend that each shared pair belongs completely to the more electronegative atom, and the oxidation number is the charge the atom would then carry.

Oxidation number: the charge an atom would have if all of its bonds were fully ionic. A positive oxidation number means the atom has lost electrons (or electron density); a negative oxidation number means it has gained them.

Always write the sign in front of the number, for example +3 or -2. This distinguishes an oxidation number from an ionic charge, which is written with the number first (Fe^{3+}).

1.2 The rules

Apply these rules in order. A rule higher in the list wins if two rules disagree.

1. An atom in an uncombined element has oxidation number 0. This applies to Na, Fe, H_2 , O_2 , Cl_2 , S_8 and P_4 .
2. For a simple (monatomic) ion, the oxidation number equals the charge on the ion: Na^+ is +1, Cl^- is -1, Al^{3+} is +3.
3. The oxidation numbers in a neutral compound add up to 0. In a polyatomic ion they add up to the charge on the ion.
4. Fluorine is always -1 in its compounds, because it is the most electronegative element.
5. Group 1 metals are always +1 and Group 2 metals are always +2 in their compounds. Aluminium is +3.
6. Hydrogen is +1, except in metal hydrides such as NaH and CaH_2 , where it is -1.
7. Oxygen is -2, except in peroxides such as H_2O_2 and Na_2O_2 (-1) and in OF_2 (+2, because fluorine wins).
8. Chlorine, bromine and iodine are -1, except when combined with oxygen or with a more electronegative halogen, when they take positive values.



Worked example 1: oxidation numbers in ions and compounds

- (a) S in H_2SO_4 : $2(+1) + \text{S} + 4(-2) = 0$, so $\text{S} = +6$.
- (b) Cr in $\text{Cr}_2\text{O}_7^{2-}$: $2\text{Cr} + 7(-2) = -2$, so $2\text{Cr} = +12$ and $\text{Cr} = +6$.
- (c) Mn in MnO_4^- : $\text{Mn} + 4(-2) = -1$, so $\text{Mn} = +7$.
- (d) N in NH_4^+ : $\text{N} + 4(+1) = +1$, so $\text{N} = -3$.
- (e) S in $\text{S}_4\text{O}_6^{2-}$: $4\text{S} + 6(-2) = -2$, so $4\text{S} = +10$ and $\text{S} = +2.5$. A fractional value is an average: the four sulfur atoms are not all in the same environment.

1.3 Using oxidation numbers in names

Where an element can have more than one oxidation number, the name shows it as a Roman numeral in brackets. For a metal ion, the numeral follows the metal: iron(II) sulfate contains Fe^{2+} , iron(III) chloride contains Fe^{3+} . For an oxoanion, the numeral follows the anion name and refers to the central atom.

Ion	Oxidation number of central atom	Systematic name
ClO^-	$\text{Cl} = +1$	chlorate(I)
ClO_3^-	$\text{Cl} = +5$	chlorate(V)
NO_2^-	$\text{N} = +3$	nitrate(III)
NO_3^-	$\text{N} = +5$	nitrate(V)
SO_3^{2-}	$\text{S} = +4$	sulfate(IV)
SO_4^{2-}	$\text{S} = +6$	sulfate(VI)
MnO_4^-	$\text{Mn} = +7$	manganate(VII)
$\text{Cr}_2\text{O}_7^{2-}$	$\text{Cr} = +6$	dichromate(VI)

So NaClO is sodium chlorate(I), KMnO_4 is potassium manganate(VII) and Na_2SO_3 is sodium sulfate(IV).

2. Redox in terms of electrons and oxidation number

2.1 Definitions

Redox means reduction and oxidation happening together. Electrons lost by one species must be gained by another, so one cannot happen without the other.

Oxidation is the loss of electrons, or an increase in oxidation number.

Reduction is the gain of electrons, or a decrease in oxidation number.

