

Cambridge AS & A Level · Chemistry 9701 · Notes

Electrochemistry

AS

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Read first: Atoms, molecules and stoichiometry, Chemical bonding

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What you need to know

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

1. **Work out the oxidation number of an element** in any compound or ion, using a short set of rules.
2. **Use changes in oxidation number to balance equations**: the total increase in oxidation number must equal the total decrease.
3. **Explain and use the words redox, oxidation, reduction and disproportionation**, both in terms of electrons (lost or gained) and in terms of oxidation numbers (going up or down).
4. **Explain and use the terms oxidising agent and reducing agent**, and pick them out in an equation.
5. **Read and write Roman numerals in names**, such as iron(III) chloride or potassium manganate(VII), where the numeral is the oxidation number of one element.

This is the AS part of electrochemistry. Electrolysis, electrode potentials, cells and the Nernst equation are the A Level topic (Electrochemistry, section 24 of the syllabus), not this one.

Understand it

Oxidation and reduction as electron transfer

When magnesium is dropped into copper(II) sulfate solution, the blue colour fades and copper appears. Each magnesium atom gives two electrons to a copper(II) ion:



- **Oxidation is loss of electrons** (magnesium is oxidised).
- **Reduction is gain of electrons** (copper(II) ions are reduced).

The two always happen together: electrons given away by one species must be taken by another. A reaction in which both happen is a **redox** reaction (**re**duction + **ox**idation). Each line above is a **half-equation**: it shows one half of the transfer, with the electrons written in. Adding them, the electrons cancel and you get the ionic equation $\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu}$.

Oxidation numbers

With ions like Mg^{2+} it is easy to see who lost electrons. In covalent molecules and ions like SO_4^{2-} no electrons fully move, so chemists keep count with **oxidation numbers** (also called oxidation states). Imagine every bond is ionic: the bonding electrons all go to the more electronegative atom. The charge each atom would then carry is its oxidation number.

The rules, in order of priority:

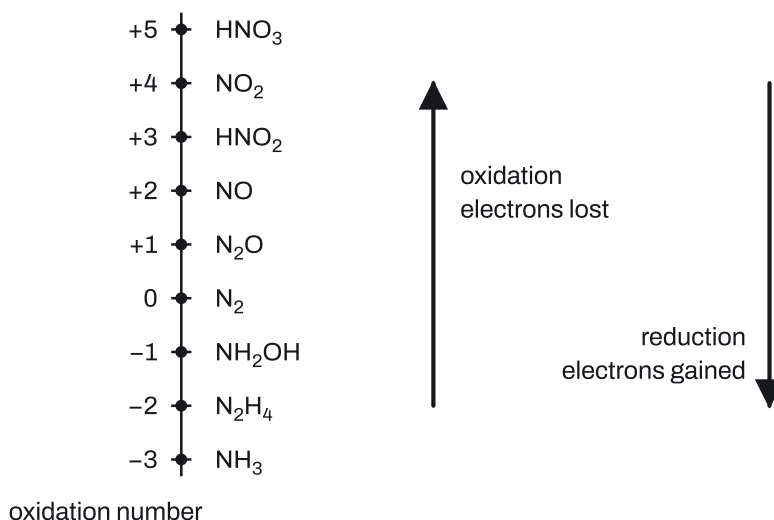
1. An **uncombined element** is 0: Na, O_2 , Cl_2 , S_8 , P_4 .
2. The oxidation numbers in a **compound add up to 0**; in an **ion they add up to its charge**. A simple ion's oxidation number is its charge (Fe^{3+} is +3, Cl^- is -1).
3. **Fluorine** is always -1 in compounds (it is the most electronegative element).
4. **Group 1** metals are +1, **Group 2** are +2, **aluminium** is +3.
5. **Hydrogen** is +1, except in metal hydrides such as NaH and CaH_2 , where it is bonded to a less electronegative metal and is -1.
6. **Oxygen** is -2, except in peroxides such as H_2O_2 (-1) and in OF_2 (+2, because fluorine wins).
7. **Chlorine, bromine and iodine** are -1, except when bonded to oxygen or fluorine (or a more electronegative halogen), when they are positive.

