Course Companion

A-Level Chemistry

Every topic handout in one volume

全部专题讲义合集

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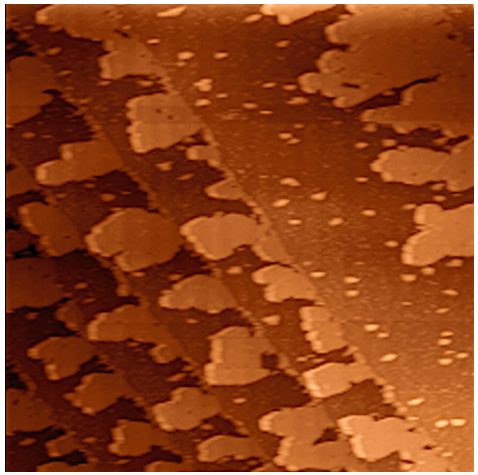
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Atomic structure

A-Level Chemistry

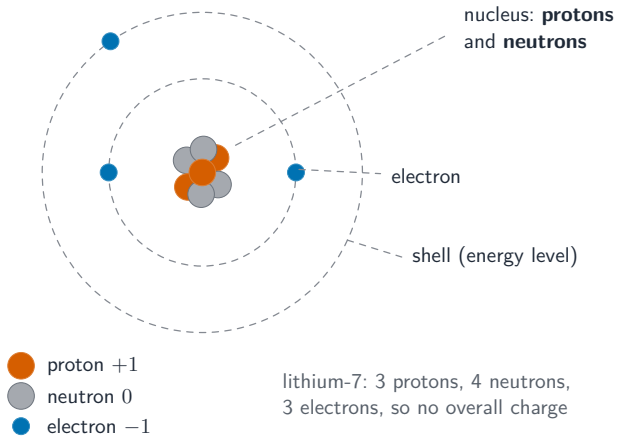
What an atom is made of



A scanning tunnelling microscope can image individual atoms.

Everything is made of **atoms** 原子. An atom is mostly empty space. At its centre is a tiny, heavy **nucleus** 原子核. The nucleus holds two kinds of particle: **protons** 质子 and **neutrons** 中子. Around the nucleus, in the empty space, move the **electrons** 电子. The electrons stay in **shells** 壳层 – layers at set distances from the nucleus.

The nucleus is very small but holds almost all the mass. The electrons take up almost all the space but have almost no mass.



An atom is mostly empty space: protons and neutrons sit in the tiny central nucleus, while electrons move in shells around it

Relative charge and relative mass

We compare the three particles using **relative charge** 相对电荷 and **relative mass** 相对质量. These are simple numbers, not real units.

Particle	Relative charge	Relative mass
proton	+1	1
neutron	0	1
electron	−1	$\frac{1}{1836}$ (about 0)

A proton and a neutron have almost the same mass. An electron is about 1836 times lighter. The proton is positive, the electron is negative, and the neutron has no charge – it is **neutral** 中性.

Proton number and nucleon number

Two numbers describe the nucleus:

- the **proton number** 质子数 (also called the **atomic number** 原子序数), symbol Z – the number of protons.
- the **nucleon number** 核子数 (also called the **mass number** 质量数), symbol A – the total number of protons and neutrons. Protons and neutrons are both **nucleons** 核子.

So the number of neutrons is $A - Z$.

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Counting particles in an atom or ion

For a neutral atom, the number of electrons equals the number of protons, which equals Z.

An **ion** 离子 is an atom that has lost or gained electrons, so it has a charge:

- a positive ion has fewer electrons than protons.
- a negative ion has more electrons than protons.

Example: $^{27}_{13}Al^{3+}$ has 13 protons, $27 - 13 = 14$ neutrons, and $13 - 3 = 10$ electrons (it lost 3 electrons to become 3+).

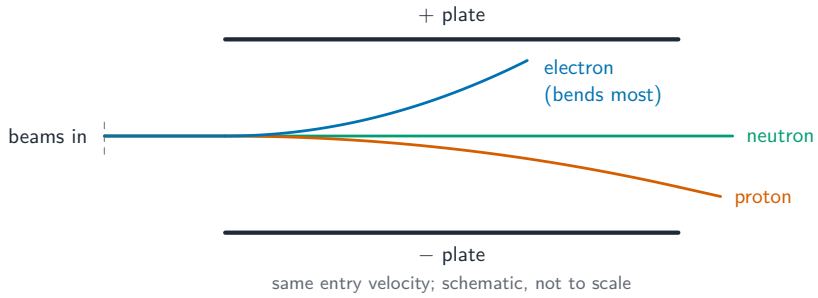
How mass and charge are spread out

Almost all the mass sits in the nucleus, because protons and neutrons are heavy and electrons are very light. All the positive charge is in the nucleus (the protons). The negative charge is spread out in the shells (the electrons).

Beams of particles in an electric field

Imagine beams of protons, neutrons and electrons moving at the same speed into an **electric field** 电场 between two charged plates:

- the proton beam bends towards the negative plate (protons are positive).
- the electron beam bends the other way, towards the positive plate. It bends much more, because the electron is far lighter – the same force gives a bigger **deflection** 偏转 to a smaller mass.
- the neutron beam goes straight through. It has no charge, so the field gives it no force.



In an electric field the proton bends towards the − plate and the electron bends the opposite way and far more (it is much lighter); the neutron passes straight through

For particles moving at the same speed, the angle of deflection is proportional to $\frac{\text{charge}}{\text{mass}}$: a bigger charge bends more, a bigger mass bends less.

Worked example. A beam of protons ($^1H^+$) is deflected through 8° in an electric field. Predict the deflection, at the same speed, of (a) $^2H^+$, (b) $^4He^{2+}$, (c) $^3He^{2+}$. Compare charge ÷ mass with the proton's value of $1 \div 1 = 1$.

- (a) $1 \div 2 = 0.5$, so about 4°, towards the negative plate.
- (b) $2 \div 4 = 0.5$, so also about 4°, towards the negative plate.
- (c) $2 \div 3 = 0.67$, so about 5.3°, towards the negative plate.

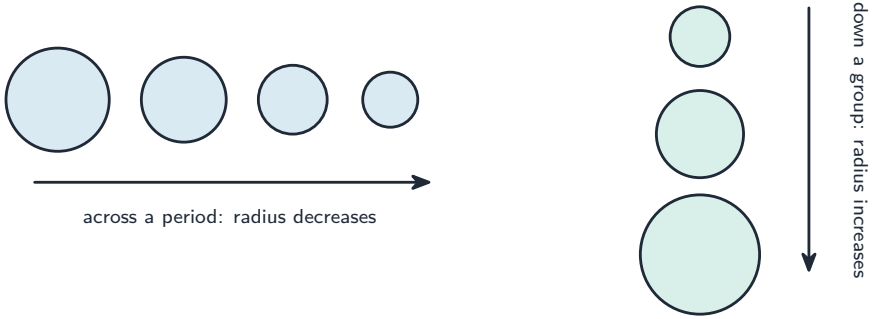
An electron has charge ÷ mass about 1840 times the proton's (in the opposite sense), which is why it bends so much more, towards the positive plate.

Atomic radius and ionic radius

The **atomic radius** 原子半径 is the size of an atom. The **ionic radius** 离子半径 is the size of an ion.

Across a **period** 周期 (left to right), the atomic radius gets **smaller**. The **nuclear charge** 核电荷 (the pull from the protons) rises, but the electrons go into the same outer shell, so the **shielding** 屏蔽 by inner shells stays about the same. The stronger pull draws the outer shell inwards.

Down a **group** 族 (top to bottom), the atomic radius gets **larger**. Each step down adds a new shell, so the outer electrons are further out and feel more shielding from the nucleus.



Across a period the atoms shrink (stronger nuclear pull on the same outer shell); down a group they grow (each step adds a shell)

For ions:

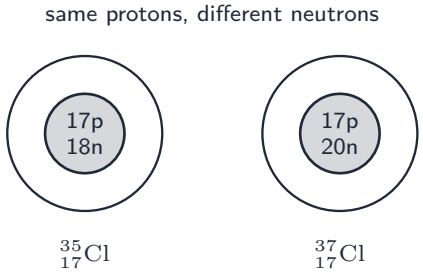
- a positive ion (**cation** 阳离子) is smaller than its atom. Electron loss reduces electron-electron repulsion and increases the attraction for the remaining electrons. The whole outer occupied shell may be lost, but not every electron loss empties a shell.

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- a negative ion (**anion** 阴离子) is larger than its atom. It has gained electrons, so there is more **repulsion** 排斥 between the electrons.
- among ions that have the same number of electrons, the one with more protons is smaller.

Isotopes

Isotopes 同位素 are atoms of the same element with the same number of protons but a different number of neutrons. So isotopes have the same proton number Z but a different nucleon number A.



Two chlorine isotopes: same protons, different neutrons

We write an isotope as ${}^{A}_{Z}X$: the nucleon number A on top, the proton number Z below. For example, chlorine has two main isotopes, $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

Same chemical properties

Chemical properties 化学性质 depend on the electrons, especially the outer electrons. Isotopes of one element have the same number of electrons arranged in the same way. So they react in exactly the same way – they have the same chemical properties.

Different physical properties

Some **physical properties** 物理性质 depend on mass, so they differ between isotopes. A heavier isotope has more neutrons, so more mass, and therefore a higher **density** 密度. (The syllabus limits this difference to mass and density.)

Electrons, energy levels and orbitals

Electrons are arranged in shells, sub-shells and orbitals.



Hydrogen emits light only at discrete, characteristic wavelengths – its line emission spectrum.

Shells and the principal quantum number

Each shell is labelled by the **principal quantum number** 主量子数 $n = 1, 2, 3, \ldots$ A larger n generally means greater spatial extent, but n alone does not put all sub-shells of a multi-electron atom into energy order. The configurations and ionisation processes assessed in these sections are ground-state species from hydrogen to krypton.

Sub-shells and orbitals

Each shell is split into **sub-shells** 亚层, named s, p and d. Each sub-shell is built from **orbitals** 轨道. An orbital is a small region that can hold up to two electrons.

Sub-shell	Number of orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10

So an s sub-shell holds 2 electrons, a p sub-shell holds 6, and a d sub-shell holds 10.

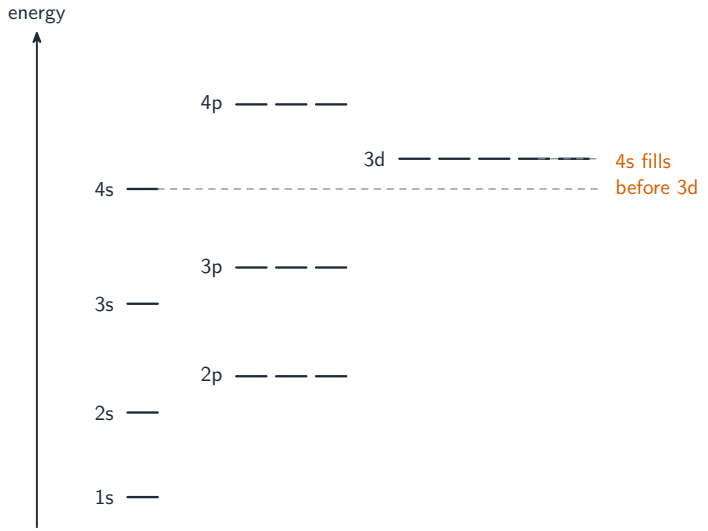
Order of increasing energy

Electrons occupy the lowest-energy available arrangement. The usual neutral-atom filling sequence for the sub-shells studied here is:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$

4s is reached before 3d in this usual construction sequence. The ordering is not fixed in every occupied atom or ion; apply the separate 4s-first removal rule for transition-metal cations.

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The usual neutral filling order; it must not be used to claim that 4s is always lower than occupied 3d levels

Electronic configuration

The **electronic configuration** 电子排布 lists how many electrons are in each sub-shell. The lowest-energy arrangement is the **ground state** 基态.

For iron (Fe, $Z = 26$):

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$$

You can write a shorthand using the nearest **noble gas** 稀有气体 in square brackets:

$$[\mathrm{Ar}]\,3d^6\,4s^2$$

Here [Ar] stands for the full configuration of argon. Chromium and copper are exceptions to mechanically placing two electrons in 4s: Cr is $[\mathrm{Ar}]3d^5 4s^1$ and Cu is $[\mathrm{Ar}]3d^{10}4s^1$. Both totals and ground-state occupations matter.

For ions, you add or remove electrons. One key rule: when a transition metal forms a positive ion, it loses its 4s electrons **before** its 3d electrons. So Fe^{3+} is $[\mathrm{Ar}]\,3d^5$.

> **Worked example.** Write the full electronic configurations of S^{2-}, Cr^{3+} and Cu^{2+}.

- S^{2-}: sulfur has 16 electrons; the ion has 18: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$, the same as argon.
- Cr^{3+}: start from Cr, $[\mathrm{Ar}]\,3d^5\,4s^1$, and remove the 4s electron first, then two 3d: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$.

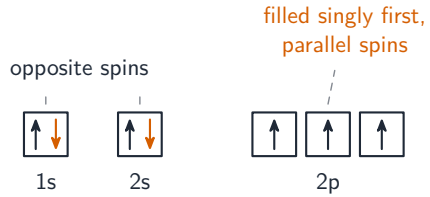
- Cu^{2+}: start from Cu, $[Ar]\,3d^{10}\,4s^1$; remove 4s, then one 3d: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$.

Always write the **atom** first, then take electrons away; removing them from the end of a configuration written in filling order gives wrong answers such as $Cu^{2+} = [Ar]\,3d^7\,4s^2$.

Electrons in boxes

The **electrons in boxes** notation draws each orbital as a box and each electron as an arrow. Two electrons in the same orbital must point opposite ways, because each electron has a property called **spin** 自旋, and a shared orbital needs opposite spins.

Within a sub-shell, electrons fill empty orbitals one at a time, with parallel arrows, before any orbital gets a second electron. Spreading out like this keeps the electrons apart and lowers the repulsion between them.



Electrons in boxes for nitrogen ($1s^2\,2s^2\,2p^3$): paired electrons point opposite ways, and the 2p orbitals fill singly with parallel spins

For oxygen, $2p^4$ has one pair and two singly occupied orbitals. The n = 2 shell also contains the 2s pair, so it contains two pairs altogether. A whole-shell question and a named-sub-shell question have different counting boundaries.

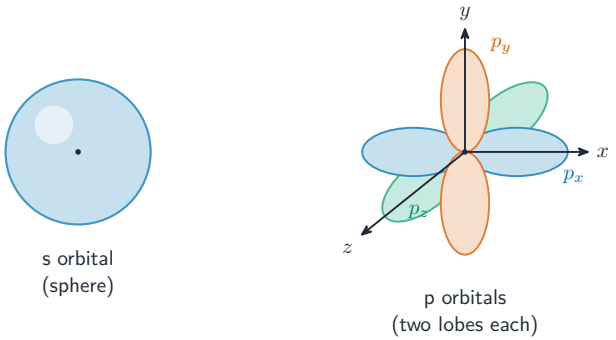
Why the configuration takes this shape

Electrons fill from low energy to high energy because that gives the most stable (lowest-energy) atom. Within a sub-shell they spread out singly first to reduce the repulsion between the negative electrons.

Shapes of s and p orbitals

- an s orbital is a **sphere** 球形 centred on the nucleus.
- a p orbital has two lobes, like a dumbbell, pointing along one axis. The three p orbitals point along three directions at right angles (the x, y and z axes).

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An s orbital is a sphere; each p orbital is a dumbbell, and the three p orbitals point along the x, y and z axes

Free radicals

A **free radical** 自由基 is a species with one or more **unpaired electrons** 未成对电子. Many free radicals are reactive, but the defining feature is an unpaired electron, not reactivity alone or a net charge.

Ionisation energy

First ionisation energy

The **first ionisation energy** 第一电离能 (IE) is the energy needed to remove one electron from each atom in one mole of gaseous atoms, forming one mole of gaseous +1 ions.

Starting from separate gaseous atoms isolates electron removal without adding energy for breaking a solid or molecule into atoms. The unit is kJ mol^{-1}. As an equation, for an element X:

$$X(g) \rightarrow X^+(g) + e^-$$

The (g) shows the species is a gas.

Successive ionisation energies

After removing one electron, you can remove another. The second ionisation energy removes one electron from each +1 ion:

$$X^+(g) \rightarrow X^{2+}(g) + e^-$$

You can keep going. These are the **successive ionisation energies** 逐级电离能. Each is larger than the one before, because every electron is pulled away from a more positive ion.

What ionisation energy depends on

Ionisation energy comes from the attraction between the positive nucleus and the outer electron. Three main factors set how strong that attraction is:

- **nuclear charge**: more protons pull the electrons more strongly, so the ionisation energy is higher.
- **atomic radius**: the further the outer electron sits from the nucleus, the weaker the pull, so the ionisation energy is lower.
- **shielding**: inner shells block some of the pull on the outer electron. More inner shells mean more shielding and a lower ionisation energy.

There is a smaller effect too – **spin-pair repulsion** 自旋成对排斥. When two electrons share one orbital, they push each other a little, so one is easier to remove.

Trends in first ionisation energy

Across a period, the first ionisation energy generally **rises**. The nuclear charge grows while shielding stays about the same, so the outer electrons are held more tightly.

Down a group, the first ionisation energy **falls**. Lower elements have more shells, so more shielding and a larger radius, and the outer electron is easier to remove.

The dips are evidence for sub-shells

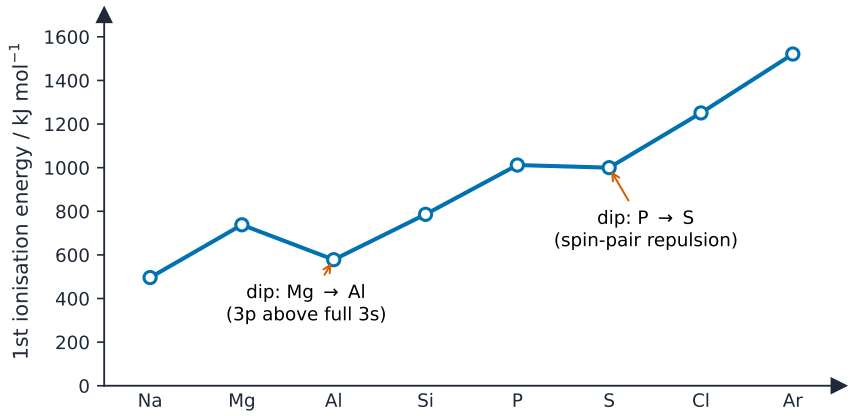
The rise across a period is not smooth. Two small dips appear, and you should be able to explain both:

- **Group 2 to Group 13** (for example Mg to Al): the electron removed from Al comes from a 3p sub-shell, which is higher in energy than the full 3s sub-shell in Mg. A 3p electron is easier to remove, so the value dips.
- **Group 15 to Group 16** (for example P to S): in S, one 3p orbital now holds a pair of electrons. Spin-pair repulsion makes one of them easier to remove, so the value dips.

These dips are evidence that sub-shells exist.

> **Worked example.** The first ionisation energies of nitrogen and oxygen are 1402 and 1314 kJ mol^{-1}. Explain why oxygen's is **lower**, even though oxygen has more protons. Nitrogen is $1s^2\,2s^2\,2p^3$: each 2p orbital holds one electron. Oxygen is $1s^2\,2s^2\,2p^4$: one 2p orbital holds a **pair**. The electron removed from oxygen is one of that pair, and the **repulsion** between the two paired electrons makes it easier to remove. This outweighs the effect of the extra proton. The electrons are in the same sub-shell with similar shielding, so do not explain it by distance or shielding.

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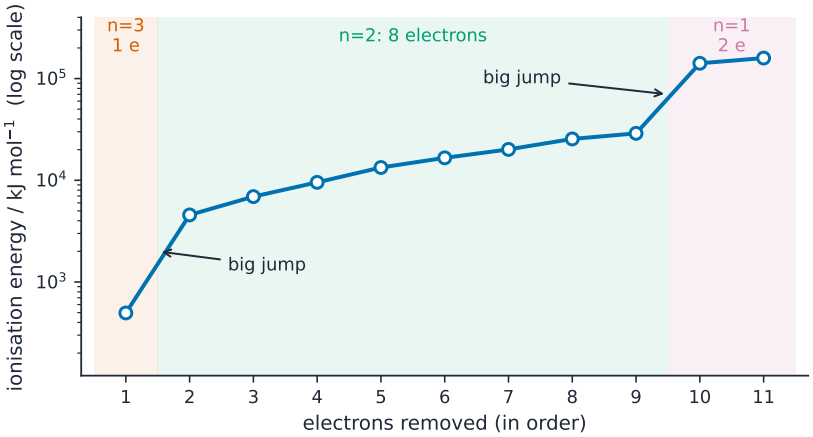
1st IE generally rises Na → Ar · dips at Al (new *p* orbital) and S (pair repulsion)

First ionisation energy rises across Period 3 but dips at Al and at S – evidence that sub-shells exist

Successive ionisation energies are evidence for shells

If you plot the successive ionisation energies of one element, the values rise, with **big jumps** at certain points. A big jump happens when the next electron must come from a shell closer to the nucleus.

For main-group atoms, count the electrons removed before the first inner-shell jump to find the outer-shell count. Counts 1 and 2 correspond to Groups 1 and 2; counts 3–8 correspond to Groups 13–18, with helium as the two-electron Group 18 exception. The first jump alone does not establish the period: use the number of occupied shells from fuller data or additional information about the atom.



big jump = next electron from a shell closer to the nucleus (shell structure)

Successive ionisation energies of sodium (log scale): the big jumps reveal the $2, 8, 1$ *shell structure*

Electrons removed before the first big jump	Group
1	Group 1
2	Group 2
3	Group 13

Worked example. The first five successive ionisation energies of an element are 590, 1150, 4940, 6480 and 8120 $\mathrm{kJ\,mol^{-1}}$. Which group is it in? Look for the **big jump**, not the biggest number. From the 1st to the 2nd the value roughly doubles, which is a normal rise. From the 2nd (1150) to the 3rd (4940) it more than quadruples: that is the jump. So **two** electrons come off easily before it, the outer shell holds 2 electrons, and the element is in **Group 2**. Count the electrons removed **before** the jump, and explain the jump properly: the next electron is being pulled from a shell **closer to the nucleus**, not from a different element.

Common mistakes.

- Leaving out the state symbols in an ionisation-energy equation. The atoms and ions are **gaseous**: $\mathrm{Na(g) \rightarrow Na^{+}(g) + e^{-}}$.
- Writing the equation as $\mathrm{X(g) + e^{-} \rightarrow X^{-}(g)}$. That is electron **gain**; ionisation **removes** an electron.
- Removing 3d electrons before 4s when a transition metal forms an ion. The **4s** electrons go first: $\mathrm{Fe^{2+}}$ is $\mathrm{[Ar]\,3d^{6}}$, not $\mathrm{[Ar]\,3d^{4}\,4s^{2}}$.
- Writing chromium as $\mathrm{[Ar]\,3d^{4}\,4s^{2}}$ or copper as $\mathrm{[Ar]\,3d^{9}\,4s^{2}}$. Both are exceptions: Cr is $\mathrm{3d^{5}\,4s^{1}}$ and Cu is $\mathrm{3d^{10}\,4s^{1}}$.

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- Explaining the Mg → Al dip by spin-pair repulsion. The Al electron is removed from a **3p** sub-shell, higher in energy than Mg's 3s; spin-pair repulsion explains the **P → S** dip.
- Saying successive ionisation energies rise "because there are fewer electrons". Each electron is removed from an increasingly **positive ion**, so it is held more strongly; a big jump shows a new, inner **shell**.
- Saying the electron beam bends towards the negative plate. Electrons are negative, so they bend towards the **positive** plate, and more sharply than protons because their mass is far smaller.

Exam tips

- Define **isotopes** in full: atoms of the same element with the same number of protons but a different number of neutrons – the mark scheme wants both halves.
- 4s fills **before** 3d, but electrons are **removed from 4s first** when forming ions, so $\mathrm{Fe^{3+}}$ is $\mathrm{[Ar]3d^{5}}$ (not $\mathrm{[Ar]3d^{3}4s^{2}}$).
- In successive ionisation energies, a **big jump** marks the start of a new (inner) shell – use the jumps to place the element in its group.
- Explain every ionisation-energy trend with the same three factors: **nuclear charge, distance and shielding**, plus sub-shell effects for the small dips.
- Learn the exact reason first ionisation energy of oxygen is **below** nitrogen: oxygen's **paired 2p electrons repel**, so one is easier to remove.

Atoms, molecules and stoichiometry

A-Level Chemistry

Relative masses of atoms and molecules

Atoms 原子 are far too light to weigh in grams, so we compare every mass to one standard. The standard is the **unified atomic mass unit** 统一原子质量单位 (symbol u), defined as exactly one twelfth of the mass of one carbon-12 atom.

Using this unit, we state masses as simple numbers:

- the **relative atomic mass** 相对原子质量 A_r of an element is the average mass of its atoms compared with $\frac{1}{12}$ of a carbon-12 atom. It is an average over all the **isotopes** 同位素, weighted by how common each one is.
- the **relative isotopic mass** 相对同位素质量 is the mass of one atom of a single isotope, compared with $\frac{1}{12}$ of a carbon-12 atom.
- the **relative molecular mass** 相对分子质量 M_r of a **molecule** 分子 is the sum of the relative atomic masses of all its atoms.
- the **relative formula mass** 相对式量 is the same idea for a substance that is not made of molecules (such as an ionic compound). Add up the relative atomic masses shown in the formula.



$$A_r = \frac{(75 \times 35) + (25 \times 37)}{100} = 35.5$$

Relative atomic mass is a weighted average: chlorine's two isotopes (75% ^{35}Cl, 25% ^{37}Cl) average to A_r = 35.5

To find A_r from isotope data, multiply each isotope mass by its percentage, add these up, and divide by 100.

Worked example. Chlorine is 75% ^{35}Cl and 25% ^{37}Cl. Find its relative atomic mass.

$$A_r = \frac{(75 \times 35) + (25 \times 37)}{100} = \frac{2625 + 925}{100} = 35.5.$$

Worked example. A mass spectrometer shows copper is 69.2% ^{63}Cu and 30.8% ^{65}Cu. Find its relative atomic mass.

$$A_r = \frac{(69.2 \times 63) + (30.8 \times 65)}{100} = \frac{4359.6 + 2002.0}{100} = 63.6.$$

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The mole and the Avogadro constant



A modern electronic balance measures mass – the basis of mole calculations.

Chemists count particles in groups called moles, just as we count eggs in dozens.

One **mole** 摩尔 (symbol mol) is the amount of substance that contains exactly $6.02214076 \times 10^{23}$ particles. That number is the **Avogadro constant** 阿伏伽德罗常量, usually rounded to three significant figures:

$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

So one mole of anything contains 6.02×10^{23} particles. (The older definition, the number of atoms in exactly 12 g of carbon-12, gives the same number to far more figures than you will ever need.) The particles may be atoms, molecules or **ions** 离子 – always say which.

The mass of one mole in grams equals the relative mass (A_r or M_r). This is the **molar mass** 摩尔质量, with units g mol^{-1}. The key equation is:

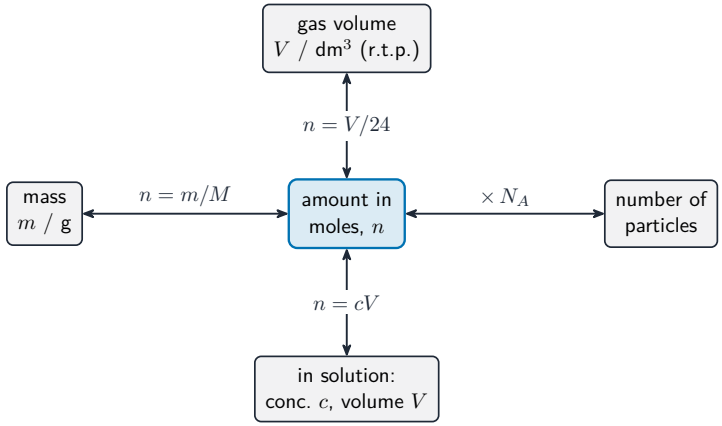
$$n = \frac{m}{M}$$

where n is the amount in moles, m is the mass in grams, and M is the molar mass.

Worked example. How many moles are in 8.0 g of methane, CH_4? (A_r: C = 12, H = 1.)

The molar mass is $M = 12 + 4(1) = 16$ g mol^{-1}, so

$$n = \frac{m}{M} = \frac{8.0}{16} = 0.50 \text{ mol}.$$



The mole is the hub of every amount calculation: convert to mass ($n = m/M$), particles ($\times N_A$), gas volume ($n = V/24$) or solution ($n = cV$)

Formulas

A **compound** 化合物 is a substance made of two or more elements chemically joined.

Charges and formulas of ionic compounds

In an **ionic compound** 离子化合物 the total positive charge balances the total negative charge, so the compound is neutral overall.

You can predict the charge of many ions from the element's position in the Periodic Table:

Group	1	2	13	15	16	17
Usual ion charge	+1	+2	+3	−3	−2	−1

Hydrogen forms H^+, and the Group 18 noble gases do not normally form ions.

Some ions you must know by name and formula:

Name	Formula
nitrate	NO_3^-
carbonate	CO_3^{2-}
sulfate	SO_4^{2-}
hydroxide	OH^-
ammonium	NH_4^+
zinc	Zn^{2+}
silver	Ag^+

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Name	Formula
hydrogencarbonate	HCO_3^-
phosphate	PO_4^{3-}

For a metal that can have more than one charge, a Roman numeral shows the **oxidation number** 氧化数. For example, iron(II) is Fe^{2+} and iron(III) is Fe^{3+}. To write a formula, balance the charges: iron(III) oxide is Fe_2O_3, because two Fe^{3+} balance three O^{2-}.

Equations and state symbols

A chemical equation must be **balanced** 配平 – the same number of each kind of atom on both sides. Add **state symbols** 状态符号 to show the state of each species: (s) solid, (l) liquid, (g) gas, and (aq) **aqueous** 水溶液 (dissolved in water).

An **ionic equation** 离子方程式 shows only the ions and molecules that actually change. The ions that do not change are **spectator ions** 旁观离子, and you leave them out. For example, the reaction that forms silver chloride is:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Empirical and molecular formulas

The **empirical formula** 实验式 is the simplest whole-number ratio of the atoms of each element in a compound. The **molecular formula** 分子式 shows the actual number of atoms of each element in one molecule.

For example, ethane has empirical formula CH_3 but molecular formula C_2H_6.

Hydrated and anhydrous solids

Some solids hold water inside their crystals. This water is the **water of crystallisation** 结晶水. A solid that contains it is **hydrated** 水合的; the same solid with the water removed is **anhydrous** 无水的.

For example, hydrated copper(II) sulfate is $CuSO_4 \cdot 5H_2O$. Heating it drives off the water to leave anhydrous $CuSO_4$.

> **Worked example: finding the water of crystallisation.** 2.46 g of hydrated magnesium sulfate, $MgSO_4 \cdot xH_2O$, is heated until its mass stops changing. 1.20 g of anhydrous $MgSO_4$ is left. Find x. (M_r: $MgSO_4 = 120.4$, $H_2O = 18.0$.)

The water lost is $2.46 - 1.20 = 1.26$ g. Then $n(MgSO_4) = 1.20/120.4 = 0.00997$ mol and $n(H_2O) = 1.26/18.0 = 0.0700$ mol. The ratio is $0.0700/0.00997 = 7.02$, so $x = 7$: the formula is $MgSO_4 \cdot 7H_2O$. You heat **to constant mass** (heat, cool, weigh, and repeat until two masses agree) to be sure all the water has gone.

Calculating empirical and molecular formulas

To find the empirical formula from masses (or percentages by mass):

1. divide each element's mass by its A_r to get the moles.
2. divide all the mole values by the smallest one.
3. round to the nearest whole numbers – that ratio is the empirical formula.

To get the molecular formula, you also need M_r. Find how many times the empirical formula mass fits into M_r, then multiply the formula by that number.

> **Worked example.** A compound is 40.0% carbon, 6.7% hydrogen and 53.3% oxygen by mass. Find its empirical formula. (A_r: C = 12, H = 1, O = 16.)

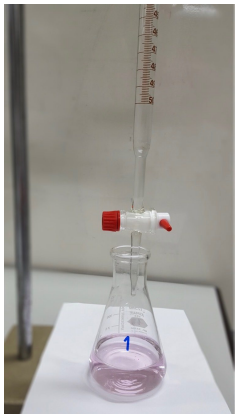
Take 100 g and divide each mass by its A_r to get moles: C = 40.0/12 = 3.33, H = 6.7/1 = 6.7, O = 53.3/16 = 3.33. Dividing through by the smallest (3.33) gives a ratio C : H : O = 1 : 2 : 1, so the empirical formula is CH_2O.

element	% by mass	÷ A_r → moles	÷ smallest (3.33)	ratio
C	40.0	40.0/12 = 3.33	1.0	1
H	6.7	6.7/1 = 6.7	2.0	2
O	53.3	53.3/16 = 3.33	1.0	1

empirical formula CH_2O - if $M_r = 180$, it fits $180/30 = 6$ times: molecular formula $C_6H_{12}O_6$

The empirical-formula recipe: divide by Ar, divide by the smallest, read off the ratio

Reacting masses and volumes



A titration finds reacting volumes precisely.

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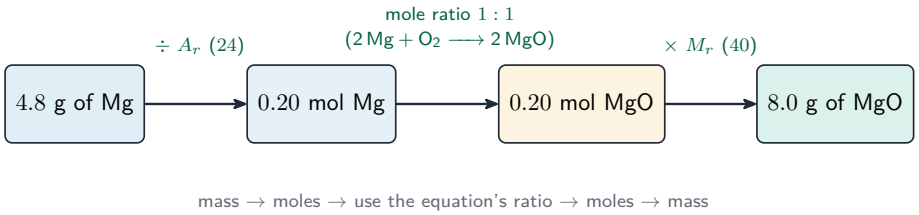
Reacting masses and percentage yield

The numbers in front of each species in a balanced equation give the mole ratio – this is the **stoichiometry** 化学计量. To find a reacting mass: change the known mass to moles, use the mole ratio to find the moles you want, then change back to mass.

> **Worked example.** What mass of magnesium oxide forms when 4.8 g of magnesium burns completely? $2Mg + O_2 \rightarrow 2MgO$. ($A_r$: Mg = 24, O = 16.)

Moles of Mg = 4.8/24 = 0.20 mol. The ratio Mg : MgO is 1 : 1, so 0.20 mol of MgO forms. Its molar mass is 24 + 16 = 40 g mol^{-1}, so

$$m = nM = 0.20 \times 40 = 8.0 \text{ g}.$$



The mole bridge: mass to moles, ratio, then back to mass

In real reactions you usually get less product than the maximum. The **percentage yield** 产率 compares the amount you actually made with the most you could make:

$$\text{percentage yield} = \frac{\text{actual amount of product}}{\text{maximum possible amount}} \times 100\%$$

For example, if the student burning 4.8 g of magnesium above collects only 6.8 g of magnesium oxide, the yield is $\frac{6.8}{8.0} \times 100 = 85\%$. Some of the product may escape as smoke, or some magnesium may not burn.

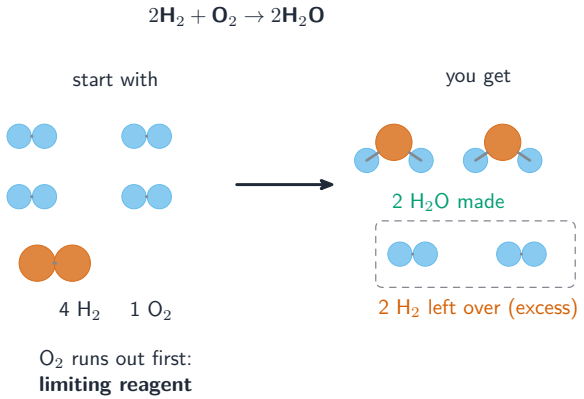
Limiting and excess reagent

When two reactants are mixed, one usually runs out first. The **limiting reagent** 限量试剂 is the one that runs out – it decides how much product forms. The other is the **excess reagent** 过量试剂, because there is more than enough of it. Always base the calculation on the limiting reagent.

To find it: work out the moles of each reactant, divide each by its number in the equation, and the smallest result is the limiting reagent.

> **Worked example.** 5.6 g of iron is heated with 4.0 g of sulfur: Fe + S → FeS. Find the mass of iron(II) sulfide formed and the mass of the reactant left over. (A_r: Fe = 55.8, S = 32.1.)

$n(\text{Fe}) = 5.6/55.8 = 0.1004$ mol and $n(\text{S}) = 4.0/32.1 = 0.1246$ mol. The ratio is 1 : 1, so iron runs out first: iron is the **limiting reagent**. The FeS formed is $0.1004 \times 87.9 = 8.8$ g. Sulfur left over: $(0.1246 - 0.1004) \times 32.1 = 0.78$ g. Keep the extra digit until the end: rounding both amounts to 0.100 and 0.125 first would give 0.80 g.



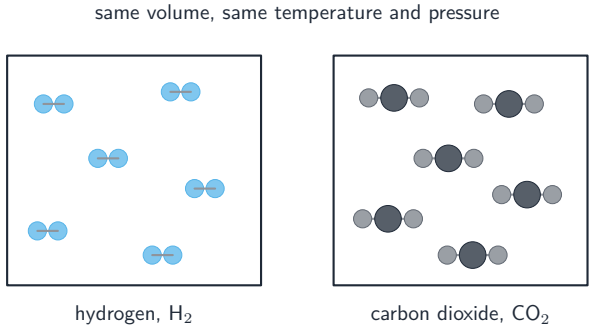
The limiting reagent runs out first and decides how much product forms; the leftover reactant is in excess

Volumes of gases

At the same temperature and pressure, equal volumes of any gases contain equal numbers of molecules. At room temperature and pressure (r.t.p.), one mole of any gas takes up 24.0 dm^3, so:

$$n = \frac{V}{24.0} \qquad (V \text{ in dm}^3 \text{ at r.t.p.})$$

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the same **number** of molecules (6 each), even though CO_2 is bigger

Equal volumes of gases at the same temperature and pressure hold equal numbers of molecules, whatever the gas

This is used when burning **hydrocarbons** 碳氢化合物 (compounds of only carbon and hydrogen), where you compare gas volumes.

Because equal volumes hold equal numbers of moles, the **volumes** of gases react in the same ratio as the numbers in the equation. You do not need to change them to moles.

> **Worked example.** 20 cm^3 of a gaseous hydrocarbon C_xH_y burns completely in oxygen. It uses 80 cm^3 of oxygen and makes 60 cm^3 of carbon dioxide (all volumes at r.t.p., so the water formed is a liquid). Find the formula.

The general equation is $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right)\text{O}_2 \rightarrow x\,\text{CO}_2 + \frac{y}{2}\,\text{H}_2\text{O}$. Divide the volumes by 20: 1 volume of hydrocarbon gives 3 volumes of CO_2, so $x = 3$. It uses 4 volumes of O_2, so $x + \frac{y}{4} = 4$, and $y = 4$. The hydrocarbon is C_3H_4.

> **Worked example: deducing the equation.** 0.540 g of a metal M (with $A_r = 27.0$) reacts with excess hydrochloric acid, giving 0.720 dm^3 of hydrogen at r.t.p. Deduce the equation. $n(\text{M}) = 0.540/27.0 = 0.0200$ mol and $n(\text{H}_2) = 0.720/24.0 = 0.0300$ mol. The ratio M : H_2 is $0.0200 : 0.0300 = 2 : 3$. Three H_2 need six H atoms, so six HCl, and the six Cl^- go to two M: $2\text{M} + 6\text{HCl} \rightarrow 2\text{MCl}_3 + 3\text{H}_2$. The metal forms M^{3+} ions (it is aluminium).

Volumes and concentrations of solutions

The **concentration** 浓度 of a solution is the amount of **solute** 溶质 in each cubic decimetre of **solution** 溶液, measured in mol dm^{-3}:

$$n = c \times V$$

where c is the concentration and V is the volume in dm^3. Remember that 1000 cm^3 =

1 dm^3.

> **Worked example.** In a titration, 25.0 cm^3 of sodium hydroxide solution is exactly neutralised by 20.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid: $\mathrm{NaOH} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}$. Find the concentration of the sodium hydroxide.

Moles of HCl $= cV = 0.100 \times \dfrac{20.0}{1000} = 2.00 \times 10^{-3}$ mol. The ratio is 1 : 1, so there are 2.00×10^{-3} mol of NaOH in 25.0 cm^3:

$$c = \frac{n}{V} = \frac{2.00 \times 10^{-3}}{25.0/1000} = 0.0800 \text{ mol dm}^{-3}.$$

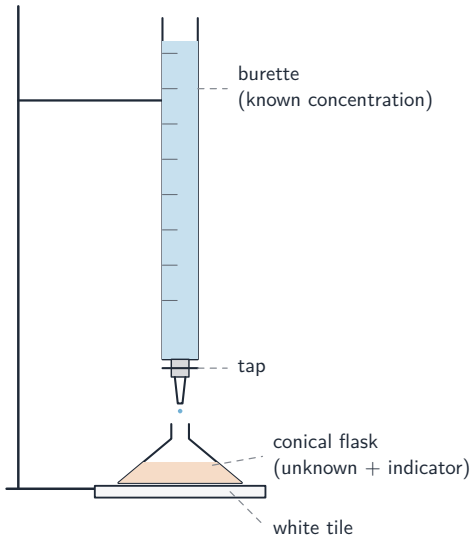
This is the basis of a **titration** 滴定, where you find an unknown concentration by reacting it with a solution whose concentration you already know.

> **Worked example: a 1 : 2 ratio and a volumetric flask.** A student dissolves a sample of sodium carbonate in water and makes the solution up to 250 cm^3 in a volumetric flask. 25.0 cm^3 of this solution needs 22.40 cm^3 of 0.100 mol dm^{-3} HCl: $\mathrm{Na_2CO_3} + 2\mathrm{HCl} \rightarrow 2\mathrm{NaCl} + \mathrm{H_2O} + \mathrm{CO_2}$. Find the mass of sodium carbonate dissolved. (M_r of $\mathrm{Na_2CO_3} = 106.0$.)

1. $n(\mathrm{HCl}) = 0.100 \times 22.40/1000 = 2.240 \times 10^{-3}$ mol.
2. The ratio is 1 : 2, so $n(\mathrm{Na_2CO_3})$ in 25.0 $\mathrm{cm}^3 = 1.120 \times 10^{-3}$ mol.
3. The flask holds 250 cm^3, ten times as much: 1.120×10^{-2} mol.
4. Mass $= 1.120 \times 10^{-2} \times 106.0 = 1.19$ g.

Step 3 is the one most often missed: the titration uses only a **portion** of the solution that was made.

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In a titration a burette adds a solution of known concentration to the unknown in the conical flask, until the indicator changes

Significant figures

Give your answer to a sensible number of **significant figures** 有效数字 – usually match the data in the question. Do not write more digits than the data supports, and do not round so early that you lose accuracy.

Common mistakes.

- Rounding an empirical ratio such as 1 : 1.5 or 1 : 1.33 to whole numbers straight away. Multiply first: 1 : 1.5 = 2 : 3 and 1 : 1.33 = 3 : 4.
- Using the molar mass of the formula **unit** for a hydrate without its water. $\mathrm{CuSO_4 \cdot 5H_2O}$ has $M_r = 159.6 + 5 \times 18.0 = 249.6$.
- Choosing the limiting reagent by the smaller mass, or the smaller number of moles alone. Divide each amount in moles by its **coefficient** first; the smaller result is limiting.
- Using 24 dm^3 for a gas that is not at room temperature and pressure, or for a solution. The molar volume applies only to **gases at r.t.p.**; otherwise use $pV = nRT$.
- Forgetting to change cm^3 to dm^3 in a concentration calculation. 25.0 cm^3 = 0.0250 dm^3.
- Dividing the hydrate mass by the anhydrous M_r. Find the water's mass by **subtraction**, then the moles of each part separately.

- Forgetting to scale up from the titrated portion (25.0 cm^3) to the whole solution made (250 cm^3).
- Writing state symbols as (aq) for a pure liquid. Water and ethanol on their own are **(l)**; (aq) means dissolved in water.

Exam tips

- Convert volumes to dm^3 **before** using concentration (25.0 cm^3 = 0.0250 dm^3); the missing ÷1000 is the most common titration error.
- Use the **balancing numbers** as the mole ratio between species – never the M_r values.
- Empirical formula: divide each mass/percentage by A_r, then by the **smallest**, then scale to whole numbers; use M_r to reach the molecular formula.
- For gases at r.t.p. use volume = moles × 24 dm^3; quote the equation you use every time.
- Give the answer to the same **significant figures** as the data (usually 3) and always include units.

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Chemical bonding

A-Level Chemistry

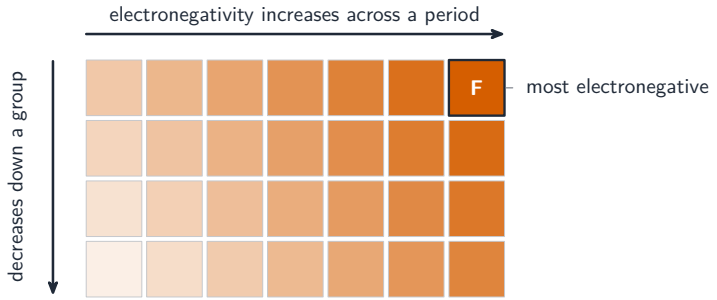
Electronegativity

Electronegativity 电负性 is the power of an atom to attract the **electrons** 电子 in a bond towards itself.