An oxidising agent (oxidant) is a species that oxidises another species by accepting electrons from it. The oxidising agent is itself reduced.

A reducing agent (reductant) is a species that reduces another species by giving electrons to it.

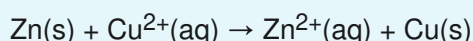
The reducing agent is itself oxidised.

The electron definition and the oxidation number definition always agree. If an atom loses electrons, its oxidation number rises by the number of electrons lost. The oxidation number definition is more useful for covalent reactions, where no full electron transfer takes place, for example in the combustion of methane (C goes from -4 in CH_4 to $+4$ in CO_2).

2.2 Identifying redox in an equation

Write the oxidation number above each element on both sides. Any element whose number changes has been oxidised or reduced. If no oxidation numbers change, the reaction is not redox. Precipitation and acid-base neutralisation reactions are not redox.

Worked example 2: identifying the oxidising and reducing agents



Zn: $0 \rightarrow +2$. Zinc loses two electrons, so zinc is oxidised. Zinc is the reducing agent.

Cu: $+2 \rightarrow 0$. Copper(II) ions gain two electrons, so they are reduced. Cu^{2+} is the oxidising agent.

Exam tip: name the species exactly as it appears in the equation. Say " Cu^{2+} ions are the oxidising agent", not "copper is the oxidising agent".

2.3 Half-equations

A half-equation shows either the oxidation or the reduction on its own, with electrons written in. Each half-equation must balance for atoms and for charge.

- Oxidation: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- Reduction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- Oxidation of halide: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
- Reduction of halogen: $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$

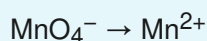
3. Balancing redox equations

There are two reliable methods. Use whichever the question suggests; if it does not suggest one, the half-equation method is safer for reactions in aqueous solution.

3.1 Building a half-equation in acidic solution

1. Balance the atoms of the element that changes oxidation number.
2. Balance oxygen by adding H_2O to the side that needs oxygen.
3. Balance hydrogen by adding H^+ to the side that needs hydrogen.
4. Balance charge by adding electrons to the more positive side.
5. Check: the number of electrons should equal the total change in oxidation number.

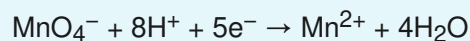
Worked example 3: the manganate(VII) half-equation



Mn is already balanced. Add $4\text{H}_2\text{O}$ to the right for the oxygen: $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

Add 8H^+ to the left for the hydrogen: $\text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

Charge on left: $-1 + 8 = +7$. Charge on right: $+2$. Add 5e^- to the left:



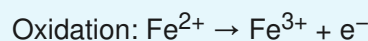
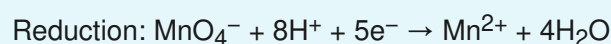
Check: Mn goes from $+7$ to $+2$, a change of 5, matching the 5 electrons.

The dichromate(VI) half-equation is built the same way: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$. Each of the two chromium atoms falls from $+6$ to $+3$, so six electrons are needed in total.

3.2 Combining half-equations

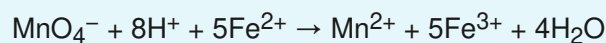
Multiply one or both half-equations so that the electrons lost equal the electrons gained, then add them and cancel anything that appears on both sides. Electrons must never appear in the final equation.

Worked example 4: manganate(VII) oxidising iron(II)



Multiply the oxidation by 5 so that 5 electrons are released: $5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + 5\text{e}^-$

Add and cancel the electrons:



Check charge: left = $-1 + 8 + 10 = +17$; right = $+2 + 15 = +17$. Balanced.

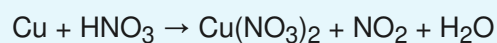
This 1 : 5 ratio is the basis of manganate(VII) titrations for iron.

3.3 The oxidation number method

This method is quicker for reactions written with full formulae.