Then find the unknown one by making the total come out right. For sulfur in SO_4^{2-} : $x + 4(-2) = -2$, so $x = +6$. Always write the sign, even for positive numbers: +6, not 6.

Species	Working	Oxidation number
SO_4^{2-}	$x - 8 = -2$	S is +6
NH_4^+	$x + 4 = +1$	N is -3
$\text{Cr}_2\text{O}_7^{2-}$	$2x - 14 = -2$	Cr is +6
H_2O_2	$2 + 2x = 0$	O is -1
NaClO_3	$1 + x - 6 = 0$	Cl is +5
Fe_3O_4	$3x - 8 = 0$	Fe averages $+\frac{8}{3}$

The last row shows that an **average** oxidation number can be a fraction. It means the atoms are not all the same: Fe_3O_4 contains one Fe^{2+} and two Fe^{3+} ions ($2 + 3 + 3 = 8$). When a question asks which **actual** oxidation numbers are present, find whole numbers that give the right total.

One element can take many oxidation numbers. Nitrogen runs all the way from -3 to +5:



Oxidation and reduction as changes in oxidation number

Losing electrons makes an atom more positive, so:

- **Oxidation** is an **increase** in oxidation number.
- **Reduction** is a **decrease** in oxidation number.

The size of the change is the number of electrons each atom lost or gained. Nitrogen going from NH_3 (−3) to NO (+2) loses 5 electrons per atom. Moving up the scale in the diagram is oxidation; moving down is reduction.

A reaction is **redox** only if some oxidation numbers change. Acid–base reactions, precipitations and most decompositions of carbonates change none: in $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$, Ca stays +2, C stays +4 and O stays −2, so it is not redox. Any reaction where an element turns into a compound, or a compound gives an element, **is** redox, because an element is 0 and the combined form usually is not.

Oxidising agents and reducing agents

An **oxidising agent** oxidises something else, so it **takes electrons** from it and is **itself reduced** (its oxidation number goes down). A **reducing agent** gives electrons away, so it is **itself oxidised** (its oxidation number goes up).

In $\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu}$, Cu^{2+} is the oxidising agent and Mg is the reducing agent.

The agent is the **whole reactant species** that contains the changing atom: in acidified manganate(VII), the oxidising agent is MnO_4^- (or KMnO_4), not "Mn" and not the acid. Common oxidising agents are O_2 , Cl_2 , $\text{MnO}_4^-/\text{H}^+$, $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ and concentrated HNO_3 ; common reducing agents are metals, H_2 , C, CO, I^- and Fe^{2+} .

The same substance can play either part depending on its partner. Hydrogen peroxide (O at −1) is an oxidising agent when it becomes water (−2) and a reducing agent when it becomes oxygen gas (0). Hydrogen is usually a reducing agent ($0 \rightarrow +1$), but with a very reactive metal it forms a hydride and is reduced ($0 \rightarrow -1$).

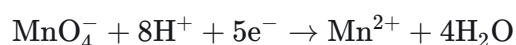
), so there it is the oxidising agent.

Half-equations with oxygen and hydrogen

Many oxidising agents contain oxygen that ends up in water. To write their half-equations in **acid**:

1. Balance the atom that changes.
2. Add H_2O to balance oxygen.
3. Add H^+ to balance hydrogen.
4. Add electrons to balance the charge. Their number should equal the change in oxidation number $\times$ atoms.

For manganate(VII) becoming manganese(II): $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$, then 8H^+ on the left, then charge: left $-1 + 8 = +7$, right $+2$, so 5e^- on the left.



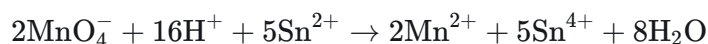
Check: Mn goes from $+7$ to $+2$, a gain of 5 electrons. ✓

In **alkaline** solution there is almost no H^+ . Balance as if in acid, then add the same number of OH^- to both sides and turn each $\text{H}^+ + \text{OH}^-$ pair into H_2O . Alternatively balance oxygen with OH^- and hydrogen with H_2O directly.