Three factors decide how electronegative an atom is:

- **nuclear charge** 核电荷: more protons pull the bonding electrons more strongly.
- **atomic radius** 原子半径: the closer the bond is to the nucleus, the stronger the pull.
- **shielding** 屏蔽 by inner shells and sub-shells: more inner electrons weaken the pull on the bonding electrons.

So electronegativity **rises** across a period (more nuclear charge, smaller radius) and **falls** down a group (larger radius, more shielding). Fluorine is the most electronegative element.



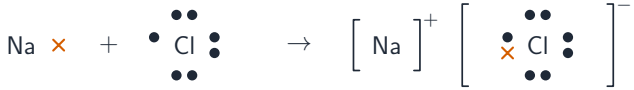
Electronegativity rises across a period and falls down a group, so fluorine is the most electronegative element

You can use the difference in **Pauling electronegativity** 鲍林电负性 values to predict the bond type. A large difference gives an **ionic** bond; a small difference gives a **covalent** bond.

Ionic bonding

Ionic bonding 离子键 is the **electrostatic attraction** 静电引力 between oppositely charged **ions** 离子 – positive **cations** 阳离子 and negative **anions** 阴离子.

It forms when a metal gives electrons to a non-metal. Good examples are sodium chloride (NaCl), magnesium oxide (MgO) and calcium fluoride (CaF_2). The ions pack into a regular giant **lattice** 晶格, held together by the attraction in every direction.



sodium gives its outer electron (×) to chlorine

Ionic bonding in NaCl: sodium transfers its single outer electron to chlorine, giving Na^+ and a full-octet Cl^-

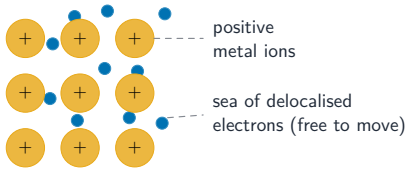


A real crystal of rock salt (halite, NaCl); the cubic shapes mirror the giant ionic lattice inside

Metallic bonding

Metallic bonding 金属键 is the electrostatic attraction between positive metal ions and a "sea" of **delocalised electrons** 离域电子.

The outer electrons are free to move through the whole metal. This explains why metals conduct electricity and are strong.



Metallic bonding: positive metal ions sit in a sea of delocalised electrons that are free to move

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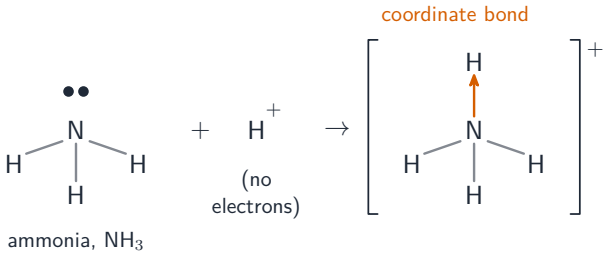
Covalent and coordinate bonding

Covalent bonding 共价键 is the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons.

Simple molecules with covalent bonds include H_2, O_2, N_2, Cl_2, HCl, CO_2, NH_3, CH_4, C_2H_6 and C_2H_4. A double bond shares two pairs; a triple bond (as in N_2) shares three pairs.

Atoms in Period 3 and below can **expand the octet** 扩展八隅体 – hold more than eight electrons in their outer shell. Examples are SO_2, PCl_5 and SF_6.

A **coordinate bond** 配位键 (also called a dative covalent bond) is a covalent bond where both shared electrons come from the same atom. For example, when ammonia and hydrogen chloride gases meet, the lone pair on the nitrogen forms a coordinate bond to H^+, making the ammonium ion NH_4^+. Coordinate bonds also join the two halves of the Al_2Cl_6 molecule.



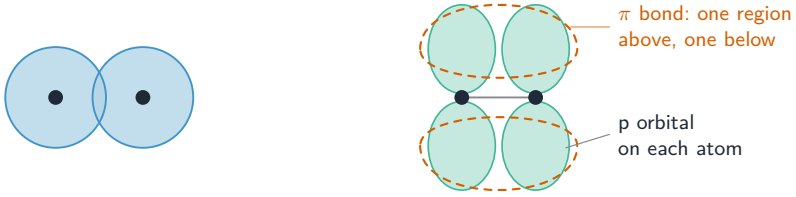
A coordinate (dative) bond: nitrogen's lone pair forms the fourth N–H bond, both electrons coming from N

Sigma and pi bonds

Covalent bonds form when **orbitals** 轨道 overlap:

- a **sigma bond** σ 键 forms by the direct, head-on **overlap** 重叠 of orbitals between the two atoms.
- a **pi bond** π 键 forms by the sideways overlap of two p orbitals, above and below the sigma bond.

A single bond is one sigma bond. A double bond (as in C_2H_4) is one sigma plus one pi bond. A triple bond (as in N_2 and HCN) is one sigma plus two pi bonds.



A σ bond forms by direct head-on overlap; a π bond forms by the sideways overlap of two p orbitals, above and below

Hybridisation

Hybridisation 杂化 mixes orbitals in the same shell to make new, equal orbitals for bonding:

- sp: two equal orbitals, used in a linear molecule.
- sp^2: three equal orbitals, used in a flat molecule like C_2H_4.
- sp^3: four equal orbitals, used in CH_4.

Bond energy and bond length

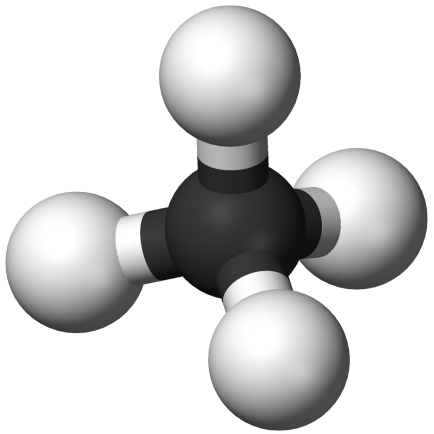
- **bond energy** 键能 is the energy needed to break one mole of a particular covalent bond in the gas state.
- **bond length** 键长 is the distance between the centres of the two bonded atoms.

A shorter bond is usually stronger (higher bond energy). Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds. Stronger bonds make a molecule harder to react.

Shapes of molecules

To work out a shape, use **VSEPR theory** 价层电子对互斥理论: the pairs of electrons around the central atom push apart as far as possible, because like charges repel.

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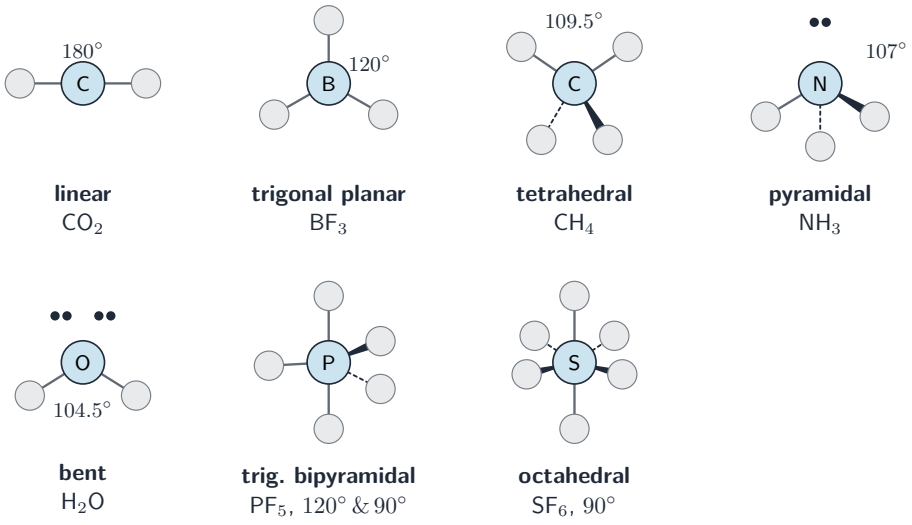


A molecular model shows the three-dimensional shape of a covalent molecule.

A **lone pair** 孤对电子 (not in a bond) pushes more strongly than a **bonding pair** 成键电子对. For ammonia and water, lone-pair repulsion reduces the **bond angle** 键角 below 109.5°; 2.5° per lone pair is a rough guide for these examples, not a universal rule.

Molecule	Shape	Bond angle
CO_2	**linear** 直线形	180°
BF_3	**trigonal planar** 平面三角形	120°
CH_4	**tetrahedral** 四面体形	109.5°
NH_3	**pyramidal** 三角锥形	107°
H_2O	**bent** 角形	104.5°
PF_5	**trigonal bipyramidal** 三角双锥形	120° and 90°
SF_6	**octahedral** 八面体形	90°

NH_3 has one lone pair and H_2O has two, which is why their angles drop below the 109.5° of CH_4. You can predict the shapes of similar molecules and ions in the same way.



The seven shapes from VSEPR theory; the lone pairs on NH_3 and H_2O push harder, squeezing the bond angle below 109.5°

Worked example. Predict the shape and bond angle of NH_3 and of H_2O. Nitrogen has 5 outer electrons and forms 3 bonds, leaving **3 bonding pairs and 1 lone pair** - four pairs in total, so they start from the tetrahedral 109.5°. The lone pair repels more strongly and squeezes the angle by about 2.5°, giving a **pyramidal** shape at about 107°. Oxygen forms 2 bonds and keeps **2 lone pairs**: still four pairs, but now two squeezes, so the shape is **bent** at about 104.5°. Count **all** the pairs to fix the basic geometry, use the known approximate angles for these examples, and name the shape from the **atoms** - NH_3 has four pairs but is pyramidal, not tetrahedral.

Counting pairs in an ion. Start with the outer electrons of the central atom, add one for each atom bonded to it by a single bond (H or a halogen), then **subtract** one for each positive charge or **add** one for each negative charge. Halve the total to get the number of pairs; the pairs not used in bonds are lone pairs.

Worked example. Predict the shapes of NH_4^+, H_3O^+ and PCl_6^-.

- NH_4^+: $5+4-1=8$ electrons, so 4 pairs, all bonding: **tetrahedral**, 109.5°. It has the same shape and electron count as CH_4.
- H_3O^+: $6+3-1=8$ electrons, so 4 pairs, 3 bonding and 1 lone pair: **pyramidal**, about 107°, like NH_3.
- PCl_6^-: $5+6+1=12$ electrons, so 6 pairs, all bonding: **octahedral**, 90°, like SF_6.

Molecules and ions with the same number of electron pairs around the central atom, arranged in the same way, have the same shape.

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Intermolecular forces

Intermolecular forces 分子间作用力 are the forces *between* **molecules** 分子. They are much weaker than the ionic, covalent and metallic bonding *inside* substances.

Bond polarity and dipoles

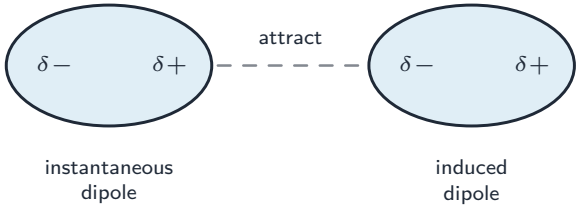
When two atoms with different electronegativity share a bond, the electrons sit closer to the more electronegative atom. The bond then has a **polarity** 极性: one end is slightly negative ($\delta-$) and the other slightly positive ($\delta+$). This separation of charge is a **dipole** 偶极.

If the dipoles in a molecule do not cancel, the whole molecule has a **dipole moment** 偶极矩 and is polar. If they cancel by symmetry (as in CO_2), the molecule is non-polar.

Van der Waals' forces

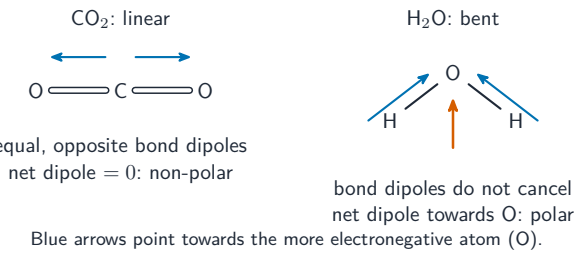
Van der Waals' forces 范德华力 is the general name for all intermolecular forces. There are two main types.

The first type is the instantaneous dipole–induced dipole force, also called the **London dispersion force** 伦敦色散力. Moving electrons make a brief **instantaneous dipole** 瞬时偶极, which then creates a matching **induced dipole** 诱导偶极 in a nearby molecule. These forces act between all molecules and get stronger when there are more electrons.



A London force: a momentary dipole in one molecule induces a dipole in its neighbour, so they attract – this acts between all molecules

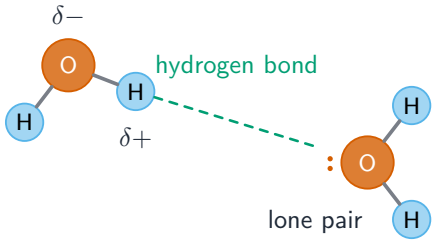
The second type is the permanent dipole–permanent dipole force. It acts between molecules that are always polar, because each one has a **permanent dipole** 永久偶极.



Check both the bonds and the shape: polar bonds can belong to a non-polar molecule.

Hydrogen bonding

Hydrogen bonding 氢键 is a strong, special case of permanent dipole forces. It forms when hydrogen is bonded to a very electronegative atom – nitrogen, oxygen or fluorine – and is attracted to a lone pair on an N, O or F atom in a neighbour. Look for N–H and O–H groups, as in ammonia and water.



Hydrogen bonding in water: a δ+ hydrogen is attracted to a lone pair on the δ− oxygen of a neighbouring molecule

Hydrogen bonding explains the strange behaviour of water:

- its high melting and **boiling point** 沸点, because many hydrogen bonds must be broken.
- its high **surface tension** 表面张力.
- ice is **less dense** than liquid water, because hydrogen bonds hold the molecules in an open, spread-out structure, so ice floats.

> **Worked example (comparing boiling points).** The hydrogen halides boil at: HF 20 °C, HCl −85 °C, HBr −67 °C, HI −35 °C. Explain the pattern.

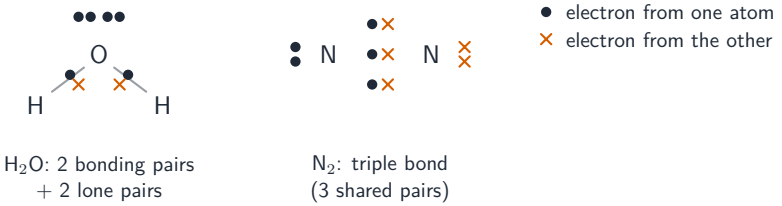
From HCl to HI the molecules have **more electrons**, so the instantaneous dipole–induced dipole (London) forces get stronger and more energy is needed to separate the molecules: the boiling point rises, even though the bonds become **less** polar. HF breaks the pattern: F is so electronegative that HF molecules form **hydrogen bonds**

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to each other, which are much stronger than the London forces, so its boiling point is far higher than expected. In an answer, name the force, say which substance has more of it and why, and link it to the **energy** needed to overcome it.

Dot-and-cross diagrams

A **dot-and-cross diagram** 点叉图 shows the outer electrons of each atom, using dots for one atom and crosses for the other. This makes it clear where each bonding electron came from. You can draw them for ionic, covalent and coordinate bonding, including molecules with an expanded octet or an odd number of electrons.



Covalent dot-and-cross: each shared pair is one electron from each atom. Water has two bonding pairs and two lone pairs; nitrogen shares three pairs (a triple bond)

Common mistakes.

- Saying the molecules' covalent bonds break when a simple molecular substance boils. Only the **intermolecular forces** between molecules are overcome; the covalent bonds inside stay whole.
- Drawing a hydrogen bond to any H atom. The hydrogen bond goes from an H that is bonded to **N, O or F** to a **lone pair** on an N, O or F of another molecule; show the lone pair and the δ+/δ− charges, with the three atoms in a straight line.
- Counting lone pairs on the outer atoms when predicting a shape. Only the bonding and lone pairs on the **central** atom set the shape.
- Calling a molecule with polar bonds polar without checking its shape. In symmetrical CO_2 and BF_3 the dipoles cancel, so the molecules are **non-polar**.
- Giving water a bond angle of 109.5° or 107°. Two lone pairs squeeze it to about **104.5°**: tetrahedral 109.5°, one lone pair 107°, two lone pairs 104.5°.
- Saying a coordinate bond is weaker than a normal covalent bond. Once formed it is the **same** as any other covalent bond; only the origin of the shared pair differs.
- Forgetting the charge when counting the electron pairs of an ion: take one electron away for each + charge and add one for each − charge.
- Saying a double bond is twice as strong as a single bond. The extra π **bond** is weaker than the σ bond, because its sideways overlap is smaller.

Exam tips

- For **shapes**, count bonding pairs and lone pairs, name the shape, then give the exact bond angle (e.g. NH_3: pyramidal, 107°) – each lone pair lowers the angle by about 2.5°.
- A **dative (coordinate) bond** has both electrons from one atom (e.g. NH_4^+, H_3O^+); draw the arrow from the lone pair.
- Name the intermolecular force precisely: **hydrogen bonding** needs H bonded to N, O or F; otherwise it is permanent-dipole or induced-dipole (van der Waals). Never call van der Waals forces "bonds".
- Explain a physical property by stating **which forces are broken**, not just "strong bonds".

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States of matter

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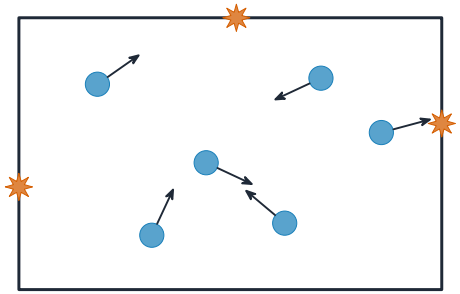
The gaseous state



Boiling turns liquid water into steam – a change between states of matter.

Where gas pressure comes from

Gas molecules move fast in all directions. They keep hitting – **colliding** 碰撞 with – the walls of their container. Each hit gives the wall a tiny push. The **pressure** 压强 of the gas is the overall result of these many collisions on the walls.



fast particles collide with the walls; the many pushes make the **pressure**

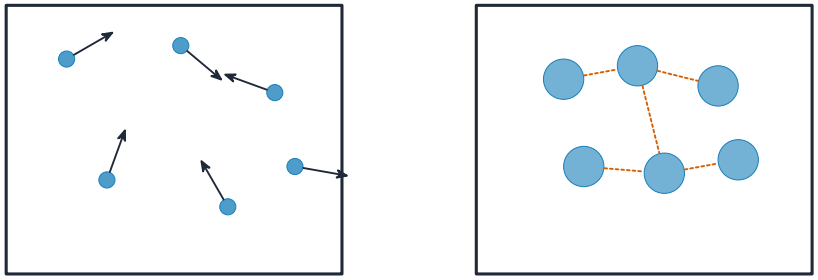
Gas pressure: fast molecules move in all directions and collide with the walls; the many tiny pushes add up to the pressure

Ideal gases

An **ideal gas** 理想气体 is a simple model. We assume two things:

- the particles themselves take up zero volume.
- there are no **intermolecular forces** 分子间作用力 of attraction between the particles.

A **real gas** 实际气体 follows this model closely at low pressure and high temperature. It behaves least like an ideal gas at high pressure and low temperature, when the particles are squeezed close together and the forces between them start to matter.



ideal gas (model)
point particles, *no* forces

real gas: high p, low T
real size + attractions (dashed)

An ideal gas is a model: point particles with no forces between them. A real gas behaves least like this at high pressure and low temperature, when the particles are crowded and their real size and attractions start to matter

The ideal gas equation

The **ideal gas equation** 理想气体方程 links pressure, volume, amount and temperature:

$$pV = nRT$$

where p is the pressure in Pa, V is the volume in m^3, n is the amount in moles, T is the temperature in **kelvin** 开尔文 (K), and R is the **gas constant** 气体常量 ($8.31\ J\ K^{-1}\ mol^{-1}$).

Always change the units first: °C to K (add 273), and cm^3 or dm^3 to m^3.

> **Worked example.** Find the volume of 0.50 mol of an ideal gas at 27 °C and 100 kPa. ($R = 8.31\ J\ K^{-1}\ mol^{-1}$.)

Convert first: $T = 300$ K, $p = 1.00 \times 10^5$ Pa. Then

$$V = \frac{nRT}{p} = \frac{0.50 \times 8.31 \times 300}{1.00 \times 10^5} = 0.0125\ m^3\ (= 12.5\ dm^3).$$

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You can also use the equation to find a **molar mass** 摩尔质量. Since $n = m/M$:

$$pV = \frac{m}{M}RT \qquad \Rightarrow \qquad M = \frac{mRT}{pV}$$

This lets you work out M_r from the mass (or the density) of a gas.

> **Worked example.** A flask holds 0.96 g of a gas in 600 cm^3 at 100 kPa and 27 °C. Find the molar mass of the gas. ($R = 8.31\ J\ K^{-1}\ mol^{-1}$.)

Convert: $V = 6.00 \times 10^{-4}\ m^3$, $T = 300$ K. Then

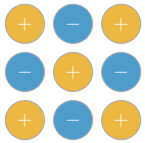
$$M = \frac{mRT}{pV} = \frac{0.96 \times 8.31 \times 300}{(1.00 \times 10^5)(6.00 \times 10^{-4})} \approx 40\ g\ mol^{-1}.$$

Bonding and structure

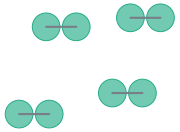


Quartz is a giant covalent structure of silicon and oxygen.

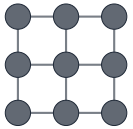
How a substance behaves depends on how its particles are joined. There are four main structures of a **crystalline solid** 晶体.



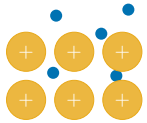
giant ionic
NaCl: high m.p.,
conducts when molten



simple molecular
I_2, ice: low m.p.,
weak forces between



giant covalent
diamond, SiO_2: very
high m.p., insulating



giant metallic
copper: high m.p.,
conducts (solid + molten)

The four structures of a crystalline solid – the structure decides the melting point, conductivity and solubility

Giant ionic

A **giant ionic** 离子晶体 structure is a huge regular **lattice** 晶格 of positive and negative **ions** 离子, held together by strong attraction in every direction. Examples are sodium chloride and magnesium oxide.

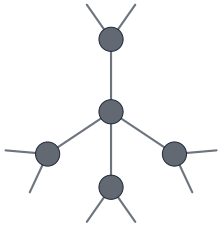
Simple molecular

A **simple molecular** 分子晶体 structure is made of small **molecules** 分子. The bonds inside each molecule are strong, but the intermolecular forces between the molecules are weak. Examples are iodine (I_2), **fullerene** 富勒烯 (C_{60}) and ice.

Giant molecular

A **giant molecular** 原子晶体 structure (also called giant covalent) is a huge network of atoms joined by strong **covalent bonds** 共价键. Examples are **silicon(IV) oxide** 二氧化硅, **graphite** 石墨 and **diamond** 金刚石.

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diamond
every C bonded to 4:
rigid 3D network, very hard



graphite
layers slide; spare
electrons let it conduct

Two giant covalent forms of carbon: diamond is a rigid 3D network (very hard); graphite has sliding layers and spare electrons that conduct



A real diamond in the rock it grew in. That whole crystal is one giant molecule – a single unbroken network of carbon atoms, each bonded to four others. Breaking it means breaking countless strong covalent bonds, which is why diamond is the hardest natural material

Giant metallic

A **giant metallic** 金属晶体 structure is a lattice of positive metal ions in a "sea" of **delocalised electrons** 离域电子. An example is copper.



A piece of pure copper metal. The shine, and the way metals conduct and bend, all come from that giant lattice of copper ions sitting in a shared sea of delocalised electrons

Physical properties

The structure decides the physical properties:

Structure	Melting/boiling point	Conducts electricity?	Solubility in water
giant ionic	high	only when molten or dissolved	usually soluble
simple molecular	low	no	usually low
giant molecular	very high	no (except graphite)	insoluble
giant metallic	high	yes (solid and molten)	insoluble

- **melting point** 熔点 and **boiling point** 沸点 are high when strong forces (ionic, covalent or metallic) must be broken, and low when only weak intermolecular forces break.
- **electrical conductivity** 导电性 needs charged particles that can move – ions that are free (when molten or dissolved) or delocalised electrons. Graphite conducts because some of its electrons are delocalised.
- **solubility** 溶解度 in water is usually high for ionic solids and low for molecular and giant covalent solids.

You can work backwards too: from the melting point, conductivity and solubility of an unknown substance, deduce the type of structure and bonding it has.

Substance	Melting point / °C	Conducts as solid?	Conducts when molten?	Soluble in water?
P	801	no	yes	yes
Q	1610	no	no	no
R	114	no	no	no
S	1083	yes	yes	no

Worked example (deducing structure from data). Use the table to deduce the structure and bonding in P, Q, R and S. Give a reason for each.

- **P: giant ionic.** It has a high melting point (strong attraction between ions in every direction) and conducts only when molten, when its ions are free to move. Solubility in water fits too (sodium chloride matches these data).
- **Q: giant molecular.** It has a very high melting point, because many strong covalent bonds must be broken, and it never conducts, because it has no ions and no delocalised electrons (silicon(IV) oxide matches).
- **R: simple molecular.** It has a low melting point, because only weak intermolecular forces are broken, not the covalent bonds inside each molecule; there are no charged particles to conduct (iodine matches).
- **S: giant metallic.** It conducts as a solid and when molten, because of its delocalised electrons, and has a high melting point from the strong attraction between the ions and the electrons (copper matches).

The key test is **conductivity**: conducts as a solid → metallic (or graphite); conducts only when molten → ionic; never conducts → molecular, and the melting point then separates simple from giant.

Ice is a special simple molecular solid: each water molecule forms hydrogen bonds to four others in an open, regular lattice. This holds the molecules further apart than in liquid water, so ice is **less dense** than water and floats. **Fullerene** C_{60} is also simple molecular, so it has a much lower melting point than diamond or graphite, although all three are pure carbon.

Common mistakes.

- Using kPa and dm^3 with $R = 8.31$. With this value of R, pressure must be in **Pa** and volume in $\mathbf{m}^3$: 600 $cm^3 = 6.00 \times 10^{-4}$ m^3.
- Using °C. Temperature must be in **kelvin**; at 27 °C, $T = 300$ K.
- Saying real gases deviate at high temperature. Deviation is greatest at **high pressure and low temperature**, when the particles are close together and move slowly, so their volume and attractions matter.

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- Saying graphite does not conduct because it is covalent. Each carbon uses three electrons in bonds, and the fourth is **delocalised** between the layers, so graphite conducts along the layers.
- Calling ice or iodine a giant structure because they are solids. They are **simple molecular**: small molecules held together by weak intermolecular forces.
- Saying ionic solids conduct when solid. The ions are fixed in the lattice; they conduct only when **molten or dissolved**, when the ions can move.

Exam tips

- Use **SI units** in $pV = nRT$: pressure in Pa, volume in m^3 ($cm^3 \times 10^{-6}$), temperature in K ($°C + 273$).
- State the **ideal-gas assumptions** (negligible molecular volume, no intermolecular forces) and when real gases deviate (high pressure, low temperature).
- Link each property to structure: giant ionic (high m.p., conducts molten), giant covalent (very high m.p.), simple molecular (low m.p.), giant metallic (conducts, malleable).
- Graphite conducts because each carbon has a **delocalised** electron; diamond does not – a favourite comparison.

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Chemical energetics

A-Level Chemistry

Enthalpy change, ΔH



Burning fuel is exothermic, releasing energy to the surroundings.



An instant cold pack uses an endothermic reaction that takes in heat.

Every chemical reaction takes in or gives out energy. This energy change, measured at constant pressure, is the **enthalpy change** 焓变, with symbol ΔH.

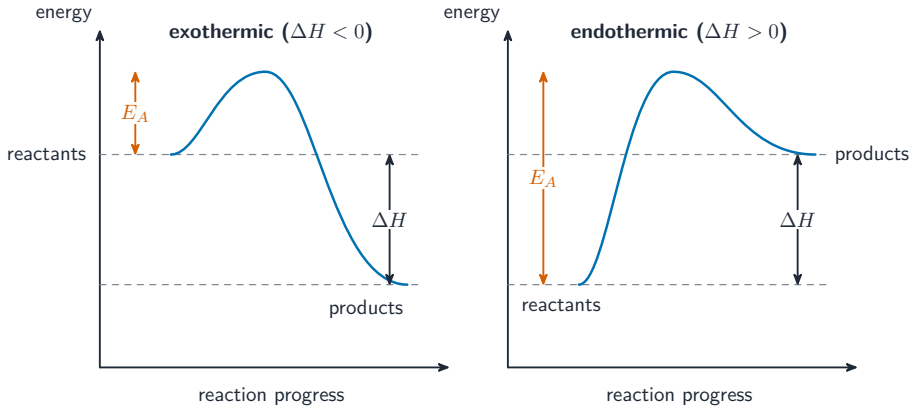
- in an **exothermic** 放热 reaction the system gives out heat, so the products have less energy than the reactants and ΔH is **negative**.
- in an **endothermic** 吸热 reaction the system takes in heat, so the products have more energy than the reactants and ΔH is **positive**.

Reaction pathway diagrams

A **reaction pathway diagram** 反应路径图 shows the energy of the reactants and products, and the energy "hill" between them. The height of the hill is the **activation energy** 活化能 – the least energy the particles need before they can react.

- exothermic: products sit **lower** than reactants ($\Delta H < 0$).
- endothermic: products sit **higher** than reactants ($\Delta H > 0$).

On the diagram, draw E_a as an arrow from the reactants' level **up to the top of the hill**, and ΔH as an arrow from the reactants' level to the products' level (pointing down for exothermic). The reverse reaction climbs the same hill from the products' side, so its activation energy is $E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H$. For example, if $E_a = +75$ kJ mol^{-1} and $\Delta H = -50$ kJ mol^{-1}, the reverse reaction has $E_a = 75 - (-50) = +125$ kJ mol^{-1}.



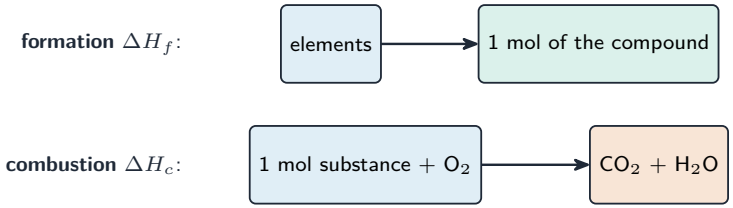
Exothermic reactions end lower than they start ($\Delta H < 0$); endothermic reactions end higher ($\Delta H > 0$)

Standard conditions and types of enthalpy change

Energy values are compared under **standard conditions** 标准条件: 298 K and 101 kPa, shown by the symbol $^{\ominus}$. Each substance is in its normal physical state at those conditions.

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Symbol	Name	Definition (per mole, under standard conditions)
$\Delta H_r^{\ominus}$	**enthalpy change of reaction** 反应焓变	for the amounts shown in the equation
$\Delta H_f^{\ominus}$	**enthalpy change of formation** 生成焓变	one mole of a compound forms from its elements
$\Delta H_c^{\ominus}$	**enthalpy change of combustion** 燃烧焓变	one mole of a substance burns completely in oxygen
$\Delta H_{\text{neut}}^{\ominus}$	**enthalpy change of neutralisation** 中和焓变	one mole of water forms from an acid and an alkali



Don't confuse them: formation builds 1 mol of a compound from its elements; combustion burns 1 mol of a substance in oxygen

Energy from breaking and making bonds

During a reaction, old bonds break and new bonds form. **Breaking** a bond needs energy (endothermic); **making** a bond releases energy (exothermic). The enthalpy change of the reaction is the difference between the two:

$$\Delta H_r = \sum(\text{bond energies broken}) - \sum(\text{bond energies made})$$

The **bond energy** 键能 is the energy needed to break one mole of a particular bond in the gas state, so it is always positive. Some bond energies are exact (for one specific molecule); others are averages taken over many different molecules, so calculations using them are only approximate.

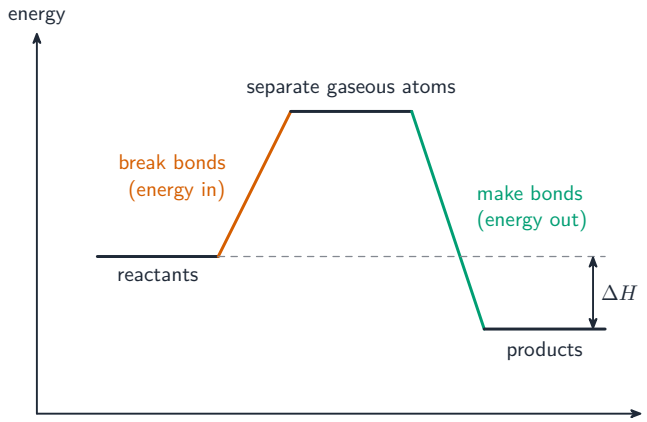
> **Worked example.** Use bond energies to find ΔH for $H_2 + Cl_2 \rightarrow 2HCl$. Bond energies (kJ mol^{-1}): H–H = 436, Cl–Cl = 242, H–Cl = 431.

$$\Delta H = \sum(\text{broken}) - \sum(\text{made}) = (436 + 242) - (2 \times 431) = 678 - 862 = -184 \text{ kJ mol}^{-1}.$$

> **Worked example: counting every bond.** Use bond energies to estimate ΔH_c of methane, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (all gases). Bond energies (kJ mol^{-1}): C–H = 410, O=O = 496, C=O = 805, O–H = 460. Draw out the structures and count: four C–H and two O=O break; two C=O (in CO_2) and four O–H (two in each water) form.

$$\Delta H = (4 \times 410 + 2 \times 496) - (2 \times 805 + 4 \times 460) = 2632 - 3450 = -818 \text{ kJ mol}^{-1}.$$

The data-book value is −890 kJ mol^{-1}. The answers differ because the C–H and O–H values are **averages**, and because bond energies apply to **gases**, while under standard conditions the water formed is a liquid: condensing it gives out extra energy.



Breaking bonds takes energy in; making bonds gives energy out. ΔH is the difference between the two

Measuring enthalpy change in the lab

When a reaction heats up (or cools down) a known mass of water or solution, the heat transferred is:

$$q = mc\Delta T$$

where m is the mass, c is the **specific heat capacity** 比热容 (how much energy raises 1 g by 1 K), and ΔT is the temperature change. The enthalpy change per mole is then:

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$$\Delta H = -\frac{mc\Delta T}{n}$$

The minus sign makes ΔH negative when the temperature rises (an exothermic reaction).

> **Worked example.** Burning 0.50 g of methanol ($M_r = 32$) raises the temperature of 100 g of water by 18 °C. Find the enthalpy change of combustion per mole. ($c = 4.18$ J g^{-1} K^{-1}.)

The heat released is $q = mc\Delta T = 100 \times 4.18 \times 18 = 7520$ J. The amount burnt is $n = 0.50/32 = 0.0156$ mol, so

$$\Delta H_c = -\frac{q}{n} = -\frac{7520}{0.0156} \approx -480 \text{ kJ mol}^{-1}.$$

The data-book value for methanol is −726 kJ mol^{-1}, so this result is much less exothermic. The usual reasons are **heat lost** to the air and to the can, **incomplete combustion** (soot on the can), and fuel **evaporating** from the wick before it is weighed again.

> **Worked example: neutralisation in solution.** 25.0 cm^3 of 2.00 mol dm^{-3} HCl is added to 25.0 cm^3 of 2.00 mol dm^{-3} NaOH in a polystyrene cup. The temperature rises by 13.5 K. Find ΔH_{neut}.

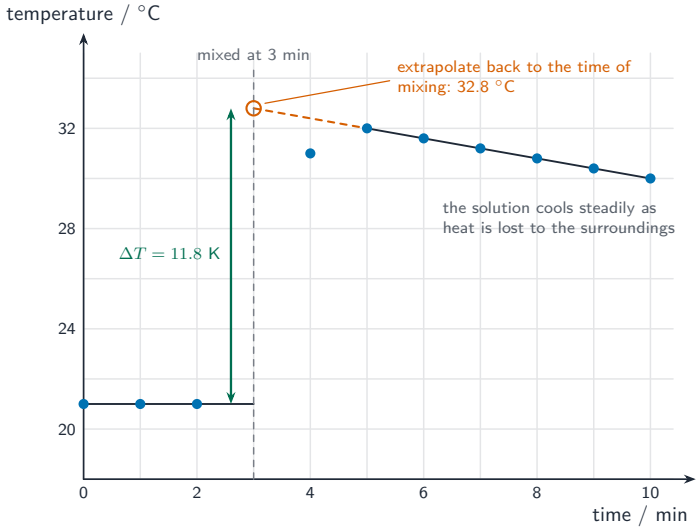
Take the solution as water: the total volume is 50.0 cm^3, so $m = 50.0$ g (density 1.00 g cm^{-3}). Then $q = 50.0 \times 4.18 \times 13.5 = 2820$ J. The water formed is $n = 0.0250 \times 2.00 = 0.0500$ mol, so

$$\Delta H_{\text{neut}} = -\frac{2820}{0.0500} = -56\,400 \text{ J mol}^{-1} = -56.4 \text{ kJ mol}^{-1}.$$

Use the **total** mass of both solutions, and the moles of the reagent that is **not** in excess (here both are equal).

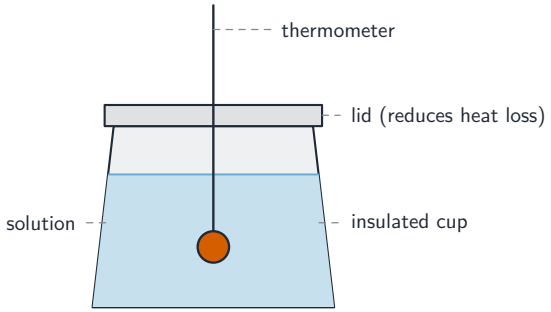
Correcting for heat loss

A reaction in a cup takes time, and heat leaks out while it happens, so the highest thermometer reading is too low. To correct for this, read the temperature every minute for a few minutes **before** mixing, mix at a set time (with no reading then), and keep reading for several minutes **after**. Plot temperature against time, draw a straight line through the cooling points, and **extrapolate** 外推 it back to the time of mixing. The temperature change is from the starting line to that extrapolated value.



Extrapolate the cooling line back to the moment of mixing: that corrects the highest temperature for the heat lost while the reaction was going on

Here the highest reading was only 32.0 °C, a rise of 11.0 K; the extrapolation gives 11.8 K. Other ways to improve the experiment are a **lid** on the cup, a second cup around it as insulation, and a thermometer that reads to 0.1 °C. A thermometer read to ±0.5 °C is used twice for ΔT, so a rise of 11.8 K has a percentage uncertainty of $(2 \times 0.5)/11.8 \times 100 = 8.5\%$.



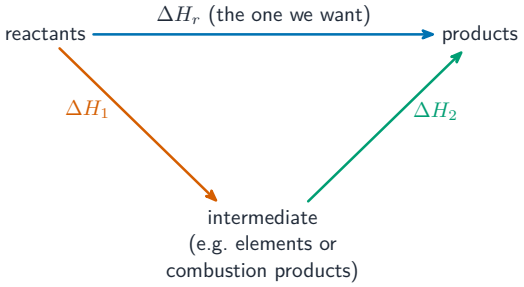
An insulated cup and a thermometer measure the temperature change of a known mass of solution

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Hess's law

Hess's law 盖斯定律 says that the total enthalpy change for a reaction is the same, no matter which route you take from reactants to products. This is because energy is conserved.

This lets you draw an **energy cycle** 能量循环: link the reactants and products by a direct step and by an indirect route, then add the steps so that both routes give the same total.



$$\Delta H_r = \Delta H_1 + \Delta H_2$$

The direct route equals the indirect route, so $\Delta H_r = \Delta H_1 + \Delta H_2$

Hess's law is useful in two ways:

- it lets you find an enthalpy change that you **cannot** measure directly (for example, the formation of a compound that forms slowly or with side reactions).
- it lets you calculate ΔH_r from bond energy data, or from formation or combustion data given in the question.

Worked example. Carbon, hydrogen and methane can all be burnt, but carbon and hydrogen will not react to make methane, so $\Delta H_f(\mathrm{CH_4})$ cannot be measured directly. Find it from these enthalpy changes of combustion (kJ mol^{-1}): C = −394, $\mathrm{H_2}$ = −286, $\mathrm{CH_4}$ = −890.

1. Write the reaction you want across the top: $\mathrm{C(s) + 2H_2(g) \rightarrow CH_4(g)}$.
2. Both sides burn to the same products, $\mathrm{CO_2 + 2H_2O}$, so draw that at the bottom of the cycle. Burning the elements goes **down** from the left; burning methane goes down from the right.
3. The two routes from the elements to $\mathrm{CO_2 + 2H_2O}$ must have the same total:

$$\Delta H_f(\mathrm{CH_4}) + (-890) = -394 + 2(-286),$$

$$\Delta H_f(\mathrm{CH_4}) = -394 - 572 + 890 = -76 \text{ kJ mol}^{-1}.$$

Worked example: a cycle from two experiments. The enthalpy change for $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4{\cdot}5H_2O(s)$ cannot be measured directly: the solid does not take up exactly five water molecules each, and the reaction is slow. Instead, each solid is dissolved in water, and the two enthalpy changes of solution are measured: anhydrous $CuSO_4$, $\Delta H_1 = -66$ kJ mol^{-1}; $CuSO_4{\cdot}5H_2O$, $\Delta H_2 = +11$ kJ mol^{-1}. Both solids give the **same** solution, $CuSO_4(aq)$, so draw it at the bottom of the cycle. The direct route is the hydration followed by dissolving the hydrate, and the other route is dissolving the anhydrous solid:

$$\Delta H_{\text{hyd}} + \Delta H_2 = \Delta H_1 \;\Rightarrow\; \Delta H_{\text{hyd}} = -66 - (+11) = -77 \text{ kJ mol}^{-1}.$$

The two short rules that come from these cycles are:

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}), \qquad \Delta H_r = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products}).$$

Common mistakes.

- Swapping the two rules: formation data is products **minus** reactants, combustion data is reactants **minus** products. If unsure, draw the cycle.
- Forgetting to multiply by the number in the equation. Above, there are **two** moles of H_2, so $\Delta H_c(H_2)$ is counted twice.
- Giving an element a non-zero enthalpy of formation. ΔH_f of an element in its standard state, such as $O_2(g)$, is zero.
- In $q = mc\Delta T$, using the mass of the fuel or of the solid added. m is the mass of the **water or solution** that is heated.
- Using the volume of only one solution in a neutralisation. m is the mass of **all** the liquid in the cup.
- Leaving out bonds that do not seem to change. Count **every** bond in the reactants and products; for example, two O=O break for each CH_4 burnt.
- Forgetting that q is in joules. Divide by 1000 to get kJ before dividing by moles.
- Expecting a bond-energy answer to match the data book exactly. Bond energies are **average** values over many compounds, so the answer is only approximate.

Exam tips

- Define each enthalpy change with its **exact standard conditions** (e.g. combustion = one mole burned completely in excess oxygen).
- Use $\Delta H = \sum$(bonds broken) $- \sum$(bonds made); breaking is endothermic (+), making is exothermic (−) – getting the sign the wrong way round is the classic error.
- In $q = mc\Delta T$ use the mass of the **water/solution**, then divide by moles and add the minus sign for an exothermic reaction.

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- For an experiment, explain a low result by **heat loss** (and, for fuels, incomplete combustion), and correct it by **extrapolating** a temperature-time graph.
- Draw **Hess cycles** with arrows the same way round, follow the alternative route, and always give ΔH a sign and units (kJ mol^{-1}).

Electrochemistry

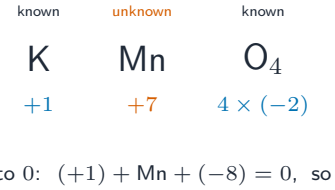
A-Level Chemistry

Oxidation number

The **oxidation number** 氧化数 (also called the oxidation state) shows how many **electrons** 电子 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.



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^-.

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

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Harder cases. The rules still work when there are two atoms of the unknown element, or when the answer is not a whole number:

Species	Working	Oxidation number
$Cr_2O_7^{2-}$	$2x + 7(-2) = -2$, so $2x = 12$	Cr = +6
$S_2O_3^{2-}$ (thiosulfate)	$2x + 3(-2) = -2$, so $2x = 4$	S = +2 (average)
$S_4O_6^{2-}$ (tetrathionate)	$4x + 6(-2) = -2$, so $4x = 10$	S = +2.5 (average)
H_2O_2	$2(+1) + 2x = 0$	O = −1 (a peroxide)
NaH	$+1 + x = 0$	H = −1 (a metal hydride)
NH_4^+	$x + 4(+1) = +1$	N = −3

A fractional value such as +2.5 is an **average**: in $S_4O_6^{2-}$ the sulfur atoms are not all in the same state, but the average is what the rules give and what you use to balance equations.

Names with Roman numerals. The numeral gives the oxidation number of the element just before it: iron(III) sulfate is $Fe_2(SO_4)_3$; copper(I) oxide is Cu_2O; in an anion the numeral follows the "-ate" name, so sodium chlorate(V) is $NaClO_3$ (Cl = +5) and sodium chlorate(I) is NaClO (Cl = +1). Manganate(VII) is MnO_4^-; dichromate(VI) is $Cr_2O_7^{2-}$.

Redox in terms of electrons



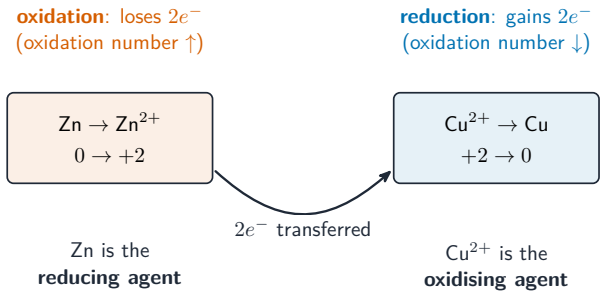
A battery uses redox reactions to push electrons round a circuit.