1. Find the elements whose oxidation numbers change and write the change for each.
2. Choose multipliers so that the total increase equals the total decrease.
3. Put these numbers in front of the species that change.
4. Balance the remaining atoms (often spectator ions, then H and O) by inspection.

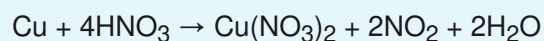
Worked example 5: copper with concentrated nitric acid



Cu: $0 \rightarrow +2$, an increase of 2. N: $+5$ in $\text{HNO}_3 \rightarrow +4$ in NO_2 , a decrease of 1.

So 2 NO_2 are formed for every Cu: $\text{Cu} + ? \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + ? \text{H}_2\text{O}$

Nitrogen on the right: 2 in $\text{Cu}(\text{NO}_3)_2 + 2$ in $\text{NO}_2 = 4$, so 4HNO_3 . Hydrogen: 4 on the left, so $2\text{H}_2\text{O}$.



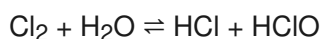
Check oxygen: left 12; right $6 + 4 + 2 = 12$. Balanced. Notice that only two of the four nitric acid molecules are reduced; the other two simply provide nitrate ions.

4. Disproportionation

Disproportionation is a redox reaction in which the same element in the same species is simultaneously oxidised and reduced.

To prove that a reaction is disproportionation, show one element starting at a single oxidation number and ending at two different ones, one higher and one lower.

4.1 Chlorine and water



Chlorine goes from 0 to -1 in HCl (reduced) and from 0 to $+1$ in HClO, chloric(I) acid (oxidised). Chloric(I) acid is the species that kills bacteria in water treatment.

4.2 Chlorine and cold dilute sodium hydroxide



Chlorine goes from 0 to -1 (NaCl) and from 0 to $+1$ (NaClO, sodium chlorate(I)). The resulting solution is household bleach.

4.3 Chlorine and hot concentrated sodium hydroxide



Chlorine goes from 0 to -1 (NaCl) and from 0 to $+5$ (NaClO₃, sodium chlorate(V)). The ratio 5 : 1 follows directly from oxidation numbers: five chlorine atoms each gain one electron to balance one chlorine atom that loses five.

4.4 Other examples

- Hydrogen peroxide decomposing: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. Oxygen goes from -1 to -2 and from -1 to 0.
- Copper(I) ions in aqueous solution: $2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$. Copper goes from $+1$ to 0 and from $+1$ to $+2$.

5. Electrolysis: the basic ideas

5.1 Key terms

Electrolysis is the decomposition of an ionic compound, when molten or in aqueous solution, by passing an electric current through it.

Electrolyte: a molten ionic compound or a solution containing ions that conducts electricity and is decomposed by it.

Anode: the positive electrode, where oxidation takes place.

Cathode: the negative electrode, where reduction takes place.

A useful memory aid: "An Ox, Red Cat", meaning anode oxidation, reduction cathode.

In the external circuit, current is carried by electrons moving through the wires. In the electrolyte, current is carried by moving ions: cations (positive) move to the cathode, anions (negative) move to the anode. A solid ionic compound does not conduct because its ions are fixed in the lattice.

Inert electrodes, usually graphite or platinum, take no part in the reaction. Active electrodes, such as copper in copper(II) sulfate solution, can themselves be oxidised at the anode.

5.2 Electrolysis of molten compounds

A molten binary ionic compound contains only one kind of cation and one kind of anion, so the products are easy to predict: the metal forms at the cathode and the non-metal at the anode.

Worked example 6: molten lead(II) bromide with graphite electrodes

Cathode (reduction): $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$. Molten lead collects at the bottom.

Anode (oxidation): $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$. Brown bromine vapour is seen.

Overall: $\text{PbBr}_2 \rightarrow \text{Pb} + \text{Br}_2$

In the same way, molten sodium chloride gives sodium at the cathode ($\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$) and chlorine at the anode ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$).