Combining half-equations

To get the full ionic equation, multiply each half-equation so that the **electrons lost equal the electrons gained**, add them, and cancel anything on both sides. With tin(II) ions as the reducing agent, $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$:

- manganate(VII) half-equation $\times 2$ (gains 10e^-);
- tin half-equation $\times 5$ (loses 10e^-);



Check the charge: left $-2 + 16 + 10 = +24$, right $+4 + 20 = +24$. ✓ No electrons appear in a full equation.

Balancing with oxidation numbers

You don't always need half-equations. Copper reacts with hot concentrated sulfuric acid to give copper(II) sulfate, sulfur dioxide and water.

1. **Find the changes.** Cu: $0 \rightarrow +2$ (up 2). S: $+6 \rightarrow +4$ in SO_2 (down 2).
2. **Make the total up equal the total down.** 1 Cu (up 2) balances 1 S reduced (down 2). So $\text{Cu} + \dots \rightarrow \text{CuSO}_4 + \text{SO}_2$.
3. **Balance the rest by inspection.** One more H_2SO_4 supplies the sulfate that stays unchanged in CuSO_4 , so there are $2\text{H}_2\text{SO}_4$, and the hydrogen ends up as $2\text{H}_2\text{O}$:



Notice that only **some** of the acid is reduced; the rest acts as an acid. This is why "moles of acid" and "moles of electrons" are not the same thing.

Disproportionation

Disproportionation is a redox reaction in which **the same element**, starting in **one** oxidation state, is **both oxidised and reduced**: some atoms go up and some go down.

- Copper(I) in water: $2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$. Copper goes from +1 to 0 (reduced) and from +1 to +2 (oxidised).
- Chlorine in cold dilute alkali: $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$. Chlorine goes from 0 to -1 and from 0 to +1.
- 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.

Because electrons lost = electrons gained, the numbers of atoms going each way are fixed by the sizes of the changes. In hot alkali, chlorine gives chloride ($0 \rightarrow -1$, down 1) and chlorate(V) ($0 \rightarrow +5$, up 5), so for every one atom that goes up, five go down:



The reverse, where the same element in two different oxidation states meets in the middle (such as iodine at +5 in IO_3^- and at -1 in I^- both becoming I_2), is **not** disproportionation.

Roman numerals in names

When an element can have more than one oxidation number, the name shows which one with a **Roman numeral** in brackets straight after it:

- FeCl_2 is iron(II) chloride and FeCl_3 is iron(III) chloride;
- KMnO_4 is potassium manganate(VII): Mn is +7;
- NaClO_3 is sodium chlorate(V) and NaClO is sodium chlorate(I);
- Na_2SO_3 is sodium sulfate(IV) (sulfite) and Na_2SO_4 is sodium sulfate(VI).

The numeral is the oxidation number of **that one element**, not the charge on the ion: the manganate(VII) ion has a charge of -1. Negative oxidation numbers are not written this way, and a numeral is not needed for elements with only one common oxidation number (sodium chloride, not sodium(I) chloride).

Key facts and formulas

There is no formula list for this topic: you must learn all of these.

Formula	Status
Element = 0; sum in a compound = 0; sum in an ion = its charge	Learn it
F = -1; Group 1 = +1; Group 2 = +2; Al = +3	Learn it

Formula	Status
H = +1 (but –1 in metal hydrides); O = –2 (but –1 in peroxides, +2 in OF ₂)	Learn it
Cl, Br, I = –1 unless bonded to O or F	Learn it
Oxidation: loss of electrons, oxidation number increases	Learn it
Reduction: gain of electrons, oxidation number decreases	Learn it
Oxidising agent: accepts electrons, is itself reduced	Learn it
Reducing agent: donates electrons, is itself oxidised	Learn it
Electrons per formula unit = change in oxidation number × number of atoms that change	Learn it
Total increase in oxidation number = total decrease (electrons lost = electrons gained)	Learn it
Acid half-equations: balance O with H ₂ O, H with H ⁺ , charge with e [–]	Learn it
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ and $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Learn it

Useful oxidation numbers to recognise quickly: S is +4 in SO₂ and SO₃^{2–}, +6 in SO₄^{2–}; N is –3 in NH₃, +3 in NO₂[–], +5 in NO₃[–]; Mn is +4 in MnO₂, +6 in MnO₄^{2–}, +7 in MnO₄[–]; Cr is +3 in Cr³⁺ and +6 in both CrO₄^{2–} and Cr₂O₇^{2–}.

