Electrochemistry

Oxidation numbers, redox in terms of electron transfer and change in oxidation number, disproportionation, oxidising and reducing agents, and balancing redox equations.

6.1 Redox processes: electron transfer and changes in oxidation number (oxidation state)

Oxidation numbers

The **oxidation number** is the charge an atom would have if the bonding were completely ionic. The rules are:

1. An element on its own is 0, including in O_2 and S_8.
2. The sum for a neutral compound is 0; for an ion it equals the charge on the ion.
3. Group 1 is +1, Group 2 is +2, Al is +3 and F is −1.
4. H is +1 (−1 in metal hydrides). O is −2 (−1 in peroxides such as H_2O_2, and +2 in OF_2).
5. Cl, Br and I are −1 unless combined with oxygen or a more electronegative halogen.

A **Roman numeral** shows the oxidation number: manganese(VII) in MnO_4^-, chromium(VI) in $Cr_2O_7^{2-}$ and sulfur(VI) in SO_4^{2-}.

Redox definitions

- **Oxidation** is loss of electrons, or an **increase** in oxidation number.
- **Reduction** is gain of electrons, or a **decrease** in oxidation number.
- **Redox** is a reaction in which both happen. The **oxidising agent** is reduced (it takes electrons) and the **reducing agent** is oxidised (it gives electrons).
- **Disproportionation** is when a single species is both oxidised and reduced, as in $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$ (Cl goes from 0 to −1 and to +1) and $2H_2O_2 \rightarrow 2H_2O + O_2$.

OIL RIG: Oxidation Is Loss, Reduction Is Gain (of electrons).

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Balancing redox equations

Find the change in oxidation number for each species, multiply so that the total increase equals the total decrease, then balance the rest with H^+ and H_2O (in acid solution).

> **TRY IT**
>
> Balance $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$.

Mn goes from +7 to +2 (gain of 5) and Fe from +2 to +3 (loss of 1), so use $5Fe^{2+}$ for each MnO_4^-:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

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

Assigning oxidation numbers systematically

Oxidation numbers are an electron-bookkeeping model, not necessarily the real charge on an atom in a molecule. Oxygen in water is assigned −2 even though a water molecule is covalent. A monatomic ion's oxidation number does equal its charge. To find an unknown value in a polyatomic species, add all oxidation-number contributions and equate the sum to the overall charge.

Worked example: in $Cr_2O_7^{2-}$ let each Cr be x. Seven oxygens contribute −14, so $2x - 14 = -2$ and $x = +6$. In NH_4^+, four hydrogens contribute +4, so $x + 4 = +1$ and nitrogen is −3. The subscript tells you how many atoms contribute; it is not itself an oxidation number.

Check exceptions before applying a rule mechanically. Oxygen is −1 in a peroxide because the O–O unit has total charge 2−. Hydrogen is −1 in ionic metal hydrides such as NaH. Elements are zero even when their molecules are diatomic or larger: the subscript in Cl_2 does not give chlorine an oxidation number of two.

> **TRY IT**
>
> Find nitrogen's oxidation number in NO_3^- and sulfur's in SO_3^{2-}.

Answer: For nitrate, $x + 3(-2) = -1$, so N is +5. For sulfite, $x + 3(-2) = -2$, so S is +4. Give signs, not just magnitudes.

Identifying the agent and the species changed

An oxidising agent **causes another substance to lose electrons** by accepting them itself. Therefore it is reduced. A reducing agent donates electrons and is oxidised. Name the complete reacting species when asked for the agent, then state the relevant element's oxidation-number change as evidence.

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Worked example: in $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, zinc changes from 0 to +2 and loses two electrons. It is the reducing agent. Copper(II) changes from +2 to 0 and gains those electrons, so Cu^{2+} is the oxidising agent. Sulfate ions in a copper sulfate solution would be spectators, not the oxidising species.

A reaction can involve oxygen without being redox. In $CuO + 2HCl \rightarrow CuCl_2 + H_2O$, copper remains +2, oxygen −2, hydrogen +1 and chlorine −1. This is an acid–base reaction with no oxidation-number change. Conversely, electron transfer can occur without oxygen being present at all.

> **TRY IT**
>
> In $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$, identify the oxidising and reducing agents.

Answer: Cl_2 is reduced from 0 to −1 and is the oxidising agent. Br^- is oxidised from −1 to 0 and is the reducing agent. Both changes occur in the same reaction, with two electrons transferred overall.

Constructing half-equations in acid solution

Use a repeatable sequence: balance the element other than H and O, balance O with water, balance H with H^+, then balance total charge with electrons. Finally check every atom and the charge. Electrons belong on the left of a reduction half-equation and on the right of an oxidation half-equation.

Worked example — dichromate reduction: begin $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$. Add seven waters on the right and fourteen protons on the left. The left charge is now +12, while the right is +6, so add six electrons to the left:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Iron(II) oxidation is $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Multiply this entire equation by six and add it to the reduction equation, cancelling electrons:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

The 1 : 6 ratio follows from electron conservation and can be used in titration calculations. Electrons must cancel out of an ordinary overall redox equation; leaving six electrons on one side indicates incomplete combination.

> **TRY IT**
>
> Combine $I_2 + 2e^- \rightarrow 2I^-$ with $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$.

Answer: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. Each side contains two iodine atoms, four sulfur atoms, six oxygens and total charge 4−. The iodine-to-thiosulfate mole ratio is 1 : 2.

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Recognising disproportionation

In disproportionation, atoms of the **same starting element in one species** end up at both higher and lower oxidation numbers. Merely having two oxidation states among the products is insufficient unless the starting species undergoes both changes. In cold dilute alkali, chlorine starts at 0 and forms chloride (−1) and chlorate(I) (+1). Equal one-electron changes give a 1 : 1 ratio of these chlorine-containing products.

Worked example: in $2H_2O_2 \rightarrow 2H_2O + O_2$, oxygen begins at −1. Some becomes −2 in water and some becomes 0 in oxygen gas. Hydrogen remains +1 throughout. The peroxide is both an oxidising and a reducing agent in this decomposition.

> **TRY IT**
>
> Is $2Mg + O_2 \rightarrow 2MgO$ disproportionation? Explain using oxidation numbers.

Answer: No. Magnesium is only oxidised, from 0 to +2, while oxygen is only reduced, from 0 to −2. It is redox, but no single starting species is both oxidised and reduced.

Chapter check: distinguish a charge from an oxidation number, name each agent, and balance atoms and charge independently. These half-equation skills underpin **electrode potentials and electrolysis** and **transition-metal titrations**.

References and further reading

Scope follows section 6 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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