6. Electrolysis of aqueous solutions

6.1 Why aqueous solutions are different

Water is very slightly ionised: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. An aqueous electrolyte therefore contains at least two cations (the metal ion and H^+) and at least two anions (the non-metal ion and OH^-). At each electrode only one of them is discharged, and which one depends on how easily each is reduced or oxidised and on concentration. Water molecules themselves can also be reduced or oxidised directly; the products are the same.

6.2 At the cathode

- If the metal is less reactive than hydrogen (for example copper or silver), the metal is deposited: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$; $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$.
- If the metal is more reactive than hydrogen (for example sodium, potassium, magnesium, calcium, aluminium), hydrogen gas is given off instead: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, or written with water, $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$.

The second form explains why the solution around the cathode becomes alkaline: hydroxide ions are left behind. At A Level you will meet the full explanation in terms of standard electrode potentials, $E^\ominus$: the species with the more positive reduction potential is reduced. (Metals near hydrogen, such as zinc and lead, can be deposited from concentrated solutions; questions will tell you if this is expected.)

6.3 At the anode (inert electrodes)

- If a halide is present in reasonable concentration, the halogen is formed: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$; $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$; $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$.
- If there is no halide (sulfate, nitrate) or the chloride is very dilute, oxygen is given off: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$, or written with water, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$.

The second form explains why the solution around the anode becomes acidic when oxygen is released. Sulfate and nitrate ions are not discharged in aqueous solution.

6.4 The effect of concentration with chloride ions

With concentrated sodium chloride solution, the main product at the anode is chlorine. With very dilute sodium chloride solution, the main product is oxygen. In between, a mixture forms. The higher the concentration of Cl^- ions, the more they are favoured for discharge.

6.5 Summary of common examples (inert electrodes unless stated)

Electrolyte	Cathode product	Anode product	What is left in solution
dilute $\text{H}_2\text{SO}_4(\text{aq})$	H_2	O_2	more concentrated H_2SO_4 (water is used up)
concentrated $\text{NaCl}(\text{aq})$	H_2	Cl_2	$\text{NaOH}(\text{aq})$
$\text{CuSO}_4(\text{aq})$	Cu	O_2	$\text{H}_2\text{SO}_4(\text{aq})$; blue colour fades
$\text{CuSO}_4(\text{aq})$, copper electrodes	Cu	anode dissolves as Cu^{2+}	$\text{CuSO}_4(\text{aq})$, unchanged concentration
$\text{CuCl}_2(\text{aq})$, concentrated	Cu	Cl_2	water; solution becomes paler
$\text{AgNO}_3(\text{aq})$	Ag	O_2	$\text{HNO}_3(\text{aq})$

Worked example 7: dilute sulfuric acid

Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

For every 4 electrons, 2 mol H_2 and 1 mol O_2 form, so the volume of hydrogen is twice the volume of oxygen. Overall the reaction is $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, the electrolysis of water.

7. Electrolysis of brine: the diaphragm cell

Brine is concentrated aqueous sodium chloride. Its electrolysis is one of the largest-scale chemical processes because it makes three useful products at once: chlorine, hydrogen and sodium hydroxide.

7.1 The cell

- Anode: titanium (coated), which resists attack by chlorine.
- Cathode: steel mesh.
- Diaphragm: a porous barrier between the anode and cathode compartments, traditionally asbestos, now usually a polymer-based material. It lets solution flow through but keeps the gases apart.
- Brine is fed into the anode compartment. Its level is kept higher on the anode side, so liquid flows steadily through the diaphragm from the anode side to the cathode side.

7.2 The electrode reactions

Anode (oxidation): $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

Cathode (reduction): $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

Overall: $2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) + 2\text{NaOH}(\text{aq})$

7.3 Why the diaphragm matters

- It keeps hydrogen and chlorine apart. A mixture of the two can react explosively, especially in light.
- The flow of liquid from anode to cathode stops hydroxide ions moving back to the anode compartment. If chlorine met hydroxide ions, it would disproportionate to chlorate(I) and chloride (section 4.2), wasting product and contaminating the solution.