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (75 questions, 2021–2025), the types came up this often. 12 of the 75 questions mix types, so the counts add up to more than 75.

Question type	Questions
Oxidation numbers: calculate, compare or find the change	22
Balance a redox equation	20
Identify or explain oxidising and reducing agents	13
Amounts, products or formulas from electron transfer	12
Decide what is oxidised or reduced, or whether a reaction is redox	11
Disproportionation	9
Redox titration calculations	3
Roman numerals in names	1

1. Oxidation numbers: calculate, compare or find the change (22 questions)

- Write the known oxidation numbers from the rules (F, Group 1 and 2, Al, H, O, then halogens).
- Call the unknown *x*, multiply each by how many atoms there are, and set the total equal to 0 (compound) or the charge (ion).

3. Solve and write the answer with its sign.

Variations you will meet:

- **The change in oxidation number** between two species: new minus old, with a sign. For $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ nitrogen goes from -3 to $+3$, a change of $+6$.
- **Which element changes the most**, or which species has the highest oxidation number: work each one out; don't guess from the formula.
- **Average oxidation numbers** in species with several atoms of the same element, like $\text{S}_3\text{O}_6^{2-}$ ($3x - 12 = -2$, so $x = +\frac{10}{3}$) or Fe_3O_4 ($+\frac{8}{3}$). A fraction is fine as an average.
- **Two different oxidation states in one compound**: find whole numbers that give the total. In Fe_3O_4 the only way to share $+8$ among three iron atoms using $+2$ and $+3$ is $2 + 3 + 3$.
- **Unusual species**: use electronegativity. In a hydride of a metal, H is -1 ; in a compound of two non-metals, the more electronegative atom gets the negative number (in POCl_3 , O is -2 and Cl is -1 , so P is $+5$).
- **Put species in order** of oxidation number: work out each, then sort.

2. Balance a redox equation (20 questions)

By oxidation numbers (fastest for multiple choice):

1. Find the element that goes up and the element that goes down, and the change **per atom**.
2. Multiply by the number of those atoms in each formula to get the change **per formula unit**.
3. Choose multipliers so that the total increase equals the total decrease.
4. Balance oxygen with H_2O , then hydrogen with H^+ (acid) or, in alkali, add OH^- and H_2O .
5. **Check the charge** on both sides.

By half-equations (when you are given them, or asked to "construct" an equation):

1. Write or copy each half-equation.
2. Multiply so the electrons are equal, add, and cancel H^+ , H_2O or OH^- that appear on both sides.
3. Check atoms and charge. There must be no electrons left.

Variations you will meet:

- **"Which equation is correct?"** Check electrons first (the changes must balance), then charge. A wrong option often balances atoms but not charge, or has the wrong ratio of the two reactants.
- **Find one coefficient or a ratio** (such as $x : y$, or the smallest number of H^+): you still have to balance the whole equation, then read it off.
- **Alkaline conditions**: OH^- appears as a product or reactant, with water on the other side. For manganate(VII) becoming MnO_2 in alkali: $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$.
- **A compound gives an element**, such as iodide to iodine: remember $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ (two electrons per I_2).

- **Species with two atoms of the changing element**, like N_2O_3 (N is +3) or $\text{P}_2\text{O}_7^{4-}$ (P is +5): the change per ion is the change per atom $\times 2$.

3. Identify or explain oxidising and reducing agents (13 questions)

1. Find which element goes **down** in oxidation number: the reactant containing it is the **oxidising agent**.
2. Find which element goes **up**: the reactant containing it is the **reducing agent**.
3. In a written answer, name the species and give the reason: " Br_2 is the oxidising agent because bromine's oxidation number decreases from 0 to -1 " or "because it gains electrons".