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

- **oxidation** 氧化 is the **loss** of electrons. The oxidation number goes **up**.
- **reduction** 还原 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** 电子转移 is why we call it a redox reaction.

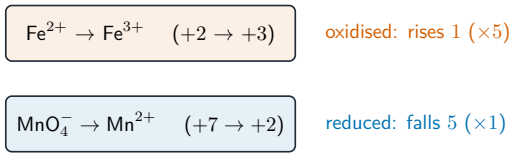


Redox is electron transfer: the reducing agent loses electrons (oxidised, number up); the oxidising agent gains them (reduced, number down)

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.



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

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

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 ($4\,H_2O$) and hydrogen with H^+ ($8\,H^+$):

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

Half-equations

A redox equation can be split into two **half-equations** 半反应方程式, one for the oxidation and one for the reduction, each showing the electrons. To write the reduction half-equation for manganate(VII) in acid:

1. write the species: $MnO_4^- \rightarrow Mn^{2+}$.
2. balance oxygen by adding H_2O: $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$.
3. balance hydrogen by adding H^+: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$.
4. balance the charge by adding electrons to the more positive side: the left is $-1+8 = +7$, the right is +2, so add $5e^-$ on the left.

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

The number of electrons (5) equals the change in oxidation number of Mn ($+7 \rightarrow +2$) – a useful check. The oxidation half-equation is $Fe^{2+} \rightarrow Fe^{3+} + e^-$. To combine them, multiply so the electrons are equal (here the iron half-equation ×5), add, and cancel the electrons.

> **Worked example.** Write the overall equation for dichromate(VI) oxidising iron(II) in acid. Cr falls from +6 to +3, and there are two Cr atoms, so the total fall is $2 \times 3 = 6$; each Fe rises by 1, so 6 Fe^{2+} are needed. The reduction half-equation is

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

and adding $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$ gives

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

Check the charge: left $-2 + 14 + 12 = +24$; right $+6 + 18 = +24$.

> **Worked example (a metal and an acid).** Copper reacts with concentrated nitric acid to give copper(II) ions and nitrogen dioxide. Balance $Cu + NO_3^- + H^+ \rightarrow Cu^{2+} + NO_2 + H_2O$. Cu rises from 0 to +2 (a rise of 2); N falls from +5 to +4 (a fall of 1). So 2 NO_3^- for each Cu. Balancing O and H:

$$Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2NO_2 + 2H_2O.$$

Disproportionation

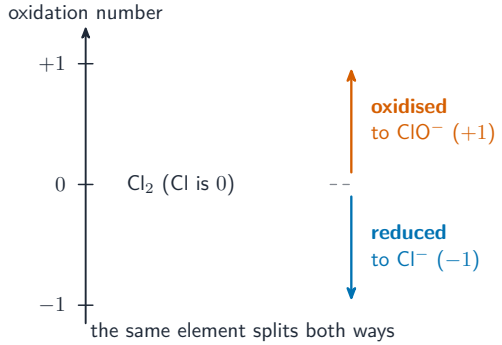
Disproportionation 歧化 is a special redox reaction in which the **same** element is both oxidised and reduced at the same time. For example, when chlorine reacts with cold water, some chlorine atoms are reduced (to Cl^-) and others are oxidised (to ClO^-).

$$Cl_2 + H_2O \rightarrow HCl + HClO \qquad (0 \rightarrow -1 \text{ and } 0 \rightarrow +1)$$

With cold dilute sodium hydroxide the same happens: $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$. With **hot** concentrated sodium hydroxide, chlorine goes further, up to +5:

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

Check with oxidation numbers: five Cl atoms each fall by 1 (a total fall of 5), and one Cl rises by 5 – they balance. Other examples: copper(I) in water, $2Cu^+ \rightarrow Cu + Cu^{2+}$; and hydrogen peroxide decomposing, $2H_2O_2 \rightarrow 2H_2O + O_2$, where oxygen goes from -1 to both -2 and 0.



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

Oxidising and reducing agents

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

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Rusting is the oxidation of iron by oxygen.

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

> **Worked example.** In the reaction $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$, identify the oxidising agent and the reducing agent. Iron falls from +3 to +2, so Fe^{3+} is **reduced** – it is the **oxidising agent**. Iodine rises from -1 to 0, so I^- is **oxidised** – it is the **reducing agent**. Name the **species** (Fe^{3+}, I^-), not just the element, and say which way its oxidation number changes.

Common oxidising agents: MnO_4^-/H^+, $Cr_2O_7^{2-}/H^+$, the halogens, O_2, concentrated H_2SO_4, H_2O_2. Common reducing agents: reactive metals, H_2, C and CO, Fe^{2+}, I^-, SO_2.

Common mistakes.

- Saying the oxidising agent is oxidised. An **oxidising agent** takes electrons, so it is itself **reduced**; in the manganate(VII)/iron(II) reaction, MnO_4^- is the oxidising agent and is reduced to Mn^{2+}.
- Writing an oxidation number as a charge, such as 2+ for iron(II). Write the **sign first**: +2. Charges on ions are written number-first (Fe^{2+}).
- Giving oxygen -2 in hydrogen peroxide. In peroxides oxygen is -1; in OF_2 it is even +2, because fluorine always wins.
- Balancing the atoms but not the charge. Check that the total charge is the same on both sides: in the manganate(VII) equation, $-1 + 10 + 8 = +17$ on the left and $+2 + 15 = +17$ on the right.
- Calling every reaction with an element in two products disproportionation. The **same** element must start in **one** oxidation state and go both up and down.

Exam tips

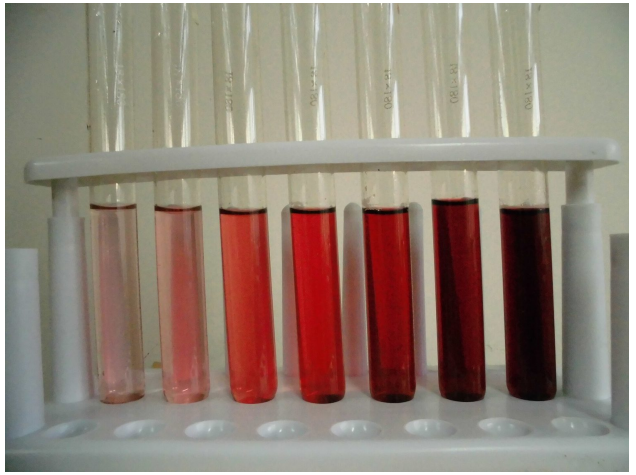
- Apply the oxidation-number rules in order: O is -2 **except** in peroxides (-1); H is $+1$ **except** in metal hydrides (-1).
- In a redox equation the **total increase equals the total decrease** in oxidation number – use this to fix the ratio, then balance O with H_2O and H with H^+.
- An **oxidising 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.
- To write a half-equation: balance the element, then O with H_2O, then H with H^+, then charge with e^-. The number of electrons equals the change in oxidation number (times the number of atoms).
- Always check that the charges balance as well as the atoms.

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Equilibria

A-Level Chemistry

Reversible reactions and dynamic equilibrium



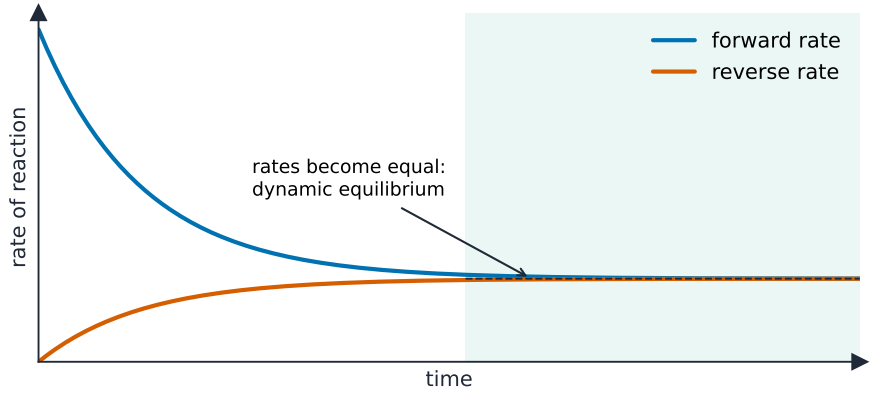
Cobalt chloride changes colour as its equilibrium shifts.

A **reversible reaction** 可逆反应 can go both ways. The **forward reaction** 正反应 makes products; the **reverse reaction** 逆反应 turns products back into reactants. We show this with the sign $\rightleftharpoons$.

In a **closed system** 封闭系统 (nothing enters or leaves), the reaction reaches a **dynamic equilibrium** 动态平衡 when:

- the rate of the forward reaction equals the rate of the reverse reaction.
- the concentrations of reactants and products stay constant.

It is called *dynamic* because both reactions are still happening – they just cancel out. A closed system is needed, or products would escape and equilibrium could never be reached.



at equilibrium: $\text{rate}_f = \text{rate}_r \cdot K_c = \frac{[\text{products}]}{[\text{reactants}]}$

At dynamic equilibrium the forward and reverse rates have become equal, so the concentrations stay constant

Le Chatelier's principle

Le Chatelier's principle 勒夏特列原理 says: if you change a system at equilibrium, the position of **equilibrium** 平衡 moves to oppose (reduce) that change.

Change you make	Which way the equilibrium moves
increase concentration of a reactant	towards the products
increase pressure	towards the side with fewer gas molecules
increase temperature	towards the **endothermic** direction
add a **catalyst** 催化剂	no shift (it speeds up both ways equally)

A catalyst lets equilibrium be reached faster, but it does **not** change the position of equilibrium.

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the equilibrium shifts to *oppose* the change you make

increase [reactant]	→ towards the **products**
increase pressure	→ to the **fewer-gas-molecules** side
increase temperature	→ in the **endothermic** direction

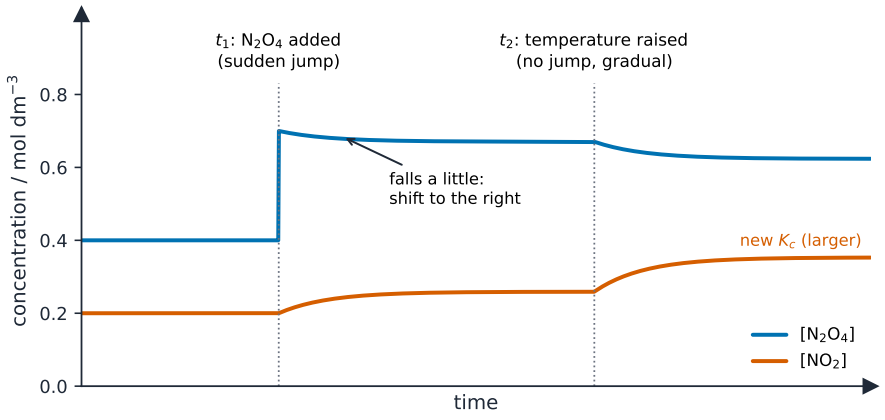
a **catalyst** speeds both directions equally, so it gives *no shift*

Le Chatelier's principle: the equilibrium always shifts to oppose the change you make

Explaining a shift with K_c. At A level, "it opposes the change" is not enough; explain it with the constant. Take $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, where the forward reaction is endothermic and

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

- **Concentration change.** At equilibrium $[\text{N}_2\text{O}_4] = 0.40$ and $[\text{NO}_2] = 0.20$ mol dm^{-3}, so $K_c = 0.20^2/0.40 = 0.10$. Extra N_2O_4 raises its concentration to 0.70. Now $\dfrac{0.20^2}{0.70} = 0.057$, which is **smaller** than K_c. The temperature has not changed, so K_c is still 0.10: some N_2O_4 must turn into NO_2 until the fraction is 0.10 again. The equilibrium moves to the right.
- **Temperature change.** Raising the temperature favours the endothermic direction, here the forward one. This time K_c itself **changes** (from 0.10 to about 0.20), so the mixture moves to the right until it fits the new value.



$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, forward endothermic · NO_2 changes twice as much as N_2O_4

Adding a substance makes its line jump at once; a temperature change makes both lines move gradually, because it changes K_c

Reading and sketching these graphs.

- A substance that is **added** or removed jumps vertically at that moment; the other lines do not jump.
- After the jump, the lines bend towards new steady values and become flat again: a new equilibrium.
- The changes follow the equation: here $[NO_2]$ rises by **twice** as much as $[N_2O_4]$ falls $(1:2)$.
- A temperature change gives **no** jump, only gradual changes.
- An increase in pressure made by compressing the gas makes **every** gas line jump up, because all the concentrations rise together. Then the shift towards fewer gas molecules follows.

Common mistakes.

- Saying that adding a reactant "increases K_c". Only temperature changes K_c; a concentration or pressure change moves the **position**.
- Saying the system goes back to the **original** concentrations. The shift only partly undoes the change: in the graph $[N_2O_4]$ ends at 0.67, not 0.40.
- Saying a catalyst "gives more product". It gives the same equilibrium mixture, only sooner.
- Predicting the temperature effect without checking the sign of ΔH. Find which direction is endothermic first.

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Equilibrium constants

For a reaction at equilibrium, the **equilibrium constant** 平衡常数 links the amounts of products and reactants. For the reaction $aA + bB \rightleftharpoons cC + dD$:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

where the square brackets mean concentration in mol dm^{-3}.

Worked example. At equilibrium the mixture $H_2 + I_2 \rightleftharpoons 2HI$ has $[H_2] = 0.20$, $[I_2] = 0.20$ and $[HI] = 1.6$ mol dm^{-3}. Find K_c.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{1.6^2}{0.20 \times 0.20} = 64$$

(no units here, because the concentration powers cancel top and bottom).

Worked example (ICE table). 1.00 mol each of H_2 and I_2 are sealed in a 1.00 dm^3 flask; at equilibrium 0.20 mol of H_2 remains. Set out an **ICE table** (Initial, Change, Equilibrium):

	H_2	I_2	$2HI$
Initial	1.00	1.00	0
Change	−0.80	−0.80	+1.60
Equilibrium	0.20	0.20	1.60

0.80 mol of H_2 reacted, so $2 \times 0.80 = 1.60$ mol HI formed. In the 1.00 dm^3 flask the concentrations equal the moles, so $K_c = \dfrac{1.60^2}{0.20 \times 0.20} = 64$.

Worked example (volume not 1 dm^3, and units). 0.50 mol of PCl_5 is heated in a sealed 2.0 dm^3 flask: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. At equilibrium there is 0.20 mol of Cl_2. Calculate K_c.

	PCl_5	PCl_3	Cl_2
Initial / mol	0.50	0	0
Change / mol	−0.20	+0.20	+0.20
Equilibrium / mol	0.30	0.20	0.20
Concentration / mol dm^{-3}	0.15	0.10	0.10

Divide each number of moles by the **volume**, 2.0 dm^3, before using the expression:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.10 \times 0.10}{0.15} = 0.067 \text{ mol dm}^{-3}$$

The units are $\dfrac{(\text{mol dm}^{-3})^2}{\text{mol dm}^{-3}} = \text{mol dm}^{-3}$. Work them out by cancelling, every time: they depend on the equation.

> **Worked example (finding an equilibrium amount).** For $H_2 + I_2 \rightleftharpoons 2HI$ at this temperature $K_c = 64$. A mixture at equilibrium has $[H_2] = [I_2] = 0.10$ mol dm^{-3}. Find [HI]. Rearrange the expression: $[HI]^2 = K_c[H_2][I_2] = 64 \times 0.10 \times 0.10 = 0.64$, so $[HI] = 0.80$ mol dm^{-3}.

Which substances appear. In a **heterogeneous** 多相 equilibrium (more than one phase), leave **solids** out of the expression, because their concentration does not change. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_c = [CO_2]$ and $K_p = p(CO_2)$. Water is left out when it is the solvent, but included when it is a reactant or product in a gas mixture or in a mixture of organic liquids (as in esterification).

For reactions of gases, we use **partial pressure** 分压 instead of concentration. The partial pressure of a gas is the share of the total pressure that it provides. It is found from the **mole fraction** 摩尔分数 (the fraction of all the moles that are that gas):

$$\text{partial pressure} = \text{mole fraction} \times \text{total pressure}$$

The constant written with partial pressures is K_p.

> **Worked example.** A gas mixture holds 2.0 mol of N_2 and 6.0 mol of H_2 at a total pressure of 200 kPa. Find the partial pressure of each gas.

There are 8.0 mol in total, so

$$p(N_2) = \frac{2.0}{8.0} \times 200 = 50 \text{ kPa}, \qquad p(H_2) = \frac{6.0}{8.0} \times 200 = 150 \text{ kPa}.$$

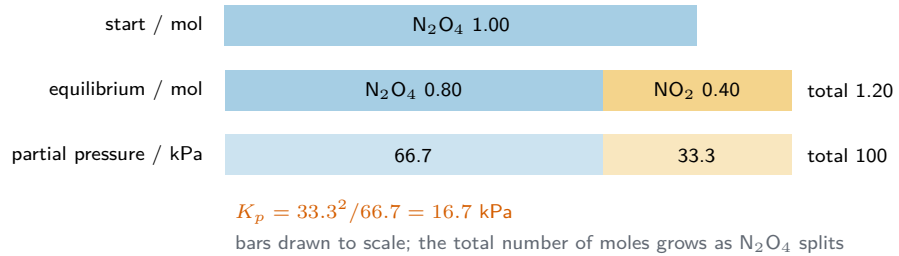
> **Worked example (a numeric K_p).** For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ the equilibrium partial pressures are $p(N_2) = 20$, $p(H_2) = 40$ and $p(NH_3) = 10$ kPa. Then
>
> $$K_p = \frac{p(NH_3)^2}{p(N_2)\,p(H_2)^3} = \frac{10^2}{20 \times 40^3} = 7.8 \times 10^{-5} \text{ kPa}^{-2},$$
>
> the units coming from $\dfrac{\text{kPa}^2}{\text{kPa} \times \text{kPa}^3} = \text{kPa}^{-2}$.

> **Worked example (K_p from the amount that reacts).** 1.00 mol of N_2O_4 is allowed to reach equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, at a total pressure of 100 kPa. At equilibrium 20% of the N_2O_4 has dissociated. Calculate K_p.

1. Moles at equilibrium: N_2O_4: $1.00 - 0.20 = 0.80$; NO_2: $2 \times 0.20 = 0.40$; total $= 1.20$ mol.
2. Mole fractions: N_2O_4: $0.80/1.20 = 0.667$; NO_2: $0.40/1.20 = 0.333$.

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3. Partial pressures: 66.7 kPa and 33.3 kPa (they add up to the total, 100 kPa: a useful check).
4. $K_p = \dfrac{p(NO_2)^2}{p(N_2O_4)} = \dfrac{33.3^2}{66.7} = 16.7$ kPa.



Moles, then mole fractions, then partial pressures: the total number of moles changes on the way.

The usual slip is to forget that the number of moles of gas changes as the reaction goes, so the **total** moles must be found again at equilibrium.

Only **temperature** changes the value of K_c or K_p. Changing concentration or pressure shifts the position of equilibrium but leaves the constant unchanged; adding a catalyst changes **neither** the constant nor the position – it only makes equilibrium arrive faster.

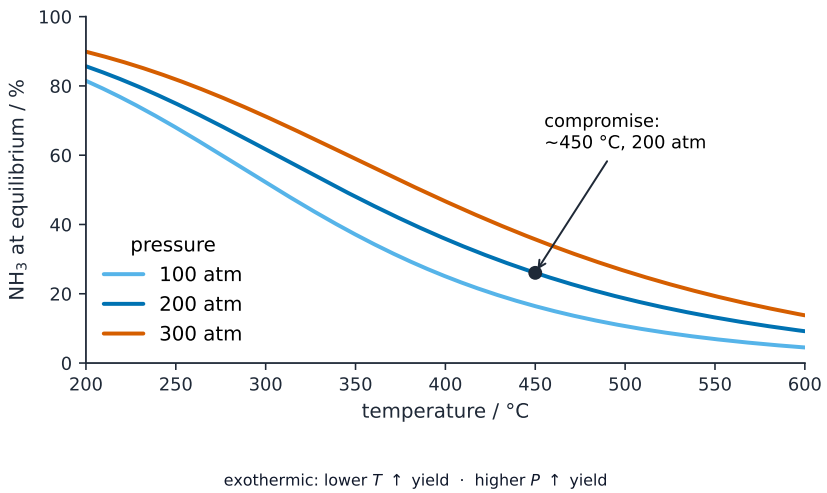
The Haber and Contact processes



Ammonia for fertiliser is made by the Haber process in large industrial plants like this one.

These two industrial processes are chosen by balancing yield, rate and cost using Le Chatelier's principle.

- the **Haber process** 哈伯法 makes ammonia: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (exothermic). It uses about 450 °C, 200 atm and an iron catalyst. A low temperature would give more ammonia but too slowly, so a moderate temperature is a compromise.
- the **Contact process** 接触法 makes sulfur trioxide: $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (exothermic). It uses about 450 °C, near 1–2 atm and a vanadium(V) oxide catalyst.



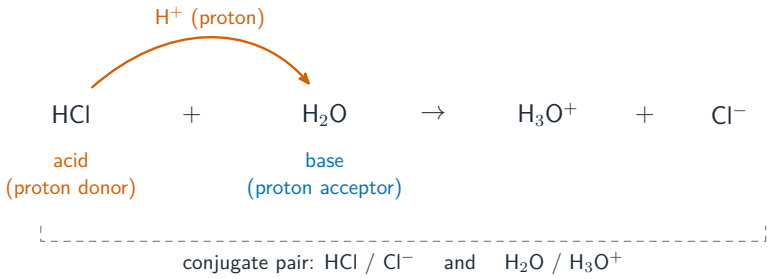
The Haber equilibrium gives more ammonia at lower temperature and higher pressure; about 450 °C and 200 atm is the working compromise

Acids and bases: the Brønsted–Lowry theory

A **proton** 质子 is simply an H^+ ion. The Brønsted–Lowry theory defines acids and bases by what they do with protons:

- an **acid** 酸 is a **proton donor** 质子供体 (it gives away H^+).
- a **base** 碱 is a **proton acceptor** 质子受体 (it takes H^+). A base that dissolves in water is called an alkali.

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Brønsted–Lowry: the acid donates a proton (H^+) to the base, making two conjugate acid–base pairs

> **Worked example (conjugate pairs).** Identify the acid–base pairs in $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. In the forward direction water **donates** a proton to ammonia, so water is the acid and ammonia the base. The pairs differ by one H^+: NH_4^+/NH_3 (acid/base) and H_2O/OH^- (acid/base). Water is a base when it reacts with HCl but an acid here: it can do both.

Common acids you must know: hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3) and ethanoic acid (CH_3COOH). Common alkalis: sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonia (NH_3).

Strong and weak acids and bases

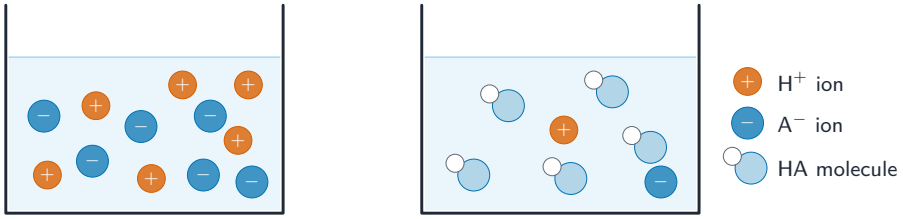
This is about how fully an acid or base splits up in water – not how concentrated it is.

- a **strong acid** 强酸 or **strong base** 强碱 is fully **dissociated** 解离 in water (almost every molecule splits into ions).
- a **weak acid** 弱酸 or **weak base** 弱碱 is only partly dissociated (most molecules stay whole).

The equations show the difference: a full arrow for a strong acid, an equilibrium arrow for a weak one.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \qquad CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Sodium hydroxide is a strong base (fully dissociated into Na^+ and OH^-). Ammonia is a weak base: only a small fraction of its molecules accept a proton from water, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, and the equilibrium lies well to the left.



strong acid
fully dissociated: many ions

weak acid
mostly molecules: few ions

Same concentration, different ionisation: a strong acid is fully dissociated into ions; a weak acid stays mostly as whole molecules

The **pH** scale measures how acidic a solution is: pure water is pH 7, acids are below 7, and alkalis are above 7. A strong acid has a lower pH than a weak acid of the same concentration.

You can tell strong and weak acids apart by:

- **reaction with a reactive metal**: a strong acid fizzes faster.
- **pH**: measured with a pH meter or **universal indicator** 通用指示剂.
- **electrical conductivity**: a strong acid conducts better, because it has more ions.

Neutralisation, salts and titration curves

Neutralisation 中和 happens when the hydrogen ions from an acid react with the hydroxide ions from an alkali:

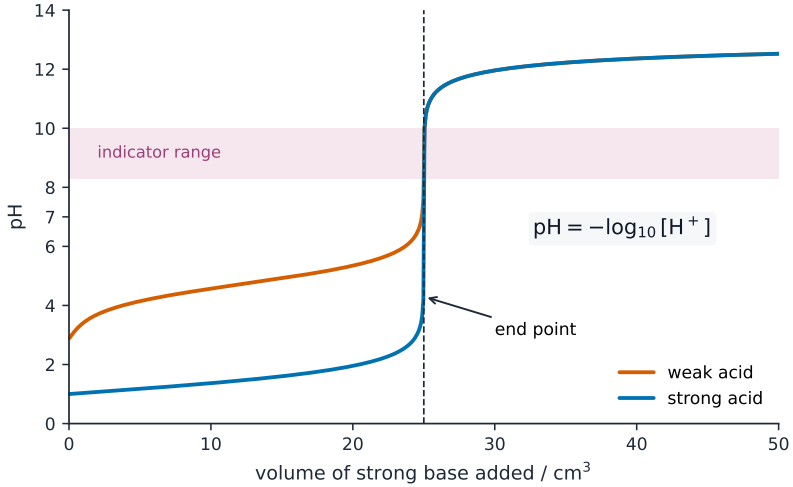
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

A **salt** 盐 is also formed, from the rest of the acid and base.

In a **titration** 滴定 you add one solution to another and follow the pH. The **titration curve** 滴定曲线 has a steep, almost vertical jump near the end point. The exact shape depends on whether each reactant is strong or weak.

To pick an **indicator** 指示剂, choose one whose colour change falls inside that steep jump. For a strong acid with a strong base most indicators work; for a weak acid with a strong base you need one that changes in the higher pH range.

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Titration curves each have a steep pH jump at the end point. The weak-acid jump sits higher, so the indicator must change colour in that range

The four curves. For 25 cm^3 of acid with an alkali of the same concentration added (examples: strong acid HCl, weak acid CH_3COOH, strong base NaOH, weak base NH_3):

Acid + base	Start pH	Steep section	Equivalence pH
strong + strong	about 1	pH 3 to 11	7
weak + strong	about 3	pH 7 to 11	above 7 (about 9)
strong + weak	about 1	pH 3 to 7	below 7 (about 5)
weak + weak	about 3	**no** steep section	about 7

Choosing an indicator from data. An indicator changes colour over a range of about 2 pH units. It is suitable if the whole range lies **inside the steep section** of the curve, so one drop of alkali changes its colour.

Indicator	Colour change range (pH)
methyl orange	3.1–4.4
bromothymol blue	6.0–7.6
phenolphthalein	8.3–10.0

Worked example. A weak acid is titrated with sodium hydroxide; the curve rises steeply from pH 7.5 to pH 11. Which indicator? **Phenolphthalein**: its range, 8.3–10.0, lies within the steep section. Methyl orange would change colour long before the equivalence point, while the curve is still rising slowly. For a strong acid with a weak base (steep from about 3 to 7), choose **methyl orange**. For a weak acid with a weak base, **no** indicator gives a sharp end-point; follow the titration with a pH meter instead.

Exam tips

- Define **dynamic equilibrium** with all three points: forward and reverse rates equal, concentrations constant, closed system.
- Answer **Le Chatelier** questions by stating the change, the direction of shift, and the reason; a **catalyst does not shift** the position (it speeds both rates).
- Write K_c as **products over reactants**, each raised to its balancing number; include state symbols to decide what appears.
- Justify Haber/Contact conditions as a **compromise** between yield, rate and cost – do not just quote them.
- Brønsted: acid = **proton donor**, base = proton acceptor; conjugate pairs differ by one H^+.
- In a K_c calculation, change moles to **concentrations** (divide by the volume) before substituting, and work out the units by cancelling.
- In a K_p calculation, find the **total** moles at equilibrium again, then mole fractions, then partial pressures.
- Pick an indicator whose whole colour-change range sits inside the **vertical section** of the titration curve.

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Reaction kinetics

A-Level Chemistry

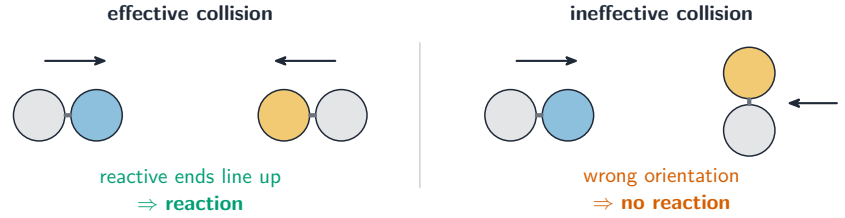
Rate of reaction

The **rate of reaction** 反应速率 is how fast reactants turn into products. We measure it as the change in concentration (or amount) in each unit of time.

To react, particles must **collide** 碰撞. The **collision frequency** 碰撞频率 is how often the particles hit each other. But not every collision leads to a reaction:

- an **effective collision** 有效碰撞 has enough energy *and* the correct direction, so a reaction happens.
- a **non-effective collision** 无效碰撞 does not have enough energy, or the particles hit at the wrong angle, so nothing happens.

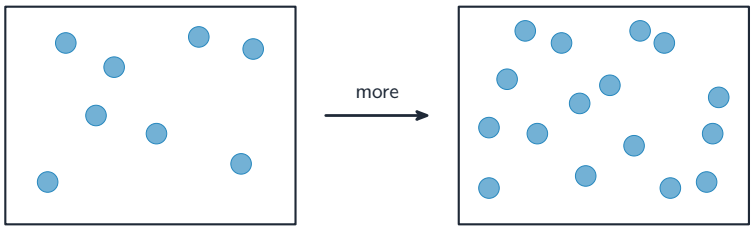
So the rate depends on the **frequency of effective collisions** – how many useful collisions happen each second.



A collision only reacts with the right orientation and enough energy (coloured ends = the reactive part)

Concentration and pressure

If you increase the concentration of a solution (or the pressure of a gas), the particles are packed closer together. They collide more often, so there are more effective collisions each second, and the rate goes up.



More particles in the same volume collide more often, so the rate rises

You can calculate a rate from experimental data – for example, the volume of gas made divided by the time taken.

Worked example. A reaction gives off carbon dioxide. In the first 30 s, 48 cm^3 of gas is collected. Find the average rate of reaction over this time.

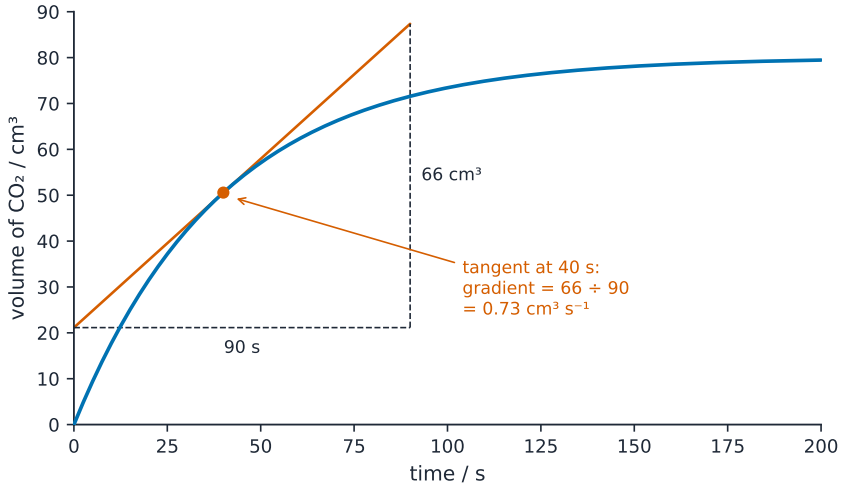
$$\text{average rate} = \frac{\text{volume of gas}}{\text{time}} = \frac{48}{30} = 1.6 \text{ cm}^3\,\text{s}^{-1}.$$

The rate is fastest at the start (the graph is steepest there) because the reactants are most concentrated, then it slows as they are used up.

Rate at one instant: drawing a tangent

An average rate hides how the rate changes. The rate at a particular **instant** is the **gradient** 斜率 of the curve at that time. Draw a **tangent** 切线 – a straight line that just touches the curve at that point, with the curve the same distance from it on each side – then make a large right-angled triangle on it and divide the rise by the run.

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The rate at one instant is the gradient of the tangent to the curve at that time

Worked example. From the graph above, find the rate at 40 s and compare it with the initial rate. The tangent at 40 s rises 66 cm^3 over 90 s, so the rate is $66 \div 90 = 0.73$ $cm^3\,s^{-1}$. A tangent at $t = 0$ is much steeper (about 2.0 $cm^3\,s^{-1}$), because the acid is most concentrated at the start. The curve becomes flat when one reactant is used up: the rate is then zero, and the final volume (80 cm^3) shows the total amount of product. Use the largest triangle you can, because reading small distances from a graph gives a large percentage error.

Units of rate. A rate is a change divided by a time, so its unit is the unit of what you measured divided by the unit of time: $cm^3\,s^{-1}$ for a gas volume, $g\,s^{-1}$ for a loss of mass, and $mol\,dm^{-3}\,s^{-1}$ for a change in concentration.

Ways to follow a reaction

What changes	Method	Example
a gas is given off	collect it in a gas syringe (or over water) and read the volume at regular times	$CaCO_3$ + HCl; Mg + HCl
a gas escapes from an open flask	stand the flask on a balance and record the **loss in mass**	$CaCO_3$ + HCl (works best with a dense gas, CO_2)
a colour changes	measure the absorbance with a **colorimeter** 比色计	iodine fading, I_2 + propanone
a precipitate forms	time how long until a cross under the flask disappears; rate $\propto 1/t$	thiosulfate + acid, giving sulfur
the concentration of acid or alkali changes	take samples, stop the reaction by cooling or diluting (**quenching**), and titrate	ester hydrolysis

Worked example (reciprocal time). Sodium thiosulfate reacts with acid to give a sulfur precipitate. At a thiosulfate concentration of 0.10 mol dm^{-3}, the cross disappears after 40 s; at 0.20 mol dm^{-3}, after 20 s. Compare the rates. The same amount of sulfur must form each time to hide the cross, so rate $\propto 1/t$: $1/40 = 0.025$ s^{-1} and $1/20 = 0.050$ s^{-1}. Doubling the concentration **doubles** the rate, because the particles collide twice as often.

Temperature and activation energy

The **activation energy** 活化能 (E_A) is the minimum energy a collision needs in order to be effective.

The **Boltzmann distribution** 玻尔兹曼分布 is a graph showing how the energies of the molecules are spread out at one temperature. The curve starts at the origin, rises to a peak, then falls away in a long tail. The total area under the curve is the total number of molecules. Only the molecules to the right of E_A have enough energy to react.

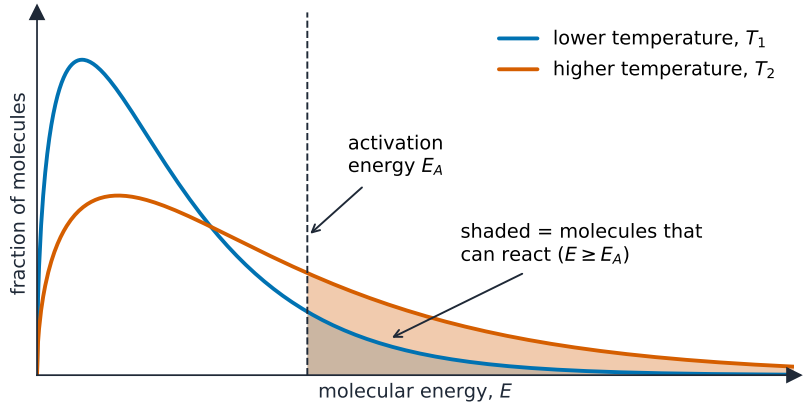
When you raise the temperature:

- the curve flattens and spreads to the right, so a **much larger fraction** of molecules now have energy greater than E_A.
- the molecules also move faster and collide more often.

The first effect is the bigger one. This is why a small rise in temperature gives a large rise in rate.

How to sketch the Boltzmann distribution. Label the axes: **number of molecules** (y) against **energy** (x). Start the curve at the **origin** (no molecule has zero energy); draw a peak that is not symmetrical, with a long tail on the right that gets closer and closer to the x-axis but **never touches** it (a few molecules have very high energy). Mark E_A well to the right of the peak, and shade the area under the curve beyond it. At a higher temperature, draw the second curve with a **lower** peak further to the right and a higher tail beyond E_A; the two curves must enclose the **same area**.

Worked example. Use the Boltzmann distribution to explain why increasing the temperature increases the rate. [3 marks] At a higher temperature the molecules have a higher average energy, so the distribution shifts to the right (and the peak is lower). A **greater proportion** of molecules now have energy **equal to or greater than** E_A (more area beyond E_A). So there are more **effective collisions per unit time**, and the rate increases. (The molecules also collide more often, but this is a much smaller effect.)



higher T ⇒ more molecules with $E \geq E_A$

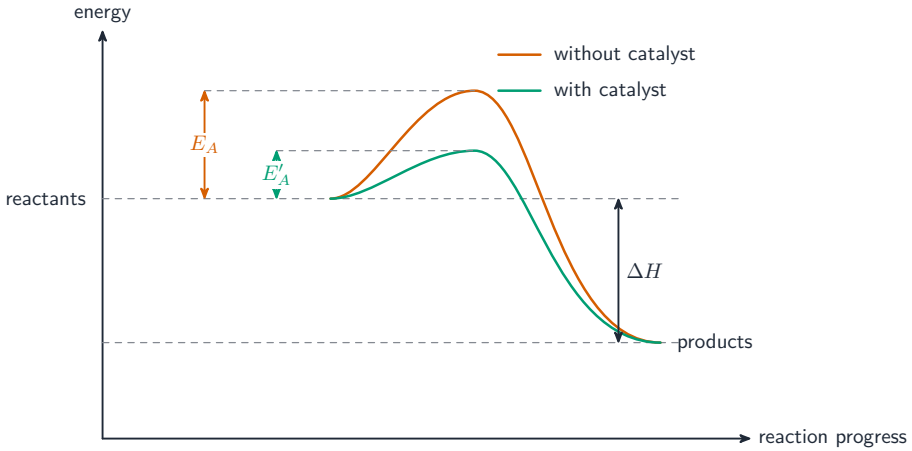
At higher temperature the curve spreads to the right, so a larger fraction of molecules can react

Catalysts

A **catalyst** 催化剂 speeds up a reaction but is not used up itself. **Catalysis** 催化作用 is the name for this action.

A catalyst works by giving the reaction a different **reaction mechanism** 反应机理 – a new route with a **lower** activation energy. On the Boltzmann distribution, lowering E_A moves the line to the left, so more molecules now have enough energy. This means more effective collisions each second, and a faster rate.

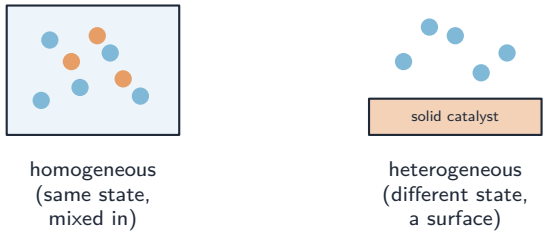
On a **reaction pathway diagram** 反应路径图, the catalysed route has a lower energy "hill". The enthalpy change of the reaction, ΔH, is **not** changed by the catalyst.



A catalyst gives a route with lower activation energy; the enthalpy change is unchanged

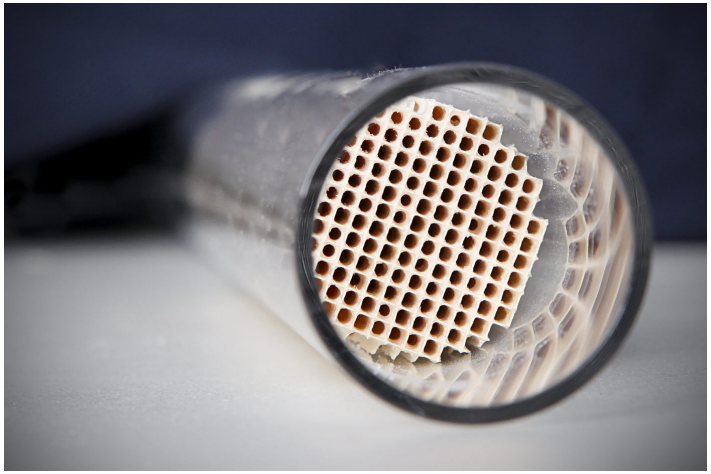
There are two types:

- a **homogeneous catalyst** 均相催化剂 is in the **same** physical state as the reactants – for example, an acid catalyst dissolved in a solution of liquids.
- a **heterogeneous catalyst** 多相催化剂 is in a **different** state from the reactants – for example, solid iron speeding up the reaction of gases in the Haber process.



A homogeneous catalyst is mixed in with the reactants (same state); a heterogeneous catalyst is a separate surface (different state), where reactants meet and react

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A car's catalytic converter is a heterogeneous catalyst; its honeycomb gives a huge surface area

How a heterogeneous catalyst works. The reacting gas molecules are **adsorbed** 吸附 onto the surface of the solid: they form weak bonds to the catalyst atoms. This weakens the bonds inside the reactant molecules and holds them close together in a good position to react. After the reaction, the products are **desorbed** 脱附 (they leave the surface), freeing the active sites for more reactant. The catalyst is made into a fine powder, a mesh or a honeycomb to give a large **surface area**. Examples: iron in the Haber process; platinum, palladium and rhodium in a catalytic converter; nickel for adding hydrogen to alkenes. A homogeneous catalyst instead forms an **intermediate** 中间体 with one reactant, which then reacts to give the product and the catalyst back (for example H^+ in esterification, or Fe^{2+} in the iodide–peroxodisulfate reaction).

Reading a reaction pathway diagram. On an energy profile, E_A is measured from the **reactants** up to the top of the hill, and ΔH from the reactants to the **products**. For the **reverse** reaction, E_A is measured from the products to the top. So for an exothermic reaction, $E_A(\text{reverse}) = E_A(\text{forward}) + |\Delta H|$.

> **Worked example.** A reaction has $\Delta H = -92\ \text{kJ mol}^{-1}$ and $E_A = +230\ \text{kJ mol}^{-1}$; a catalyst lowers E_A to $+80\ \text{kJ mol}^{-1}$. State the activation energy of the reverse reaction with the catalyst, and the effect of the catalyst on ΔH. Reverse $E_A = 80+92 = 172\ \text{kJ mol}^{-1}$. ΔH is unchanged ($-92\ \text{kJ mol}^{-1}$), because the reactants and products are the same and so are their energies. The catalyst lowers the activation energy of the forward and reverse reactions by the **same** amount ($150\ \text{kJ mol}^{-1}$), so it speeds up both.

The catalyst on the Boltzmann distribution. Draw a **single** curve (the temperature is unchanged) and mark two activation energies, E_A and a smaller $E_{A,\text{cat}}$ to its left. The extra shaded area between them is the extra fraction of molecules that can

now react.

Common mistakes.

- Drawing the higher-temperature Boltzmann curve with a **taller** peak. The number of molecules is the same, so the area under both curves is the same: the new peak is **lower** and further right.
- Moving the curve when a catalyst is added. The molecules have the same energies, so the curve does not change; the E_A line moves to the **left**.
- Saying higher concentration gives the particles more energy. Their energies are unchanged; they are closer together, so they collide **more often**.
- Writing "more collisions" without time. Rate depends on the number of effective collisions **per second** (their frequency).
- Saying a catalyst gives the particles more energy, or is used up. It gives a different route with a lower E_A and is made again at the end.

Exam tips

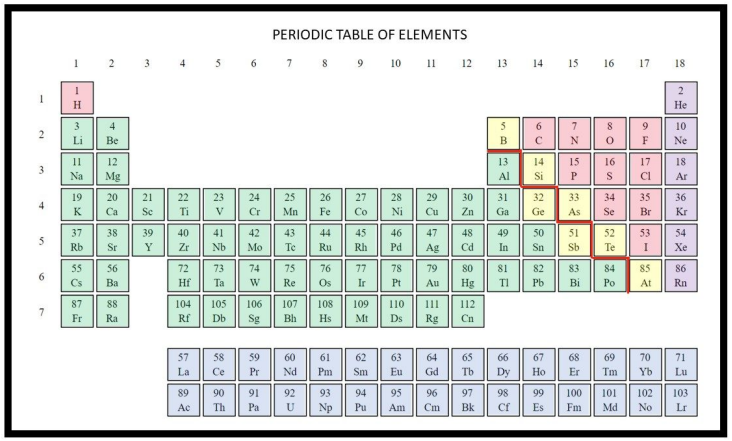
- Explain rate changes with **collision theory** – more frequent and/or more energetic **effective collisions**.
- On a **Boltzmann distribution** mark E_A, shade to its right, and show the curve **flatten and shift right** at higher temperature; it starts at the origin, and its high-energy tail never meets the energy axis.
- A **catalyst** gives an alternative route with **lower** E_A and does **not** change ΔH.
- Say why a small temperature rise gives a large rate rise: a **much greater proportion** of molecules now exceed E_A (the main effect).
- For a rate at one time, draw a tangent and find its gradient with a large triangle; give the unit.
- When the cross disappears, rate $\propto 1/\text{time}$.
- Heterogeneous catalysis: adsorption → bonds weakened → reaction → desorption.

