Redox and oxidation numbers

Oxidation numbers and their rules, oxidation and reduction as electron transfer, oxidising and reducing agents, disproportionation, and half-equations.

Oxidation numbers

The **oxidation number** of an atom is the charge it would have if all the bonding were ionic. Rules (apply in order):

1. Atoms in an **uncombined element** are 0, including in molecules like O_2 and S_8.
2. The sum of oxidation numbers in a **neutral compound** is 0; in an **ion** it equals the charge.
3. **Group 1** is +1 and **Group 2** is +2 in compounds.
4. **Fluorine** is −1 in all its compounds.
5. **Hydrogen** is +1, except in metal hydrides (such as NaH), where it is −1.
6. **Oxygen** is −2, except in peroxides (such as H_2O_2) where it is −1, and in OF_2 where it is +2.
7. **Chlorine, bromine and iodine** are −1, except when bonded to oxygen or fluorine.

> **TRY IT**
>
> Find the oxidation number of chromium in $Cr_2O_7^{2-}$ and of sulfur in SO_4^{2-}.

$Cr_2O_7^{2-}$: $2x + 7(-2) = -2$, so $2x = +12$ and $x = +6$. SO_4^{2-}: $x + 4(-2) = -2$ so $x = +6$.

In names, a Roman numeral shows the oxidation number: iron(III) chloride is $FeCl_3$; potassium manganate(VII) is $KMnO_4$. Given the number you can write the formula: copper(I) oxide is Cu_2O.

Oxidation and reduction

	Electrons	Oxidation number
Oxidation	Loss	Increases
Reduction	Gain	Decreases

(**OIL RIG**: oxidation is loss, reduction is gain.)

An **oxidising agent** gains electrons (and is reduced). A **reducing agent** loses electrons (and is oxidised).

Metals form positive ions by losing electrons, so their oxidation number increases. Non-metals form negative ions by gaining electrons, so theirs decreases.

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NOTE

In magnesium burning, $2Mg + O_2 \rightarrow 2MgO$: magnesium goes from 0 to +2 (oxidised, a reducing agent) and oxygen goes from 0 to −2 (reduced, an oxidising agent).

Disproportionation

A **disproportionation** reaction is one in which an element in a single species is **simultaneously oxidised and reduced**.

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl$$

Chlorine goes from 0 to +1 in $HClO$ (oxidised) and from 0 to −1 in HCl (reduced). Other examples are Cu_2O with dilute acid (copper(I) to copper(0) and copper(II)) and hydrogen peroxide decomposing.

To show disproportionation, give the starting oxidation number and both of the new numbers, one higher and one lower, for the same element.

Oxidation numbers can also be used to classify any reaction as **redox** (some oxidation number changes) or not.

Ionic half-equations

A **half-equation** shows the electrons gained or lost by one species.

1. Write the species before and after.
2. Balance the atoms other than O and H.
3. Balance O with H_2O.
4. Balance H with H^+ (in acid).
5. Balance charge with electrons.

TRY IT

Write the half-equation for manganate(VII) ions reduced to manganese(II) ions in acid.

$MnO_4^- \rightarrow Mn^{2+}$. Add $4H_2O$ to the right to balance oxygen. Add $8H^+$ to the left to balance hydrogen. Charge on the left is $-1 + 8 = +7$, on the right $+2$, so add $5e^-$ to the left:

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

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Combining half-equations

To make a full ionic equation, multiply the half-equations so that the electrons **cancel**, then add them and cancel any species that appears on both sides.

For MnO_4^- with $Fe^{2+} \rightarrow Fe^{3+} + e^-$, multiply the iron half-equation by 5:

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

Check that the atoms and the total charge are the same on each side. Both sides here have a charge of $+17$.

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