Variations you will meet:

- **"Define oxidising agent"**: a species that accepts (gains) electrons from another species, so it oxidises it and is itself reduced.
- **Which equation shows X acting as an oxidising agent?** Work out X's oxidation number before and after in each option: you want the one where it goes **down**.
- **Catalyst or agent?** A species used up in one step and made again in a later step is a **catalyst**, not an oxidising or reducing agent overall.
- **"Role of" a reagent** in a titration or organic reaction (such as I_2 taking hydrogen from an organic molecule): if it gains electrons or its oxidation number falls, it is an oxidising agent.

4. Amounts, products or formulas from electron transfer (12 questions)

These all rest on one fact: **moles of electrons lost = moles of electrons gained**.

1. For each reactant, find the electrons transferred per mole (change per atom $\times$ atoms per formula).
2. Set up the balance: $n_1 \times e_1 = n_2 \times e_2$.
3. Solve for the unknown: an amount, a new oxidation number, or a formula that fits it.

Variations you will meet:

- **How many moles of A react with 1 mol of B?** Divide the electrons B takes by the electrons each A gives.
- **Two parts of one compound both change.** Add the electrons. In copper(I) sulfide being oxidised to Cu^{2+} and SO_4^{2-} , each Cu loses 1 and S goes from -2 to $+6$ (loses 8), so one Cu_2S gives $2 + 8 = 10$ electrons.
- **Deduce the product.** Given the mole ratio of reactants, find the electrons one side gives, and so the new oxidation number of the other element; then pick the formula with that oxidation number. If only some of an acid is reduced, use step 3 of "Balancing with oxidation numbers" in Understand it: the rest stays as, say, nitrate in the salt.
- **A chain of reactions** (A oxidises B, then the product is titrated by C): the electrons pass along, so you can link A to C directly through the electron count.
- **Organic oxidations**: each O atom added or each pair of H atoms removed counts as 2 electrons lost by the organic molecule.

5. Decide what is oxidised or reduced, or whether a reaction is redox (11 questions)

1. Write the oxidation number of **every** element on both sides.
2. Any element whose number rises is oxidised; any whose number falls is reduced; unchanged ones are neither.
3. If nothing changes, it is **not** a redox reaction.

Variations you will meet:

- **The same element appears in more than one reactant or product:** track each atom separately. In $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$, iodine in IO_3^- is reduced ($+5 \rightarrow 0$) and iodine in I^- is oxidised ($-1 \rightarrow 0$), so iodine is both oxidised and reduced.
- **"Identify the type of reaction"** between an element and another element: it is redox; explain with the changes in oxidation number.
- **Spectator elements:** oxygen in an oxide, or sulfur in a sulfate that stays sulfate, usually doesn't change. Check rather than assume.

6. Disproportionation (9 questions)

1. Find an element whose atoms **start in one oxidation state** and **end in two**, one higher and one lower.
2. For the ratio of products, use electrons: (number going up) $\times$ (size of increase) = (number going down) $\times$ (size of decrease).

Variations you will meet:

- **"Which reaction is disproportionation?"** It must be redox, and the same element must go both up and down. Two different elements changing, or one element changing in one direction only, is not disproportionation.
- **"Explain why this reaction is a disproportionation":** give the starting oxidation number and **both** final ones, and say one is an increase (oxidation) and one a decrease (reduction) of the same element.
- **Find the ratio or the amounts** of the two products: if the increase is $+2$ and the decrease is -1 , twice as many atoms are reduced as oxidised.

7. Redox titration calculations (3 questions)

1. **Moles of titrant** = concentration $\times$ volume in dm^3 ($\text{cm}^3 \div 1000$).
2. **Use the balanced equation** (from half-equations if needed) to find moles of the other reactant.
3. **Scale up** to the whole solution if only a portion was titrated (for example $\times 250/25.0$), then convert to a concentration or mass.

Manganate(VII) needs no indicator (its purple colour just stays at the end point); iodine is usually titrated with thiosulfate, $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$, with starch near the end.

8. Roman numerals in names (1 question)

1. Work out the oxidation number of the element that can vary.
2. Write it as a Roman numeral in brackets straight after that element's name: potassium chromate(VI) for K_2CrO_4 .
3. Remember the numeral is the oxidation number of that element, **not** the charge of an ion and not the number of atoms.

