Electrochemistry

A-Level Chemistry

Oxidation number

The **oxidation number** (also called the oxidation state) shows how many **electrons** an atom has lost or gained compared with the free element. You work it out using simple rules:

- an uncombined element has an oxidation number of 0.
- a simple ion has an oxidation number equal to its charge (so Mg^{2+} is $+2$).
- Group 1 is always $+1$, Group 2 is always $+2$.
- hydrogen is $+1$ (but -1 in metal hydrides).
- oxygen is -2 (but -1 in peroxides).
- fluorine is always -1.
- the oxidation numbers in a neutral compound add up to 0; in an ion they add up to the charge.

A Roman numeral shows the size of the oxidation number of an element, for example iron(II) means $+2$ and manganese(VII) in $KMnO_4$ means $+7$.

known	unknown	known
K	Mn	O_4
$+1$	$+7$	$4 \times (-2)$

they sum to 0: $(+1) + \text{Mn} + (-8) = 0$, so $\text{Mn} = +7$

Assigning an oxidation number: fix the known atoms (K = +1, O = −2 each), then use "they sum to zero" to find the unknown (Mn = +7)

Worked example. Find the oxidation number of sulfur in the sulfate ion, SO_4^{2-}.

Each oxygen is -2, so the four oxygens give $4 \times (-2) = -8$. In an ion the numbers add up to the charge, here -2. If sulfur is x:

$$x + (-8) = -2 \quad \Rightarrow \quad x = +6.$$

Worked example. Find the oxidation number of nitrogen in the nitrate ion, NO_3^-.

$$x + 3 \times (-2) = -1 \quad \Rightarrow \quad x - 6 = -1 \quad \Rightarrow \quad x = +5.$$

Redox in terms of electrons

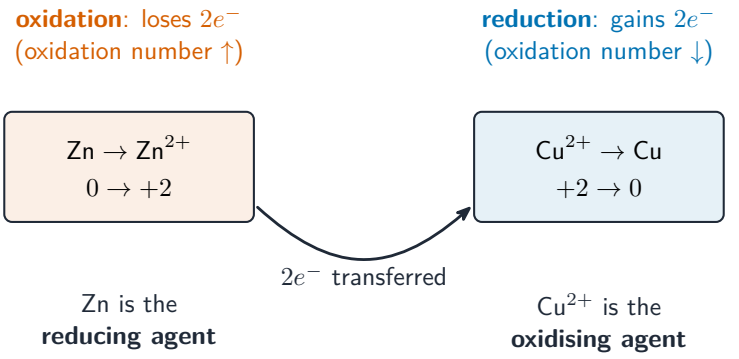
A battery uses redox reactions to push electrons round a circuit.

A **redox** reaction is one where electrons move from one species to another.

- **oxidation** is the **loss** of electrons. The oxidation number goes **up**.
- **reduction** is the **gain** of electrons. The oxidation number goes **down**.

A useful memory aid is **OIL RIG**: Oxidation Is Loss, Reduction Is Gain.

Oxidation and reduction always happen together, because the electrons lost by one species are gained by another. This **electron transfer** is why we call it a redox reaction.



Redox is electron transfer: the reducing agent loses electrons (oxidised, number up); the oxidising agent gains them (reduced, number down)

Using oxidation numbers to balance equations

Changes in oxidation number help you balance a redox equation:

1. find the element whose oxidation number **rises** (it is oxidised) and the one whose number **falls** (it is reduced).
2. the total rise must equal the total fall, because every electron lost is gained somewhere.
3. choose the ratio of the two species so the rise and fall match, then balance the rest of the equation.

$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} \quad (+2 \rightarrow +3)$ oxidised: rises 1 ($\times 5$)

$\mathrm{MnO_4^-} \rightarrow \mathrm{Mn^{2+}} \quad (+7 \rightarrow +2)$ reduced: falls 5 ($\times 1$)

5 electrons lost = 5 gained $\Rightarrow$ ratio **5 $\mathrm{Fe^{2+}}$: 1 $\mathrm{MnO_4^-}$**

Balancing a redox equation: the total rise in oxidation number must equal the total fall, which fixes the ratio

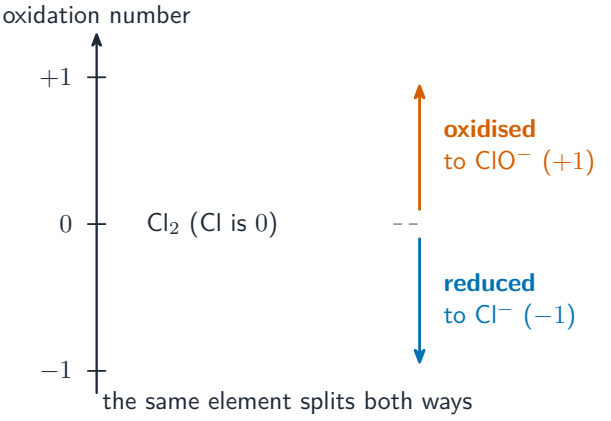
> **Worked example.** Balance the reaction of manganate(VII) with iron(II) in acid: $\mathrm{MnO_4^-} + \mathrm{Fe^{2+}} + \mathrm{H^+} \rightarrow \mathrm{Mn^{2+}} + \mathrm{Fe^{3+}} + \mathrm{H_2O}$.

Manganese falls from +7 to +2 (a fall of 5); iron rises from +2 to +3 (a rise of 1). To make the total fall equal the total rise, take 5 iron ions for every 1 manganate ion. Then balance oxygen with water ($4\,\mathrm{H_2O}$) and hydrogen with $\mathrm{H^+}$ ($8\,\mathrm{H^+}$):

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

Disproportionation

Disproportionation is a special redox reaction in which the **same** element is both oxidised and reduced at the same time. For example, when chlorine reacts with cold water, some chlorine atoms are reduced (to $\mathrm{Cl^-}$) and others are oxidised (to $\mathrm{ClO^-}$).



Disproportionation: chlorine (0) is both oxidised to ClO^- (+1) and reduced to Cl^- (−1) at once

Oxidising and reducing agents

Rusting is the oxidation of iron by oxygen.

- an **oxidising agent** takes electrons away from another species. In doing so, it is itself reduced.
- a **reducing agent** gives electrons to another species. In doing so, it is itself oxidised.

So in any redox reaction, the oxidising agent causes the oxidation of the other species, while the reducing agent causes the reduction.

Exam tips

- Apply the oxidation-number rules in order: O is -2 **except** in peroxides (-1); H is $+1$ **except** in metal hydrides (-1).
- In a redox equation the **total increase equals the total decrease** in oxidation number – use this to fix the ratio, then balance O with H_2O and H with H^+.
- An **oxidising agent is itself reduced**; name both what is oxidised/reduced *and* the agent for full marks.
- **Disproportionation** is the same element both oxidised and reduced – show both oxidation-number changes.