7.4 The sodium hydroxide product

The liquid leaving the cathode compartment is a fairly dilute solution of sodium hydroxide that still contains a lot of unreacted sodium chloride. It is concentrated by evaporation; most of the sodium chloride, being less soluble, crystallises out and is recycled. The final sodium hydroxide still contains a little chloride. Modern plants increasingly use the membrane cell instead, in which an ion-exchange membrane lets only Na^+ ions through, giving purer sodium hydroxide.

8. Extraction of aluminium

Aluminium is too reactive to be extracted by reduction with carbon, so it is extracted by electrolysis.

8.1 The process

- The ore, bauxite, is purified to give aluminium oxide, Al_2O_3 (alumina).
- Aluminium oxide melts at over 2000°C . To save energy it is dissolved in molten cryolite, Na_3AlF_6 , which allows the cell to run at roughly 950°C .
- The cell is a steel tank lined with carbon (graphite), which acts as the cathode. Large carbon blocks dipping into the electrolyte act as the anodes.

8.2 The electrode reactions

Cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$. Molten aluminium sinks to the bottom and is tapped off.

Anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$

Overall: $2\text{Al}_2\text{O}_3 \rightarrow 4\text{Al} + 3\text{O}_2$

8.3 Why the anodes must be replaced

At the high temperature of the cell, the oxygen formed at the anode reacts with the carbon anodes: $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ (some carbon monoxide also forms). The anodes therefore burn away and are replaced regularly. This is one of the main running costs, along with the very large amount of electrical energy needed.

Exam tip: three marks often come from three separate points: cryolite lowers the operating temperature (energy saving), the anodes are oxidised to CO_2 (so replaced), and the large current makes electricity the major cost. Keep them as separate sentences.

9. Purification of copper

Copper used for electrical wiring must be very pure, because impurities increase its resistance. Copper made by smelting is purified by electrolysis.

9.1 The cell

- Anode: a block of impure copper.
- Cathode: a thin sheet of pure copper.
- Electrolyte: copper(II) sulfate solution acidified with dilute sulfuric acid.

9.2 The electrode reactions

Anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$. The impure anode gets smaller.

Cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$. Pure copper builds up on the cathode.

9.3 What happens to the impurities

- Metals more reactive than copper, such as zinc, iron and nickel, are oxidised at the anode and go into solution as ions (for example $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$). They stay in solution because they are harder to reduce than Cu^{2+} , so they are not deposited at the cathode.
- Metals less reactive than copper, such as silver, gold and platinum, are not oxidised. They fall to the bottom of the cell as anode sludge (anode slime), which is collected and is a valuable source of these metals.

Because some of the electrons released at the anode come from impurity metals rather than copper, slightly less copper dissolves than is deposited. The concentration of Cu^{2+} in the electrolyte therefore falls slowly over time, and the electrolyte must be topped up or replaced.

10. Faraday calculations

10.1 Charge, current and the Faraday constant

$Q = I \times t$, where Q is charge in coulombs (C), I is current in amperes (A) and t is time in seconds (s).

The Faraday constant, F , is the charge carried by one mole of electrons. $F = 9.65 \times 10^4 \text{ C mol}^{-1}$.

$F = L \times e$, where L is the Avogadro constant and e is the charge on one electron.

Use the values given on your data sheet: $F = 9.65 \times 10^4 \text{ C mol}^{-1}$, $L = 6.02 \times 10^{23} \text{ mol}^{-1}$, $e = 1.60 \times 10^{-19} \text{ C}$. Check the current data booklet in case more significant figures are given.

10.2 The method

1. Convert time to seconds.
2. Calculate charge: $Q = I \times t$.
3. Calculate moles of electrons: $n(\text{e}^-) = Q \div F$.
4. Use the half-equation to convert moles of electrons into moles of product.
5. Convert to mass ($\times M$) or gas volume ($\times 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room temperature and pressure).