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) Deduce the oxidation number of the stated element in each species.

(i) nitrogen in hydrazine, N_2H_4 (ii) chlorine in Cl_2O_7 (iii) sulfur in $\text{Na}_2\text{S}_2\text{O}_5$ (iv) hydrogen in CaH_2 **[4]**

(b) Name KIO_4 , using a Roman numeral to show the oxidation number of iodine. **[1]**

(a)(i) H is +1: $2x + 4 = 0$, so N is -2 . **B1**

(ii) O is -2 : $2x - 14 = 0$, so Cl is $+7$. **B1**

(iii) Na is $+1$, O is -2 : $2 + 2x - 10 = 0$, so S is $+4$. **B1**

(iv) Ca is $+2$ and hydrogen is bonded to a metal: $2 + 2x = 0$, so H is -1 . **B1**

(b) $1 + x - 8 = 0$, so I is $+7$: potassium iodate(VII). **B1**

Example 2

Iodate(V) ions, IO_3^- , react with hydrazine, N_2H_4 , in acidic solution. The products are iodine, nitrogen gas and water.

(a) State the change in oxidation number of iodine and of nitrogen. **[2]**

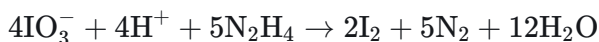
(b) Use these changes to construct the balanced ionic equation. **[2]**

(c) Identify the reducing agent. Explain your answer. **[1]**

(a) Iodine: $+5 \rightarrow 0$, a decrease of 5. **B1** Nitrogen: $-2 \rightarrow 0$, an increase of 2. **B1**

(b) Per formula: each IO_3^- gains 5 electrons; each N_2H_4 (two N atoms) loses $2 \times 2 = 4$. The lowest common multiple is 20, so 4 IO_3^- react with 5 N_2H_4 . **M1**

Balance the rest: 4 I give 2I_2 ; 10 N give 5N_2 ; 12 O give $12\text{H}_2\text{O}$ (24 H), and the left has 20 H in hydrazine, so add 4H^+ :

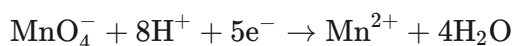


Charge: left $-4 + 4 = 0$, right 0. ✓ **A1**

(c) N_2H_4 (hydrazine), because the oxidation number of nitrogen increases (it loses electrons). **B1**

Example 3

Nitrite ions, NO_2^- , are oxidised to nitrate ions, NO_3^- , by acidified manganate(VII) ions.



(a) Construct the half-equation for the oxidation of nitrite ions in acidic solution. **[1]**

(b) Construct the ionic equation for the reaction. **[1]**

(c) A 250 cm^3 solution of sodium nitrite, NaNO_2 , is made. A 25.0 cm^3 portion needs 18.40 cm^3 of $0.0200 \text{ mol dm}^{-3}$ KMnO_4 to react completely. Calculate the concentration of nitrite ions in the solution. **[3]**

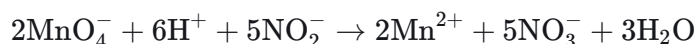
(d) Calculate the mass of sodium nitrite used to make the 250 cm^3 of solution. [M_r : NaNO_2 , 69.0] **[2]**

(a) N goes from +3 to +5, so 2 electrons are lost. Balance O with water, H with H^+ :



B1

(b) Manganate(VII) $\times 2$ (10e^- gained) and nitrite $\times 5$ (10e^- lost). Adding gives 16H^+ and $5\text{H}_2\text{O}$ on the left and 10H^+ and $8\text{H}_2\text{O}$ on the right; cancelling leaves



B1 (charge: $-2 + 6 - 5 = -1$ on both sides).

(c) $n(\text{MnO}_4^-) = 0.0200 \times \frac{18.40}{1000} = 3.68 \times 10^{-4} \text{ mol}$. **M1**

$n(\text{NO}_2^-) = \frac{5}{2} \times 3.68 \times 10^{-4} = 9.20 \times 10^{-4} \text{ mol}$. **M1** for using the 5 : 2 ratio.