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The Periodic Table: chemical periodicity

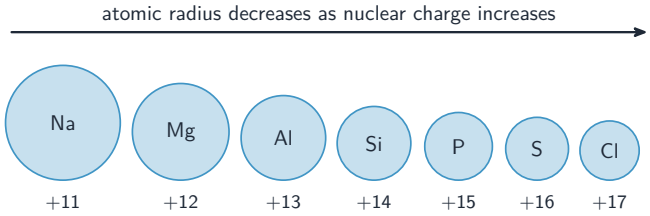
A-Level Chemistry

Physical properties across Period 3



Properties repeat in a regular pattern across each period of the table.

Periodicity 周期性 means that properties repeat in a regular pattern as you go across each **period** 周期 of the Periodic Table. Period 3 (Na to Ar) is the standard example.



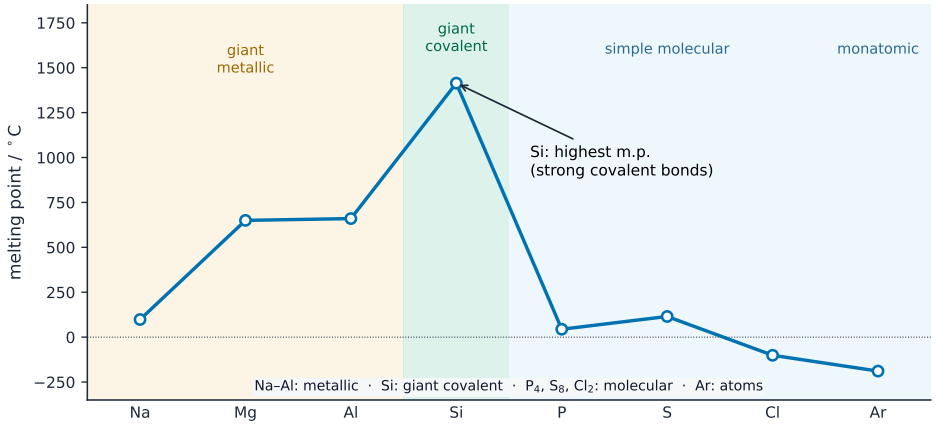
Atomic radius decreases across Period 3: the rising nuclear charge pulls the same outer shell inwards

Property	Trend across Period 3
atomic radius 原子半径	gets smaller (more nuclear charge pulls the same shell in)
ionic radius 离子半径	positive ions are small; from P^{3-} onwards the negative ions are larger
melting point 熔点	rises to a peak at silicon, then falls sharply
electrical conductivity 导电性	high for Na, Mg, Al; almost zero from Si onwards

The melting point and conductivity follow from the structure and bonding:

- **Na, Mg, Al** are **giant metallic** 金属晶体. Melting points rise (Na → Al) because each atom gives more delocalised electrons and the ions get smaller, so the bonding is stronger. They conduct well.
- **Si** is **giant molecular** 原子晶体 (giant covalent). It has the highest melting point, because strong covalent bonds must be broken. It barely conducts.
- **P, S, Cl, Ar** are **simple molecular** 分子晶体 (or single atoms). Their melting points are low, because the only forces that break are the weak **van der Waals' forces** 范德华力 **between** the molecules - the strong covalent bonds **inside** each molecule are never broken at all. They do not conduct.

Name **van der Waals' forces** when you explain that drop: it is the marking point, and "the covalent bonds are weak" is the error that loses it. Melting S_8 pulls whole molecules apart from each other; it does not touch a single S–S bond. Their sizes still follow the molecule: S_8 melts higher than P_4 because it is bigger, with more electrons and so stronger van der Waals' forces, while Ar (a single atom) is lowest of all.



Melting point across Period 3 peaks at silicon (giant covalent); it is high for the metals and low for the simple molecular elements

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Chemical properties across Period 3

Reactions with oxygen, chlorine and water

With **oxygen**:

$$4Na + O_2 \rightarrow 2Na_2O \qquad 2Mg + O_2 \rightarrow 2MgO \qquad 4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \rightarrow P_4O_{10} \qquad S + O_2 \rightarrow SO_2$$

With **chlorine**:

$$2Na + Cl_2 \rightarrow 2NaCl \qquad Mg + Cl_2 \rightarrow MgCl_2 \qquad 2Al + 3Cl_2 \rightarrow 2AlCl_3$$

$$Si + 2Cl_2 \rightarrow SiCl_4 \qquad 2P + 5Cl_2 \rightarrow 2PCl_5$$

With **water** (only Na and Mg react):

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \qquad Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

Sodium reacts fast; magnesium reacts only very slowly with cold water. Heated magnesium reacts quickly with **steam** 水蒸气, burning with a bright white light to give the oxide instead:

$$Mg + H_2O(g) \rightarrow MgO + H_2$$

What you see when the elements are heated in oxygen:

- **sodium** – burns with a bright **yellow-orange** flame, giving a white solid;
- **magnesium** – burns with a **brilliant white** flame, giving a white powder;
- **aluminium** – powder burns brightly, but a solid piece is protected by its thin oxide layer and reacts slowly;
- **phosphorus** – white phosphorus catches fire in air at room temperature, burning with a bright flame and dense **white fumes** of P_4O_{10};
- **sulfur** – burns with a **blue** flame, giving a colourless, choking gas, SO_2.

SO_3 is made from SO_2 and more oxygen only with a catalyst ($2SO_2 + O_2 \rightleftharpoons 2SO_3$, as in the Contact process).

Oxidation number of the oxides and chlorides

The **oxidation number** 氧化数 of the Period 3 element in its oxide or chloride rises across the period, because it equals the number of outer-shell (**valence shell** 价层) **electrons** 电子 the atom uses in bonding:

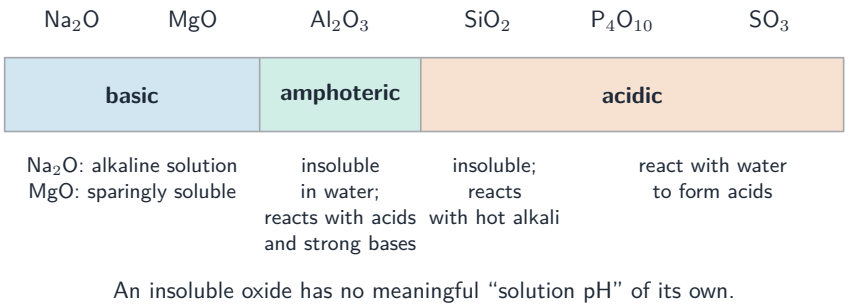
Oxides	Na_2O	MgO	Al_2O_3	P_4O_{10}	SO_2 / SO_3
oxidation number	+1	+2	+3	+5	+4 / +6

The chlorides NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5 show oxidation numbers +1 to +5 in the same way.

Oxides with water, and acid–base behaviour

Across the period the **oxides** 氧化物 change from basic to acidic:

Oxide	With water	Acid–base nature	Approximate pH
Na_2O	$Na_2O + H_2O \rightarrow 2NaOH$	basic	13–14
MgO	$MgO + H_2O \rightarrow Mg(OH)_2$	basic	9–10
Al_2O_3	insoluble	**amphoteric** 两性	7
SiO_2	insoluble	weakly acidic	7
P_4O_{10}	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$	acidic	1–2
SO_3	$SO_3 + H_2O \rightarrow H_2SO_4$	strongly acidic	0–1



The Period 3 oxides change from basic (the metals) through amphoteric (Al_2O_3) to acidic (the non-metals)

Metal oxides (left) are basic; non-metal oxides (right) are acidic. Al_2O_3 and its **hydroxide** 氢氧化物 $Al(OH)_3$ are amphoteric – they react with **both** acids and bases:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

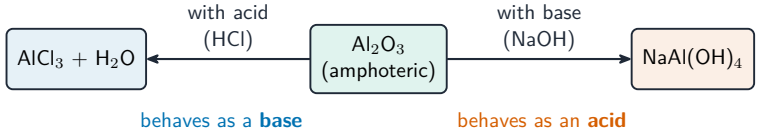
$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

The other oxides react with acids or bases according to their nature:

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- basic oxides react with acids: $MgO + 2HCl \rightarrow MgCl_2 + H_2O$ and $Na_2O + 2HCl \rightarrow 2NaCl + H_2O$;
- acidic oxides react with bases: $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ (only with hot, concentrated NaOH), $P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$, $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$ and $SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$.

The hydroxides follow the same pattern. NaOH and $Mg(OH)_2$ are basic and react only with acids. $Al(OH)_3$ is amphoteric: $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$ and $Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$. This is why a white precipitate of $Al(OH)_3$ dissolves again when **excess** NaOH(aq) is added.

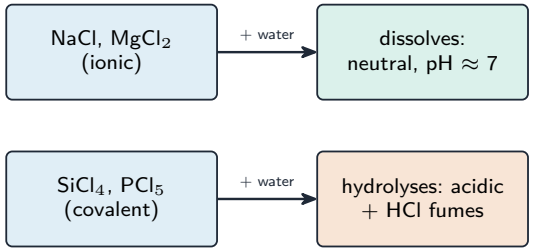


Aluminium oxide is amphoteric – it reacts with acids (behaving as a base) and with bases (behaving as an acid)

Chlorides with water

- NaCl and $MgCl_2$ are ionic. They simply dissolve, giving a near-neutral solution: pH 7 for NaCl, and about 6.5 for $MgCl_2$, because the small Mg^{2+} ion slightly polarises the water molecules around it.
- $AlCl_3$ is in between. The very small, highly charged Al^{3+} ion **polarises** 使极化 the water molecules around it so strongly that they lose H^+, giving an acidic solution of about **pH 3**: $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$. With only a little water, solid $AlCl_3$ gives steamy fumes of HCl.
- $SiCl_4$ and PCl_5 are covalent. They undergo **hydrolysis** 水解 (react with water) to make acidic solutions and fumes of HCl:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \qquad PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$



The ionic chlorides just dissolve (neutral); the covalent chlorides react with water (hydrolyse) to give an acidic solution and HCl fumes

Explaining the trends

These trends follow from the change in bonding and **electronegativity** 电负性. On the left, the elements are metals with low electronegativity, so their oxides and chlorides are ionic and basic (or neutral). On the right, the elements are non-metals with high electronegativity, so their oxides and chlorides are covalent and acidic. You can use a chloride's or oxide's properties (melting point, conductivity, effect on water) to suggest whether its bonding is ionic or covalent.

Worked example. Predict the pH when Na_2O, Al_2O_3 and SO_3 are each added to water. Acid-base character follows the **metal to non-metal** change across Period 3. Na_2O is ionic and basic: it dissolves to give NaOH, so the pH is about **13**. SO_3 is covalent and acidic: it reacts to give H_2SO_4, so the pH is about **1**. Al_2O_3 sits at the changeover - it is **amphoteric** and essentially **insoluble** in water, so the pH stays about **7**. The trap is that last one: amphoteric does **not** mean neutral, it means the oxide reacts with acids **and** with alkalis - it simply does not react with water.

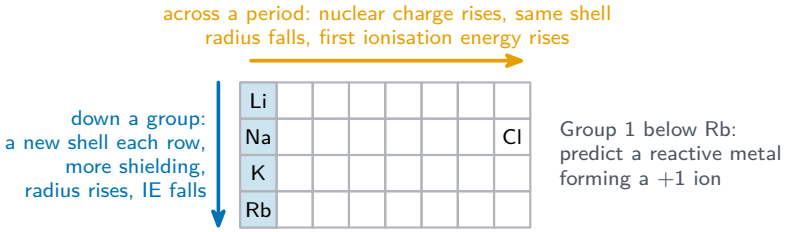
Worked example (identify the element). Element X is in Period 3. Its oxide has a very high melting point, does not dissolve in water, and reacts with hot, concentrated NaOH(aq) but not with dilute acids. Its chloride is a liquid that fumes in moist air. Identify X and explain each observation. The high melting point means a **giant** structure; reacting only with a base means the oxide is **acidic**, so it is not a metal oxide; the fuming liquid chloride is a **covalent** chloride hydrolysed by water: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$. So X is **silicon**, and the oxide is the giant covalent SiO_2. (An aluminium oxide would also react with acids; a phosphorus or sulfur oxide would be molecular, with a low melting point.)

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Periodicity of other elements

The same idea works for any group. If you know the pattern down a group and across a period, you can:

- **predict** the properties of an element from its position (for example, a Group 1 element will be a reactive metal forming a +1 ion).
- **deduce** the likely position and identity of an unknown element from its physical and chemical properties.



Two directions, two reasons: use them to predict an element from its position.

Common mistakes.

- Explaining the atomic-radius trend by "more electrons". Across the period the electrons go into the **same shell** with similar shielding, while the nuclear charge rises, so the outer electrons are pulled closer.
- Explaining silicon's high melting point with intermolecular forces. Silicon is a **giant covalent** lattice: melting means breaking many strong covalent bonds.
- Saying Al_2O_3 gives a neutral solution because it is amphoteric. It is **insoluble**, so the pH stays 7; "amphoteric" means it reacts with both acids and bases.
- Saying SiO_2 is basic because it does not dissolve. SiO_2 is **weakly acidic**: it reacts with hot, concentrated NaOH but not with acids.
- Saying $SiCl_4$ dissolves in water like NaCl. Covalent chlorides are **hydrolysed**, giving steamy fumes of HCl and an acidic solution.
- Giving the same oxidation number to sulfur in both of its oxides. Sulfur is +4 in SO_2 and +6 in SO_3.

Exam tips

- Always pair the **trend with its reason**: atomic radius falls across Period 3 (rising nuclear charge, similar shielding).
- Explain the **melting-point pattern** by structure: giant metallic (Na→Al), giant covalent (Si, highest), then simple molecular (P_4, S_8, Cl_2) and monatomic (Ar).

- Oxides go **basic** → **amphoteric** (Al_2O_3) → **acidic** across the period; link to ionic-to-covalent bonding.
- For reactions of oxides/chlorides with water, give the **products and the resulting pH**.

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Group 2

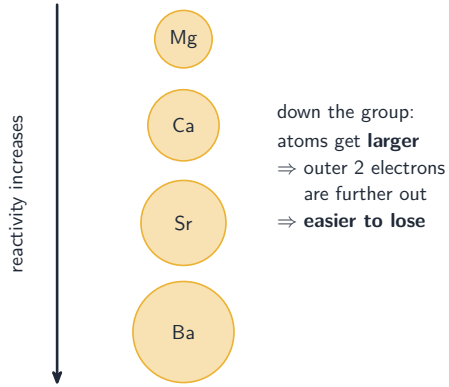
A-Level Chemistry

The Group 2 metals



Limestone is calcium carbonate – a compound of the Group 2 metal calcium.

Group 族 2 holds the metals magnesium, calcium, strontium and barium. They all have two outer electrons, which they lose to form 2+ ions. Going **down** the group, the atoms get larger and the outer electrons are easier to lose, so the metals get **more reactive** – their **reactivity** 反应活性 increases down the group.



Reactivity increases down Group 2: larger atoms hold their two outer electrons less tightly, so they are lost more easily

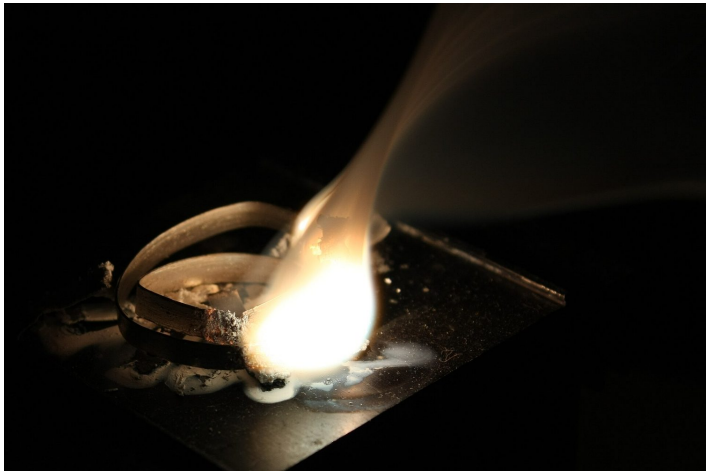
Element	Atomic radius / nm	Ionic radius of M^{2+} / nm	1st + 2nd ionisation energy / kJ mol^{-1}	Melting point / °C
Mg	0.160	0.072	2189	650
Ca	0.197	0.100	1735	842
Sr	0.215	0.113	1614	777
Ba	0.224	0.136	1468	727

Down the group each atom has one more shell of electrons, so the radius increases. The outer electrons are further from the nucleus and better **shielded** 屏蔽 by the inner shells, so although the nuclear charge rises, the attraction for the outer electrons falls and the ionisation energies **decrease**. This is why reactivity increases. Melting points show no smooth trend: metallic bonding generally weakens down the group as the 2+ ions get larger, but magnesium is out of line because its crystal structure is different.

Reactions of the elements

With **oxygen**, they burn to form an oxide:

$$2Mg + O_2 \rightarrow 2MgO$$



Magnesium burns in air with a brilliant white flame, forming white magnesium oxide

With **water**, they form a hydroxide and hydrogen. The reaction gets faster down the group:

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

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Magnesium is slow with cold water but reacts fast with steam, giving MgO and H_2.

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$

Metal	With cold water	What you see
Mg	very slow	a few bubbles over hours; burns brightly in steam, leaving white MgO
Ca	steady	fizzing; the metal sinks and rises; a cloudy white suspension of $Ca(OH)_2$ forms (it is only slightly soluble)
Sr	fast	vigorous fizzing; the solution becomes alkaline
Ba	very fast	very vigorous fizzing; a clear, strongly alkaline solution ($Ba(OH)_2$ is soluble)

Because the hydroxides become more soluble down the group, the solution formed in water has a **higher pH** further down: about pH 10 for a saturated solution of $Mg(OH)_2$, about pH 12 for $Ca(OH)_2$, and higher still for $Ba(OH)_2$.

With **dilute hydrochloric or sulfuric acid**, they form a salt and hydrogen:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \qquad Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

With sulfuric acid the reaction slows down the group, because the **sulfates** 硫酸盐 formed (such as $BaSO_4$) are insoluble and coat the metal.

Reactions of the compounds

The **oxides** 氧化物 and **hydroxides** 氢氧化物 are basic. They react with water and with dilute acids:

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

The **carbonates** 碳酸盐 react with dilute acids to give a salt, water and carbon dioxide:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

The oxides react with water to give the hydroxide; calcium oxide (quicklime) does this very **exothermically**, hissing and crumbling: $CaO + H_2O \rightarrow Ca(OH)_2$. The carbonates are insoluble in water and do not react with it.

With **sulfuric acid**, the reactions of calcium, strontium and barium compounds stop quickly, because an insoluble sulfate forms a coating:

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

$MgSO_4$ is soluble, so magnesium carbonate keeps fizzing until it has all reacted.

> **Worked example.** A Group 2 carbonate QCO_3 is added in excess to dilute sulfuric acid; the mixture is filtered and the filtrate evaporated to give QSO_4 crystals. Identify Q. The sulfate must be **soluble**, or it would stay in the filter paper with the excess carbonate (and coat it, stopping the reaction). Only $MgSO_4$ is soluble, so Q is **magnesium**. To make insoluble $BaSO_4$ instead, mix solutions of a soluble barium salt and a soluble sulfate, then filter, wash and dry the precipitate.

Comparing reactions with acid. $MgCO_3$ and $Mg(OH)_2$ both dissolve in dilute HCl to give a colourless solution of $MgCl_2$ and water (a similarity). Only the carbonate **fizzes**, because it also gives off CO_2 (a difference).

Uses that follow from the chemistry. Calcium hydroxide (slaked lime) and calcium carbonate (powdered limestone) are bases used to raise the pH of acidic soil and lakes. Magnesium hydroxide is the antacid "milk of magnesia" – its low solubility makes it a mild base that will not damage the stomach. Calcium hydroxide is manufactured from calcium carbonate: heat it to CaO, then add water.

Thermal decomposition

Thermal decomposition 热分解 means breaking a compound apart by heating it.

- the carbonates break into the oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

- the **nitrates** 硝酸盐 break into the oxide, brown nitrogen dioxide gas and oxygen:

$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$

The **thermal stability** 热稳定性 of both the carbonates and the nitrates **increases** down the group. A larger metal ion pulls less on the carbonate or nitrate ion, so the compound is harder to break apart – it needs a higher temperature. So magnesium carbonate decomposes most easily, and barium carbonate is the hardest.

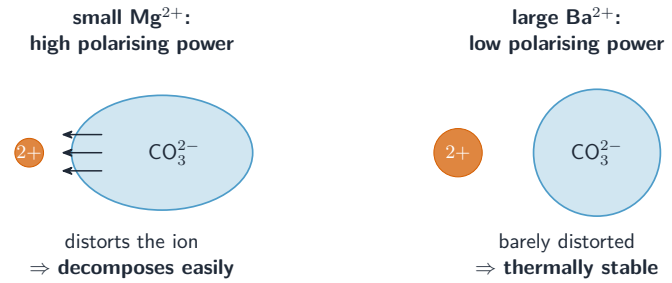
Identifying a solid by heating. Three white solids, $MgCO_3$, $Mg(NO_3)_2$ and MgO, can be told apart by heating each in a test tube:

Solid	What you see on heating	Test on the gas
$MgCO_3$	a colourless gas; the white solid remains (now MgO)	CO_2 turns limewater milky
$Mg(NO_3)_2$	**brown** fumes of NO_2 (often the solid melts first)	the O_2 also given off relights a glowing splint
MgO	no change	no gas

Of the Group 2 compounds, only the nitrates give **two** gases on heating. A nitrate that decomposes easily ("low thermal stability") must be near the top of the group,

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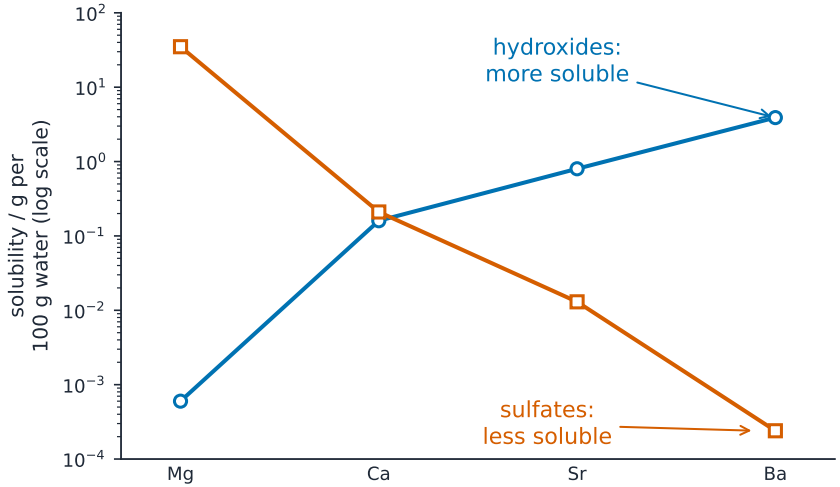
so magnesium nitrate.



Thermal stability rises down the group: a small cation polarises (distorts) the carbonate ion more, weakening it so it decomposes more easily

Trends in solubility

Compound	Trend in solubility 溶解度 down the group
hydroxides	**increase** ($Mg(OH)_2$ almost insoluble; $Ba(OH)_2$ soluble)
sulfates	**decrease** ($MgSO_4$ soluble; $BaSO_4$ insoluble)



Down Group 2 the hydroxides become more soluble while the sulfates become less soluble (note the log scale)

From these trends you can predict the properties of the next element down, radium, and of its compounds.

The low solubility of $Mg(OH)_2$ explains a test: adding aqueous ammonia (a weak alkali, low $[OH^-]$) to $MgCl_2(aq)$ gives a white precipitate of $Mg(OH)_2$, but $BaCl_2(aq)$ gives none, because $Ba(OH)_2$ is too soluble to precipitate at that hydroxide concentration. The low solubility of $BaSO_4$ gives the **sulfate test**: add acidified $BaCl_2(aq)$, and a white precipitate forms if sulfate ions are present.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Worked example (predicting). Radium is below barium. Write an equation for radium with water, and predict how it compares with calcium. $Ra(s) + 2H_2O(l) \rightarrow Ra(OH)_2(aq) + H_2(g)$. Radium reacts **faster**: more vigorous fizzing, and a clear solution with no white suspension, because $Ra(OH)_2$ is more soluble than $Ca(OH)_2$. The reason: a radium atom is larger, with its outer electrons further from the nucleus and more shielded, so the first and second ionisation energies are lower and the electrons are lost more easily. Predict also: $RaSO_4$ is even less soluble than $BaSO_4$; $RaCO_3$ needs an even higher temperature to decompose.

Worked example. $MgCO_3$ decomposes at about 540 °C and $BaCO_3$ at about 1360 °C. Explain the trend and predict where $CaCO_3$ sits. Going **down** Group 2 the cation gets **larger**, so its charge is spread over a bigger surface and its **polarising power** falls. A less polarising cation distorts the carbonate ion less, so the C-O bond is weakened less and more heat is needed to break it. Thermal stability therefore **increases down the group**, and $CaCO_3$, lying between Mg and Ba, decomposes at an intermediate temperature of about 900 °C. Argue the whole chain - **cation size, then polarising power, then distortion of the anion**; "it is more reactive" explains nothing here.

Common mistakes.

- Saying magnesium and steam give $Mg(OH)_2$. With **steam** magnesium gives the **oxide**: $Mg + H_2O \rightarrow MgO + H_2$; the hydroxide forms only with cold water.
- Explaining the rise in reactivity by "more electrons". The outer electrons are further from the nucleus and better **shielded**, so the first and second ionisation energies fall and the electrons are lost more easily.
- Saying barium reacts more slowly with sulfuric acid because it is less reactive. Barium is **more** reactive; the reaction slows because insoluble $BaSO_4$ coats the metal.
- Writing Group 2 formulas with a 1+ ion, such as CaOH or $MgNO_3$. The ion is 2+: $Ca(OH)_2$, $Mg(NO_3)_2$.
- Writing "a gas is given off" as an observation. Say what you **see**: fizzing (effervescence), the metal getting smaller, a white solid forming.

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Exam tips

- Reactivity **increases down** Group 2: ionisation energy falls as atoms get larger, so electrons are lost more easily.
- Reactions with water become **more vigorous** down the group; Mg reacts slowly with cold water but fast with steam ($\rightarrow$ MgO).
- Hydroxides get **more soluble** down the group; sulfates get **less soluble** ($BaSO_4$ insoluble – the basis of the sulfate test).
- Write equations with the correct +2 ion and state the observations (fizzing, dissolving).
- Heating identifies: carbonate $\rightarrow$ CO_2 only (limewater); nitrate $\rightarrow$ brown NO_2 + O_2 (glowing splint); oxide $\rightarrow$ no change.
- To make a salt by "excess solid + acid, filter, evaporate", the salt must be **soluble**; insoluble salts such as $BaSO_4$ are made by precipitation.
- For any "predict" question about radium or beryllium, carry each trend one step further and give the reason (size $\rightarrow$ shielding $\rightarrow$ ionisation energy, or cation size $\rightarrow$ polarising power).

Group 17

A-Level Chemistry

Physical properties of the halogens



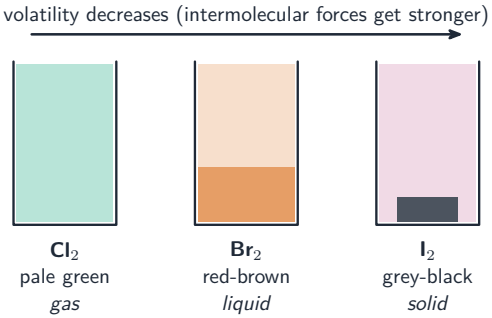
Bromine is a Group 17 halogen – a dark liquid that gives off an orange vapour.

The **halogens** 卤素 are the **Group** 族 17 elements. They exist as diatomic molecules (Cl_2, Br_2, I_2). Going down the group:

Element	Colour and state at room temperature
chlorine	pale green gas
bromine	red-brown liquid
iodine	grey-black solid (purple vapour)

The **volatility** 挥发性 (how easily a substance turns to vapour) **decreases** down the group: chlorine is a gas, but iodine is a solid. This is because the molecules get larger and have more electrons, so the **instantaneous dipole** 瞬时偶极 and **induced dipole** 诱导偶极 forces between them get stronger. Stronger forces are harder to break, so the boiling point rises and volatility falls.

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Down Group 17 the halogens change from a pale green gas to a red-brown liquid to a grey-black solid as volatility falls

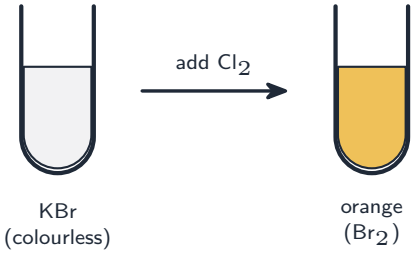
The **bond energy** 键能 (bond strength) of the X–X molecules generally falls from Cl_2 to I_2, because the shared electrons are further from the nuclei in the larger atoms. The values (kJ mol^{-1}) are Cl–Cl 242, Br–Br 193 and I–I 151.

Chemical properties of the halogens and hydrogen halides

Halogens as oxidising agents

Each halogen reacts by gaining one electron to form a 1− ion, so it acts as an **oxidising agent** 氧化剂. This power **decreases** down the group, because the larger atoms attract an extra electron less strongly. A more reactive halogen can push out a less reactive one from its salt:

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$$



Chlorine displaces bromine: the solution turns orange

The ionic equation leaves out the spectator K^+: $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$. Chlorine gains electrons (it is reduced, $0 \rightarrow -1$) and the bromide ions lose them (oxidised,

$-1 \rightarrow 0$).

Halogen added	to $Cl^-(aq)$	to $Br^-(aq)$	to $I^-(aq)$
Cl_2	no reaction	orange-yellow (Br_2)	brown (I_2)
Br_2	no reaction	–	brown (I_2)
I_2	no reaction	no reaction	–

In water, bromine and iodine solutions can look alike (both yellow to brown). To tell them apart, shake the mixture with a little **cyclohexane**, a non-polar solvent that does not mix with water: the top layer turns **orange** with bromine but **purple** with iodine.

Reactions with hydrogen

Each halogen reacts with hydrogen to form a **hydrogen halide** 卤化氢:

$$H_2 + Cl_2 \rightarrow 2HCl$$

The reaction gets less vigorous down the group: chlorine reacts explosively in light, bromine needs heat, and iodine reacts slowly and only partly.

Thermal stability of the hydrogen halides

The **thermal stability** 热稳定性 of the hydrogen halides **decreases** down the group. The H–X bond gets weaker as the halogen atom gets larger, so HI breaks apart on gentle heating while HCl is very stable.

Hydrogen halide	H–X bond energy / kJ mol^{-1}	Effect of heating
HCl	431	stable even at high temperature
HBr	366	decomposes a little when strongly heated
HI	299	decomposes with a hot glass rod: purple I_2 vapour

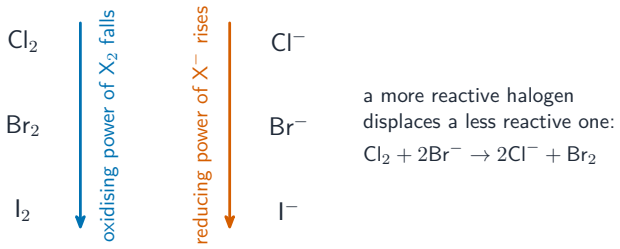
The larger the halogen atom, the longer the H–X bond and the less the bonding pair is attracted by the halogen nucleus, so the bond is weaker. For example, a hot wire pushed into HI gives $2HI \rightarrow H_2 + I_2$, and violet fumes appear.

Reactions of the halide ions

Halide ions as reducing agents

A **halide ion** 卤离子 (such as Cl^-) can give away an electron, acting as a **reducing agent** 还原剂. This power **increases** down the group, because a larger ion holds its outer electron less tightly.

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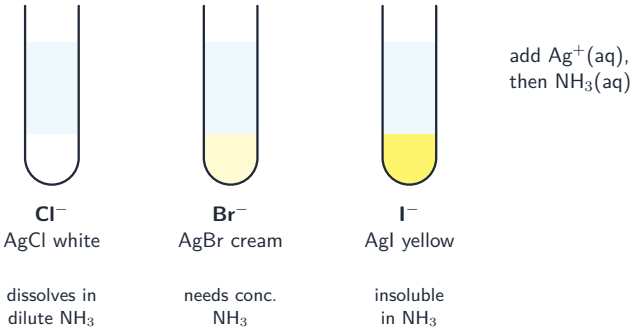
Two opposite trends: the oxidising power of the halogens falls down the group, while the reducing power of the halide ions rises

Reaction with aqueous silver ions

Add aqueous silver nitrate, then aqueous **ammonia** 氨, to identify the halide from the colour of the silver halide **precipitate** 沉淀:

Halide	Precipitate with Ag^+	Solubility in ammonia
Cl^-	white	dissolves in dilute ammonia
Br^-	cream	dissolves only in concentrated ammonia
I^-	yellow	insoluble in ammonia

The ionic equation is the same for each, for example $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Cream and yellow can be hard to tell apart by eye, so the ammonia step is what confirms the halide.



Silver halide precipitates: AgCl is white, AgBr cream and AgI yellow – and their solubility in ammonia confirms which halide is present



The silver halide test: AgCl is white, AgBr cream and AgI yellow

Reaction with concentrated sulfuric acid

All the halides first give the hydrogen halide. The lower halides are then oxidised by the acid, because they are stronger reducing agents:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

- chloride gives only HCl (no redox).
- bromide also gives some brown Br_2 and SO_2.
- iodide gives I_2 and the smelly gases H_2S and SO_2, because I^- is the strongest reducing agent.

The redox steps, with the oxidation number of sulfur:

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O \qquad (S: +6 \rightarrow +4)$$

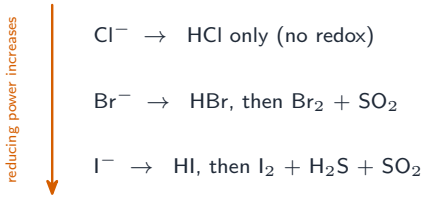
$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O \qquad (S: +6 \rightarrow +4)$$

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O \qquad (S: +6 \rightarrow -2)$$

The further sulfur's oxidation number falls, the stronger the reducing agent must be. Only iodide is strong enough to take sulfur down to -2 in H_2S (iodide can also give yellow solid sulfur, oxidation number 0).

Observations: steamy fumes of the hydrogen halide in every case; with bromide, **orange-brown** fumes of bromine and a choking gas (SO_2); with iodide, **purple** fumes or a black solid (iodine), and a **bad-egg** smell (H_2S).

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With concentrated sulfuric acid, chloride gives only HCl, but bromide and iodide (stronger reducing agents) are also oxidised to the halogen

Reactions of chlorine



Chlorine is added to pool water to kill microbes.

With sodium hydroxide

With **cold, dilute** sodium hydroxide, chlorine reacts to form chloride and chlorate(I):

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

With **hot, concentrated** sodium hydroxide, it forms chloride and chlorate(V):

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

In both, the **oxidation number** 氧化数 of chlorine goes both up and down (from 0), so both are **disproportionation** 歧化 reactions.

Worked example. Use oxidation numbers to show that the reaction of chlorine with hot NaOH is balanced. In NaCl chlorine is -1, and in $NaClO_3$ it is $+5$ (sodium $+1$, three oxygens -6). Each Cl atom that goes to NaCl **gains** 1 electron; each Cl atom that goes to $NaClO_3$ **loses** 5. The electrons must balance, so for every 1 chlorate(V) there must be 5 chlorides: 5NaCl and $1NaClO_3$, which needs six Cl atoms, that is $3Cl_2$.

cold, dilute NaOH

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$$

Cl: $0 \longrightarrow -1$ and $+1$; chlorate(I)

hot, concentrated NaOH

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

Cl: $0 \longrightarrow -1$ and $+5$; chlorate(V)

In each row, chlorine is both reduced and oxidised: disproportionation.

The conditions change the oxidised product; chloride forms in both reactions.

Chlorine in water purification

A little chlorine is added to water for **water purification** 水净化. It reacts with water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

This is also a disproportionation: chlorine goes from 0 to $+1$ in HOCl and to -1 in HCl. Chloric(I) acid, HOCl, is a weak acid and partly dissociates:

$$HOCl \rightleftharpoons H^+ + ClO^-$$

The active species HOCl and ClO^- kill **bacteria** 细菌, making the water safe to drink. Only a small amount is added, because chlorine is toxic.

Worked example. Solid NaCl, NaBr and NaI are each warmed with concentrated H_2SO_4. Predict the products. **Reducing power increases down the group**, so how far each halide reduces the sulfuric acid differs. Cl^- is too weak to reduce it at all, so you get only steamy HCl - an acid-base reaction. Br^- reduces it a little: HBr plus brown Br_2 and SO_2. I^- is the strongest reducing agent: HI plus I_2, and it drives the sulfur all the way down to H_2S, with its bad-egg smell. **Every** halide gives the hydrogen halide first; the extra products appear only where the halide is a strong enough **reducing agent** to attack the sulfur.

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Common mistakes.

- Saying the halogens' boiling points rise because the covalent bonds get stronger. Boiling separates **molecules**: the instantaneous dipole–induced dipole forces between them get stronger with more electrons. From chlorine to iodine, the X–X bond gets **weaker**; fluorine is an exception because its F–F bond is unusually weak.
- Mixing up the two trends. **Halogens** (oxidising agents) get weaker down the group; **halide ions** (reducing agents) get stronger.
- Testing for halide ions without acidifying. Add dilute **HNO_3** first to remove carbonate and other ions that also give precipitates; do not use HCl, which adds chloride.
- Calling the reaction of chlorine with cold NaOH a displacement. Chlorine (oxidation number 0) goes to -1 in NaCl and $+1$ in NaClO at the same time: **disproportionation**.
- Giving chlorine the oxidation number $+3$ in $NaClO_3$. Oxygen is -2 three times and sodium is $+1$, so chlorine is $+5$: chlorate(V).
- Saying iodide and concentrated sulfuric acid give only HI. I^- is a strong reducing agent, so it reduces the acid to SO_2 and H_2S and is oxidised to I_2.

Exam tips

- Halogens get **less reactive down** the group (harder to gain an electron); oxidising power decreases.
- **Displacement**: a more reactive halogen displaces a less reactive halide – state the colour change.
- Test halide ions with $AgNO_3$: white (Cl^-), cream (Br^-), yellow (I^-), then confirm with dilute/concentrated ammonia.
- With concentrated H_2SO_4, give the **oxidation number of sulfur** in each product: SO_2 is $+4$, S is 0, H_2S is -2.
- Chlorine with water and with cold NaOH are **disproportionation** – show the oxidation-number changes.

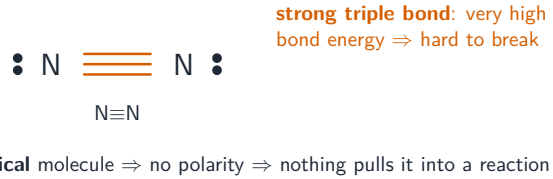
Nitrogen and sulfur

A-Level Chemistry

Why nitrogen is unreactive

Nitrogen gas, N_2, makes up most of the air but reacts with very little. There are two reasons:

- the two nitrogen atoms are joined by a **triple bond** 三键, which has a very high **bond energy** 键能. A lot of energy is needed to break it.
- the molecule has no **polarity** 极性 – it is perfectly symmetrical, so it has no permanent dipole. London dispersion attractions still act between nitrogen molecules.



Nitrogen is unreactive for two reasons: a very strong triple bond, and a symmetrical, non-polar molecule

Ammonia and the ammonium ion



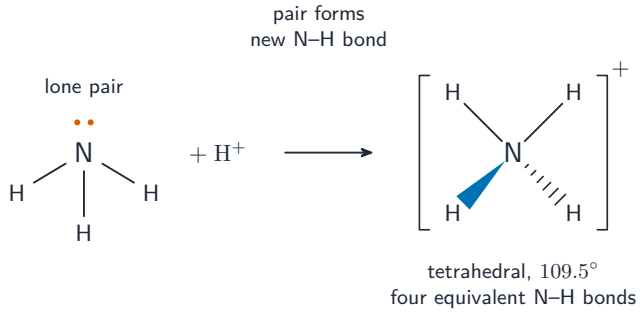
Ammonia is converted into nitrogen fertilisers in industrial plants on a huge scale.

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Basicity of ammonia

The **basicity** 碱性 of ammonia (its ability to act as a base) comes from the **lone pair** 孤对电子 of electrons on the nitrogen atom. Using the Brønsted–Lowry theory, ammonia is a base because this lone pair can accept a **proton** 质子 (H^+):

$$NH_3 + H^+ \rightarrow NH_4^+$$



Ammonia acts as a base because the lone pair on its nitrogen accepts a proton, making the ammonium ion

The ammonium ion

When the lone pair forms a bond to H^+, it makes the **ammonium ion** 铵离子, NH_4^+. Because both shared electrons came from the nitrogen, this new bond is a **coordinate bond** 配位键. The ion has four identical N–H bonds and a tetrahedral shape.

Displacement of ammonia from its salts

If you warm an ammonium salt with a base (such as sodium hydroxide), you push out ammonia gas. This is an acid–base **displacement** 置换:

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$$

The sharp smell of ammonia, and damp red litmus turning blue, is a test for an ammonium salt.

Oxides of nitrogen and air pollution

Where they come from

Oxides of nitrogen (NO and NO_2, together called NO_x) come from two sources:

- **natural**: lightning gives enough energy for nitrogen and oxygen in the air to combine.

- **man-made**: the high temperature inside an **internal combustion engine** 内燃机 makes nitrogen and oxygen react:

$$N_2 + O_2 \rightarrow 2NO$$

The reaction needs a very high temperature because the N≡N bond is so strong. Once in the air, NO is slowly oxidised to brown NO_2:

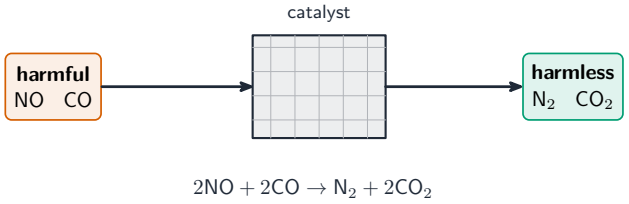
$$2NO + O_2 \rightarrow 2NO_2$$

Removing them from car exhaust

A **catalytic converter** 催化转化器 cleans the **exhaust gases** 尾气. It lets the harmful gases react together to form harmless ones:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

The catalyst is a thin layer of metals such as platinum, palladium and rhodium, spread over a **honeycomb** 蜂窝状 support to give a large surface area. The gases **adsorb** onto the metal surface, react, and the products leave the surface. Unburned hydrocarbons are oxidised in the converter too, for example $C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$.



In a catalytic converter the harmful gases NO and CO react over the catalyst to form harmless N_2 and CO_2

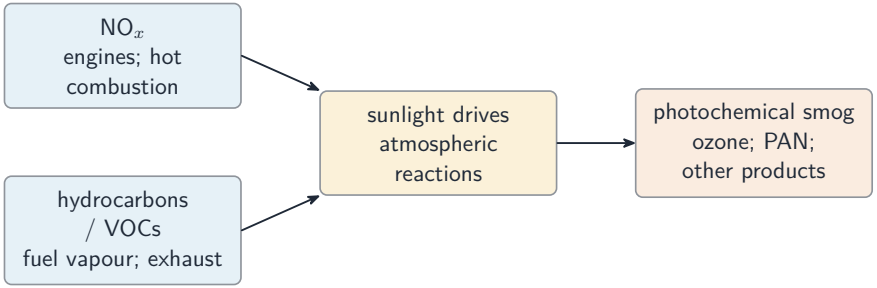
Photochemical smog

In sunlight, NO and NO_2 take part in reactions with unburned **hydrocarbons** that form pollutants including ozone and peroxyacetyl nitrate (PAN). PAN is a harmful part of **photochemical smog** 光化学烟雾, the haze seen over busy cities (its brown colour comes from NO_2).

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Photochemical smog over a big city. The brown layer is trapped low down, exactly where the traffic fumes are – sunlight turns those nitrogen oxides and unburned hydrocarbons into the haze you can see



A process map, not a balanced equation.
Ozone is formed in the air; brown NO_2 contributes to visible haze.

Primary emissions feed reactions in the air; the products are secondary pollutants.

Acid rain

The oxides of nitrogen also help make **acid rain** 酸雨 in two ways:

- directly: NO_2 dissolves in rain to form nitric acid.
- as a catalyst: NO_2 speeds up the oxidation of atmospheric **sulfur dioxide** 二氧化硫 (SO_2) into SO_3, which then forms sulfuric acid in the rain.

The direct route, with oxygen and water:

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

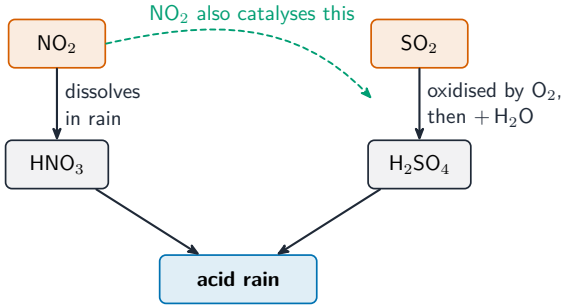
Worked example. Explain, with equations, how NO_2 acts as a catalyst in the formation of acid rain from SO_2. First NO_2 oxidises SO_2, and is itself reduced to NO:

$$NO_2 + SO_2 \rightarrow NO + SO_3$$

Then the NO is oxidised back by oxygen in the air:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2$$

Adding the two steps gives the overall reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$: the NO_2 cancels out, because it is used in the first step and **regenerated** in the second, which is what makes it a catalyst. The SO_3 then dissolves in rain: $SO_3 + H_2O \rightarrow H_2SO_4$. Marks are given for both equations **and** for the word "regenerated".