Run the method backwards to find a time or a current from a mass.

Worked example 8: mass of copper deposited

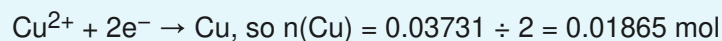
A current of 2.00 A is passed through copper(II) sulfate solution for 30.0 minutes. Calculate the

mass of copper deposited at the cathode. (A_r : Cu = 63.5)

$$t = 30.0 \times 60 = 1800 \text{ s}$$

$$Q = 2.00 \times 1800 = 3600 \text{ C}$$

$$n(e^-) = 3600 \div 96\,500 = 0.03731 \text{ mol}$$



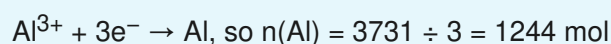
$$\text{mass} = 0.01865 \times 63.5 = 1.18 \text{ g}$$

Worked example 9: mass of aluminium per hour

An aluminium cell runs at $1.00 \times 10^5 \text{ A}$. Calculate the mass of aluminium produced in one hour. (A_r : Al = 27.0)

$$Q = 1.00 \times 10^5 \times 3600 = 3.60 \times 10^8 \text{ C}$$

$$n(e^-) = 3.60 \times 10^8 \div 96\,500 = 3731 \text{ mol}$$



$$\text{mass} = 1244 \times 27.0 = 3.36 \times 10^4 \text{ g} = 33.6 \text{ kg}$$

Worked example 10: finding the Avogadro constant by experiment

A student electrolyses copper(II) sulfate solution using copper electrodes. A steady current of 0.500 A flows for 40.0 minutes and the anode loses 0.395 g. Calculate a value for the Avogadro constant. (A_r : Cu = 63.5; $e = 1.60 \times 10^{-19} \text{ C}$)

$$Q = 0.500 \times 2400 = 1200 \text{ C}$$

$$n(\text{Cu}) = 0.395 \div 63.5 = 6.22 \times 10^{-3} \text{ mol}, \text{ so } n(e^-) = 2 \times 6.22 \times 10^{-3} = 1.244 \times 10^{-2} \text{ mol}$$

$$\text{Charge per mole of electrons (an experimental } F) = 1200 \div 1.244 \times 10^{-2} = 9.65 \times 10^4 \text{ C mol}^{-1}$$

$$\text{Number of electrons in } 1200 \text{ C} = 1200 \div 1.60 \times 10^{-19} = 7.50 \times 10^{21}$$

$$L = 7.50 \times 10^{21} \div 1.244 \times 10^{-2} = 6.03 \times 10^{23} \text{ mol}^{-1}$$

Exam tip: the most common error is forgetting step 4. Always write the half-equation and read the electron ratio from it: 1 for Ag and Na, 2 for Cu, H_2 and Cl_2 , 3 for Al, 4 for O_2 .

Quick check

- State the oxidation number of the named element in each of the following: (a) S in $\text{Na}_2\text{S}_2\text{O}_3$ (b) Mn in K_2MnO_4 (c) N in N_2H_4 (d) O in OF_2 (e) H in LiAlH_4 . [5]
- Give the systematic names, including oxidation numbers, of (a) NaClO_3 (b) KNO_2 (c) $\text{Fe}_2(\text{SO}_4)_3$. [3]
- Iron(III) ions react with iodide ions: $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$. Identify the oxidising agent and explain your answer in terms of both electrons and oxidation numbers. [3]
- Acidified dichromate(VI) ions oxidise iron(II) ions to iron(III) ions and are reduced to