$[\text{NO}_2^-] = \frac{9.20 \times 10^{-4}}{25.0/1000} = 0.0368 \text{ mol dm}^{-3}$. **A1**

(d) Moles in 250 cm^3 : $0.0368 \times 0.250 = 9.20 \times 10^{-3} \text{ mol}$. **M1**

Mass = $9.20 \times 10^{-3} \times 69.0 = 0.635 \text{ g}$ (3 s.f.). **A1**

Example 4

White phosphorus, P_4 , reacts with hot aqueous sodium hydroxide to form phosphine, PH_3 , and dihydrogenphosphate(I) ions, $H_2PO_2^-$.

(a) Deduce the oxidation number of phosphorus in PH_3 and in $H_2PO_2^-$. **[2]**

(b) Explain why this reaction is a disproportionation. **[1]**

(c) Deduce the mole ratio of PH_3 to $H_2PO_2^-$ formed, and construct the equation for the reaction of P_4 with OH^- and H_2O . **[2]**

(d) In a separate reaction, 0.600 mol of hydroxylamine, NH_2OH , reduces exactly 1.20 mol of Fe^{3+} ions to Fe^{2+} . The only nitrogen-containing product is an oxide of nitrogen. Deduce the oxidation number of nitrogen in this oxide and suggest its formula. **[3]**

(a) In PH_3 : $x + 3 = 0$, so P is -3 . **B1** In $H_2PO_2^-$: $2 + x - 4 = -1$, so P is $+1$. **B1**

(b) Phosphorus starts at 0 in P_4 and is both reduced (to -3 in PH_3) and oxidised (to $+1$ in $H_2PO_2^-$). **B1**

(c) Each P reduced gains 3 electrons; each P oxidised loses 1. So three P atoms are oxidised for every one reduced: $PH_3 : H_2PO_2^- = 1 : 3$. **M1**



A1 ($P\ 4 = 4$; $O\ 6 = 6$; $H\ 9 = 9$; charge $-3 = -3$).

(d) Oxidation number of N in NH_2OH : $x + 2 - 2 + 1 = 0$, so -1 . **B1**

Electrons gained by iron: $1.20 \times 1 = 1.20$ mol. Each NH_2OH therefore loses $1.20 \div 0.600 = 2$ electrons. **M1**

N goes from -1 to $+1$, so the oxide is N_2O (O is -2 , $2(+1) - 2 = 0$). **A1**

Common mistakes

- **Forgetting that an element is zero.** Cl_2 , O_2 and metals are 0. Giving Cl_2 the -1 of chloride hides a real change in oxidation number and makes a redox reaction look like it isn't one.
- **Mixing up the agent and what happens to it.** The oxidising agent is **reduced**; the reducing agent is **oxidised**. "Reducing agent" was a common wrong answer where the species gained electrons: check which way its oxidation number moves.
- **Naming an element instead of the species.** The oxidising agent is $Cr_2O_7^{2-}$ (or potassium dichromate(VI)), not "chromium" or "Cr(VI)", and not the acid.
- **Defining an oxidising agent vaguely.** "Something that oxidises" or "adds oxygen" is not enough. Say it **accepts electrons** (or its oxidation number decreases) and so it is itself reduced.
- **Unbalanced charge.** Half-equations and ionic equations must balance for atoms **and** charge. Reports mention H^+ written on the wrong side of an oxidation half-equation, and electrons left in a full equation.

- **Per atom versus per formula.** In $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$ each Cr gains 3, so each dichromate gains 6. The same for I_2 : two electrons per molecule, not one.
- **Explaining disproportionation with the definition only.** Reports note many answers define the word but don't apply it. Quote the element's starting oxidation number and both final ones.
- **Wrong signs and forgetting halogens can be positive.** Chlorine in oxoanions (ClO^- , ClO_3^-) is positive; "−3" and "−5" for chlorine were common errors. Always write + for positive oxidation numbers.
- **Calling a non-redox reaction redox** (or the other way round). An acid–base reaction, a precipitation or the thermal decomposition of a carbonate changes no oxidation numbers. Check every element.
- **Using the wrong mole ratio in titrations.** After finding moles of manganate(VII), multiply by the ratio from the balanced equation (such as $\frac{5}{2}$), not by 1.