Nitrogen and sulfur oxides make acid rain: NO_2 forms nitric acid directly and also catalyses the oxidation of SO_2 to sulfuric acid

Worked example. A white solid is warmed with aqueous NaOH, and a gas is released that turns damp red litmus blue. Identify the gas and the ion in the solid, and explain the reaction. The only common gas that turns damp red litmus **blue** is **ammonia**, NH_3, so the solid contains the **ammonium ion**, NH_4^+. The hydroxide ion is the stronger base, so it takes the proton back from the ammonium ion:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

This is the standard test for NH_4^+. Always say the litmus is **damp**: the ammonia must dissolve in the water before it can show its basicity, so dry litmus would give no colour change at all.

Common mistakes.

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- Saying nitrogen is unreactive because it is a gas or because its atoms have full shells. The reason is the very strong **N≡N triple bond** (and the molecule's lack of polarity).
- Testing for ammonia with dry litmus or blue litmus. Use **damp red** litmus, which turns blue; the ammonia must dissolve in the water first.
- Saying the coordinate bond in NH_4^+ is different from the other three N–H bonds. Once formed, all **four** bonds are identical.
- Saying NO_x come from nitrogen in the fuel. Most come from **nitrogen in the air**, which reacts with oxygen at the high temperature of the engine.
- Saying NO_2 is used up when it helps form acid rain from SO_2. It acts as a **catalyst** and is regenerated: $NO_2 + SO_2 \rightarrow NO + SO_3$, then $NO + \frac{1}{2}O_2 \rightarrow NO_2$.

Exam tips

- N_2 is unreactive because of its **strong triple bond** (very high bond energy) – state this exactly.
- **Ammonia** is a base and a ligand because of its **lone pair**; the ammonium ion forms by a dative bond.
- Explain how **oxides of nitrogen** form (high temperature in engines) and their link to acid rain and photochemical smog.
- Give balanced equations and correct observations for reactions of ammonia and the ammonium ion.

An introduction to AS Level organic chemistry

A-Level Chemistry

Formulas, functional groups and naming



Crude oil is a complex mixture of hydrocarbons – the feedstock for organic chemistry.

A **hydrocarbon** 碳氢化合物 is a compound of only carbon and hydrogen. **Alkanes** 烷烃 are the simplest hydrocarbons and have no functional group.

A **functional group** 官能团 is the reactive part of a molecule. It decides the physical and chemical properties of the compound, so molecules with the same functional group behave alike (for example the –OH group in alcohols).

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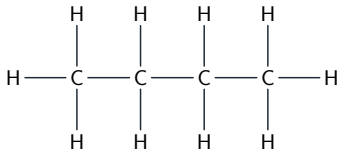
Types of formula

Formula	What it shows
general formula 通式	the pattern for a whole family, e.g. alkanes are C_nH_{2n+2}
molecular formula 分子式	the actual number of each atom, e.g. C_4H_{10}
structural formula 结构式	the groups in order, e.g. $CH_3CH_2CH_2CH_3$
displayed formula 展开式	every atom and every bond drawn out
skeletal formula 骨架式	lines for bonds; carbons at corners, hydrogens on carbon not shown

molecular C_4H_{10}

structural $CH_3CH_2CH_2CH_3$

displayed



skeletal



The same molecule (butane) shown four ways – molecular, structural, displayed and skeletal – each hiding more detail than the last

You can read off the **empirical formula** 实验式 (simplest ratio) from any of these.

Reading a skeletal formula. Every corner and every line end is a carbon atom. Carbon makes four bonds, so the number of hydrogens on each carbon is 4 minus the bonds drawn to it (a double line counts as two). For example, cyclohexene is a hexagon with one double line. The two carbons of the C=C each have three bonds drawn (two in the double line, one single), so each has 1 H; the other four carbons each have two bonds drawn, so each has 2 H. That gives C_6H_{10}, and the empirical formula is C_3H_5.

Naming

Use systematic **nomenclature** 命名法: a stem for the number of carbons (meth-, eth-, prop-, but-, pent-, hex- for 1 to 6), an ending for the functional group, and numbers to show where groups are.

Class	Group	Ending or prefix	Example
alkene	C=C	-ene	but-1-ene, $CH_2{=}CHCH_2CH_3$
halogenoalkane	–X	chloro-, bromo-, iodo-	2-bromopropane, $CH_3CHBrCH_3$
alcohol	–OH	-ol	propan-2-ol, $CH_3CH(OH)CH_3$
aldehyde	–CHO	-al	propanal, CH_3CH_2CHO
ketone	C=O in chain	-one	butanone, $CH_3COCH_2CH_3$
carboxylic acid	–COOH	-oic acid	ethanoic acid, CH_3COOH

Class	Group	Ending or prefix	Example
ester	–COO–	alkyl -oate	methyl propanoate, $CH_3CH_2COOCH_3$
acyl chloride	–COCl	-oyl chloride	ethanoyl chloride, CH_3COCl
amine	$–NH_2$	-amine	ethylamine, $CH_3CH_2NH_2$
amide	$–CONH_2$	-amide	ethanamide, CH_3CONH_2
nitrile	–CN	-nitrile	propanenitrile, CH_3CH_2CN

The rules, in order:

1. Find the **longest chain** that contains the functional group. Its length gives the stem. For aldehydes, acids, nitriles and amides, the carbon of the group is **carbon 1** and counts in the chain.
2. Number the chain from the end that gives the functional group the **lowest** number.
3. Name side chains (methyl, ethyl) and halogens as **prefixes**, in alphabetical order, each with its number. Use di- and tri- for repeats: 2,2-dimethyl.
4. Use commas between numbers and hyphens between numbers and words.

> **Worked example.** Name (a) $CH_3CH(CH_3)CH_2OH$, (b) $CH_3CH_2CH{=}CHCH_3$, (c) $CH_3CHClCH(CH_3)COOH$.

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(a) The longest chain through the OH carbon has three carbons; number from the OH end so the OH is on C1, and the methyl is on C2: **2-methylpropan-1-ol**. (b) Five carbons; numbering from the right puts the C=C between C2 and C3, rather than C3 and C4: **pent-2-ene**. (c) The COOH carbon is C1, so the chain has four carbons, a methyl on C2 and a chlorine on C3. In alphabetical order (chloro before methyl): **3-chloro-2-methylbutanoic acid**.

Characteristic organic reactions

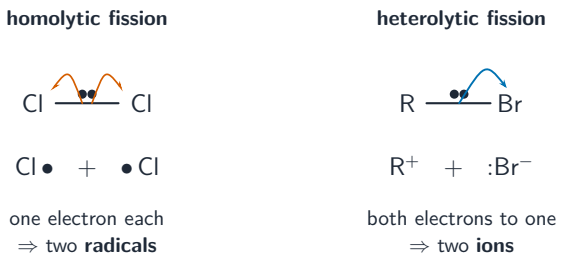
Some key terms

- a **homologous series** 同系列 is a family of compounds with the same functional group and general formula, where successive members differ by CH_2.
- a **saturated** 饱和 compound has only single C–C bonds; an **unsaturated** 不饱和 compound has a C=C double bond (or a triple bond).

Breaking bonds

A covalent bond can break in two ways:

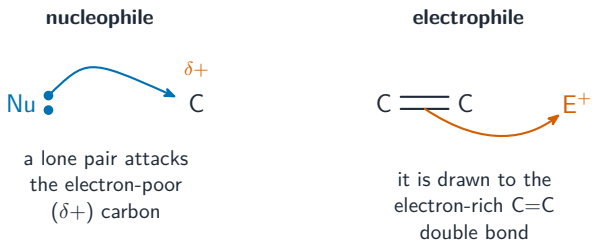
- **homolytic fission** 均裂: the bond splits evenly, one electron to each atom. This makes two **free radicals** 自由基 (species with an unpaired electron).
- **heterolytic fission** 异裂: the bond splits unevenly, both electrons going to one atom. This makes two ions.



Homolytic fission gives one electron to each atom (two radicals); heterolytic fission gives both electrons to one atom (two ions)

Attacking species

- a **nucleophile** 亲核试剂 is an electron-pair donor: it uses a lone pair to form a bond to an electron-poor centre. A nucleophile can be neutral, such as ammonia, or negative, such as hydroxide.
- an **electrophile** 亲电试剂 is an electron-pair acceptor: it accepts a pair from an electron-rich region, such as the pi bond of C=C.



A nucleophile uses its lone pair to attack an electron-poor centre; an electrophile is drawn to an electron-rich one such as a C=C bond

Types of reaction

Reaction	What happens
addition 加成	two molecules join to make one
substitution 取代	one atom or group is swapped for another
elimination 消去	a small molecule is removed, making a double bond
hydrolysis 水解	a molecule is split apart by water
condensation 缩合	two molecules join and a small molecule (such as water) is lost

For organic redox, the symbol [O] stands for one oxygen atom from an oxidising agent, and [H] for one hydrogen atom from a reducing agent.

Worked classification. Ethene plus HBr makes bromoethane by addition; bromoethane plus hydroxide replaces Br with OH by substitution; ethanol losing water to make ethene is elimination. Ester plus water giving acid and alcohol is hydrolysis, while acid plus alcohol giving ester and water is condensation. Classify from the structural change and the role of water.

Types of mechanism

A free-radical reaction happens in three steps: **initiation** 引发 (radicals are made), **propagation** 增长 (radicals react and make new radicals), and **termination** 终止 (two radicals join and stop the chain).

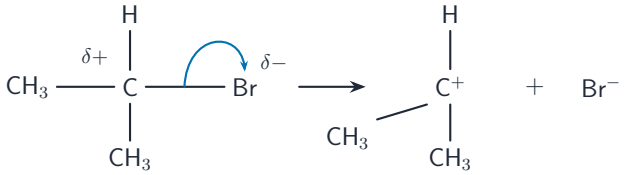
The main mechanisms you meet are **free-radical substitution** 自由基取代 (alkanes), **electrophilic addition** 亲电加成 (alkenes), **nucleophilic substitution** 亲核取代 (halogenoalkanes) and **nucleophilic addition** 亲核加成 (carbonyls). In mechanisms, a full **curly arrow** 弯箭头 shows a pair of electrons moving; it starts at a bond or a **lone pair** 孤对电子.

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Follow the electron pair in a substitution

A full curly arrow starts on a bond or a lone pair and shows **two** electrons moving. A half-headed arrow shows one electron moving in a radical step. Do not start an arrow at a positive charge.

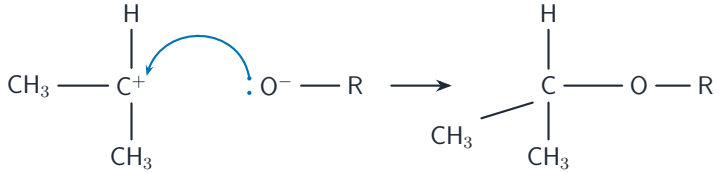
Past-paper application: 9701/24 N25 Q3(b)(ii). The question states an S_N1 mechanism for 2-bromopropane with $(CH_3)_2CHO^-$. Follow the stated mechanism. First show the $\delta+$ carbon and $\delta-$ bromine, then move the C–Br pair to bromine. This gives a carbocation and Br^-.



Bond pair moves to Br; the carbon intermediate has a positive charge.

Full curly arrow from the C–Br bond to Br; the intermediate carbon has a positive charge.

Next, move a lone pair on the nucleophile's oxygen to the positive carbon. A new C–O bond forms. In the figure, R means $CH(CH_3)_2$.



An oxygen lone pair forms the C–O bond. Here R = $CH(CH_3)_2$.

The arrow begins at the lone pair; it shows electron movement, not the movement of an entire molecule.

For the worksheet's 2-bromo-2-methylpropane case, the same two-stage pattern gives a tertiary carbocation, then attack by OH^-. Three alkyl groups help stabilise the positive charge by their electron-releasing effect. A primary carbocation is much less stable. In the worksheet's 1-bromobutane S_N2 case, attack and C–Br breaking occur together in one stage, without a carbocation intermediate. Draw both pair-moving arrows in that stage.

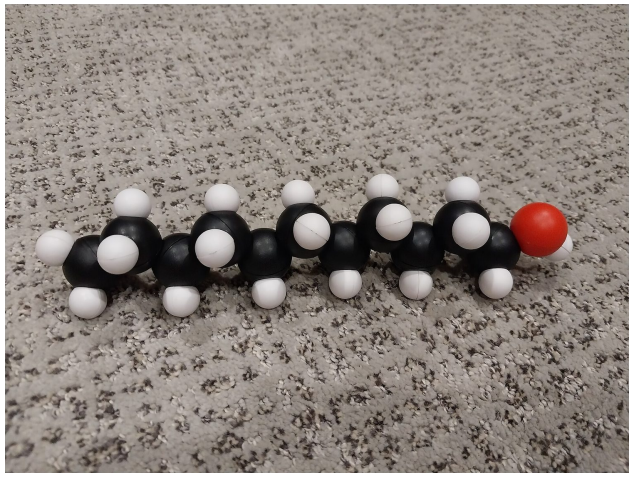
Identify radical stages from what they do

For methane and chlorine under UV light: initiation $Cl_2 \rightarrow 2Cl\cdot$ makes radicals. Propagation $Cl\cdot + CH_4 \rightarrow HCl + \cdot CH_3$, followed by $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$, consumes and regenerates one radical in each step. Termination $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl$ consumes two radicals without making a new radical.

Common mistakes in mechanisms.

- Drawing a curly arrow from the electrophile to the C=C bond. Arrows always point the way the **electrons** move: from the electron-rich double bond **to** the electrophile.
- Starting an arrow at an atom or at a charge. Start it at a **lone pair** (draw the lone pair) or at the middle of a **bond**.
- Leaving out charges and dipoles. Show $\delta+$ and $\delta-$ on the polar bond, the charge on the carbocation, and the charge on the ion that leaves.
- Thinking a nucleophile must be negative. Ammonia and water are neutral but have a lone pair, so they are nucleophiles.
- Using full arrows for radical steps. One electron moving is shown with a **half-headed** (fish-hook) arrow.
- Saying termination makes "nothing". It joins two radicals into a stable molecule, for example $2 \cdot CH_3 \rightarrow C_2H_6$, which is one reason free-radical substitution gives a mixture of products.

Shapes of organic molecules



Organic molecules have definite three-dimensional shapes.

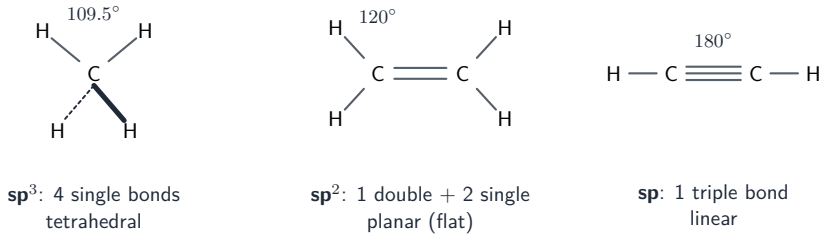
Organic molecules can be straight-chained, branched or **cyclic** 环状 (in a ring).

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The shape around a carbon depends on its **hybridisation** 杂化:

Hybridisation	Bonds	Shape	Angle
sp^3	4 single	tetrahedral	109.5°
sp^2	1 double + 2 single	**planar** 平面 (flat)	120°
sp	1 triple (or 2 doubles)	linear	180°

Every single bond is a **sigma bond** σ 键, made by direct overlap. A double bond is one sigma bond plus one **pi bond** π 键, made by sideways overlap of p orbitals. Ethene is planar because of its sp^2 carbons.



sp^3: 4 single bonds tetrahedral

sp^2: 1 double + 2 single planar (flat)

sp: 1 triple bond linear

The shape at a carbon follows from its hybridisation: sp^3 is tetrahedral (109.5°), sp^2 is planar (120°), sp is linear (180°)



σ bond: head-on overlap

π bond: sideways overlap of p orbitals

Sigma density lies on the internuclear axis; pi density is on both sides of it.

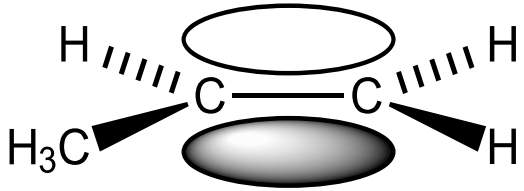
Work locally, then count the whole molecule

Past-paper application: 9701/14 N25 Q6. In propyne, CH_3–C ≡ CH, the methyl carbon has four bonding regions: sp^3, tetrahedral, 109.5°. Each triple-bond carbon has two regions: sp, linear, 180°. A multiple bond counts as one region for shape. The molecule therefore contains sp and sp^3 carbons, not sp^2.

For bond counts, each bonded atom pair contributes one σ bond. A double bond adds one π; a triple bond adds two π bonds. Methane has four σ and no π bonds. Ethene has **five** σ (four C–H and one C–C) and **one** π. Ethyne has three σ and two π bonds. Include the C–H bonds when counting the whole molecule.

Past-paper application: 9701/12 N25 Q25. Methanal, $H_2C{=}O$, has three bonding regions around carbon: sp^2, trigonal planar, approximately 120°. All four atoms are in a plane. It has three σ bonds (two C–H and one C–O) plus one π bond. Both original statements are correct: answer A.

Orbital drawing: 9701/24 N25 Q3(a)(iv). The original scheme shows the π overlap above and below the propene framework:



Sideways overlap of parallel p orbitals forms one pi bond with two regions of density; the regions are not separate pi bonds.

Transfer to a non-organic molecule: 9701/12 N25 Q5. The question states that each N in N_2 is sp hybridised. Of its two sp orbitals, one holds a lone pair and one forms a head-on sp–sp σ overlap. The two remaining p orbitals form two π bonds by sideways overlap. The original answer is B.

Isomerism

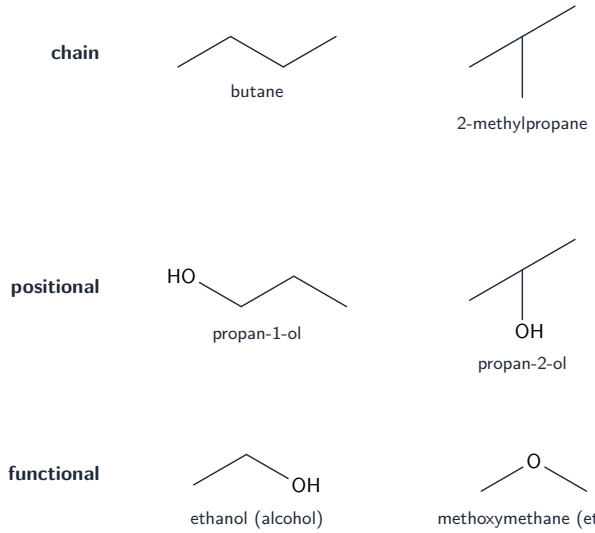
Isomers are compounds with the same molecular formula but a different arrangement of atoms. This is called **isomerism** 异构.

■ Structural isomerism

In **structural isomerism** 结构异构 the atoms are joined in a different order. There are three kinds:

- **chain isomerism** 链异构: the carbon chain is branched in different ways.
- **positional isomerism** 位置异构: the functional group is on a different carbon.
- **functional group isomerism** 官能团异构: the atoms form a different functional group (for example an alcohol and an ether).

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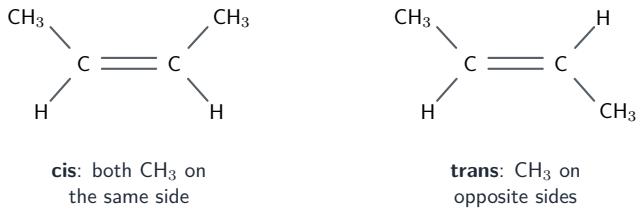


The three kinds of structural isomerism – chain, positional and functional-group – each pair sharing the same molecular formula

■ Stereoisomerism

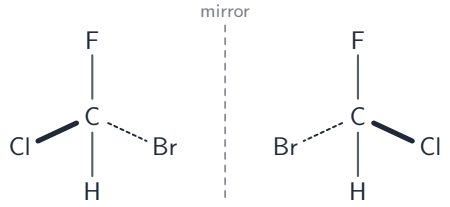
In **stereoisomerism** 立体异构 the atoms are joined in the same order but point in different directions in space.

- **geometrical isomerism** 几何异构 (cis/trans) happens at a C=C double bond. The pi bond stops the two carbons rotating (**restricted rotation** 受限旋转), so groups are fixed on the same side (**cis** 顺式) or opposite sides (**trans** 反式).



Cis–trans isomerism at a C=C bond: the methyl groups are fixed on the same side (cis) or opposite sides (trans) because the bond cannot rotate

- **optical isomerism** 旋光异构 happens at a **chiral** 手性 carbon – a **chiral centre** 手性中心 is a carbon with four different groups attached. Such a carbon gives two mirror-image forms called **enantiomers** 对映体. A molecule may have more than one chiral centre.



enantiomers: mirror images that cannot be superimposed
(the central carbon has 4 different groups)

Optical isomerism: a carbon with four different groups gives two mirror-image forms (enantiomers) that cannot be superimposed

Chiral centres in rings. Check each ring carbon by walking round the ring both ways from it. In methylcyclohexane, the carbon holding the CH_3 has H, CH_3, and two ring paths that are **identical**, so it is **not** chiral. In 2-methylcyclohexan-1-ol, C1 (holding the OH) has OH, H, a ring path that meets the methyl carbon at once, and a path that does not: four different groups, so it **is** chiral, and C2 is chiral for the same reason. A ring also stops rotation, so two groups on neighbouring ring carbons can be on the same face (**cis**) or opposite faces (**trans**) of the ring, as in 1,2-dimethylcyclohexane.

From a molecular formula you can deduce the possible isomers by trying different chains, positions and functional groups.

> **Worked example.** Draw all the isomers of C_4H_9Br and say which shows optical isomerism. Work through the chains in order. The straight chain of four carbons gives two positions for Br: **1-bromobutane**, $CH_3CH_2CH_2CH_2Br$, and **2-bromobutane**, $CH_3CH_2CHBrCH_3$. The branched chain (three carbons with a methyl) also gives two: **1-bromo-2-methylpropane**, $(CH_3)_2CHCH_2Br$, and **2-bromo-2-methylpropane**, $(CH_3)_3CBr$. That is four structural isomers. Only 2-bromobutane has a carbon with four different groups (H, Br, CH_3 and C_2H_5), so it exists as two enantiomers: five isomers in all. Check for repeats by naming each one: two drawings with the same name are the same molecule.

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> **Worked example.** Explain why but-2-ene shows **cis-trans** (E/Z) isomerism but but-1-ene does not. Stereoisomerism at a C=C needs two things: restricted rotation about the double bond (both alkenes have that), **and** two **different** groups on **each** of the two double-bond carbons. In but-2-ene, $CH_3CH{=}CHCH_3$, each double-bond carbon carries an H and a CH_3 - different, so the methyl groups can sit on the same side (**cis** / **Z**) or on opposite sides (**trans** / **E**). In but-1-ene, $CH_2{=}CHCH_2CH_3$, the first carbon carries **two hydrogens** - identical, so swapping them changes nothing and only one form exists. Test **each** double-bond carbon separately: two identical groups on **either** carbon kills the isomerism, however different the other carbon may be.

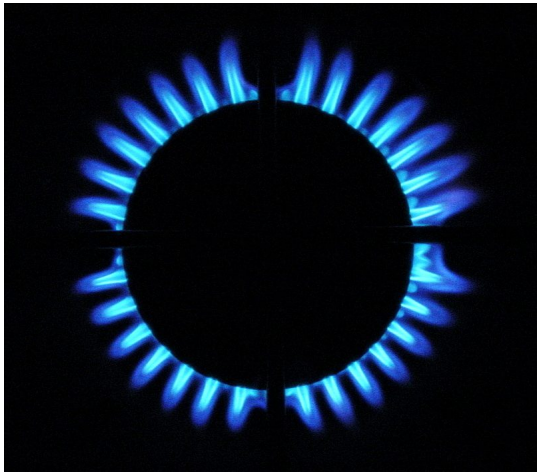
Exam tips

- Know the difference between **general, molecular, structural, displayed and skeletal** formulas – questions ask for a specific one.
- Name systematically: longest chain, lowest locants, substituents alphabetical; a wrong locant loses the mark.
- Classify each reaction by **type and reagent** (addition, substitution, elimination, oxidation).
- **E/Z isomerism** needs restricted rotation about a C = C **and** two different groups on each carbon.

Hydrocarbons

A-Level Chemistry

Alkanes



Natural gas – mainly methane, the simplest alkane – burns on a stove.

Alkanes 烷烃 are saturated hydrocarbons (general formula C_nH_{2n+2}).

Making alkanes

- **hydrogenation** 氢化: add hydrogen to an **alkene** 烯烃, using a Pt or Ni catalyst and heat.
- **cracking** 裂化: break a long-chain alkane into shorter ones by heating with Al_2O_3.

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3 \qquad \text{(Ni catalyst, about 150 °C)}$$

$$C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4 \qquad \text{(hot } Al_2O_3\text{)}$$

Cracking always gives at least one **alkene**: an alkane has too few hydrogen atoms to make two smaller alkanes.

> **Worked example.** $C_{14}H_{30}$ is cracked to give octane, C_8H_{18}, and three molecules of one other product. Find that product. Carbon: $14-8=6$ left over; hydrogen: $30-18=12$ left over. Shared between three molecules, each has 2 C and 4 H, so the product is ethene, C_2H_4: $C_{14}H_{30} \rightarrow C_8H_{18} + 3C_2H_4$.

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Combustion

In **combustion** 燃烧 an alkane burns in oxygen:

- **complete combustion** 完全燃烧 (plenty of oxygen) gives carbon dioxide and water.
- **incomplete combustion** 不完全燃烧 (not enough oxygen) gives water plus toxic **carbon monoxide** 一氧化碳 (CO) and soot (carbon).

$$\text{complete: alkane} + O_2 \rightarrow CO_2 + H_2O$$

$$\text{incomplete: alkane} + \text{less } O_2 \rightarrow CO + \text{soot} + H_2O$$

Complete combustion gives CO_2 and water; incomplete also gives CO and soot

$$CH_4 + 1\tfrac{1}{2}\,O_2 \rightarrow CO + 2H_2O \qquad CH_4 + O_2 \rightarrow C + 2H_2O$$

You are often asked to **write the balanced equation**. Balance it in a fixed order - **carbon first, then hydrogen, and oxygen last** - because oxygen is the only element left on just one side:

$$C_6H_{14} + 9\tfrac{1}{2}\,O_2 \rightarrow 6\,CO_2 + 7\,H_2O$$

The 6 carbons fix $6\,CO_2$; the 14 hydrogens fix $7\,H_2O$; counting the oxygens on the right gives $12+7=19$, so the left needs $19\div 2=9\frac{1}{2}$. A **half** of O_2 is perfectly acceptable in this equation - and if the question asks for whole numbers, simply double everything ($2\,C_6H_{14} + 19\,O_2 \rightarrow 12\,CO_2 + 14\,H_2O$).

Free-radical substitution

Alkanes react with chlorine or bromine by **free-radical substitution** 自由基取代, in **ultraviolet light** 紫外线. For ethane and chlorine the mechanism has three steps:

- **initiation** 引发 – UV light splits the halogen into two **free radicals** 自由基: $Cl_2 \rightarrow 2\,Cl\cdot$ This kind of break is **homolytic fission** 均裂: the bond splits **evenly**, one electron going to each atom, which is what makes two radicals. (The opposite, **heterolytic fission** 异裂, sends **both** electrons to one atom and makes a pair of **ions** - that is what happens in the polar mechanisms such as electrophilic addition.) Examiners ask for this word by name, so use it.
- **propagation** 增长 – radicals react and make new radicals:

$$Cl\cdot + C_2H_6 \rightarrow C_2H_5\cdot + HCl \qquad C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$$

- **termination** 终止 – two radicals join, ending the chain: $Cl\cdot + C_2H_5\cdot \rightarrow C_2H_5Cl$

Any two radicals can meet in termination, so there are three possible steps:

$$\mathrm{Cl}\cdot + \mathrm{Cl}\cdot \rightarrow \mathrm{Cl_2} \qquad \mathrm{C_2H_5}\cdot + \mathrm{Cl}\cdot \rightarrow \mathrm{C_2H_5Cl} \qquad \mathrm{C_2H_5}\cdot + \mathrm{C_2H_5}\cdot \rightarrow \mathrm{C_4H_{10}}$$

The small amount of **butane** found in the products is evidence for this mechanism: it can only form when two ethyl radicals join. A Cl· can also attack the chloroethane already made, giving $\mathrm{C_2H_4Cl_2}$ and further products, so the reaction gives a **mixture**. Using an excess of ethane makes this less likely.

1. initiation

$$\mathrm{Cl_2} \xrightarrow{\text{UV}} 2\,\mathrm{Cl^\bullet}$$

UV light splits Cl–Cl into two radicals

2. propagation

$$\mathrm{Cl^\bullet} + \mathrm{C_2H_6} \longrightarrow \mathrm{C_2H_5^\bullet} + \mathrm{HCl}$$

$$\mathrm{C_2H_5^\bullet} + \mathrm{Cl_2} \longrightarrow \mathrm{C_2H_5Cl} + \mathrm{Cl^\bullet}$$

each radical makes a new radical, so the chain continues

3. termination

$$\mathrm{Cl^\bullet} + \mathrm{C_2H_5^\bullet} \longrightarrow \mathrm{C_2H_5Cl}$$

two radicals join, ending the chain

Free-radical substitution in three steps: initiation makes radicals, propagation carries the chain, and termination ends it

Why cracking is useful, and why alkanes are unreactive

Cracking turns heavy fractions of **crude oil** 原油 into more useful, lower-M_r alkanes and alkenes. (A **fraction** 馏分 is a group of molecules with a similar boiling-point range.) Crude oil contains more of the heavy fractions than people need, and less petrol than people need, so cracking matches supply to **demand**. The shorter alkanes are used as fuels such as petrol, and the alkenes are the starting materials for polymers and other chemicals.

Alkanes are generally unreactive, especially towards polar reagents. This is because the C–H and C–C bonds are strong and have little **polarity** 极性, so there is no charge to attract an attacking species.

Environmental effects

Burning alkanes in an internal combustion engine gives off carbon monoxide, oxides of nitrogen and unburnt hydrocarbons. A catalytic converter removes these by turning them into harmless gases.

- **Carbon monoxide, CO**, comes from incomplete combustion of the fuel. It is toxic: it binds to haemoglobin, so the blood carries less oxygen.
- **Oxides of nitrogen, $\mathbf{NO_x}$**, form because $\mathrm{N_2}$ and $\mathrm{O_2}$ from the air react at the high temperature in the engine: $\mathrm{N_2 + O_2 \rightarrow 2NO}$, then $\mathrm{2NO + O_2 \rightarrow 2NO_2}$. They cause acid rain and photochemical smog.

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- **Unburnt hydrocarbons** are fuel that passes through without burning. They cause photochemical smog, and some are carcinogens.

The **catalytic converter** 催化转化器 holds platinum and rhodium on a ceramic honeycomb, which gives a large surface area. On its surface, CO and NO react together, and the hydrocarbons are oxidised:

$$\mathrm{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

$$\mathrm{C_8H_{18} + 12\tfrac{1}{2}\,O_2 \rightarrow 8CO_2 + 9H_2O}$$

In the first reaction, CO is **oxidised** (carbon goes from +2 to +4) while NO is **reduced** (nitrogen goes from +2 to 0).

Alkenes



Cracking heavy fractions at a refinery produces alkenes for plastics and fuels.

Alkenes have a C=C double bond (general formula $\mathrm{C_nH_{2n}}$). The double bond is the functional group, so alkenes are reactive.

Making alkenes

- **elimination** 消去 of HX from a **halogenoalkane** 卤代烷, using NaOH dissolved in ethanol, with heat.
- **dehydration** 脱水 of an **alcohol** 醇, using a hot $\mathrm{Al_2O_3}$ catalyst or concentrated sulfuric acid.
- cracking of a longer-chain alkane.

Reactions of alkenes

Most reactions are **electrophilic addition** 亲电加成 across the double bond:

Reagent and conditions	Product
H_2, Pt/Ni catalyst, heat	alkane
steam 水蒸气 (H_2O), H_3PO_4 catalyst	alcohol
a **hydrogen halide** 卤化氢 (HX), room temperature	halogenoalkane
a halogen X_2	a di-substituted alkane

The equations, using propene:

$$CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3 \qquad CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$$

$$CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CH(OH)CH_3 \qquad CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

The steam and HBr additions give mainly the product with the OH or Br on the **middle** carbon (propan-2-ol and 2-bromopropane), for the reason explained under Markovnikov's rule below. With bromine, both carbons of the old C=C gain a Br: 1,2-dibromopropane.

There are also two oxidation reactions with acidified $KMnO_4$:

- **cold, dilute** $KMnO_4$ adds two –OH groups to give a **diol** 二醇.
- **hot, concentrated** $KMnO_4$ breaks the C=C bond right apart, and what each half turns into tells you exactly where the double bond used to be.

That second reaction is worth learning properly, because it is how the exam asks you to **locate a double bond in a large molecule**. Oxidation is written with [O], meaning "an oxygen atom from the oxidising agent". Cut the molecule at the C=C, then look at **what each of the two carbons was carrying**:

The C=C carbon carries	It becomes
two alkyl groups (=CR_2)	a **ketone** 酮, $R_2C{=}O$
one alkyl and one H (=CHR)	a **carboxylic acid** 羧酸, RCOOH
two hydrogens (=CH_2)	CO_2 and water

The pattern is simply how many hydrogens that carbon had: none stops at a ketone, one is pushed on to an acid, and two are oxidised all the way to CO_2.

> **Worked example.** Give the products when $(CH_3)_2C{=}CHCH_3$ is heated with hot concentrated acidified $KMnO_4$. Cut at the C=C and take each carbon separately. The **left** carbon carries **two methyl groups** and no hydrogen, so it stops at a **ketone**: $(CH_3)_2C{=}O$, which is propanone. The **right** carbon carries **one methyl and one H**, so it goes on to a **carboxylic acid**: CH_3COOH, ethanoic acid. So:

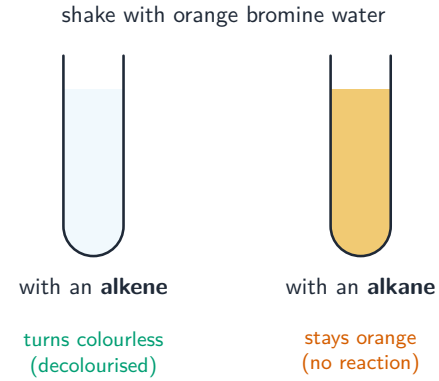
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$$(CH_3)_2C{=}CHCH_3 + 3[O] \rightarrow CH_3COCH_3 + CH_3COOH$$

Now run it **backwards**, which is the way the question is usually set. Given the products, rebuild the alkene by putting the two carbonyl carbons back together as a C=C: a ketone means that carbon had **two alkyl groups**, an acid means **one alkyl and one H**, and CO_2 means the chain **ended** in $=CH_2$. Getting CO_2 is the strongest clue of all - it can only come from a **terminal** double bond.

Test for a C=C bond

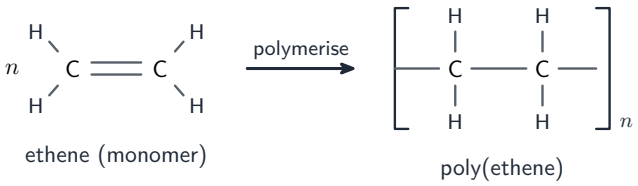
Shake the compound with orange **bromine water** 溴水. An alkene **decolourises** it (turns it colourless) by electrophilic addition. An alkane does not.



The bromine-water test: an alkene decolourises the orange bromine water, while an alkane leaves it orange

Addition polymerisation

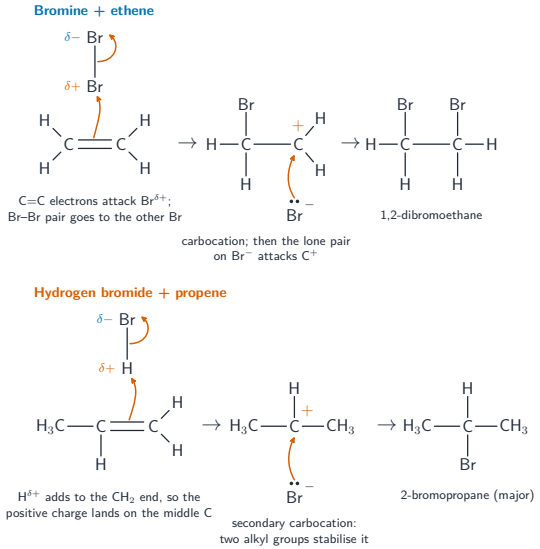
In **addition polymerisation** 加成聚合, many alkene molecules join into one long chain, with no other product. Ethene gives poly(ethene). The long-chain product is a **polymer** 聚合物. Propene gives poly(propene): $n\,CH_2{=}CHCH_3 \rightarrow -(CH_2{-}CH(CH_3))_n-$, where the CH_3 is a side group on every second carbon of the chain.



Addition polymerisation: many ethene molecules open their double bonds and join into the long chain of poly(ethene)

The mechanism and Markovnikov's rule

In electrophilic addition, the electron-rich C=C attracts an **electrophile** 亲电试剂 (an electron-pair acceptor). This forms a positive intermediate called a **carbocation** 碳正离子, which the negative part then attacks. The syllabus uses two examples: bromine with ethene, and hydrogen bromide with propene.



Electrophilic addition: the C=C attacks the δ+ atom, a carbocation forms, then the lone pair of Br^- attacks it. With propene the H goes to the CH_2 end, giving the more stable secondary carbocation

Where the δ+ comes from. Br_2 is not polar on its own. As it comes close to the C=C, the cloud of electrons in the double bond repels the electrons in Br–Br. This makes an **induced dipole** 诱导偶极: the nearer Br becomes δ+ and the further Br δ−. HBr already has a permanent dipole, with H δ+.

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Drawing it for full marks (Br_2 + ethene):

1. the dipole on Br–Br, δ+ on the Br nearer the C=C.
2. a curly arrow from the **C=C double bond** to the δ+ Br.
3. a curly arrow from the **Br–Br bond** to the δ− Br.
4. the carbocation, with a full + on the carbon that did **not** gain the Br.
5. a curly arrow from a **lone pair** on Br^- to that C^+, and the product.

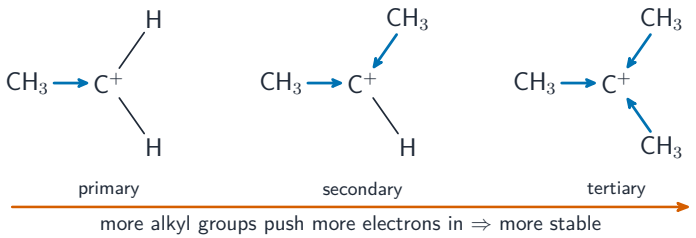
In the first step the Br–Br bond breaks **heterolytically**: both electrons go to one Br, which leaves as Br^-.

Common mistakes.

- An arrow starting at a carbon atom, not at the middle of the double bond.
- An arrow from the δ+ Br towards the C=C. The electrons move **from** the double bond **to** the electrophile.
- The + drawn on the carbon that has just bonded to Br. The **other** carbon has lost its share of the C=C pair.
- An arrow starting from the minus sign of Br^-. Draw the lone pair and start there.

With **bromine water** the carbocation meets far more water molecules than Br^- ions, so a lone pair on water often attacks it instead. The main product is then 2-bromoethanol, not 1,2-dibromoethane. The colour still goes, because the Br_2 is used up either way.

Alkyl groups push electrons towards the positive carbon – this is the **inductive effect** 诱导效应. So a carbocation with more alkyl groups is more stable: tertiary is more stable than secondary, which is more stable than primary. When HBr adds to propene, the more stable carbocation forms, so hydrogen adds to the carbon that already has more hydrogens. This pattern is **Markovnikov's rule** 马氏规则.



Markovnikov: HBr adds so the *more stable* carbocation forms

Carbocation stability rises from primary to tertiary as more alkyl groups push electrons in – the basis of Markovnikov's rule

Worked example. Predict the major product when HBr adds to propene, $CH_3CH{=}CH_2$. The H^+ adds first, and it adds in whichever way makes the **more stable carbocation**. Adding the H to the **end** carbon puts the positive charge on the middle carbon, giving a **secondary** carbocation, which is stabilised by electron-releasing alkyl groups on **two** sides. Adding it to the middle carbon would leave a less stable **primary** carbocation. The bromide ion then attacks the secondary carbocation, so the major product is **2-bromopropane**. That is Markovnikov's rule - but quote the **reason** (carbocation stability: tertiary > secondary > primary), because the rule on its own is not the explanation.

Exam tips

- **Alkanes**: free-radical substitution needs **UV light** – show initiation, propagation and termination with the radical dots.
- **Alkenes**: electrophilic addition via a **carbocation**; draw curly arrows from the C = C.
- **Markovnikov**: H adds to the carbon with more H's, via the **more stable carbocation** (alkyl groups are electron-releasing).
- In cracking questions, balance the **carbon** and **hydrogen** atoms to find a missing product; at least one product is an alkene.
- For the catalytic converter, give an equation (for example $2CO{+}2NO \rightarrow 2CO_2{+}N_2$) and say what is oxidised and what is reduced.
- Test for C = C: **bromine water decolourises** (orange → colourless) – state the observation.

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Halogen compounds

A-Level Chemistry

Halogenoalkanes

A **halogenoalkane** 卤代烷 is an alkane with one or more halogen atoms in place of hydrogen (a C–X bond, where X is a halogen).



Volatile halogenoalkanes were once widely used as refrigerants and aerosol propellants

Making halogenoalkanes

- **free-radical substitution** 自由基取代 of an alkane with Cl_2 or Br_2 in ultraviolet light.
- **electrophilic addition** 亲电加成 of an alkene with a halogen X_2 or a hydrogen halide HX.
- substitution of an **alcohol** 醇, for example by HX, by PCl_5, by PCl_3 with heat, or by $SOCl_2$.

The equations, using ethane and ethene:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl \qquad \text{(UV light)}$$

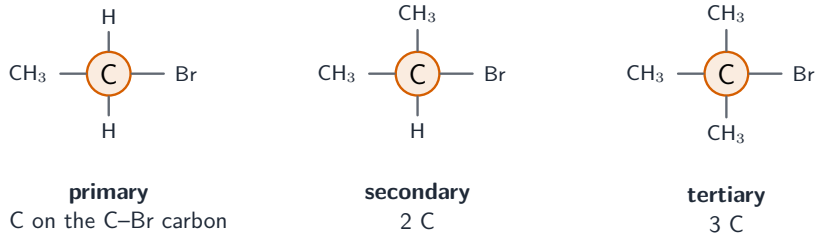
$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br \qquad CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$$

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

Free-radical substitution gives a **mixture**: the chloroethane formed can react again to give $C_2H_4Cl_2$ and further products, so it is a poor way to make one pure product. Addition to an alkene gives a single product, and an alcohol gives the halogen exactly where the OH was.

Three classes

A halogenoalkane is **primary** 伯, **secondary** 仲 or **tertiary** 叔, depending on how many carbon atoms are joined to the carbon that holds the halogen (one, two or three).



Primary, secondary and tertiary halogenoalkanes, set by how many carbons are joined to the carbon bearing the halogen

Nucleophilic substitution

The C–X bond is polar, so the carbon is slightly positive. A **nucleophilic substitution** 亲核取代 happens when a **nucleophile** 亲核试剂 (a lone-pair species) attacks that carbon and replaces the halogen.



Many halogenoalkane reactions are carried out by heating the mixture under reflux

Reagent and conditions	Product
NaOH(aq), heat	an alcohol
KCN in ethanol, heat	a **nitrile** 腈 (adds one carbon to the chain)
NH_3 in ethanol, heated under pressure	an **amine** 胺

The equations, using bromoethane:

$$C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$$

$$C_2H_5Br + KCN \rightarrow C_2H_5CN + KBr$$

$$C_2H_5Br + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4Br$$

Two moles of ammonia are used: the second one takes the HBr formed, as ammonium bromide. The nucleophiles are OH^-, CN^- and NH_3; each has a lone pair that attacks the $\delta+$ carbon.



A rotary evaporator removes solvent under reduced pressure – the step after the reaction

To **identify the halogen**, warm the halogenoalkane with **silver nitrate** 硝酸银 in ethanol. A silver halide **precipitate** 沉淀 forms, and its colour shows which halogen is present (white AgCl, cream AgBr, yellow AgI).

The silver ions do not pull the halogen off directly. **Water** in the mixture is the nucleophile: it slowly hydrolyses the halogenoalkane, which releases halide ions, and these meet the silver ions:

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$$C_2H_5Br + H_2O \rightarrow C_2H_5OH + H^+ + Br^- \qquad Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$

Ethanol is used as a **common solvent**, because the halogenoalkane does not mix with water.