- chromium(III) ions. Write the two half-equations and hence the balanced ionic equation. [3]
- Use oxidation numbers to balance this equation: $\text{H}_2\text{S} + \text{SO}_2 \rightarrow \text{S} + \text{H}_2\text{O}$. [2]
 - In acidic solution, manganate(VII) ions oxidise hydrogen peroxide to oxygen and are reduced to Mn^{2+} . The half-equation for hydrogen peroxide is $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$. Construct the overall ionic equation. [2]
 - Chlorine reacts with hot concentrated aqueous sodium hydroxide. (a) Write the equation. (b) Explain, using oxidation numbers, why this reaction is described as disproportionation. [3]
 - Predict the product at each electrode, and write the half-equations, for the electrolysis of (a) molten potassium bromide (b) aqueous silver nitrate with inert electrodes. [4]
 - Brine is electrolysed in a diaphragm cell. (a) Write the equation for the reaction at each electrode. (b) Explain two reasons why the diaphragm is needed and why the brine level is kept higher on the anode side. [5]
 - (a) Explain why aluminium oxide is dissolved in molten cryolite and why the anodes must be replaced regularly. (b) A cell runs at $1.50 \times 10^5 \text{ A}$ for 24.0 hours. Calculate the mass of aluminium produced, in tonnes. ($F = 9.65 \times 10^4 \text{ C mol}^{-1}$; $A_r: \text{Al} = 27.0$) [6]
 - (a) Describe what happens to zinc and silver impurities during the electrolytic purification of copper, and explain why the concentration of Cu^{2+} in the electrolyte slowly falls. (b) Calculate the time, in minutes, needed to deposit 5.00 g of copper at the cathode using a current of 3.00 A. ($A_r: \text{Cu} = 63.5$) [6]
 - Dilute sulfuric acid is electrolysed with platinum electrodes using a current of 0.800 A for 25.0 minutes. Calculate the volume of each gas produced, in cm^3 , at room temperature and pressure. (Molar gas volume = $24.0 \text{ dm}^3 \text{ mol}^{-1}$) [4]

- (a) $2(+1) + 2\text{S} + 3(-2) = 0$, so $2\text{S} = +4$ and $\text{S} = +2$. (b) $2(+1) + \text{Mn} + 4(-2) = 0$, so $\text{Mn} = +6$. (c) $2\text{N} + 4(+1) = 0$, so $\text{N} = -2$. (d) Fluorine is always -1 , so $\text{O} + 2(-1) = 0$ and $\text{O} = +2$. (e) $\text{Li} = +1$ and $\text{Al} = +3$, so $1 + 3 + 4\text{H} = 0$, $4\text{H} = -4$ and $\text{H} = -1$ (a hydride).
- (a) $\text{Cl}: +1 + \text{Cl} + 3(-2) = 0$, $\text{Cl} = +5$: sodium chlorate(V). (b) $\text{N}: +1 + \text{N} + 2(-2) = 0$, $\text{N} = +3$: potassium nitrate(III). (c) $\text{Fe}: 2\text{Fe} + 3(-2) = 0$, $\text{Fe} = +3$; S in sulfate is $+6$: iron(III) sulfate(VI).
- Fe^{3+} is the oxidising agent. Each Fe^{3+} ion gains one electron ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$), taking it from an iodide ion, and its oxidation number falls from $+3$ to $+2$, so Fe^{3+} is reduced. In doing so it oxidises I^- : iodine's oxidation number rises from -1 to 0 as each iodide ion loses an electron.
- Reduction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$. Oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$, multiplied by 6. Overall: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$. Charge check: left $-2 + 14 + 12 = +24$; right $6 + 18 = +24$.
- S in H_2S : $-2 \rightarrow 0$, an increase of 2. S in SO_2 : $+4 \rightarrow 0$, a decrease of 4. So two H_2S are needed for each SO_2 . That gives 3 S atoms in total, and 4 H atoms make $2\text{H}_2\text{O}$: $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$. Check O: 2 on each side.
- Reduction half-equation: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$. To match electrons, multiply this by 2 (10e^-) and the peroxide half-equation by 5 (10e^-): $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{H}_2\text{O}_2 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2 + 10\text{H}^+$. Cancel 10H^+ : $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2$. Check charge: left $-2 + 6 = +4$; right $+4$.
- (a) $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$. (b) All chlorine starts at 0 in Cl_2 . Five chlorine

atoms are reduced to -1 in NaCl and one is oxidised to $+5$ in NaClO_3 . The same element in the same species is both oxidised and reduced, which is disproportionation. (Total decrease $5 \times 1 = 5$ equals total increase $1 \times 5 = 5$.)