How to get the marks

- **"Deduce" or "calculate" an oxidation number:** show the sum ($2x - 14 = -2$), then give the value **with its sign**. A Roman numeral is accepted in some mark schemes, but a signed number is always safe.
- **"Identify the oxidising agent. Explain."** One mark usually needs **both**: the correct species, and the reason in terms of electron gain or oxidation number decrease, with the numbers.
- **"Define":** learn the wording in terms of electrons: oxidation is loss of electrons (or increase in oxidation number); an oxidising agent accepts electrons from another species.
- **"Construct an equation":** ionic equations are fine unless the question names compounds. Leave out spectator ions, cancel species on both sides, use the lowest whole-number ratio, and check charge.
- **"Explain why this is disproportionation":** name the element, give the one starting oxidation number and the two final ones, and say one is oxidation and one is reduction.
- **Titration:** write each step (moles of titrant, ratio, scaling) so method marks can be given even if an arithmetic slip happens; errors carried forward are usually allowed. Give the final answer to 3 significant figures unless the data justify more, with units.
- **Multiple choice:** work each option; many wrong options come from one small slip (using per-atom changes, missing a sign, or balancing atoms but not charge).

Quick check

1. Deduce the oxidation number of: (a) chromium in CrO_2Cl_2 ; (b) oxygen in OF_2 ; (c) phosphorus in PO_4^{3-} .
2. Name Na_2SO_3 and KNO_2 , using Roman numerals for the oxidation numbers of sulfur and nitrogen.
3. Which of these is a disproportionation, which is redox but not disproportionation, and which is not redox?
(i) $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$; (ii) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$; (iii) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$.
4. Use oxidation numbers to balance: $\dots \text{Fe}^{2+} + \dots \text{ClO}_3^- + \dots \text{H}^+ \rightarrow \dots \text{Fe}^{3+} + \dots \text{Cl}^- + \dots \text{H}_2\text{O}$.
5. Iodate(V) ions, IO_3^- , are reduced to iodide ions by tin(II) ions, which become tin(IV). How many moles of Sn^{2+} react with 1 mol of IO_3^- ?

Answers

1. (a) $x - 4 - 2 = 0$, so Cr is +6. (b) F is -1 , so $x - 2 = 0$ and O is +2. (c) $x - 8 = -3$, so P is +5.
2. S in SO_3^{2-} : $x - 6 = -2$, so +4: sodium sulfate(IV). N in NO_2^- : $x - 4 = -1$, so +3: potassium nitrate(III).
3. (ii) is disproportionation: oxygen goes from -1 to both -2 and 0 . (i) is redox but not disproportionation: Mg goes up ($0 \rightarrow +2$) and H goes down ($+1 \rightarrow 0$), two different elements. (iii) is not redox: Ca stays +2, C +4, O -2 .
4. Cl goes from +5 to -1 (gains 6); each Fe loses 1, so 6Fe^{2+} per ClO_3^- . Three O give $3\text{H}_2\text{O}$, which needs 6H^+ : $6\text{Fe}^{2+} + \text{ClO}_3^- + 6\text{H}^+ \rightarrow 6\text{Fe}^{3+} + \text{Cl}^- + 3\text{H}_2\text{O}$. Charge: $12 - 1 + 6 = 17$ and $18 - 1 = 17$. ✓
5. I goes from +5 to -1 : 6 electrons gained per IO_3^- . Each Sn^{2+} loses 2. So $6 \div 2 = 3$ mol of Sn^{2+} .

Past questions to try

- [9701/13/O/N/24 Q11](#): the ratio of two ions from oxidation number changes in alkaline solution.
- [9701/12/F/M/25 Q14](#): deducing the oxidation state of nitrogen in a product from a mole ratio.
- [9701/23/O/N/23 Q3](#): defining an oxidising agent and explaining a disproportionation.
- [9701/21/M/J/21 Q4](#): identifying the oxidising agent with oxidation numbers.