Elimination

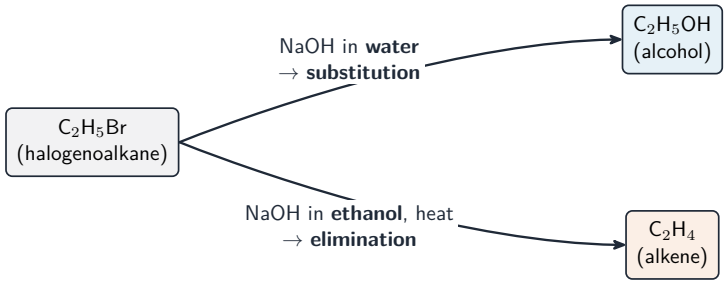
The same halogenoalkane can instead undergo **elimination** 消去 to form an **alkene** 烯烃. The conditions decide which reaction wins:

- NaOH in **water** → nucleophilic substitution → an alcohol.
- NaOH in **ethanol**, heated → elimination → an alkene.

$$C_2H_5Br + NaOH \rightarrow C_2H_4 + NaBr + H_2O$$

In elimination, the OH^- acts as a **base**: it removes an H from the carbon **next to** the C–Br carbon, the Br leaves, and a C=C forms between those two carbons.

> **Worked example.** 2-bromobutane, $CH_3CHBrCH_2CH_3$, is heated with NaOH in ethanol. Name the organic products. The Br is on C2, and both neighbours (C1 and C3) carry H atoms. Losing an H from C1 gives **but-1-ene**, $CH_2{=}CHCH_2CH_3$; losing one from C3 gives **but-2-ene**, $CH_3CH{=}CHCH_3$, as both **cis** and **trans** isomers. So three alkenes form. Some butan-2-ol also forms by substitution, because the two reactions always compete; ethanol as the solvent and a high temperature favour elimination.



The same halogenoalkane: NaOH in water substitutes to an alcohol, while NaOH in ethanol (with heat) eliminates to an alkene

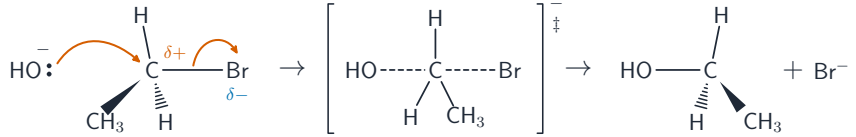
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The S_N1 and S_N2 mechanisms

Nucleophilic substitution can follow two routes:

- **S_N2**: one step. The nucleophile attacks at the same time as the halogen leaves, passing through a crowded **transition state** 过渡态 where both are half-bonded. The rate depends on both the halogenoalkane and the nucleophile.
- **S_N1**: two steps. First the C–X bond breaks to give a **carbocation** 碳正离子; then the nucleophile attacks it. The rate depends only on the halogenoalkane.

S_N2 (primary, e.g. bromoethane): one step

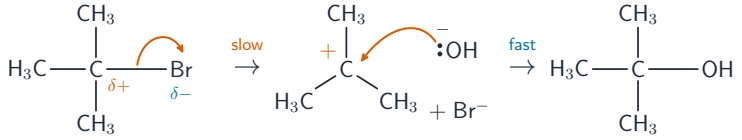


lone pair on O attacks the $\delta+$ C from the side away from Br

transition state: O–C half-formed, C–Br half-broken, charge spread

ethanol + bromide ion; the three groups have flipped

S_N1 (tertiary, e.g. 2-bromo-2-methylpropane): two steps



the C–Br bond breaks: both electrons go to Br

tertiary carbocation: three alkyl groups push electrons in and stabilise it

2-methylpropan-2-ol

S_N2 is a single step through a charged transition state; S_N1 is a slow step to a carbocation, then a fast attack

Drawing the mechanism for full marks. A **curly arrow** 弯箭头 shows a **pair** of electrons moving. It must start at a **lone pair** 孤对电子 or at a **bond**, and end where the new bond forms (or on the atom that takes the pair). For S_N2 the marks are usually:

1. the **dipole** 偶极 on the C–Br bond: $\delta+$ on C, $\delta-$ on Br.
2. a curly arrow from a **lone pair on the O** of OH^- to the $\delta+$ carbon (draw the lone pair).
3. a curly arrow from the **C–Br bond** to the Br.
4. the **transition state**: square brackets, dotted HO · · · C and C · · · Br bonds, and an overall − charge.
5. the products, including Br^-.

For S_N1 there are two steps, so two diagrams: the C–Br bond breaks first (arrow from

the bond to Br) to give the carbocation with a full + on the carbon, and then the lone pair of OH^- attacks that C^+.

Why the rate equations differ. In S_N1 the slow step involves only the halogenoalkane, so rate = k[RBr] (first order). In S_N2 both species meet in the one step, so rate = k[RBr][OH^-] (second order). The "1" and "2" in the names count the species in the **rate-determining step** 决速步骤, not the number of steps.

Common mistakes.

- An arrow starting from the minus sign or from the H of OH^-. It must start at a lone pair on the **oxygen**.
- An arrow pointing from the Br **to** the carbon. Arrows show electrons moving away from the bond, into the Br.
- Forgetting the charge on the transition state, or drawing full bonds (not dotted ones) inside the brackets.
- Drawing a transition state for S_N1. S_N1 has a real **intermediate** 中间体 (the carbocation) instead.
- Writing "aqueous NaOH" when the question wants an alkene. Elimination needs NaOH in **ethanol**, heated; aqueous NaOH gives the alcohol.
- Explaining the silver nitrate order by the polarity of the C–X bond. The order follows the **bond energy**: C–I is weakest, so it breaks fastest.
- Saying tertiary halogenoalkanes use S_N1 "because they are more reactive". The reason is that three alkyl groups **block** the back of the carbon **and** stabilise the carbocation.

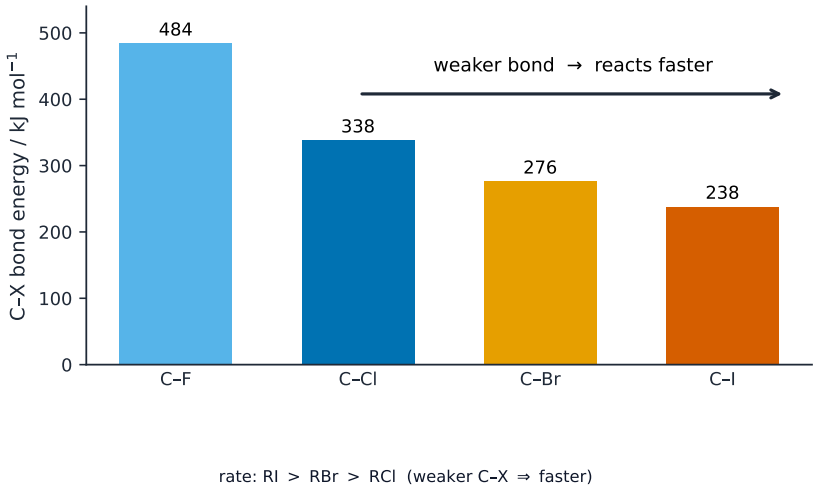
Alkyl groups push electrons towards the positive carbon (the **inductive effect** 诱导效应), so they stabilise the carbocation. The more alkyl groups on the C^+, the more the positive charge is spread out, so carbocation stability is **tertiary** > **secondary** > **primary**. This is why:

- **primary** halogenoalkanes mostly react by S_N2.
- **tertiary** halogenoalkanes mostly react by S_N1 (their carbocation is well stabilised).
- **secondary** halogenoalkanes use a mixture of the two.

Different reactivities

How fast a halogenoalkane reacts depends on the strength of the C–X bond, measured by its **bond energy** 键能. The C–I bond is the weakest, so iodoalkanes react fastest; the C–Cl bond is the strongest of the three, so chloroalkanes react slowest. So when tested with silver nitrate, an iodoalkane gives its precipitate first – its higher **reactivity** 反应活性 comes from the weaker C–X bond.

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The weaker the C–X bond, the faster the halogenoalkane reacts – so iodoalkanes react fastest and chloroalkanes slowest

The comparison experiment. Put equal amounts of 1-chlorobutane, 1-bromobutane and 1-iodobutane into three test tubes, each with ethanol. Warm them in a water bath at the same temperature (about 50 °C) beside a tube of aqueous silver nitrate, then add the same volume of silver nitrate to each and start a clock. Record the time until a precipitate appears.

Halogenoalkane	C–X bond energy / kJ mol^{-1}	Precipitate	Appears
1-chlorobutane	338	white AgCl	last (very slowly)
1-bromobutane	276	cream AgBr	second
1-iodobutane	238	yellow AgI	first

The order follows the bond energy, **not** the polarity of the bond: the C–Cl bond is the most polar, yet it reacts slowest, because breaking the strong C–Cl bond is the hard step. For a fair test keep the temperature, the volumes and the carbon chain the same, and change only the halogen. Compared in the same way, a tertiary bromoalkane gives its precipitate faster than a primary one, because it reacts by S_N1 through a stable carbocation.

Worked example. Predict the mechanism for the hydrolysis of 1-bromobutane and of 2-bromo-2-methylpropane. Classify the halogenoalkane first. 1-bromobutane is **primary**: the carbon carrying the Br is barely shielded, so the nucleophile can attack the back of it and the mechanism is S_N2 - one step, with the rate depending on **both** the halogenoalkane and the nucleophile. 2-bromo-2-methylpropane is **tertiary**: three bulky methyl groups block that attack, but they also stabilise the carbocation formed once the Br leaves, so it goes S_N1 - two steps, with the rate depending on the halogenoalkane **only**. Decide from the **class** (primary → S_N2, tertiary → S_N1), and note that the tertiary one hydrolyses **faster** despite being the more crowded.

Exam tips

- Draw **nucleophilic substitution** with a curly arrow from the nucleophile's lone pair to the $\delta+$ carbon and one from the C-X bond.
- Match mechanism to class: S_N1 (tertiary, carbocation, two steps) vs S_N2 (primary, one step, transition state).
- Reactivity is set by **bond enthalpy**: C-I is weakest, so iodoalkanes react fastest (not electronegativity).
- **Elimination** (hot, ethanolic KOH) vs **substitution** (warm, aqueous KOH) – the conditions decide the product; state them.

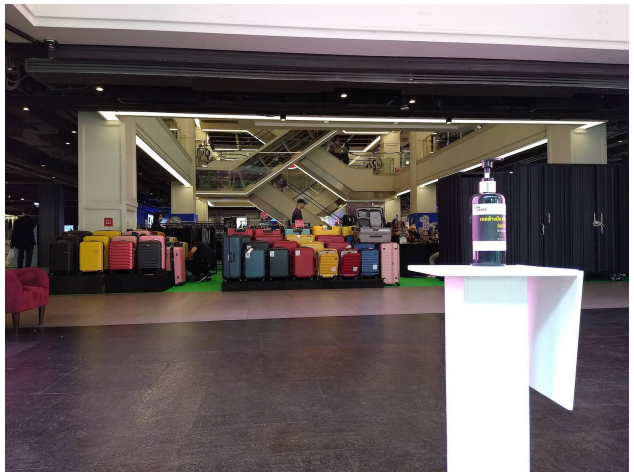
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Hydroxy compounds

A-Level Chemistry

Alcohols

An **alcohol** 醇 has the –OH (hydroxyl) functional group.



Ethanol, the alcohol in hand sanitiser, kills microbes

Making alcohols

Method	Reagents and conditions
addition of steam to an alkene	$H_2O(g)$, H_3PO_4 catalyst (**electrophilic addition** 亲电加成)
an **alkene** 烯烃 with cold dilute $KMnO_4$	gives a **diol** 二醇 (two –OH groups)
substitution of a **halogenoalkane** 卤代烷	NaOH(aq), heat
reduction 还原 of an **aldehyde** 醛 or **ketone** 酮	$NaBH_4$ or $LiAlH_4$
reduction of a **carboxylic acid** 羧酸	$LiAlH_4$
hydrolysis 水解 of an **ester** 酯	dilute acid or alkali, heat

The equations, for two-carbon examples:

$$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH \qquad (\text{steam}, H_3PO_4, \text{about } 300\,^\circ\text{C})$$

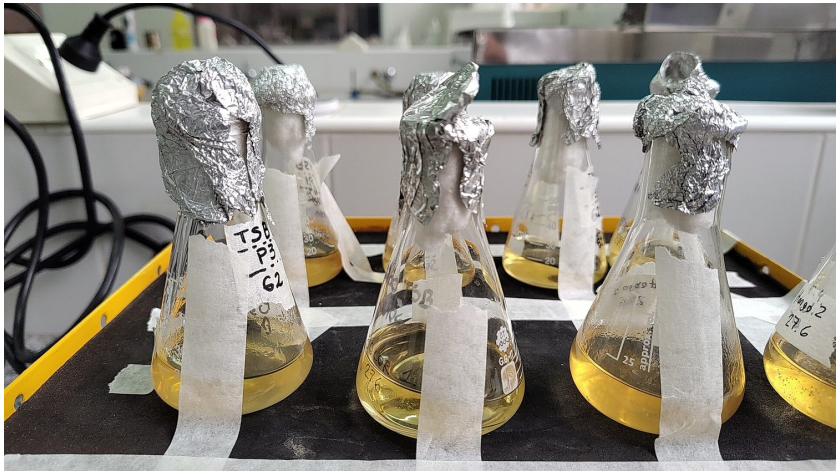
$$CH_2{=}CH_2 + [O] + H_2O \rightarrow HOCH_2CH_2OH \qquad (\text{cold dilute acidified } KMnO_4)$$

$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH \qquad CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$$

With the $KMnO_4$ the purple colour disappears, and the product, ethane-1,2-diol, has an –OH on **each** carbon of the old C=C. Reducing a ketone gives a **secondary** alcohol: propanone gives propan-2-ol.

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Industrially, ethanol is also made by fermenting sugar; fractional distillation then separates it from the water

Reactions of alcohols

- **combustion**: alcohols burn in oxygen to give carbon dioxide and water.
- **substitution** to a halogenoalkane, for example with HX, PCl_5, PCl_3 and heat, or $SOCl_2$.
- **with sodium**: alcohols react with sodium metal to give hydrogen and a sodium alkoxide – like water, but more slowly.
- **oxidation** 氧化 with acidified $K_2Cr_2O_7$ (or $KMnO_4$). The product depends on the class of alcohol (see below).
- **dehydration** 脱水 to an alkene, using a hot Al_2O_3 catalyst or concentrated acid.
- **ester formation**: an alcohol reacts with a carboxylic acid (with concentrated H_2SO_4 catalyst) to make an ester.

The equations, using ethanol:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5O^-Na^+ + H_2 \qquad (\text{sodium ethoxide})$$

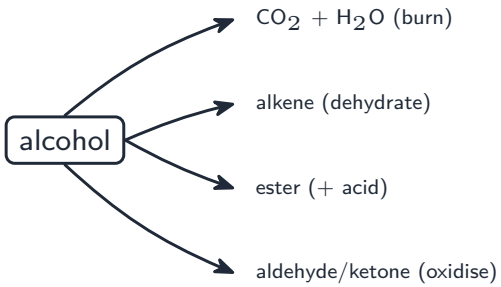
$$C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O \qquad (\text{hot } Al_2O_3, \text{ or conc. } H_2SO_4)$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \qquad (\text{ethyl ethanoate})$$

Esterification is reversible and slow, so it is heated under reflux with the acid catalyst. The ester's name puts the alcohol part first (**ethyl**) and the acid part second (**ethanoate**).

Making a halogenoalkane from an alcohol. Each reagent swaps the –OH for a halogen atom:

- **HBr(g)**, or KBr with concentrated H_2SO_4 (the acid and the salt make the HBr in the flask): $C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$.
- **PCl_5**, at room temperature: $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$. The steamy fumes of HCl are a **test for an –OH group**.
- **PCl_3**, with heat: $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$.
- **$SOCl_2$**: $C_2H_5OH + SOCl_2 \rightarrow C_2H_5Cl + SO_2 + HCl$. Both by-products are gases, so the halogenoalkane is easy to separate.

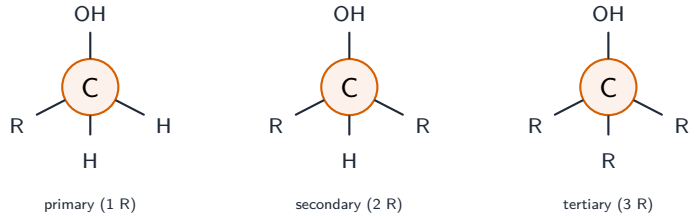


An alcohol can burn, dehydrate, esterify or be oxidised

■ Three classes and how oxidation tells them apart

An alcohol is **primary** 伯, **secondary** 仲 or **tertiary** 叔, depending on how many carbons are joined to the carbon holding the –OH. Some molecules have more than one –OH group.

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The class is set by the carbon holding the –OH: one R group makes it primary, two secondary, three tertiary – which decides how it oxidises

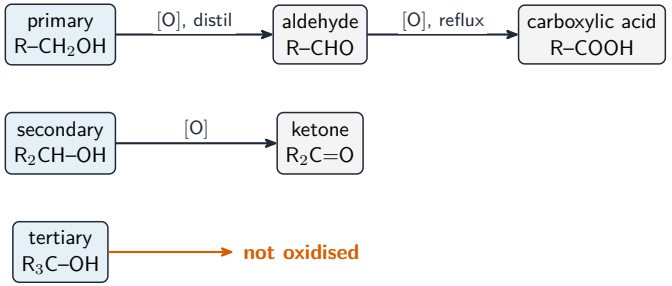
Class	Oxidation product
primary	**aldehyde** (by **distillation** 蒸馏), then **carboxylic acid** (by **reflux** 回流)
secondary	a **ketone**
tertiary	not oxidised

Write the oxidising agent as [O]:

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O \qquad \text{(distil: ethanal)}$$

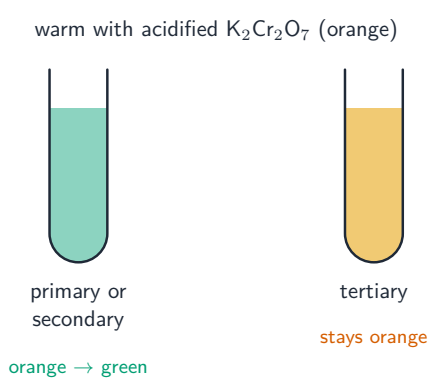
$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O \qquad \text{(reflux: ethanoic acid)}$$

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O \qquad \text{(propanone)}$$



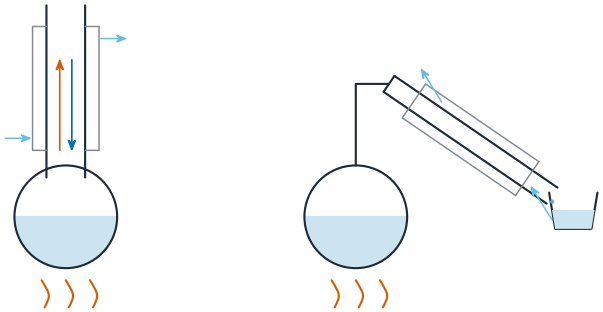
Oxidation by class: a primary alcohol gives an aldehyde then a carboxylic acid, a secondary gives a ketone, a tertiary is not oxidised

In a quick test, acidified $K_2Cr_2O_7$ turns from **orange to green** with a primary or secondary alcohol, but stays orange with a tertiary alcohol.



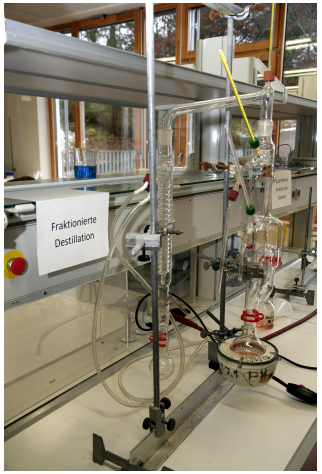
Acidified dichromate turns orange to green with a primary or secondary alcohol, but stays orange with a tertiary alcohol

- **distillation** removes the aldehyde as it forms, before it can be oxidised further.
- **reflux** keeps boiling the mixture and returning the vapour, so the alcohol is fully oxidised to the carboxylic acid.



Distillation removes the aldehyde as it forms; reflux keeps boiling and returning the vapour, fully oxidising to the acid

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A real distillation set-up: the vapour boils off, cools in the condenser and is collected – the same idea separates ethanol from a fermented mixture

The iodoform test

If you warm an alcohol that contains the $CH_3CH(OH)-$ group with alkaline aqueous iodine, you get a pale yellow precipitate of **tri-iodomethane** 三碘甲烷 (CHI_3) and the ion RCO_2^-. This is a useful test for that group.

> **Worked example.** Which of these give a yellow precipitate with alkaline iodine: ethanol, propan-1-ol, propan-2-ol, butan-2-ol, 2-methylpropan-2-ol? Look for a CH_3 on the carbon that carries the OH, **and** an H on that same carbon.

- **ethanol**, CH_3CH_2OH: yes ($CH_3CH(OH)-$ with H in place of R). It gives CHI_3 and methanoate, HCO_2^-.
- **propan-2-ol**, $CH_3CH(OH)CH_3$: yes, giving CHI_3 and ethanoate, $CH_3CO_2^-$.
- **butan-2-ol**, $CH_3CH(OH)CH_2CH_3$: yes, giving CHI_3 and propanoate, $CH_3CH_2CO_2^-$. The CH_3 becomes CHI_3; the rest of the molecule leaves as the carboxylate ion, one carbon shorter.
- **propan-1-ol**, $CH_3CH_2CH_2OH$: no. The OH carbon carries CH_2CH_3, not CH_3.
- **2-methylpropan-2-ol**, $(CH_3)_3COH$: no. The OH carbon has CH_3 groups but **no H**, so it cannot be oxidised first.

Dehydration can give more than one alkene

In dehydration the OH leaves together with an H from a carbon **next to** the OH carbon, and a C=C forms between those two carbons. If the two neighbouring carbons are different, you get different alkenes.

Worked example. Butan-2-ol, $CH_3CH(OH)CH_2CH_3$, is heated with Al_2O_3. The OH is on C2.

- An H lost from **C1** gives $CH_2{=}CHCH_2CH_3$, **but-1-ene**.
- An H lost from **C3** gives $CH_3CH{=}CHCH_3$, **but-2-ene**. But-2-ene has two different groups on each carbon of the C=C, so it exists as **cis** and **trans** isomers.

So the answer is **three** alkenes: but-1-ene, cis-but-2-ene and trans-but-2-ene. Butan-1-ol, with only one neighbouring carbon, gives only but-1-ene.

■ Acidity of alcohols

The –OH group makes alcohols very weakly acidic: they can lose the H^+ to form an RO^- ion. But their **acidity** 酸性 is **lower** than that of water. This is because the alkyl group pushes electron density onto the oxygen, which makes the RO^- ion less stable, so the alcohol holds onto its H^+ more tightly.

The evidence is the reaction with sodium. A small piece of sodium in water darts about, fizzes fast and may melt; in ethanol it sinks and fizzes **steadily**, more slowly, giving hydrogen and sodium ethoxide. The slower reaction shows that ethanol gives up H^+ less easily than water.

Worked example: two OH groups. Butane-1,3-diol is $HOCH_2CH_2CH(OH)CH_3$. Classify each OH group, and give the product of heating it under reflux with excess acidified $K_2Cr_2O_7$. Does it give the iodoform test? The OH on C1 is on a carbon with **one** carbon neighbour: **primary**. The OH on C3 has **two** carbon neighbours: **secondary**. Under reflux the primary OH is oxidised all the way to –COOH and the secondary OH becomes a ketone C=O, so the product is $HOOCCH_2COCH_3$, 3-oxobutanoic acid. The molecule contains $CH_3CH(OH)-$, so **yes**, it gives a yellow precipitate with alkaline iodine. Treat each OH group as if it were alone, then put the answers together.

Worked example. Three unlabelled bottles hold butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. How does warming each with acidified $K_2Cr_2O_7$ tell them apart? What matters is how many hydrogens sit on the **carbon carrying the OH**. Butan-1-ol is **primary** (two such hydrogens): the orange dichromate turns **green**, and by distilling you collect an **aldehyde** (butanal), or by refluxing you get the **carboxylic acid** (butanoic acid). Butan-2-ol is **secondary** (one such hydrogen): also **green**, but the product is a **ketone** (butanone), which will not oxidise further. 2-methylpropan-2-ol is **tertiary** (**no** such hydrogen): there is nothing to remove, so the dichromate stays **orange**. The colour only separates the tertiary from the other two - to split primary from secondary you must identify the **product** (an aldehyde gives a silver mirror with Tollens', a ketone does not).

Common mistakes.

- Classifying the alcohol by the number of carbons in the whole molecule. Count only the carbons joined to the **carbon carrying the OH**.

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- Writing [O] for a tertiary alcohol and giving a product. A tertiary alcohol has no H on the OH carbon, so it is not oxidised.
- Saying distillation "makes" the aldehyde. Both set-ups make the aldehyde first; distillation simply removes it before it is oxidised further.
- Missing the cis and trans isomers of but-2-ene when you list dehydration products.
- Writing the ester name the wrong way round. Ethanoic acid and ethanol make **ethyl ethanoate**: alcohol part first, acid part second.
- Writing H_2 as a product of oxidation. The H atoms removed join [O] to form **water**.
- Saying any alcohol with a CH_3 gives the iodoform test. The CH_3 must be on the **same** carbon as the OH, and that carbon needs an H.

Exam tips

- Classify the alcohol as **primary, secondary or tertiary** first – it decides the oxidation product.
- **Oxidation** with acidified $K_2Cr_2O_7$ (orange → green): primary → aldehyde (distil) → acid (reflux); secondary → ketone; tertiary → no reaction.
- Distinguish the conditions for **aldehyde vs acid** from a primary alcohol (distillation vs reflux).
- Name esters correctly (the acid part comes second, ending "-oate").

Carbonyl compounds

A-Level Chemistry

Aldehydes and ketones

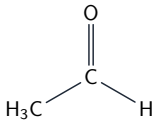
Aldehydes and ketones are **carbonyl compounds** 羰基化合物 – they contain the C=O **carbonyl** 羰基 group.

- in an **aldehyde** 醛 the carbonyl carbon is on the end of the chain (it also carries an H), written –CHO.
- in a **ketone** 酮 the carbonyl carbon is in the middle, between two other carbons.



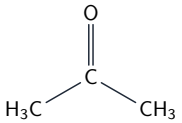
Propanone (acetone), the simplest ketone, is the solvent in nail-polish remover

aldehyde



C=O carbon on the end
(also carries an H): –CHO

ketone



C=O carbon in the middle,
between two carbons

Both have the C=O carbonyl group: in an aldehyde it is on the end of the chain (–CHO), in a ketone it is in the middle

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Making aldehydes and ketones

Both are made by the **oxidation** 氧化 of an **alcohol** 醇 with acidified $K_2Cr_2O_7$ or $KMnO_4$:

- a **primary** alcohol, with **distillation** 蒸馏, gives an aldehyde.
- a **secondary** alcohol gives a ketone.

Write the oxidising agent as [O] in a balanced equation:

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

Conditions and observations. Heat the alcohol with acidified potassium dichromate(VI); the solution turns from **orange** to **green** as $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. (With acidified $KMnO_4$ the purple colour fades.) For an aldehyde, **distil the product off as it forms**: the aldehyde has the lowest boiling point in the mixture (it has no hydrogen bonding between its molecules), so it leaves before it can be oxidised further to a carboxylic acid. Heating under **reflux** 回流 instead would give the carboxylic acid. A ketone cannot be oxidised further, so it can be distilled off at the end. A **tertiary** alcohol is not oxidised: the dichromate stays orange.

Reactions

- **reduction** 还原 with $NaBH_4$ or $LiAlH_4$ turns a carbonyl compound back into an alcohol (an aldehyde gives a primary alcohol; a ketone gives a secondary alcohol).
- reaction with **hydrogen cyanide** 氰化氢 (HCN), with KCN as **catalyst** 催化剂 and heat, adds H and CN across the C=O to make a **hydroxynitrile** 羟基腈. This adds one carbon to the chain.

Write the reducing agent as [H]:

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH \qquad CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$$

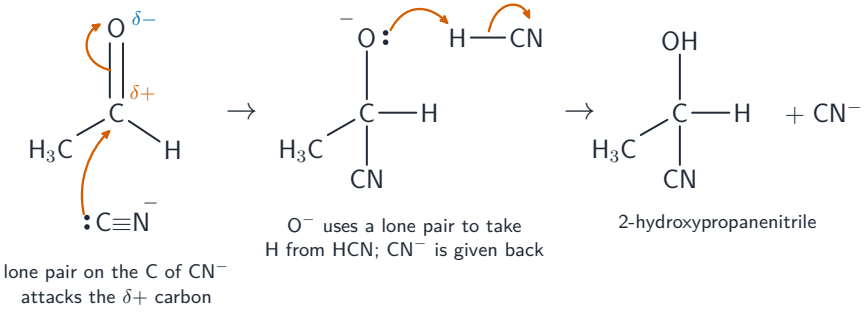
$NaBH_4$ is used in water or methanol, at room temperature. $LiAlH_4$ is a stronger reducing agent that reacts violently with water, so it is used in **dry ether**. Both supply hydride ions, H^-, which attack the $\delta+$ carbonyl carbon. They do not reduce C=C double bonds, so in a molecule with both, only the C=O is reduced. (Hydrogen with a nickel catalyst reduces both.)

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

The mechanism: nucleophilic addition

The reaction with HCN is a **nucleophilic addition** 亲核加成. Oxygen is more electronegative than carbon, so the C=O bond is polar and the carbonyl carbon is $\delta+$. HCN is a weak acid and gives very few CN^- ions, so a little KCN is added to supply them. The steps are:

1. a **lone pair** 孤对电子 on the **carbon** of CN^- attacks the $\delta+$ carbonyl carbon.
2. at the same time, one pair of the C=O double bond moves onto the oxygen, which becomes O^-.
3. the O^- uses a lone pair to take H^+ from an HCN molecule. This makes the hydroxynitrile and gives back a CN^- ion. Because CN^- is used and then given back, KCN acts as a catalyst.



Nucleophilic addition of HCN to ethanal: CN^- attacks the $\delta+$ carbonyl carbon, the C=O pair moves to O, then O^- takes H from HCN and gives CN^- back

With propanone the same steps give 2-hydroxy-2-methylpropanenitrile. The product has one more carbon atom than the aldehyde or ketone, which makes this reaction useful for making longer carbon chains.

The product is a racemic mixture. The carbonyl group and the atoms joined to it are **planar** (trigonal planar around the carbon). So the CN^- ion can attack the carbonyl carbon from **above** or **below** the plane with equal chance. With ethanal, the product 2-hydroxypropanenitrile has a **chiral** carbon (four different groups: H, CH_3, OH and CN), so the two directions of attack give the two **optical isomers** 旋光异构体 in equal amounts – a **racemic mixture** 外消旋混合物, which does not rotate plane-polarised light. With propanone the product is not chiral (the carbon carries two CH_3 groups), so there is only one product.

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> **Worked example.** Explain why the product of HCN with butanone shows no optical activity, even though it contains a chiral carbon. The carbon in $CH_3C(OH)(CN)CH_2CH_3$ has four different groups, so it is chiral. But the butanone molecule is planar at the C=O, so CN^- attacks from either face with **equal probability**; equal amounts of the two enantiomers form, and their effects on plane-polarised light cancel.

Common mistakes.

- Starting the first arrow at the N of CN^-. The lone pair that attacks is on the **carbon**, which is why the new bond is C–C.
- Drawing the arrow from the oxygen to the carbon. The C=O pair moves **towards** the more electronegative O.
- Calling this electrophilic addition, as in alkenes. The C=O carbon is $\delta+$, so it is attacked by a **nucleophile**, not an electrophile.
- Leaving the product as O^-: the mechanism is only finished when the O gains an H.

Tests for carbonyl compounds

Detecting any carbonyl

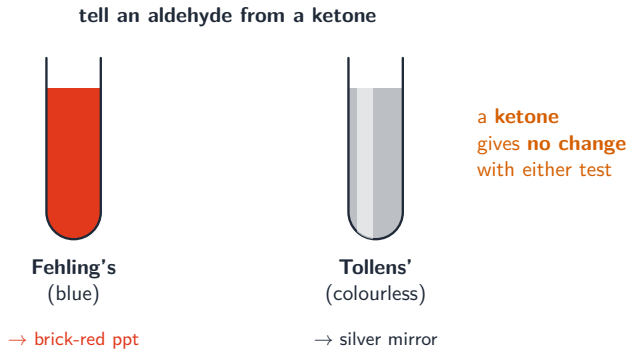
Add **2,4-DNPH** reagent (2,4-dinitrophenylhydrazine). An orange precipitate confirms that the compound is an aldehyde or a ketone.

The reaction is a **condensation** 缩合: the C=O joins to the NH_2 of 2,4-DNPH and a molecule of water is lost, giving a 2,4-dinitrophenylhydrazone. Alcohols, carboxylic acids and esters do **not** react (the C=O of acids and esters is not reactive enough). To find **which** carbonyl compound you have, filter the orange crystals, recrystallise them to purify them, and measure their **melting point**. Compare it with a table of known melting points of 2,4-dinitrophenylhydrazones: each carbonyl compound gives a derivative with its own melting point.

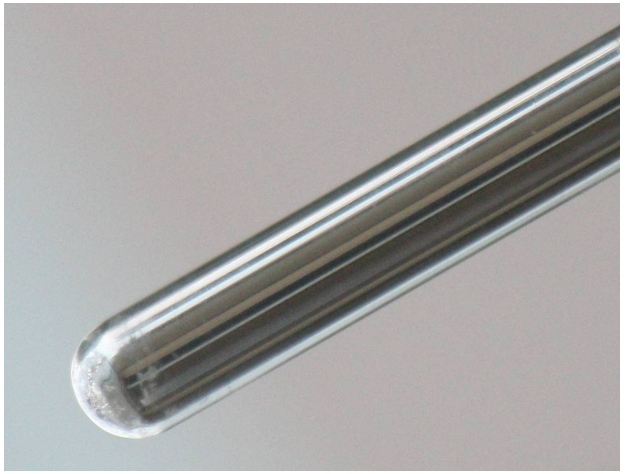
Telling an aldehyde from a ketone

Aldehydes are easily oxidised to carboxylic acids, but ketones are not. Two tests use this difference:

Test	Aldehyde	Ketone
Fehling's reagent 斐林试剂 (blue solution)	turns to a brick-red precipitate	no change
Tollens' reagent 托伦试剂 (colourless)	gives a silver mirror	no change



Telling an aldehyde from a ketone: an aldehyde gives a brick-red precipitate with Fehling's and a silver mirror with Tollens'; a ketone gives no change



A positive Tollens' test: an aldehyde coats the tube with a shiny silver mirror

What is happening in each test. Both reagents are mild **oxidising agents**; the aldehyde is oxidised to a carboxylic acid (or its anion, as the solutions are alkaline), and the reagent is reduced:

- **Fehling's**: warm with the aldehyde in a water bath. The blue complexed Cu^{2+} ions are reduced to copper(I) oxide, Cu_2O, the **brick-red** precipitate.
- **Tollens'** (ammoniacal silver nitrate, $[Ag(NH_3)_2]^+$): warm with the aldehyde in a water bath. The Ag^+ ions are reduced to **silver** metal: $Ag^+ + e^- \rightarrow Ag$, which coats the glass.
- **Ease of oxidation**: warm with acidified $K_2Cr_2O_7$. An aldehyde turns it from orange to green; a ketone leaves it orange.

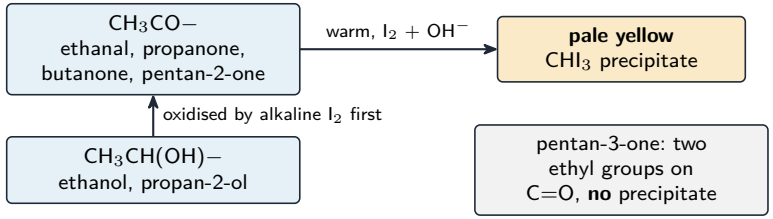
Heat these in a **water bath**, never with a flame: the organic compounds are flammable.

The iodoform test

If the compound has the CH_3CO- group, warming it with alkaline aqueous iodine gives a pale yellow precipitate of **tri-iodomethane** 三碘甲烷 (CHI_3) and the ion RCO_2^-.

$$CH_3COR + 3I_2 + 4OH^- \rightarrow CHI_3 + RCO_2^- + 3I^- + 3H_2O$$

The three H atoms of the CH_3 are replaced by I, then the CI_3 group splits off. The rest of the molecule becomes a carboxylate ion with **one carbon fewer**: propanone gives ethanoate, $CH_3CO_2^-$. Which carbonyls give a positive test? Ethanal (the only aldehyde), and all **methyl ketones** – propanone, butanone, pentan-2-one – but **not** pentan-3-one, whose C=O carries two ethyl groups. Alkaline iodine can also oxidise an alcohol with a $CH_3CH(OH)-$ group to a CH_3CO- compound, so ethanol and propan-2-ol also give the yellow precipitate.



Which compounds give the pale yellow precipitate

Worked example. A liquid gives an orange precipitate with 2,4-DNPH, gives **no** silver mirror with Tollens' reagent, and gives a yellow precipitate with alkaline aqueous iodine. Identify it. Take the tests one at a time, using each for exactly what it proves. The orange precipitate with **2,4-DNPH** proves a **carbonyl** group is present - an aldehyde or a ketone, nothing else. **No** silver mirror with Tollens' rules out an **aldehyde**, so it must be a **ketone**. The yellow precipitate in the **iodoform** test proves a CH_3CO- group: a methyl group joined directly to the carbonyl carbon. The simplest compound satisfying all three is **propanone**, CH_3COCH_3. Keep the roles straight: 2,4-DNPH finds **any** carbonyl, Tollens' separates aldehyde from ketone, and iodoform detects the **methyl group beside** the C=O.

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Worked example (choosing between isomers). Compound X, C_4H_8O, gives an orange precipitate with 2,4-DNPH and a brick-red precipitate with Fehling's solution, but no yellow precipitate with alkaline aqueous iodine. Suggest two possible structures, and say how reduction could tell them apart. The carbonyl isomers of C_4H_8O are butanal, 2-methylpropanal and butanone. Fehling's is positive, so X is an **aldehyde**, which rules out butanone. Neither aldehyde has CH_3CO-, consistent with the negative iodoform test. So X is **butanal**, $CH_3CH_2CH_2CHO$, or **2-methylpropanal**, $(CH_3)_2CHCHO$. Reduction with $NaBH_4$ gives butan-1-ol or 2-methylpropan-1-ol respectively; the melting point of the 2,4-DNPH derivative also distinguishes them.

Test	Aldehyde	Ketone	Shows
2,4-DNPH	orange precipitate	orange precipitate	any C=O (aldehyde or ketone)
Fehling's, warm	blue → brick-red	stays blue	aldehyde
Tollens', warm	silver mirror	no change	aldehyde
acidified dichromate, warm	orange → green	stays orange	aldehyde
alkaline iodine, warm	yellow precipitate for ethanal only	yellow precipitate for methyl ketones	CH_3CO- group

Exam tips

- **2,4-DNPH** gives an orange precipitate with **any** carbonyl – it tests for C = O.
- **Tollens' (silver mirror)** and **Fehling's (brick-red)** are positive for **aldehydes only** – this is how you tell aldehydes from ketones.
- Nucleophilic addition of HCN adds **one carbon** (→ hydroxynitrile); show the curly arrows.
- The **iodoform (tri-iodomethane)** test is positive for CH_3CO- groups.
- Use [O] and [H] in balanced oxidation and reduction equations; state "distil" for an aldehyde and "reflux" for a carboxylic acid.
- HCN addition to an aldehyde (or unsymmetrical ketone) gives a **racemic** mixture, because the planar C=O is attacked equally from both sides.
- $NaBH_4$ and $LiAlH_4$ reduce C=O but not C=C.

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Carboxylic acids and derivatives

A-Level Chemistry

Carboxylic acids

A **carboxylic acid** 羧酸 has the –COOH (carboxyl) functional group. It is a weak acid.



Vinegar is a dilute solution of ethanoic acid, a carboxylic acid

Making carboxylic acids

- **oxidation** 氧化 of a primary **alcohol** 醇 or an **aldehyde** 醛 with acidified $K_2Cr_2O_7$ or $KMnO_4$, with **reflux** 回流 (so it is fully oxidised).
- **hydrolysis** 水解 of a **nitrile** 腈 with dilute acid or alkali, then acidifying.
- hydrolysis of an **ester** 酯 with dilute acid or alkali and heat, then acidifying.

The equations use [O] for oxygen from the oxidising agent:

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

$$CH_3CH_2CN + 2H_2O + H^+ \rightarrow CH_3CH_2COOH + NH_4^+$$

With acidified dichromate, the colour changes from **orange to green** as $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. Under reflux the aldehyde formed first cannot escape, so it is oxidised on to the acid; to stop at the aldehyde instead, distil it off as it forms. With dilute alkali, a nitrile gives the carboxylate salt and ammonia, and the acid is released by adding a strong acid.

Worked example (a two-step synthesis). Show how to make propanoic acid from bromoethane. Propanoic acid has **three** carbon atoms and bromoethane only two, so a carbon must be added. Step 1: heat bromoethane under reflux with KCN in ethanol: a nucleophilic substitution gives **propanenitrile**, CH_3CH_2CN, and the new carbon. Step 2: heat the nitrile under reflux with dilute HCl: hydrolysis gives **propanoic acid**. Using a nitrile is the usual way to lengthen a carbon chain by one atom in these questions.

Reactions of carboxylic acids

These reactions all show that carboxylic acids are acids:

- **with a reactive metal** (a **redox** 氧化还原 reaction): gives a **salt** 盐 and hydrogen.

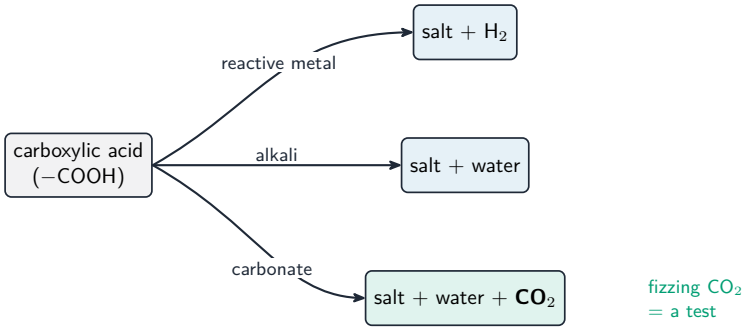
$$2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$$

- **with an alkali** (a **neutralisation** 中和): gives a salt and water.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

- **with a carbonate** 碳酸盐: gives a salt, water and carbon dioxide. The fizzing of CO_2 is a test for a carboxylic acid.

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$



Carboxylic acids behave as acids: a salt with a metal (+ H_2), with an alkali (+ water), or with a carbonate (+ water + CO_2 – the fizz is a test)

Two reactions change the functional group:

- **esterification** 酯化 with an alcohol (concentrated H_2SO_4 catalyst) gives an ester.
- **reduction** 还原 by $LiAlH_4$ gives a primary alcohol.

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$$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$$

$LiAlH_4$ is used in **dry ether**, because it reacts violently with water. A weaker reducing agent, $NaBH_4$, reduces aldehydes and ketones but does **not** reduce carboxylic acids.

Esters

An ester has the –COO– group. It often smells sweet or fruity.



Esters give many fruits and perfumes their sweet smell

Making esters

An ester forms in a **condensation** 缩合 reaction between an alcohol and a carboxylic acid, with concentrated H_2SO_4 as catalyst. A water molecule is lost, and the reaction is reversible:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$CH_3COOH \quad + \quad HOC_2H_5 \quad \rightleftharpoons \quad CH_3CO\ O\ C_2H_5 \quad + \quad H_2O$$

the –OH (acid) and –H (alcohol) leave as water; the C–O–C ester link forms

(concentrated H_2SO_4 catalyst; reversible)

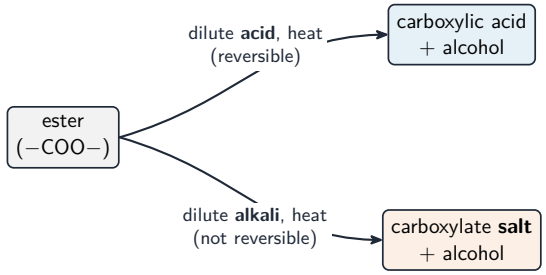
Esterification is a condensation: the –OH from the acid and the –H from the alcohol leave as water, forming the C–O–C ester link

Hydrolysis of esters

Hydrolysis splits the ester back apart. The conditions change the products:

- **dilute acid** and heat: reversible. Gives back the carboxylic acid and the alcohol.
- **dilute alkali** and heat: not reversible. Gives the alcohol and the **salt** of the carboxylic acid (the carboxylate ion).

Why alkali takes it to completion. With alkali the acid formed is at once neutralised to the carboxylate ion, $RCOO^-$. A negative ion cannot react with the alcohol, so the reverse reaction stops and all the ester is hydrolysed. To get the free carboxylic acid afterwards, add a strong acid.



Hydrolysing an ester: dilute acid (reversible) gives the carboxylic acid and alcohol; dilute alkali (not reversible) gives the carboxylate salt and alcohol

Worked example. Name the ester made from ethanol and propanoic acid, and say which part comes from which. In an ester name the **alcohol** gives the first word (the alkyl part) and the **acid** gives the second (the -oate part). Ethanol supplies C_2H_5- and propanoic acid supplies CH_3CH_2COO-, so the ester is **ethyl propanoate**, $CH_3CH_2COOC_2H_5$. It is made by refluxing the two with a concentrated H_2SO_4 catalyst, and the reaction is **reversible**, so the yield is never complete. The trap is naming it backwards: **propyl ethanoate** is a completely different ester (made from propan-1-ol and ethanoic acid). Alcohol first, acid second.

Worked example (working backwards from a formula). An ester is $HCOOCH_2CH_2CH_3$. Name it and give the products of heating it with NaOH(aq).