8. (a) Molten KBr contains only K^+ and Br^- . Cathode: $\text{K}^+ + \text{e}^- \rightarrow \text{K}$ (potassium). Anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$ (bromine). (b) Cathode: silver is less reactive than hydrogen, so $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ (silver deposited). Anode: nitrate is not discharged, so oxygen forms: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ (or $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$).

9. (a) Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$. Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. (b) The diaphragm keeps hydrogen and chlorine apart, because a mixture of them can explode. It also keeps chlorine away from the sodium hydroxide formed at the cathode; otherwise chlorine would react with hydroxide ions ($\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$), losing chlorine and contaminating the product. The higher level on the anode side makes the liquid flow from anode to cathode through the diaphragm, so OH^- ions cannot migrate back to the anode.

10. (a) Aluminium oxide has a very high melting point (over 2000°C). Dissolving it in molten cryolite gives an electrolyte that is molten at about 950°C , saving a large amount of energy. Oxygen is formed at the hot carbon anodes and reacts with them, $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, so the anodes burn away and must be replaced. (b) $t = 24.0 \times 3600 = 86\,400\text{ s}$. $Q = 1.50 \times 10^5 \times 86\,400 = 1.296 \times 10^{10}\text{ C}$. $n(\text{e}^-) = 1.296 \times 10^{10} \div 96\,500 = 1.343 \times 10^5\text{ mol}$. $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$, so $n(\text{Al}) = 1.343 \times 10^5 \div 3 = 4.477 \times 10^4\text{ mol}$. Mass = $4.477 \times 10^4 \times 27.0 = 1.21 \times 10^6\text{ g} = 1.21\text{ tonnes}$.

11. (a) Zinc is more reactive than copper, so it is oxidised at the anode ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$) and its ions stay in solution; they are not deposited at the cathode because Cu^{2+} is reduced in preference. Silver is less reactive than copper, so it is not oxidised; it falls off the anode as anode sludge. Some of the electrons supplied at the anode come from oxidising impurities such as zinc, but all the electrons at the cathode deposit copper. So more Cu^{2+} is removed at the cathode than is added at the anode, and $[\text{Cu}^{2+}]$ falls. (b) $n(\text{Cu}) = 5.00 \div 63.5 = 0.07874\text{ mol}$. $n(\text{e}^-) = 2 \times 0.07874 = 0.1575\text{ mol}$. $Q = 0.1575 \times 96\,500 = 1.520 \times 10^4\text{ C}$. $t = Q \div I = 1.520 \times 10^4 \div 3.00 = 5066\text{ s} = 84.4\text{ minutes}$.

12. $t = 25.0 \times 60 = 1500\text{ s}$. $Q = 0.800 \times 1500 = 1200\text{ C}$. $n(\text{e}^-) = 1200 \div 96\,500 = 0.01244\text{ mol}$. Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, so $n(\text{H}_2) = 0.01244 \div 2 = 6.22 \times 10^{-3}\text{ mol}$; volume = $6.22 \times 10^{-3} \times 24\,000 = 149\text{ cm}^3$ of hydrogen. Anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, so $n(\text{O}_2) = 0.01244 \div 4 = 3.11 \times 10^{-3}\text{ mol}$; volume = $3.11 \times 10^{-3} \times 24\,000 = 74.6\text{ cm}^3$ of oxygen. The $2 : 1$ ratio matches the formula of water.