1. Find the $-COO-$ and split the formula after its single-bonded O. The part with the C=O, $HCOO-$, comes from **methanoic acid**. The part on the other O, $-CH_2CH_2CH_3$, comes from **propan-1-ol**.
2. Name: alcohol part first, acid part second: **propyl methanoate**.
3. With NaOH the products are **propan-1-ol** and **sodium methanoate**, HCOONa:

$$HCOOCH_2CH_2CH_3 + NaOH \rightarrow HCOONa + CH_3CH_2CH_2OH$$

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Common mistakes.

- Reading an ester formula from left to right as "alcohol, then acid". In $CH_3COOC_2H_5$ the acid part is written first (CH_3COO-), but the name puts the alcohol part first: ethyl ethanoate.
- Counting the C of the C=O in the alcohol part. It always belongs to the acid part.
- Giving the carboxylic acid as a product of alkaline hydrolysis. Alkali gives its **salt**; you get the acid only after adding a strong acid.
- Saying concentrated H_2SO_4 is a reactant. It is a catalyst (it also removes some of the water, which helps the yield).

Exam tips

- Carboxylic acids react with carbonates to give $\mathbf{CO_2}$ (fizzing) – this distinguishes them from phenols.
- Explain acid strength via the **delocalised carboxylate ion**; electron-withdrawing groups (e.g. Cl) increase strength.
- **Esterification** (with concentrated H_2SO_4) is reversible; name esters as *alkyl alkanoate*.
- Know the products of **acid vs alkaline** hydrolysis of an ester (they differ).
- To add one carbon to a chain, go through a **nitrile**: halogenoalkane + KCN, then hydrolyse the nitrile to the carboxylic acid.
- Write oxidations with [O] and reductions with [H], and balance them.

Nitrogen compounds

A-Level Chemistry

Primary amines



Dyeing cloth: azo and amine chemistry is what puts fast, bright colour into fibres

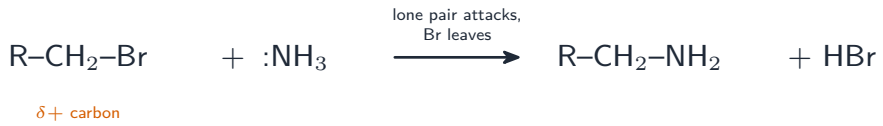
An **amine** 胺 has an $-NH_2$ group (the nitrogen replaces a hydrogen of ammonia).

Making a primary amine

Heat a **halogenoalkane** 卤代烷 with ammonia dissolved in ethanol, under pressure:

$$C_2H_5Br + NH_3 \rightarrow C_2H_5NH_2 + HBr$$

This is a **nucleophilic substitution** 亲核取代: the lone pair on the nitrogen of ammonia attacks the slightly positive carbon and pushes out the halogen. You use an excess of ammonia, or the amine made can react again.



Making a primary amine: ammonia's lone pair attacks the δ+ carbon and pushes out the halogen – a nucleophilic substitution

Why an excess of ammonia. The amine made still has a lone pair on its nitrogen, so it is a nucleophile too. If there is little ammonia, the ethylamine attacks another bromoethane:

$$C_2H_5NH_2 + C_2H_5Br \rightarrow (C_2H_5)_2NH + HBr$$

This gives a **secondary amine** 仲胺, which can react again to give a tertiary amine. A large excess of ammonia makes it much more likely that each bromoethane meets an ammonia molecule rather than an amine, so the main product is the primary amine.

Nitriles and hydroxynitriles

Making a nitrile

Heat a halogenoalkane with potassium cyanide (KCN) in ethanol:

$$C_2H_5Br + KCN \rightarrow C_2H_5CN + KBr$$

This is also a nucleophilic substitution, with the CN^- ion as the nucleophile. It is useful because it **adds one carbon** to the chain. The product is a **nitrile** 腈.

Making a hydroxynitrile

Add HCN (with KCN as catalyst, and heat) to an **aldehyde** 醛 or **ketone** 酮. The H and CN add across the C=O bond to give a **hydroxynitrile** 羟基腈. The reagent is **hydrogen cyanide** 氰化氢, and the mechanism is **nucleophilic addition** 亲核加成.

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

The product from ethanal is 2-hydroxypropanenitrile. The OH goes on the old carbonyl carbon, and the CN bonds to that **same** carbon, so the chain again gains one carbon. With a ketone such as propanone, $(CH_3)_2CO$, the product is $(CH_3)_2C(OH)CN$, 2-hydroxy-2-methylpropanenitrile.

> **Worked example.** Give the structure of the product when butanone, $CH_3COCH_2CH_3$, reacts with HCN and KCN, and state the type of reaction. The C=O carbon is carbon 2. HCN adds across the C=O: the H goes to the oxygen and the CN to the carbon. The product is $CH_3C(OH)(CN)CH_2CH_3$, which has **five** carbons. The reaction is nucleophilic addition, and the nucleophile is CN^-, which the KCN catalyst supplies.

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$$\mathrm{R{-}CH_2{-}Br} + \mathrm{CN^-} \longrightarrow \mathrm{R{-}CH_2{-}CN}$$ nucleophilic **substitution** (nitrile)

$$\mathrm{R_2C{=}O} + \mathrm{HCN} \longrightarrow \mathrm{R_2C(OH)(CN)}$$ nucleophilic **addition** (hydroxynitrile)

Two ways cyanide adds a carbon: KCN with a halogenoalkane substitutes to a nitrile; HCN with a carbonyl adds to a hydroxynitrile

Hydrolysis of nitriles

Warm a nitrile with dilute acid (or dilute alkali, then acidify). This **hydrolysis** 水解 turns the –CN group into a –COOH group, giving a **carboxylic acid** 羧酸:

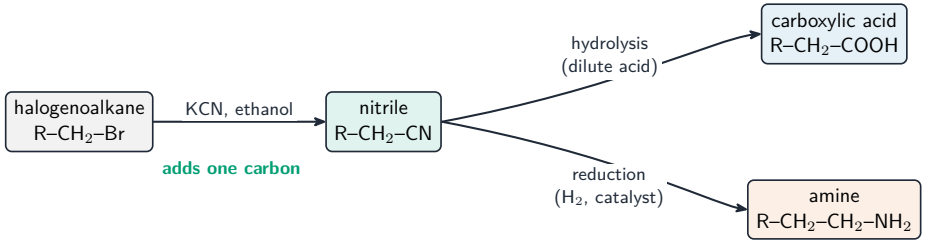
$$\mathrm{CH_3CN + 2H_2O + HCl \rightarrow CH_3COOH + NH_4Cl}$$

With **dilute alkali**, the product is first the **salt** of the acid, and ammonia gas is given off:

$$\mathrm{CH_3CN + NaOH + H_2O \rightarrow CH_3COONa + NH_3}$$

To get the free carboxylic acid, you then **acidify** with a strong acid: $\mathrm{CH_3COONa + HCl \rightarrow CH_3COOH + NaCl}$. Both routes need heating under reflux.

A nitrile can also be **reduced** by hydrogen and a catalyst to form an amine, which is the **reduction** 还原 route to a longer-chain amine.



Nitriles are a useful hub: KCN adds a carbon to make the nitrile, which then hydrolyses to a carboxylic acid or reduces to an amine

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Reducing a nitrile gives an amine; amines and diacids link up to make polyamides such as nylon – the fibre first made famous in stockings

Worked example. Starting from bromoethane, make propanoic acid. Compare the carbons first: bromoethane has 2, propanoic acid has 3, so a carbon must be **added** - and the KCN step is the reaction that does it. Step 1: warm bromoethane with **ethanolic KCN**; nucleophilic substitution gives propanenitrile, $\mathrm{CH_3CH_2CN}$, which now has 3 carbons because the CN carbon joins the chain. Step 2: reflux the nitrile with **dilute HCl**; hydrolysis gives propanoic acid. Count the carbons **before** you plan: whenever the target has exactly one more than the starting material, the nitrile route is almost always the intended answer, and remember the CN carbon is part of the new chain.

Common mistakes.

- Using **aqueous** KCN. The solvent must be ethanol; in water the hydroxide ions present give an alcohol instead.
- Naming a nitrile without counting the CN carbon. $\mathrm{CH_3CH_2CN}$ has three carbons, so it is **propanenitrile**, not ethanenitrile.
- Forgetting that the HBr made reacts with the excess ammonia (or amine) to give a salt, $\mathrm{NH_4Br}$. The equation above is the simple form.
- Giving the acid as the product of hydrolysis with **NaOH**. Alkali gives the sodium salt (and $\mathrm{NH_3}$); only after adding acid do you get the carboxylic acid.
- Mixing up the two cyanide reactions. KCN with a halogenoalkane is **substitution**; HCN with an aldehyde or ketone is **addition**.

Exam tips

- **Amines are bases** (the N lone pair accepts H^+); aliphatic amines are stronger bases than ammonia.
- Making amines: **reduce a nitrile**, or react a halogenoalkane with excess ammonia.
- **KCN adds one carbon** (halogenoalkane → nitrile) – track the carbon count carefully in synthesis routes.
- State reagents and conditions precisely for each conversion.

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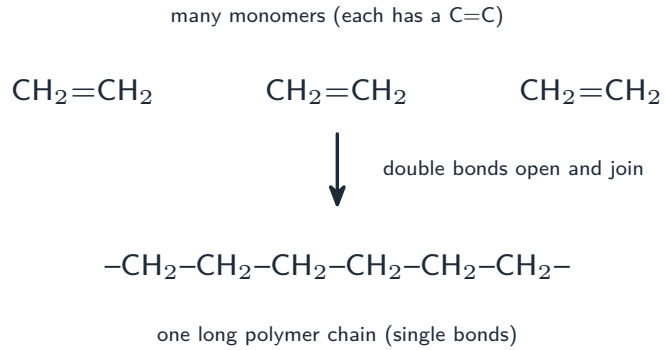
Polymerisation

A-Level Chemistry

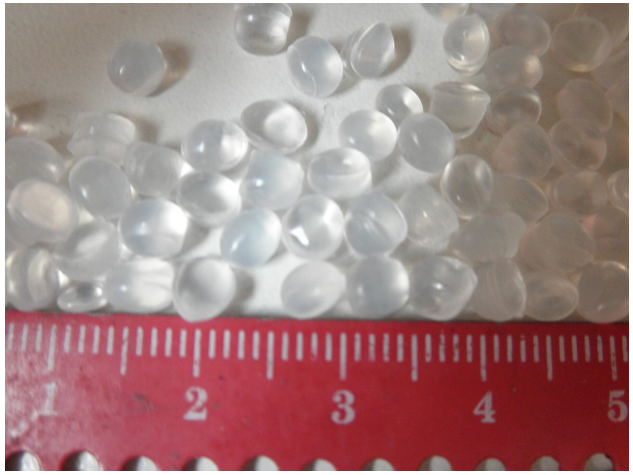
Addition polymerisation

In **addition polymerisation** 加成聚合, many small molecules join into one very long chain, with no other product made.

Each small molecule is a **monomer** 单体. It must be unsaturated – it has a C=C double bond. The double bond opens up so that the monomers can link together. The long chain that forms is the **polymer** 聚合物.



Each monomer's double bond opens, and the monomers join end to end into one long chain – with no other product made



Poly(ethene), a common addition polymer, is supplied as tiny pellets a few millimetres across; these are later melted and moulded into bottles, bags and other products

Repeat units

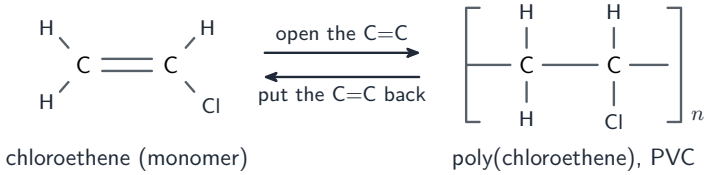
The **repeat unit** 重复单元 is the small part that is copied again and again along the chain. To find it, take the monomer, change the C=C to a single C–C, and draw bonds going out at each end.

- **poly(ethene)** 聚乙烯 is made from ethene:

$$n\,CH_2{=}CH_2 \rightarrow -(CH_2{-}CH_2)_n-$$

- **poly(chloroethene)** 聚氯乙烯 (PVC) is made from chloroethene:

$$n\,CH_2{=}CHCl \rightarrow -(CH_2{-}CHCl)_n-$$



Finding the repeat unit: change the monomer's C=C to a single bond and draw bonds out at each end; reverse it to find the monomer

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Finding the monomer

To go the other way, look at one repeat unit of the polymer, and put the C=C double bond back in. That gives you the monomer.

> **Worked example.** A polymer has the repeat unit $-(CH_2{-}CH(CH_3))_n-$. Identify the monomer and name the polymer. Reverse the rule you used to build it: rub out the bonds sticking out at each end, and turn the single C-C **in the backbone** back into a **C=C**. That gives $CH_2{=}CH(CH_3)$, which is propene - so the polymer is **poly(propene)**. Two checks catch most errors: the monomer must have the **same molecular formula** as the repeat unit (addition polymerisation adds nothing and loses nothing), and the double bond goes back into the **backbone**, never into the side group.

> **Worked example: a section of chain.** Part of a polymer chain is $-CH_2{-}CH(CN){-}CH_2{-}CH(CN){-}CH_2{-}CH(CN)-$. Identify the repeat unit and the monomer. Look for the pattern that repeats: every **two** backbone carbons carry one CN. So the repeat unit is $-(CH_2{-}CH(CN))-$. Putting the C=C back between those two carbons gives the monomer $CH_2{=}CHCN$, propenenitrile. A section of n repeat units always has $2n$ backbone carbons, so the section above holds three repeat units.

When there are two monomers. If the pattern only repeats after **four** backbone carbons, two different monomers have joined. In

$$-CH_2{-}CH_2{-}CH_2{-}CHCl{-}CH_2{-}CH_2{-}CH_2{-}CHCl-$$

split the backbone into pairs of carbons: $CH_2{-}CH_2$ comes from **ethene** and $CH_2{-}CHCl$ comes from **chloroethene**. Always cut between the pairs, never through one.

A monomer with groups on both carbons. But-2-ene, $CH_3CH{=}CHCH_3$, has a methyl group on **each** carbon of the C=C. Only those two carbons go into the backbone, so the repeat unit is $-(CH(CH_3){-}CH(CH_3))-$, with two CH_3 side groups. It is not a four-carbon chain.

The problem of disposal

Poly(alkene)s are very hard to get rid of:

- they are **non-biodegradable** 不可生物降解 – microbes cannot break them down, so they stay in the ground for a very long time.
- their **combustion** 燃烧 (burning) can release harmful gases. For example, burning PVC gives off toxic hydrogen chloride.

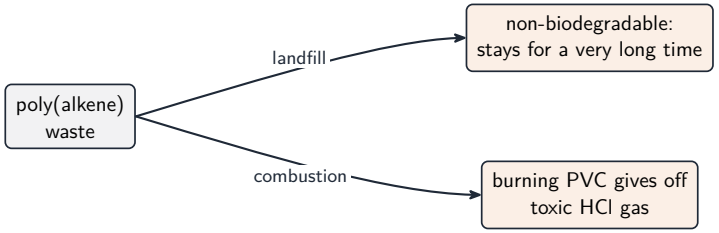
When you explain the harmful products of burning, name each one and the harm it does:

Product	Where it comes from	Why it is harmful
carbon monoxide, CO	incomplete combustion of any poly(alkene)	toxic: it stops the blood carrying oxygen
soot (carbon particles)	incomplete combustion	breathing problems
carbon dioxide, CO_2	complete combustion	a greenhouse gas
hydrogen chloride, HCl	burning PVC (it contains chlorine)	toxic; it dissolves to form acid rain

Burning in a modern incinerator recovers energy, and the HCl can be removed from the waste gases by reacting it with a base before release.



Most addition polymers are non-biodegradable, so they build up as waste in the environment



Poly(alkene) waste is hard to dispose of: it is non-biodegradable, and burning PVC releases toxic hydrogen chloride

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Common mistakes.

- Putting the side group into the backbone. In poly(propene) the backbone is $–CH_2–CH–$ and the CH_3 hangs **off** it: only the two carbons of the old C=C join the chain.
- Leaving a C=C inside the repeat unit. The double bond **opens** to make the chain, so the repeat unit has only single bonds.
- Drawing the bonds at the ends of the repeat unit stopping inside the brackets. The two **continuation bonds** must cross the brackets, with n outside.
- Calling ethene's polymer "polyethane". Name it from the **monomer**: poly(ethene), poly(propene), poly(chloroethene).
- Saying addition polymers are reactive because the monomer was. The polymer has only strong, non-polar **C–C and C–H** bonds, so it is inert.

Exam tips

- Draw the **repeat unit** in brackets with the two bonds crossing them and n outside; keep the backbone carbons.
- Deduce the **monomer from a polymer** (and vice versa) – a very common question.
- Addition polymers are **inert and non-biodegradable** – link to landfill, recycling and incineration issues.
- Do not confuse with condensation (no small molecule is lost in addition polymerisation).

Organic synthesis

A-Level Chemistry

This topic does not add new reactions. Instead it asks you to **join up** the reactions you already know, so you can build a target molecule in several steps.



Medicines are built up from simple starting materials by multi-step organic synthesis

Identifying functional groups

A molecule may have more than one **functional group** 官能团. Use the test reactions from the syllabus to identify each one, and then predict how the molecule will behave. For example:

- decolourises bromine water → a C=C double bond (an **alkene** 烯烃).
- after warming with NaOH(aq) and acidifying with dilute HNO_3, gives a precipitate with silver nitrate → a **halogenoalkane** 卤代烷.
- orange $K_2Cr_2O_7$ turns green → a primary or secondary **alcohol** 醇.
- orange precipitate with 2,4-DNPH → an **aldehyde** 醛 or **ketone** 酮.
- fizzes with a carbonate → a **carboxylic acid** 羧酸.

> **Worked example (predicting reactions).** Compound **Y** is prop-2-en-1-ol, $CH_2{=}CHCH_2OH$. Predict what you would see with each reagent, and name the product.

- **Bromine water:** orange to colourless, because Br_2 adds across the C=C, giving 2,3-dibromopropan-1-ol, $CH_2BrCHBrCH_2OH$.
- **Acidified $K_2Cr_2O_7$, distil:** orange to green, because Y is a **primary** alcohol; the aldehyde propenal, $CH_2{=}CHCHO$, distils off. The C=C is unchanged.
- **Sodium:** fizzing (H_2), from the O–H group.

- **Na_2CO_3:** no change, because Y has no carboxylic acid group.
- **2,4-DNPH:** no precipitate, because Y has no C=O; its oxidation product propenal **would** give an orange precipitate.

Treat each functional group separately, and say which group causes each result: a molecule with two groups usually gives both sets of reactions.

add this	you see	functional group
bromine water	orange → colourless	C=C (alkene)
silver nitrate	a precipitate forms	halogenoalkane
acidified $K_2Cr_2O_7$	orange → green	1°/2° alcohol
2,4-DNPH	orange precipitate	aldehyde / ketone
a carbonate	fizzes (CO_2 given off)	carboxylic acid

The standard identification tests: each reagent gives a characteristic observation that points to one functional group

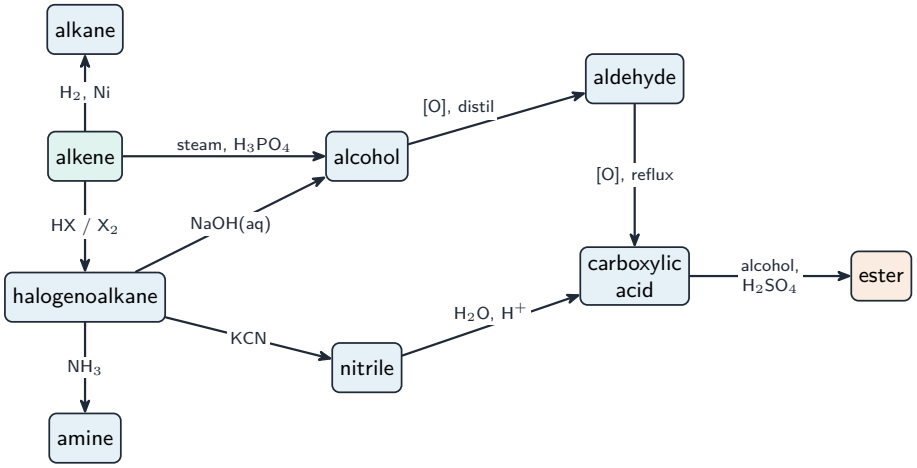
A map of the AS reactions

Each row turns one functional group into another. Learn it as a map you can travel around:

Start	Reagent and conditions	Product
alkene	H_2, Ni	alkane
alkene	HX, or X_2	halogenoalkane
alkene	steam, H_3PO_4	alcohol
halogenoalkane	NaOH(aq), heat	alcohol
halogenoalkane	KCN in ethanol, heat	a **nitrile** 腈 (adds one carbon)
halogenoalkane	NH_3 in ethanol, pressure	an **amine** 胺
alcohol	$K_2Cr_2O_7$, distil / reflux	aldehyde / carboxylic acid
alcohol	concentrated acid, heat	alkene
aldehyde or ketone	$NaBH_4$	alcohol
aldehyde or ketone	HCN, KCN	hydroxynitrile

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Start	Reagent and conditions	Product
nitrile	dilute acid, heat	carboxylic acid
carboxylic acid + alcohol	concentrated H_2SO_4	an **ester** 酯



A map of the AS reactions: each arrow turns one functional group into another. Work backwards from your target to plan a route

Planning a multi-step route

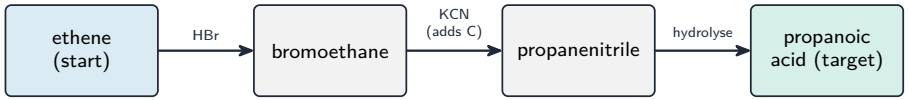
To devise a **synthetic route** 合成路线:

1. compare the target with the starting material – what has changed (the functional group, the number of carbons)?
2. work **backwards** from the target: which single reaction could make it, and from what?
3. repeat until you reach the starting material.
4. write each step with its **reagent** 试剂 and conditions.

If you need to add a carbon, use a cyanide step. These are the only AS reactions that lengthen the chain: KCN with a halogenoalkane gives a nitrile, and HCN adding to an aldehyde or ketone gives a hydroxynitrile.

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plan backwards from the target



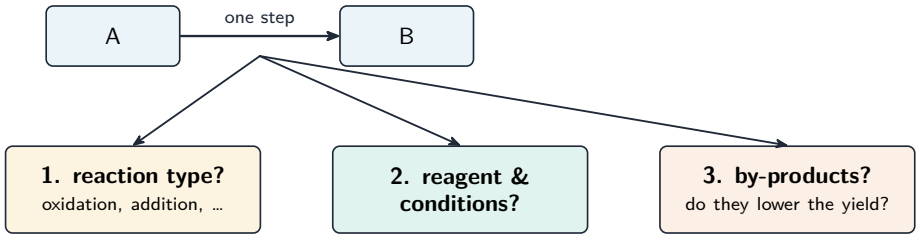
Plan a route by working backwards from the target, one reaction at a time, until you reach the starting material

Analysing a route

When you are given a route, for each step state the **type of reaction** (such as **oxidation** 氧化, **reduction** 还原, substitution, addition or elimination) and the reagent used. Also think about possible **by-products** 副产物 – for example, making an amine from a halogenoalkane also gives a mixture of further-substituted amines, so the yield of the simple amine is low.



A separating funnel splits two immiscible layers – how the organic product is recovered from the reaction mixture



e.g. a halogenoalkane → amine also makes further-substituted amines, so the simple-amine yield is low

For every step in a given route, ask its reaction type, reagent and by-products

name the reaction type at each step

oxidation	loses electrons / gains O or loses H (e.g. alcohol → acid)
reduction	gains electrons / loses O or gains H
substitution	one atom or group swaps for another
addition	two molecules join; a C=C double bond opens
elimination	a small molecule is removed; a C=C forms

also give the **reagent** for each step, and watch for **by-products** (e.g. amines over-substitute)

Name the reaction type at each step: oxidation, reduction, substitution, addition or elimination

Worked example. Devise a route from propene to propanone, CH_3COCH_3. Work **backwards** from the target. A ketone comes from oxidising a **secondary** alcohol, so the step before propanone is propan-2-ol with acidified $K_2Cr_2O_7$ under reflux. Propan-2-ol comes from propene by adding **steam** over an H_3PO_4 catalyst - and Markovnikov's rule conveniently puts the OH on the **middle** carbon, which is exactly the secondary alcohol needed. So the route is: propene, then steam with H_3PO_4, giving propan-2-ol; then acidified $K_2Cr_2O_7$ under reflux, giving propanone. Give a **reagent and its conditions** on every arrow: a route with the right intermediates but no reagents scores very little.

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Worked example (adding a carbon). Devise a route from ethanal, CH_3CHO, to 2-hydroxypropanoic acid (lactic acid), $CH_3CH(OH)COOH$. Compare the two: the target has **three** carbons and ethanal has two, so a cyanide step is needed, and the new carbon ends up as the COOH. Working backwards: a carboxylic acid can come from **hydrolysing a nitrile**, so the step before is 2-hydroxypropanenitrile, $CH_3CH(OH)CN$; that comes from adding HCN to ethanal.

1. Ethanal with HCN and a little KCN (**nucleophilic addition**): 2-hydroxypropanenitrile.
2. Heat under reflux with dilute HCl (**hydrolysis**): 2-hydroxypropanoic acid, with NH_4^+.

The product of step 1 is a **racemic mixture**: the cyanide ion can attack the flat C=O from either side, so both optical isomers form in equal amounts.

Common mistakes.

- Adding silver nitrate straight to a halogenoalkane. The halogen is bonded covalently, so there are no free halide ions: **hydrolyse** first with warm NaOH(aq), acidify with dilute HNO_3, then add $AgNO_3$.
- Oxidising to a carboxylic acid by distilling. **Distil** to collect the aldehyde as it forms; heat under **reflux** to oxidise all the way to the carboxylic acid.
- Expecting a tertiary alcohol to turn dichromate green. Tertiary alcohols are **not** oxidised, so the orange colour stays.
- Getting the wrong alcohol from steam addition. By Markovnikov's rule propene gives mainly **propan-2-ol**, not propan-1-ol.
- Using KCN in water. Use KCN in **ethanol**, heated under reflux; in water the hydroxide ions give an alcohol instead.
- Forgetting the carbon count. Only the cyanide steps add a carbon; a route that needs one more carbon must include KCN or HCN.

Exam tips

- Learn the **reagents and conditions** for each conversion – that is exactly what synthesis questions test.
- Plan multi-step routes by functional group and watch the **carbon count** (KCN adds one carbon).
- Choose the **shortest valid route** and state every reagent and condition.

Analytical techniques

A-Level Chemistry

Infrared spectroscopy

Infrared spectroscopy 红外光谱 helps you find the **functional group** 官能团 in a molecule. Each kind of bond soaks up (absorbs) infrared radiation at its own range of frequencies. Where the bond shows strong **absorption** 吸收, the spectrum has a dip.



An infrared spectrometer shines infrared through a sample and records which wavenumbers its bonds absorb

The position is measured in **wavenumber** 波数 (in cm^{-1}). You are given a data table, so you do not memorise the numbers. You just match the dips to bonds:

- a broad dip around 3200–3650 cm^{-1} → an O–H bond in an alcohol.
- a dip around 1700 cm^{-1} → a C=O bond (aldehyde, ketone, acid or ester).
- a broad dip 2500–3000 cm^{-1} together with a C=O dip → a carboxylic acid.

This is useful for checking a reaction. For example, if propene has been turned into propan-2-ol, the C=C dip should be gone and an O–H dip should appear.

The data table gives more bonds than these three. The ones you will use most:

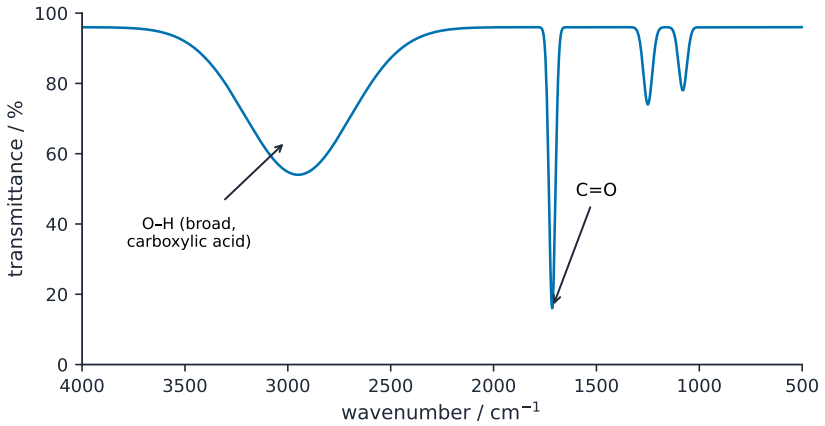
Bond	Found in	Wavenumber / cm^{-1}	What the dip looks like
O–H	alcohols, phenols	3200–3650	broad
O–H	carboxylic acids	2500–3000	very broad, over the C–H dips

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Bond	Found in	Wavenumber / cm^{-1}	What the dip looks like
N–H	amines, amides	3300–3500	medium, sharper than O–H
C–H	alkanes, most organic compounds	2850–2950	strong, sharp
C≡N	nitriles	2200–2250	sharp, medium
C=O	aldehydes, ketones, acids, esters, amides	1640–1750	strong, sharp
C=C	alkenes	1610–1680	weak to medium
C–O	alcohols, esters, acids	1040–1300	strong

Bonds absorb infrared because they **vibrate** (stretch and bend) at their own natural frequencies; a bond between heavier atoms, or a weaker bond, vibrates more slowly and absorbs at a lower wavenumber. The region below about 1500 cm^{-1} (the **fingerprint region** 指纹区) has many overlapping dips that are unique to each molecule: compare it with a database spectrum to confirm an identity.

> **Worked example.** Three compounds, propanoic acid, propan-1-ol and propanal, are tested. Spectrum X has a broad dip at 3350 and a strong dip at 1050 cm^{-1} but none near 1700. Spectrum Y has a very broad dip from 2500 to 3000 and a strong one at 1715. Spectrum Z has a strong dip at 1730 but none above 3100. Identify each. X: O–H (alcohol) and C–O, no C=O → **propan-1-ol**. Y: acid O–H plus C=O → **propanoic acid**. Z: C=O with no O–H → **propanal**. In each answer, give the **bond**, its **wavenumber**, and what it shows.



IR: dips at characteristic wavenumbers identify functional groups (e.g. C=O, O–H)

An infrared spectrum: each bond gives a dip at its own wavenumber. A broad O–H dip together with a C=O dip identifies a carboxylic acid

Mass spectrometry

In **mass spectrometry** 质谱, a molecule is turned into ions and sorted by its **mass-to-charge ratio** 质荷比 (m/e). The spectrum is a set of peaks at different m/e values.



A modern mass spectrometer: the sample is loaded at the front, then the machine ionises it and sorts the ions by their mass-to-charge ratio to give the spectrum

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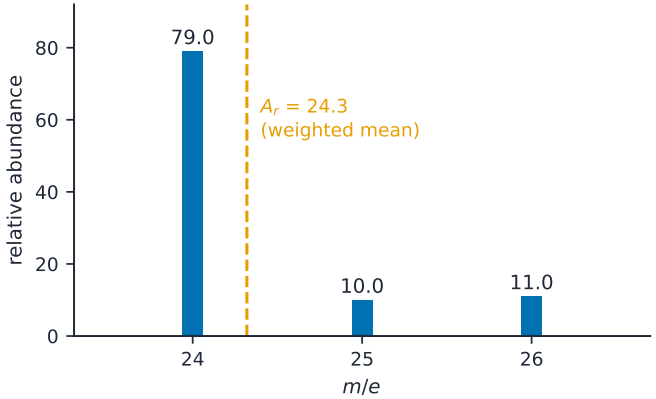
Relative atomic mass from isotopes

An element's **isotope** 同位素 mixture gives several peaks. From the **isotopic abundance** 同位素丰度 (how common each isotope is) you can find the **relative atomic mass** 相对原子质量 – a weighted average:

$$A_r = \frac{\sum(\text{isotope mass} \times \text{abundance})}{\sum \text{abundance}}$$

For example, chlorine is 75% ^{35}Cl and 25% ^{37}Cl, giving $A_r = \dfrac{35 \times 75 + 37 \times 25}{100} = 35.5$.

> **Worked example (three isotopes, from peak heights).** The mass spectrum of magnesium has peaks at m/e 24, 25 and 26 with relative heights 79.0, 10.0 and 11.0. Find A_r to one decimal place. The heights are the abundances, so



The weighted mean sits close to the tallest peak: A_r(Mg) = 24.3

$$A_r = \frac{24 \times 79.0 + 25 \times 10.0 + 26 \times 11.0}{79.0 + 10.0 + 11.0} = \frac{2432}{100} = 24.3.$$

When the heights do not add up to 100, still divide by their **sum**. Each peak is a **singly charged** ion, so m/e equals the isotope's mass.

The molecular ion and fragmentation

The peak at the highest m/e (the **molecular ion** 分子离子 peak, or **molecular ion peak** 分子离子峰, M^+) gives the relative molecular mass of the whole molecule.

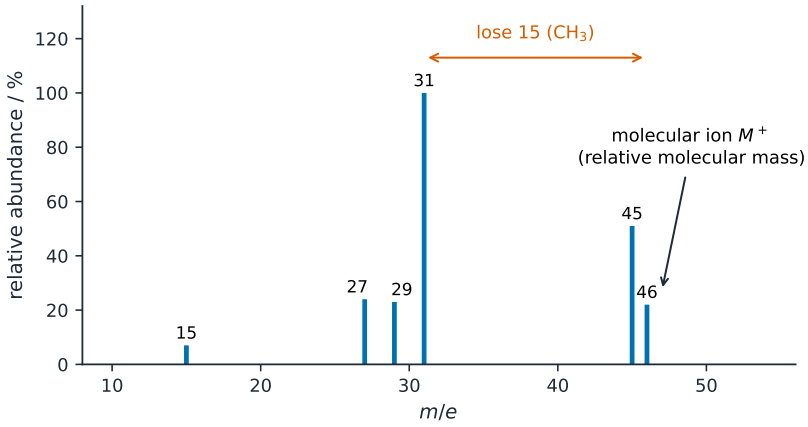
The molecule also breaks into smaller pieces – this is **fragmentation** 碎裂. The gap between two peaks tells you the mass of the lost piece, so you can suggest each **fragment** 碎片. For example, a loss of 15 means a CH_3 group was lost, and a loss of 29 means CHO or C_2H_5.

Write a fragmentation as an equation: the molecular ion splits into a **positive ion**, which is detected, and a neutral **radical** 自由基, which is not:

$$[CH_3CH_2OH]^+ \rightarrow [CH_2OH]^+ + CH_3^\bullet$$

m/e	**Likely ion**	**Suggests**
15	CH_3^+	a methyl group
29	$C_2H_5^+$ or CHO^+	an ethyl group, or an aldehyde
31	CH_2OH^+	a primary alcohol
43	CH_3CO^+ or $C_3H_7^+$	a methyl ketone, or a propyl group
45	$COOH^+$	a carboxylic acid
77	$C_6H_5^+$	a benzene ring

Worked example. Propanone and propanal both have $M_r = 58$. The spectrum of one has a base peak at $m/e = 43$ and a peak at 15; the other has large peaks at 29 and 28 but none at 43. Which is which? CH_3COCH_3 splits next to the C=O into CH_3CO^+ (43) and CH_3 (15), so the first is **propanone**. CH_3CH_2CHO splits into $C_2H_5^+$ and CHO^+, both at 29, so the second is **propanal**.



A mass spectrum: the highest-m/e peak is the molecular ion (M^+, the M_r); the gaps between peaks give the masses of the lost fragments

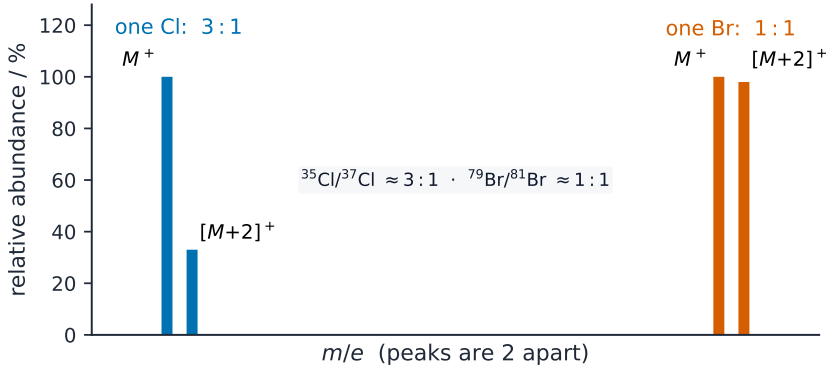
In this spectrum of ethanol the molecular ion at 46 is **small**: the tallest peak (the **base peak** 基峰) is at 31, CH_2OH^+, and even the peak at 45 (the molecule minus one H) is taller than M^+. So find M^+ as the peak with the **highest** m/e (ignoring the tiny [M + 1] peak), never as the tallest one.

The [M + 1] and [M + 2] peaks

- a small **[M + 1]** peak comes from the ^{13}C isotope. The number of carbon atoms n is:

$$n = \frac{100 \times \text{abundance of } [M+1]^+}{1.1 \times \text{abundance of } M^+}$$

- an **[M + 2]** peak shows chlorine or bromine. One chlorine gives an $[M+2]$ peak about one third the height of M^+ (from ^{37}Cl); one bromine gives an $[M+2]$ peak about the **same** height as M^+ (from ^{81}Br).



An $[M+2]$ peak two mass units above M^+ shows a halogen: one chlorine gives a 3 : 1 ratio, one bromine a 1 : 1 ratio

Worked example ([M + 1]). A hydrocarbon has M^+ at $m/e = 86$ with relative height 40.0, and an [M + 1] peak with height 2.64. Find the number of carbon atoms and the molecular formula.

$$n = \frac{100 \times 2.64}{1.1 \times 40.0} = \frac{264}{44} = 6.$$

Six carbons have mass 72, leaving $86 - 72 = 14$ for hydrogen, so the formula is C_6H_{14} (hexane or one of its isomers). Each carbon has a 1.1% chance of being ^{13}C, so the more carbons, the larger the [M + 1] peak.

Two halogen atoms. With **two** chlorine atoms there are three molecular ion peaks, M, $[M+2]$ and $[M+4]$, in the ratio about 9 : 6 : 1 (from $^{35}Cl^{35}Cl$, $^{35}Cl^{37}Cl$ and $^{37}Cl^{37}Cl$: $\frac{3}{4}\times\frac{3}{4}$, $2\times\frac{3}{4}\times\frac{1}{4}$, $\frac{1}{4}\times\frac{1}{4}$). With two bromine atoms the ratio is 1 : 2 : 1. The same patterns appear in any fragment ion that still contains the halogen atoms.

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Worked example. A compound shows a molecular ion at $m/e = 108$ and a peak of almost equal height at $m/e = 110$. Its infrared spectrum shows **no** broad absorption near 3300 cm^{-1}. Deduce its identity. Two peaks **two units apart with roughly equal heights** are the 1 : 1 signature of **one bromine** atom (from ^{79}Br and ^{81}Br); one chlorine would have given a 3 : 1 ratio instead. Take the bromine away from the molecular ion: $108 - 79 = 29$, which fits a C_2H_5 fragment. The absence of a broad peak near 3300 cm^{-1} rules out an O-H, so there is no alcohol group. The compound is **bromoethane**, C_2H_5Br. Read the $[M + 2]$ **ratio** rather than merely noting the peak: 1 : 1 means bromine, 3 : 1 means chlorine.

Common mistakes.

- Taking the tallest peak as the molecular ion. The tallest is the **base peak**; M^+ is the peak at the **highest** m/e (apart from the small [M + 1] and [M + 2] peaks).
- Writing a fragment without its charge. Only **positive ions** are detected, so write CH_3^+ or $[CH_2OH]^+$; the lost piece is a neutral radical and gives no peak.
- Reading every dip near 3000 cm^{-1} as O–H. Nearly every organic molecule has a C–H absorption near 2850–3100 cm^{-1}; an alcohol's O–H is **broad** and higher, and an acid's O–H is very broad, 2500–3000 cm^{-1}, together with a C=O.
- Getting the halogen ratios the wrong way round. One **Cl** gives $M : [M+2] \approx 3 : 1$; one **Br** gives about 1 : 1.
- Using the [M + 1] peak's height directly as the number of carbons. Divide by the M^+ height and by 1.1: $n = \dfrac{100 \times [M+1]}{1.1 \times M}$.
- Saying IR identifies the whole molecule. IR shows which **bonds** (functional groups) are present; combine it with the mass spectrum or other data to decide the structure.

Exam tips

- On an **IR spectrum** quote the **wavenumber and the bond** (O-H broad $\sim 3200 - 3600$, C=O ~ 1700); use the data booklet.
- The peak at the **highest** m/z is the molecular ion M^+ and gives the M_r.
- Explain **fragmentation**: the gap between peaks is the lost fragment (loss of 15 = CH_3, 29 = C_2H_5 or CHO).
- Learn common **isotope patterns** (Cl gives M and M+2 in about 3:1; M+1 from ^{13}C).
- Two Cl: $M : [M+2] : [M+4] \approx 9 : 6 : 1$; two Br: 1 : 2 : 1.
- Write a fragmentation as molecular ion → positive ion (detected) + radical (not detected).
- For A_r from a spectrum, divide by the sum of the peak heights, whatever it is.

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Chemical energetics

A-Level Chemistry

Lattice energy and Born–Haber cycles

These cycles use several **enthalpy changes** 焓变 (ΔH). Two new ones are:

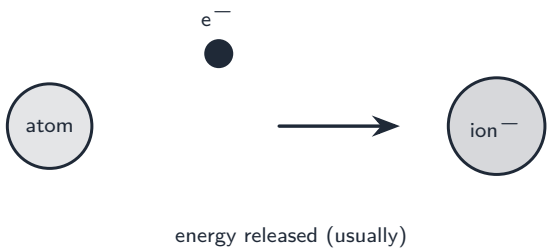
- the **enthalpy change of atomisation** 原子化焓变, ΔH_{at} – the energy to make **one mole** of gaseous atoms from an element. It is always positive (bonds must break).
- the **lattice energy** 晶格能, ΔH_{latt} – the energy change when one mole of a solid ionic lattice forms from its gaseous ions. It is always negative (strong bonds form).



An ionic solid such as sodium chloride is a giant, regular lattice of ions – the lattice energy is released when it forms

■ Electron affinity

The **first electron affinity** 电子亲和能 (EA) is the energy change when one mole of gaseous atoms each gain one electron to form one mole of 1− ions. The first EA is usually negative.

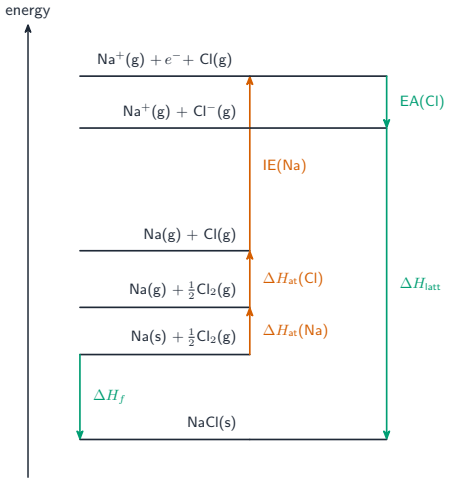


A gaseous atom gains an electron, usually releasing energy

The same factors as ionisation energy apply (nuclear charge, atomic radius, shielding). Going down Group 16 or 17, the EA becomes **less** exothermic, because the atom is larger and pulls the extra electron in less strongly. (The very top element is an exception: its atom is so small that electron repulsion makes its EA less exothermic than the one below it.)

Born–Haber cycles

A **Born–Haber cycle** 玻恩哈伯循环 is an energy cycle that links the enthalpy change of formation of an ionic solid with its atomisation, ionisation energy, electron affinity and lattice energy. Using Hess's law, you go round the cycle to find any one unknown step. (You only need +1 and +2 cations and −1 and −2 anions.)



A Born–Haber cycle for NaCl: going up costs energy (atomisation, ionisation); coming down releases it (electron affinity, and the large lattice energy)

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> **Worked example.** Find the lattice energy of sodium chloride from these data (kJ mol^{-1}): enthalpy of formation $\Delta H_f = -411$; atomisation $\Delta H_{\text{at}}(\text{Na}) = +107$ and $\Delta H_{\text{at}}(\text{Cl}) = +122$; first ionisation energy of Na $= +496$; electron affinity of Cl $= -349$.

By Hess's law the direct formation route equals the route up and round the cycle:

$$\Delta H_f = \Delta H_{\text{at}}(\text{Na}) + \Delta H_{\text{at}}(\text{Cl}) + \text{IE}_1 + \text{EA} + \Delta H_{\text{latt}},$$

so $\Delta H_{\text{latt}} = -411 - (107 + 122 + 496 - 349) = -787$ kJ mol^{-1}.

> **Worked example (a 2+ ion).** Find the lattice energy of magnesium chloride, MgCl_2, from these data (kJ mol^{-1}): $\Delta H_f = -641$; $\Delta H_{\text{at}}(\text{Mg}) = +148$; $\Delta H_{\text{at}}(\text{Cl}) = +122$; first and second ionisation energies of Mg $= +736$ and $+1450$; electron affinity of Cl $= -349$.

Count what one formula unit needs before adding anything up:

1. Mg must lose **two** electrons, so both ionisation energies go in: $736 + 1450$.
2. There are **two** Cl atoms, so the atomisation of chlorine and the electron affinity are each counted twice: 2×122 and $2 \times (-349)$.
3. Hess's law then gives

$$\Delta H_{\text{latt}} = -641 - (148 + 2(122) + 736 + 1450 + 2(-349)) = -641 - 1880 = -2521 \text{ kJ mol}^{-1}.$$

The answer is about three times the lattice energy of NaCl, because Mg^{2+} has twice the charge of Na^+ and is smaller.

> **Worked example (a 2− ion).** Find the lattice energy of magnesium oxide from these data (kJ mol^{-1}): $\Delta H_f(\text{MgO}) = -602$; $\Delta H_{\text{at}}(\text{Mg}) = +148$; first plus second ionisation energies of Mg $= +2186$; $\Delta H_{\text{at}}(\text{O}) = +249$; first electron affinity of O $= -141$; second electron affinity of O $= +798$.

Going round the cycle, $\Delta H_f = \Delta H_{\text{at}}(\text{Mg}) + (\text{IE}_1 + \text{IE}_2) + \Delta H_{\text{at}}(\text{O}) + \text{EA}_1 + \text{EA}_2 + \Delta H_{\text{latt}}$, so

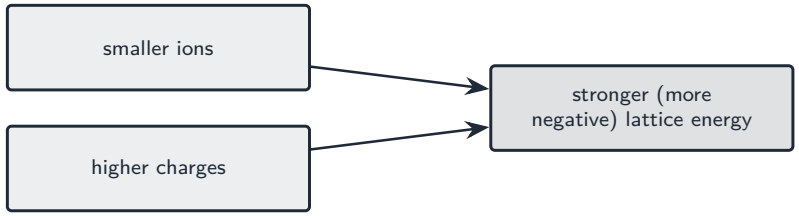
$$\Delta H_{\text{latt}} = -602 - (148 + 2186 + 249 - 141 + 798) = -602 - 3240 = -3842 \text{ kJ mol}^{-1}.$$

The **second** electron affinity is endothermic, but forming O^{2-} still pays off, because the lattice of 2+ and 2− ions is so strongly held: about five times as exothermic as the lattice energy of NaCl.

What controls the size of a lattice energy

The lattice energy is more negative (stronger) when:

- the **ionic charge** is higher (e.g. Mg^{2+} beats Na^{+}).
- the **ionic radius** is smaller.



Smaller ions and higher charges give a stronger lattice energy

Both make the attraction between the ions stronger.

Compound	Ions	Lattice energy / kJ mol^{-1}
NaCl	Na^{+}, Cl^{-}	−787
KCl	K^{+} (larger), Cl^{-}	−711
NaF	Na^{+}, F^{-} (smaller)	−918
MgO	Mg^{2+}, O^{2-} (both doubly charged)	−3842

Charge has the bigger effect: doubling both charges multiplies the attraction by about four, while a change in radius alters it by only a fraction.

Enthalpies of solution and hydration

- the **enthalpy change of hydration** 水合焓变, ΔH_{hyd} – the energy change when one mole of gaseous ions is surrounded by water to form aqueous ions. It is exothermic.
- the **enthalpy change of solution** 溶解焓变, ΔH_{sol} – the energy change when one mole of solute dissolves fully in water.

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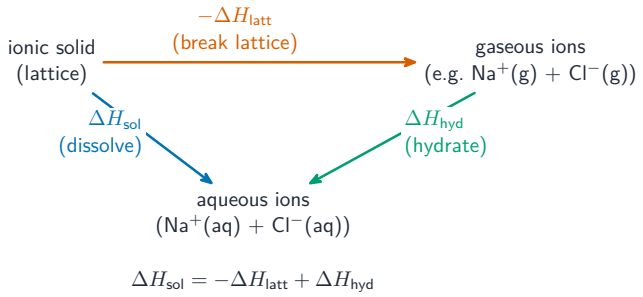


An instant cold pack feels cold because its salt dissolves endothermically (a positive ΔH_{sol}), driven by the rise in entropy

An energy cycle links the three:

$$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

(To dissolve, you first pull the lattice apart, then hydrate the ions.) Like lattice energy, ΔH_{hyd} is more exothermic for ions with a higher charge and a smaller radius: a small, highly charged ion attracts the polar water molecules more strongly (the $\delta-$ oxygen atoms towards a cation, the $\delta+$ hydrogen atoms towards an anion).



Dissolving energy cycle: pull the lattice apart (reverse lattice energy), then hydrate the gaseous ions, so $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$

Worked example. Find ΔH_{sol} of sodium chloride from: $\Delta H_{\text{latt}}(\text{NaCl}) = -787$; $\Delta H_{\text{hyd}}(Na^{+}) = -406$; $\Delta H_{\text{hyd}}(Cl^{-}) = -364$ kJ mol^{-1}.

The hydration term includes **both** ions:

$$\Delta H_{\text{sol}} = -(-787) + (-406 - 364) = 787 - 770 = +17 \text{ kJ mol}^{-1}.$$

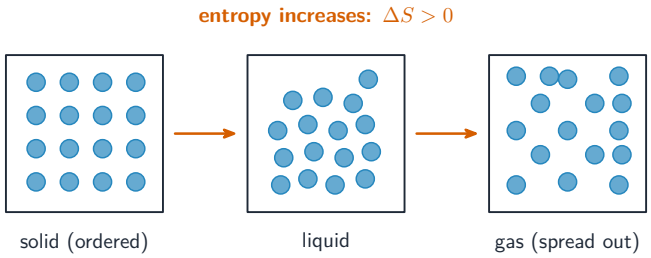
Dissolving is slightly endothermic, yet sodium chloride is very soluble: the entropy increase when the ions spread out through the water makes ΔG negative (see below).

> **Worked example (finding a hydration enthalpy).** $\Delta H_{\text{sol}}(\text{KF}) = -15$, $\Delta H_{\text{latt}}(\text{KF}) = -821$ and $\Delta H_{\text{hyd}}(\text{F}^-) = -506$ kJ mol^{-1}. Find $\Delta H_{\text{hyd}}(\text{K}^+)$. Rearranging, $\Delta H_{\text{hyd}}(\text{K}^+) = \Delta H_{\text{sol}} + \Delta H_{\text{latt}} - \Delta H_{\text{hyd}}(\text{F}^-) = -15 - 821 + 506 = -330$ kJ mol^{-1}.

Explaining a solubility trend. The solubility of the Group 2 **sulfates** falls down the group. Both terms in the cycle become less exothermic as the cation gets bigger, but by different amounts. The sulfate ion is so **large** that the distance between ion centres hardly changes from Mg^{2+} to Ba^{2+}, so the lattice energy becomes only a little less exothermic. The hydration enthalpy of the cation depends on the cation alone, and it becomes **much** less exothermic as the cation's radius grows. So ΔH_{sol} becomes more endothermic down the group, and the sulfates become less soluble. (The Group 2 hydroxides show the opposite trend: with the small OH^- ion, the lattice energy falls faster than the hydration enthalpy.)

Entropy change, ΔS

Entropy 熵 (S) measures the number of ways the particles and their energy can be arranged in a system. More ways means more "disorder".



Entropy rises from solid to liquid to gas as the particles spread into more arrangements, so ΔS is positive

The **entropy change** 熵变 (ΔS) is **positive** when disorder increases, and **negative** when it falls:

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Change	Sign of ΔS
solid → liquid → gas (melting, boiling), or dissolving	positive
a rise in temperature	positive
a reaction that makes **more** gas molecules	positive
a reaction that makes **fewer** gas molecules	negative

You can calculate it from standard entropies:

$$\Delta S^{\ominus} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$

Multiply each standard entropy by the number of moles in the equation. Elements have standard entropies too (they are **not** zero, unlike their enthalpies of formation), and $S^{\ominus}$ is in J K^{-1} mol^{-1}.

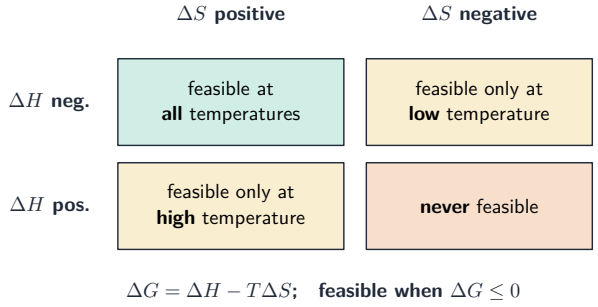
Gibbs free energy change, ΔG

The **Gibbs free energy** 吉布斯自由能 change decides whether a reaction can happen on its own:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Here T is the temperature in kelvin. A reaction is **feasible** (it can happen) when ΔG is negative or zero. The **feasibility** 可行性 therefore depends on temperature:

ΔH	ΔS	When feasible
negative	positive	at all temperatures
positive	positive	only at high temperature
negative	negative	only at low temperature
positive	negative	never



Whether a reaction is feasible ($\Delta G \leq 0$) depends on the signs of ΔH and ΔS, and sometimes on temperature

To find the changeover temperature, set $\Delta G = 0$, which gives $T = \Delta H / \Delta S$.

> **Worked example.** A reaction has $\Delta H = +120$ kJ mol^{-1} and $\Delta S = +200$ J K^{-1} mol^{-1}. Find ΔG at 298 K, and the temperature above which the reaction becomes feasible.

First match the units: $\Delta S = +0.200$ kJ K^{-1} mol^{-1}. Then

$$\Delta G = \Delta H - T\Delta S = 120 - 298 \times 0.200 = +60 \text{ kJ mol}^{-1} \quad \text{(positive, so not yet feasible).}$$

Setting $\Delta G = 0$ gives $T = \Delta H / \Delta S = 120 / 0.200 = 600$ K, so the reaction is feasible above 600 K.

> **Worked example (from standard entropies).** For the thermal decomposition $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H^\ominus = +178$ kJ mol^{-1}. Standard entropies (J K^{-1} mol^{-1}): $CaCO_3$ 93, CaO 40, CO_2 214. Find the minimum temperature for decomposition.

$$\Delta S^\ominus = (40 + 214) - 93 = +161 \text{ J K}^{-1}\text{ mol}^{-1} = +0.161 \text{ kJ K}^{-1}\text{ mol}^{-1}.$$

The sign is what you expect: a gas is made from a solid. At 298 K, $\Delta G^\ominus = 178 - 298 \times 0.161 = +130$ kJ mol^{-1}, so limestone is stable at room temperature. Decomposition becomes feasible when $\Delta G^\ominus \leq 0$: $T \geq 178 / 0.161 = 1106$ K (about 830 °C). This is why a lime kiln runs at around 1000 °C or more. The calculation assumes ΔH and ΔS stay the same as the temperature changes, which is only roughly true.

Common mistakes.

- Counting a step once when the formula needs it twice. In $MgCl_2$ the chlorine atomisation and electron affinity are both doubled, and Mg needs its first **and** second ionisation energies.
- Using the bond energy of Cl_2 for the atomisation of chlorine. ΔH_{at} makes **one mole of Cl atoms**, which is half of the bond energy ($244 \div 2 = 122$).
- Saying every electron affinity is negative. The **second** electron affinity, as in $O^-(g) + e^- \rightarrow O^{2-}(g)$, is positive: the electron is added to a negative ion, which repels it.
- Giving lattice energy a positive sign. Here lattice energy is for **forming** the lattice from gaseous ions, so it is always negative.
- Putting T in °C or ΔS in J K^{-1} mol^{-1} into $\Delta G = \Delta H - T\Delta S$. Use kelvin, and divide ΔS by 1000 first.
- Saying a reaction with $\Delta G < 0$ will happen quickly. ΔG says it is feasible; a high activation energy can still make it far too slow to see.

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Exam tips

- In a **Born-Haber cycle** get each step's direction and sign right (atomisation, ionisation +; electron affinity, lattice formation −) and apply Hess's law around it.
- In a dissolving cycle, $\Delta H_{sol} = -\Delta H_{latt} + \sum \Delta H_{hyd}$: add the hydration enthalpy of **every** ion, times the number of each in the formula.
- To explain a solubility trend, compare how fast the lattice energy and the hydration enthalpy change down the group; the one that changes more decides.
- **Lattice energy** is more exothermic for **smaller, more highly charged ions** (higher charge density).
- Predict the **sign of** ΔS from the state changes (more gas moles = more disorder).
- Use $\Delta G = \Delta H - T\Delta S$; feasible when $\Delta G \leq 0$ – convert ΔS from J K^{-1} mol^{-1} ($\div 1000$).

Electrochemistry

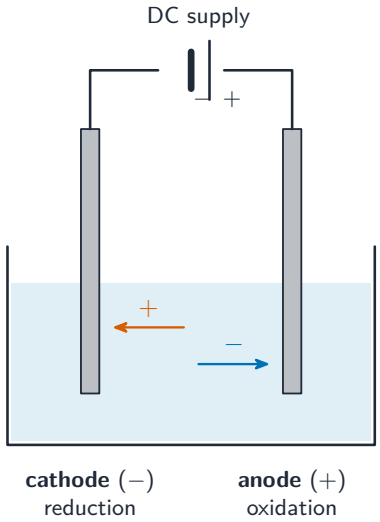
A-Level Chemistry

Electrolysis

Electrolysis 电解 uses electricity to break down a molten or aqueous **electrolyte** 电解质. Positive ions move to the negative electrode and negative ions move to the positive electrode.

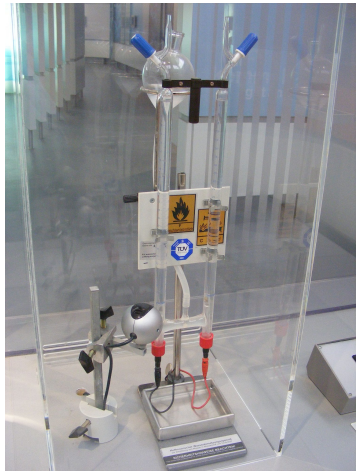
At each **electrode** 电极 a half-reaction happens:

- at the **cathode** 阴极 (negative): positive ions gain electrons (reduction).
- at the **anode** 阳极 (positive): negative ions lose electrons (oxidation).



Electrolysis: the DC supply drives positive ions to the cathode (reduction) and negative ions to the anode (oxidation)

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A Hofmann voltameter for the electrolysis of water: the power supply drives current through two electrodes, and the gas made at each one collects in its side tube

Predicting the products

- a **molten** electrolyte gives the metal at the cathode and the non-metal at the anode.
- an **aqueous** electrolyte also contains water. At the cathode, a less reactive metal is released, but for a reactive metal you get hydrogen instead. At the anode you usually get oxygen, but a concentrated halide solution gives the halogen.

molten	**aqueous**
metal at cathode non-metal at anode	also contains water, so H_2 or O_2 may form

A molten electrolyte gives the metal and non-metal; aqueous also has water

Using $E^\ominus$ to decide. In an aqueous solution, two species compete at each electrode, and the one that reacts more easily wins:

- **cathode**: the metal ion or H_2O (giving H_2). The species with the **more positive** $E^\ominus$ is reduced. Cu^{2+}/Cu (+0.34 V) is more positive than $2H_2O/H_2$ (−0.83 V, or 0.00 V for H^+/H_2), so copper is deposited; Na^+/Na (−2.71 V) is far more negative, so hydrogen forms instead.
- **anode**: the anion or H_2O (giving O_2). The species whose oxidised form has the **less positive** $E^\ominus$ is oxidised more easily. Sulfate and nitrate ions are very hard to oxidise, so oxygen forms: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

- **concentration** matters for halides. $E^{\ominus}(Cl_2/Cl^-) = +1.36$ V and $E^{\ominus}(O_2/H_2O) = +1.23$ V are close. In **concentrated** NaCl(aq) the high $[Cl^-]$ makes chloride the easier one, so chlorine forms; in **dilute** NaCl(aq), oxygen forms (often mixed with some chlorine). Bromide and iodide are oxidised easily, so they give bromine and iodine even when dilute.

Electrolyte	Cathode	Anode
molten $PbBr_2$	lead	bromine
$CuSO_4$(aq), inert electrodes	copper	oxygen
concentrated NaCl(aq)	hydrogen	chlorine
dilute NaCl(aq)	hydrogen	oxygen
dilute H_2SO_4(aq)	hydrogen	oxygen (volume ratio $H_2 : O_2 = 2 : 1$)
$CuSO_4$(aq), copper electrodes	copper	the copper anode dissolves: $Cu \to Cu^{2+} + 2e^-$

Calculations

The charge on one mole of electrons is the **Faraday constant** 法拉第常量, linked to the **Avogadro constant** 阿伏伽德罗常量 (L) and the charge on one electron (e) by $F = Le$.

The charge passed is $Q = It$ (current × time). Then:

1. moles of electrons $= Q/F$.
2. use the half-equation to find moles of product.
3. find the mass ($\times M_r$) or the gas volume.

Measuring the mass deposited for a known charge lets you work back to a value of the Avogadro constant.

Determining L by electrolysis. Weigh a clean, dry copper cathode. Electrolyse copper(II) sulfate solution with copper electrodes, using a variable resistor to keep a **constant current** read on an ammeter, for a measured time. Then wash the cathode with water, then propanone, dry and reweigh it. For example, 0.50 A for 30 min (900 C) deposits 0.296 g of copper. Moles of Cu $= 0.296/63.5 = 4.66 \times 10^{-3}$, so moles of electrons $= 2 \times 4.66 \times 10^{-3} = 9.32 \times 10^{-3}$. Number of electrons $= Q/e = 900/(1.60 \times 10^{-19}) = 5.63 \times 10^{21}$. So $L = 5.63 \times 10^{21} \div 9.32 \times 10^{-3} = 6.0 \times 10^{23}$ mol^{-1}. (Weighing the **anode** loss works too, but the anode may shed bits of copper, so the cathode gain is more reliable.)

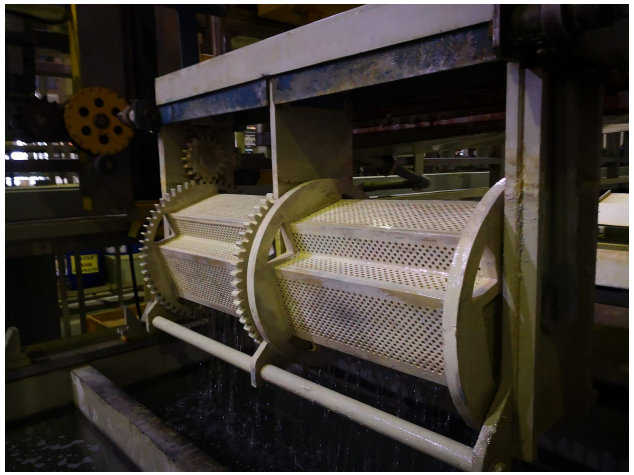
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Worked example (gas volume). Dilute sulfuric acid is electrolysed with 0.40 A for 40 min. Find the volume of oxygen at room conditions (24.0 dm^3 mol^{-1}). $Q = 0.40 \times 2400 = 960$ C; moles of electrons $= 960/96\,500 = 9.95 \times 10^{-3}$. At the anode $2H_2O \to O_2 + 4H^+ + 4e^-$, so moles of $O_2 = 9.95 \times 10^{-3}/4 = 2.49 \times 10^{-3}$, volume $= 2.49 \times 10^{-3} \times 24\,000 = 60$ cm^3. The hydrogen at the cathode needs only 2 electrons per molecule, so its volume is twice as large, 120 cm^3.

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate solution, depositing copper at the cathode: $Cu^{2+} + 2e^- \to Cu$. Find the mass of copper deposited. ($F = 96\,500$ C mol^{-1}, A_r Cu $= 64$.)

Charge passed: $Q = It = 2.0 \times (30 \times 60) = 3600$ C. Moles of electrons $= Q/F = 3600/96\,500 = 0.0373$ mol. From the half-equation, 2 mol of electrons give 1 mol of Cu, so $n(Cu) = 0.0187$ mol and

$$m = nM = 0.0187 \times 64 \approx 1.2 \text{ g}.$$

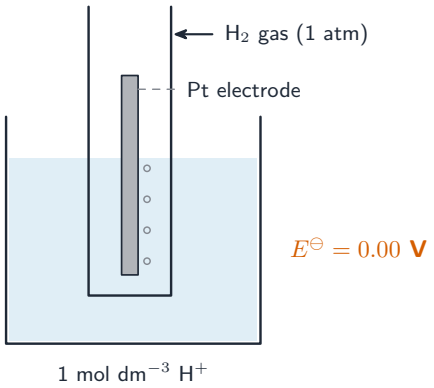


Electrolysis is used to electroplate an object with a thin, shiny layer of metal such as chromium

Standard electrode potentials and cell potentials

The **electrode potential** 电极电势 (E) of a half-cell shows how easily it is reduced. We measure it against a reference, under standard conditions, to get the **standard electrode potential** 标准电极电势 ($E^{\ominus}$), always written as a reduction.

The reference is the **standard hydrogen electrode** 标准氢电极: hydrogen gas at 101 kPa (1 atm) over platinum in 1 mol dm^{-3} H^+, defined as exactly 0.00 V.



The standard hydrogen electrode: H_2 at 1 atm over platinum in 1 mol dm^{-3} H^+, the 0.00 V reference for every electrode potential

To measure an $E^\ominus$, connect the half-cell to the standard hydrogen electrode and read the voltage. A metal sits in a solution of its ions; for two ions of the same element (such as Fe^{3+}/Fe^{2+}), a platinum electrode dips into a solution containing both.

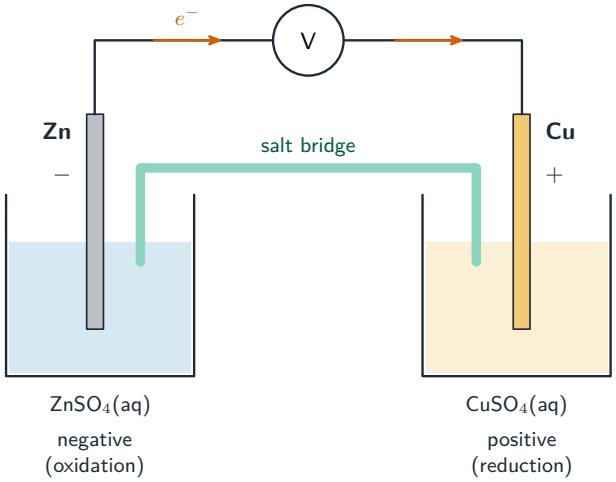
Definitions to learn word for word. The **standard electrode potential** of a half-cell is the potential difference between that half-cell and the standard hydrogen electrode, measured under **standard conditions**: 298 K, 1 mol dm^{-3} of each ion in the half-equation, and 101 kPa for any gas. The **standard cell potential** is the potential difference between two half-cells under standard conditions.

The measuring circuit. Join the two half-cells with a **salt bridge** 盐桥 – filter paper soaked in saturated potassium nitrate (KNO_3) solution. It completes the circuit by letting ions move between the solutions, without the solutions mixing; KNO_3 is used because its ions do not react or form precipitates with the ions in either half-cell. Connect the electrodes with wire through a **high-resistance voltmeter**, so almost no current flows and the cell's full potential difference is measured. For a non-metal such as chlorine, bubble the gas over a platinum electrode in a solution of its ions, $Cl^-(aq)$, at 1 mol dm^{-3}. Platinum is used because it is **inert** and conducts.

■ Combining half-cells

The **standard cell potential** 标准电池电势 is the difference between the two standard electrode potentials:

$$E^\ominus_{\text{cell}} = E^\ominus(\text{more positive}) - E^\ominus(\text{less positive})$$



A simple cell: two half-cells joined by a salt bridge, with a voltmeter. Electrons flow from the negative (Zn) electrode to the positive (Cu)

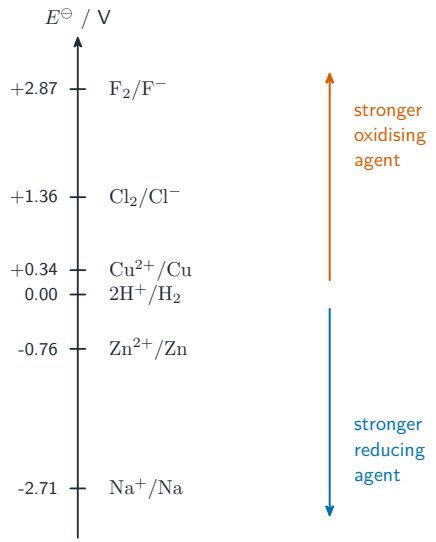
> **Worked example.** Find the standard cell potential of a cell built from the Zn^{2+}/Zn half-cell ($E^\ominus = -0.76$ V) and the Cu^{2+}/Cu half-cell ($E^\ominus = +0.34$ V).

$$E^\ominus_{\text{cell}} = E^\ominus(\text{more positive}) - E^\ominus(\text{less positive}) = (+0.34) - (-0.76) = 1.10 \text{ V}.$$

From $E^\ominus$ values you can:

- find the **polarity**: the more negative electrode is the negative terminal, and electrons flow from it through the external circuit to the positive electrode.
- judge **reactivity**: a more positive $E^\ominus$ means a better **oxidising agent** 氧化剂 (easily reduced); a more negative $E^\ominus$ means a better **reducing agent** 还原剂.

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The electrochemical series: a more positive $E^\ominus$ (top) is a stronger oxidising agent; a more negative $E^\ominus$ (bottom) is a stronger reducing agent

Feasibility and redox equations

A reaction is feasible when $E^\ominus_{\text{cell}}$ is **positive**. To build the full equation, take the two **half-equations** 半反应方程式, reverse the one that is oxidised, and add them so the electrons cancel. This $E^\ominus$ test tells you the **feasibility** 可行性 of the reaction.

You can also link it to free energy: $\Delta G^\ominus = -nE^\ominus_{\text{cell}}F$, where n is the moles of electrons.

> **Worked example (feasibility).** Will acidified manganate(VII) oxidise chloride ions to chlorine? $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$, $E^\ominus = +1.52$ V; $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$, $E^\ominus = +1.36$ V. The manganate(VII) half-cell is more positive, so it is reduced and chloride is oxidised: $E^\ominus_{\text{cell}} = 1.52 - 1.36 = +0.16$ V, positive, so the reaction is **feasible**. Multiply the manganate half-equation by 2 and the chlorine one by 5 (10 electrons each), reverse the chlorine one and add:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

This is why manganate(VII) titrations are acidified with sulfuric acid, never hydrochloric acid: the HCl would be oxidised and use up extra manganate(VII).

> **Worked example ($\Delta G^\ominus$).** For the Daniell cell, $E^\ominus_{\text{cell}} = +1.10$ V and $n = 2$. $\Delta G^\ominus = -nE^\ominus_{\text{cell}}F = -2 \times 1.10 \times 96\,500 = -212\,300$ J mol^{-1} $= -212$ kJ mol^{-1}. A positive $E^\ominus_{\text{cell}}$ always gives a negative $\Delta G^\ominus$: the two tests of feasibility agree. Remember to convert J to kJ.

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Limits of the prediction. A positive $E^\ominus_{\text{cell}}$ shows a reaction **can** happen under standard conditions, but it may not be seen: the **rate** may be very slow (a high activation energy), or the conditions may not be standard (different concentrations or temperature change E). If $E^\ominus_{\text{cell}}$ is only slightly positive (below about 0.3 V), a change in concentration can reverse the prediction.

The Nernst equation

If the concentrations are not standard, the electrode potential changes. Raising the concentration of the **oxidised** species makes E more positive. The **Nernst equation** 能斯特方程 gives the exact value:

$$E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons in the half-equation.

For a metal in contact with its ions, the reduced species is the solid metal, whose "concentration" is taken as 1, so the equation becomes

$$E = E^\ominus + \frac{0.059}{z} \log[M^{z+}]$$

> **Worked example (Nernst).** Find E for (a) a copper electrode in 0.010 mol dm^{-3} Cu^{2+}(aq) ($E^\ominus = +0.34$ V); (b) a platinum electrode in a solution with $[Fe^{3+}] = 0.10$ and $[Fe^{2+}] = 1.0$ mol dm^{-3} ($E^\ominus = +0.77$ V). (a) $E = 0.34 + (0.059/2)\log(0.010) = 0.34 + 0.0295 \times (-2) = +0.28$ V. Diluting the oxidised species makes E **less positive**: Cu^{2+} becomes a weaker oxidising agent. (b) $E = 0.77 + 0.059\log(0.10/1.0) = 0.77 - 0.059 = +0.71$ V. Each tenfold change in the ratio changes E by $0.059/z$ volts.

Qualitative reasoning. Without numbers, use Le Chatelier on the half-equation written as a reduction: adding more of the oxidised species (or removing the reduced one) pushes the equilibrium to the right, so the half-cell is reduced more readily and E becomes **more positive**.

Common mistakes.

- Using the time in minutes in $Q = It$. Time must be in **seconds**: 30 minutes is 1800 s.
- Forgetting the electrons in the half-equation. Cu^{2+} needs **2** electrons per atom, so the moles of copper are half the moles of electrons.
- Multiplying an $E^\ominus$ value when you double a half-equation to balance electrons. Electrode potentials do **not** change with the coefficients; only $\Delta G^\ominus = -nE^\ominus_{\text{cell}}F$ uses n.
- Saying a positive $E^\ominus_{\text{cell}}$ means the reaction will happen fast. It shows the reaction is **energetically** feasible; it says nothing about the **rate**, and a high activation energy can stop it happening at all.

- Calling the anode negative in electrolysis because it is negative in a cell. In **electrolysis** the anode is positive (oxidation); in a **cell** the negative terminal is where oxidation happens. Oxidation is always at the anode.
- Raising $[Cu^{2+}]$ and expecting E to fall. A higher concentration of the **oxidised** species pushes E **more positive**.
- Expecting the metal at the cathode in any aqueous solution. Reactive metals (such as sodium) are not released from aqueous solution; **hydrogen** forms instead.

Exam tips

- $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{more positive}) - E^{\ominus}(\text{less positive})$; a **positive** $E^{\ominus}_{\text{cell}}$ means the reaction is feasible.
- Quote standard conditions: **298 K,** 1 **mol dm^{-3}, 101 kPa**, platinum electrode.
- A **more negative** electrode potential means a **stronger reducing agent**; use the series to predict the direction.
- For electrolysis quantities use $Q = It$ and moles of electrons $= Q/F$.
- Aqueous electrolysis: at the cathode the more positive $E^{\ominus}$ wins (metal below hydrogen, else H_2); at the anode, halides (concentrated Cl^-) give the halogen, otherwise O_2.
- Salt bridge: $KNO_3(aq)$, to complete the circuit without mixing; high-resistance voltmeter, so no current flows.
- Nernst: $E = E^{\ominus} + (0.059/z)\log([\text{ox}]/[\text{red}])$; a metal's own "concentration" is 1.
- $\Delta G^{\ominus} = -nE^{\ominus}_{\text{cell}}F$ gives J mol^{-1}; divide by 1000 for kJ.

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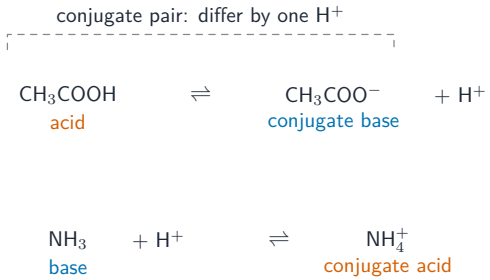
Equilibria

A-Level Chemistry

Conjugate acids and bases

When a Brønsted acid loses an H^+, what is left is its **conjugate base** 共轭碱. When a base gains an H^+, it becomes its **conjugate acid** 共轭酸. The two species that differ by just one H^+ form a **conjugate acid–base pair** 共轭酸碱对.

For example, in $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, the pair is CH_3COOH (acid) and CH_3COO^- (its conjugate base).

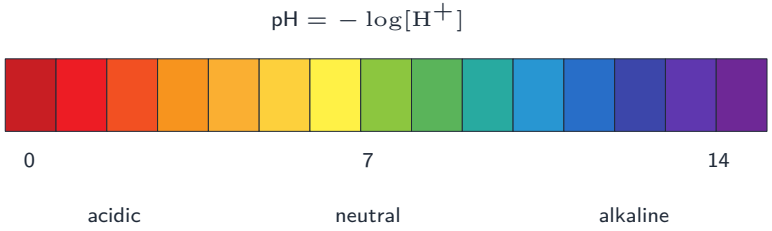


Conjugate pairs differ by one proton: an acid loses H^+ to give its conjugate base; a base gains H^+ to give its conjugate acid

Worked example. Identify the two conjugate acid–base pairs in $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. Follow each H^+. Water gives an H^+ to ammonia, so here water is the **acid** and OH^- is its conjugate base. Ammonia accepts the H^+, so it is the **base** and NH_4^+ is its conjugate acid. The pairs are H_2O/OH^- and NH_4^+/NH_3. Water can act as an acid (with NH_3) or a base (with HCl, giving H_3O^+); a species that can do both is **amphoteric** 两性.

pH and the equilibrium constants

- **pH** measures acidity: $\text{pH} = -\log[H^+]$, so $[H^+] = 10^{-\text{pH}}$.
- the **acid dissociation constant** 酸解离常数 of a weak acid HA is $K_a = \dfrac{[H^+][A^-]}{[HA]}$, and $\text{p}K_a = -\log K_a$. A larger K_a (smaller $\text{p}K_a$) means a stronger acid.
- the **ionic product of water** 水的离子积 is $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K.



The pH scale: pH = -log of the hydrogen-ion concentration



pH paper estimates the pH of a solution from the colour it turns

■ Calculating pH

- **strong acid** 强酸: fully ionised, so $[H^+]$ equals the acid concentration; then take $-\log$.
- **strong alkali** 强碱: find $[OH^-]$ from the concentration, then use $[H^+] = K_w/[OH^-]$.
- **weak acid** 弱酸: only partly ionised, so use $[H^+] = \sqrt{K_a \times [HA]}$.

> **Worked example.** Find the pH of 0.050 mol dm^{-3} hydrochloric acid (a strong acid).

It is fully ionised, so $[H^+] = 0.050$ mol dm^{-3}, giving $\text{pH} = -\log(0.050) = 1.30$.

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> **Worked example.** Find the pH of 0.10 mol dm^{-3} sodium hydroxide (a strong base). ($K_w = 1.0 \times 10^{-14}$.)

$[OH^-] = 0.10$, so $[H^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/0.10 = 1.0 \times 10^{-13}$, giving $\text{pH} = 13.0$.

> **Worked example.** Find the pH of 0.10 mol dm^{-3} ethanoic acid (a weak acid). ($K_a = 1.8 \times 10^{-5}$.)

$$[H^+] = \sqrt{K_a \times [HA]} = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3}, \qquad \text{pH} = -\log(1.3 \times 10^{-3}) = 2.87.$$

The square-root formula comes from two **assumptions**: each HA that ionises gives one H^+ and one A^-, so $[H^+] = [A^-]$ (and the H^+ from water is ignored); and so little HA ionises that [HA] at equilibrium is still about the starting concentration. Then $K_a = [H^+]^2/[HA]$.

> **Worked example (finding K_a from pH).** A 0.020 mol dm^{-3} solution of a weak acid HA has pH 3.20. Find K_a and pK_a. $[H^+] = 10^{-3.20} = 6.31 \times 10^{-4}$. $K_a = [H^+]^2/[HA] = (6.31 \times 10^{-4})^2/0.020 = 1.99 \times 10^{-5}$ mol dm^{-3}, so p$K_a = 4.70$.

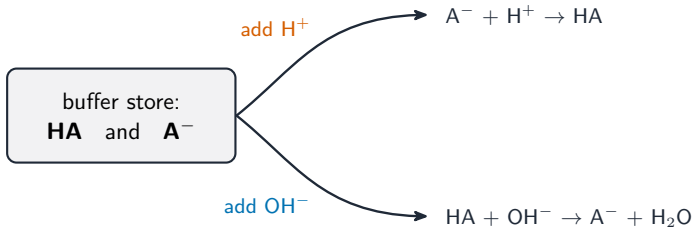
Watch the formula. A diprotic strong acid gives two H^+ per molecule: 0.050 mol dm^{-3} H_2SO_4 (treated as fully ionised) has $[H^+] = 0.10$, pH 1.00. A Group 2 hydroxide gives two OH^-: 0.010 mol dm^{-3} $Ba(OH)_2$ has $[OH^-] = 0.020$, $[H^+] = 5.0 \times 10^{-13}$, pH 12.3.

Buffer solutions

A **buffer solution** 缓冲溶液 resists a change in pH when a small amount of acid or alkali is added. You make one from a weak acid and its conjugate base (for example ethanoic acid and sodium ethanoate).

It works because the mixture holds a store of both partners:

- added H^+ is removed by the conjugate base: $CH_3COO^- + H^+ \rightarrow CH_3COOH$.
- added OH^- is removed by the weak acid: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$.



either way, the pH barely changes

A buffer holds a store of a weak acid and its conjugate base: added H^+ is mopped up by A^- and added OH^- by HA, so the pH barely changes

To find the pH, put the concentrations of the acid and its salt into the K_a expression. Buffers are important in living things – for example, HCO_3^- keeps the pH of blood close to 7.4.

The blood buffer. Carbon dioxide dissolves in blood to form carbonic acid, which is in equilibrium with hydrogencarbonate ions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

If H^+ is added (for example lactic acid from exercise), it combines with HCO_3^- and the equilibrium shifts to the **left**; the extra CO_2 is breathed out. If H^+ is removed, more H_2CO_3 ionises to replace it, shifting the equilibrium to the **right**. The pH of blood must stay between about 7.35 and 7.45, or enzymes and haemoglobin stop working properly. Other uses of buffers: shampoos, food and drinks, biological experiments and calibrating pH meters.

Making a buffer by part-neutralisation. You can also make a buffer by adding a **strong base** to an **excess** of a weak acid: some of the acid becomes its salt, and the rest is left over.

> **Worked example.** 25.0 cm^3 of 0.10 mol dm^{-3} NaOH is added to 50.0 cm^3 of 0.10 mol dm^{-3} ethanoic acid ($K_a = 1.8 \times 10^{-5}$). Find the pH. Moles of acid = 5.0×10^{-3}; moles of NaOH = 2.5×10^{-3}. The NaOH turns 2.5×10^{-3} mol of acid into ethanoate, leaving 2.5×10^{-3} mol of acid. Both are in the same volume, so the ratio of moles is the ratio of concentrations: $[H^+] = 1.8\times10^{-5}\times(2.5/2.5) = 1.8\times10^{-5}$, pH = 4.74. When exactly half the acid has been neutralised, pH = pK_a – a quick way to read pK_a from a titration curve.

> **Worked example (buffer pH).** A buffer contains 0.10 mol dm^{-3} ethanoic acid and 0.20 mol dm^{-3} sodium ethanoate. $K_a = 1.8\times10^{-5}$ mol dm^{-3}. Find its pH.

The salt is fully ionised, so $[CH_3COO^-] = 0.20$; the weak acid hardly ionises, so $[CH_3COOH] = 0.10$. Rearranging the K_a expression:

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.8\times10^{-5}\times\frac{0.10}{0.20} = 9.0\times10^{-6}, \qquad \text{pH} = 5.05.$$

Do **not** use $\sqrt{K_a[HA]}$ here: that formula assumes $[H^+] = [A^-]$, which is not true once the salt is added.

Solubility product

For a salt that barely dissolves, the **solubility product** 溶度积 (K_{sp}) is the product of the ion concentrations in a saturated solution, each raised to the power of its number in the formula:

$$K_{sp} = [Ag^+][Cl^-] \qquad K_{sp} = [Ca^{2+}][F^-]^2$$

You can find K_{sp} from the solubility, or the solubility from K_{sp}.

> **Worked example.** The solubility of calcium fluoride, CaF_2, is 2.0×10^{-4} mol dm^{-3}. Find K_{sp}.

Each CaF_2 that dissolves gives one Ca^{2+} and **two** F^-, so $[Ca^{2+}] = 2.0\times10^{-4}$ and $[F^-] = 4.0\times10^{-4}$:

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.0\times10^{-4})(4.0\times10^{-4})^2 = 3.2\times10^{-11}\ \text{mol}^3\,\text{dm}^{-9}.$$



Stalactites grow as dissolved calcium carbonate slowly comes back out of solution – a real solubility equilibrium

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The common ion effect

The **common ion effect** 同离子效应 is the way a salt becomes **less** soluble in a solution that already contains one of its ions. The extra ion pushes the dissolving equilibrium back (Le Chatelier), so less salt dissolves. You can calculate the new solubility using K_{sp} and the concentration of the common ion.

> **Worked example (common ion).** K_{sp} of silver chloride is 1.8×10^{-10} mol^2 dm^{-6}. Find its solubility (a) in pure water and (b) in 0.10 mol dm^{-3} sodium chloride. (a) $[Ag^+] = [Cl^-] = s$, so $s^2 = 1.8 \times 10^{-10}$ and $s = 1.3 \times 10^{-5}$ mol dm^{-3}. (b) Now $[Cl^-] = 0.10$ (the tiny amount from AgCl is negligible), so $[Ag^+] = 1.8 \times 10^{-10} / 0.10 = 1.8 \times 10^{-9}$ mol dm^{-3}. The solubility is about **7000 times smaller** in the salt solution.

Will a precipitate form? Work out the **ionic product** – the K_{sp} expression with the actual concentrations after mixing. If it is **greater** than K_{sp}, a precipitate forms; if it is smaller, the solution is not yet saturated and nothing precipitates.

> **Worked example.** Equal volumes of 2.0×10^{-4} mol dm^{-3} $Ca(NO_3)_2$ and 2.0×10^{-4} mol dm^{-3} NaF are mixed. Does CaF_2 ($K_{sp} = 3.2 \times 10^{-11}$) precipitate? Mixing equal volumes halves each concentration: $[Ca^{2+}] = 1.0 \times 10^{-4}$ and $[F^-] = 1.0 \times 10^{-4}$. Ionic product $= (1.0 \times 10^{-4})(1.0 \times 10^{-4})^2 = 1.0 \times 10^{-12}$, which is **less** than K_{sp}, so **no** precipitate forms.

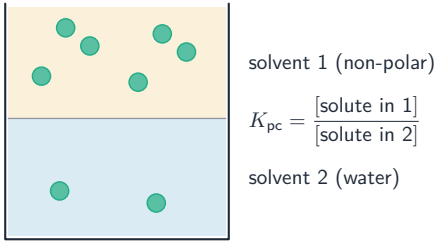
Partition coefficients

When a solute is shaken with two solvents that do not mix, it spreads between them. The **partition coefficient** 分配系数 (K_{pc}) is the ratio of its concentrations in the two layers (at constant temperature):

$$K_{pc} = \frac{[\text{solute in solvent 1}]}{[\text{solute in solvent 2}]}$$

This works when the **solute** 溶质 is in the same physical state in both solvents. The value depends on the **polarity** 极性 of the solute and of each **solvent** 溶剂: a non-polar solute dissolves more in the non-polar solvent, while a polar solute prefers the polar solvent.

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A solute shaken with two immiscible solvents spreads between them; the partition coefficient is the ratio of its concentrations in the two layers

> **Worked example (extraction).** For a solute X between hexane and water, $K_{pc} = [\text{X in hexane}]/[\text{X in water}] = 4.0$. 100 cm^3 of water contains 1.00 g of X. How much is extracted by shaking with (a) one 50 cm^3 portion of hexane, (b) two 25 cm^3 portions in turn? (a) Let x g move into the hexane: $\frac{x/50}{(1.00-x)/100} = 4.0$, so $2x = 4.0(1.00 - x)$ and $x = 0.667$ g. (b) First 25 cm^3: $\frac{x/25}{(1.00-x)/100} = 4.0$, so $4x = 4.0(1.00 - x)$ and $x = 0.500$ g, leaving 0.500 g. Second portion: $x = 0.250$ g. Total = 0.750 g. Using the same volume of solvent in **several smaller portions** extracts **more** solute than using it all at once.

Why the value depends on polarity. A polar solute (for example ammonia or a small alcohol) forms hydrogen bonds or dipole forces with water, so K_{pc} (organic : water) is **small**. A non-polar solute such as iodine forms stronger London forces with a non-polar solvent such as hexane, so K_{pc} (hexane : water) is **large**. Always say which solvent is on top of the fraction.

Common mistakes.

- Using $\sqrt{K_a[HA]}$ for a buffer. Use $[H^+] = K_a[\text{acid}]/[\text{salt}]$, because the salt supplies most of the A^-.
- In K_{sp}, doubling the concentration of the ion that appears twice but forgetting to square it, or squaring it but forgetting to double it. For CaF_2 with solubility s, $K_{sp} = s(2s)^2 = 4s^3$.
- Saying a buffer keeps the pH constant. It keeps the pH almost constant when **small** amounts of acid or alkali are added; a large amount uses up the acid or its conjugate base.
- Saying a weak acid has a high pH. A concentrated weak acid can have a lower pH than a dilute strong acid; "weak" means only partly ionised.
- Writing the conjugate base of H_2O as H_3O^+. A conjugate pair differs by one H^+: the conjugate **base** of water is OH^- and its conjugate **acid** is H_3O^+.

Exam tips

- pH $= -\log[\mathrm{H^+}]$; for a **strong acid** $[\mathrm{H^+}]$ = concentration, for a **weak acid** use $[\mathrm{H^+}] = \sqrt{K_a[\mathrm{HA}]}$.
- For a base, get $[\mathrm{H^+}]$ from $K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$.
- For a **buffer** use $[\mathrm{H^+}] = K_a \times [\text{acid}]/[\text{salt}]$ and explain how it removes added $\mathrm{H^+}/\mathrm{OH^-}$.
- Write the K_{sp} expression with the correct powers; the number of decimal places in a pH equals the significant figures of $[\mathrm{H^+}]$.
- State the two assumptions behind $[\mathrm{H^+}] = \sqrt{K_a[\mathrm{HA}]}$: $[\mathrm{H^+}] = [\mathrm{A^-}]$, and [HA] at equilibrium $\approx$ the starting concentration.
- For a part-neutralised buffer, use the **moles** of acid left and salt made; at half-neutralisation, pH $= \mathrm{p}K_a$.
- Ionic product $> K_{\mathrm{sp}} \rightarrow$ precipitate. A common ion lowers the solubility.
- For extraction with K_{pc}, let x be the mass transferred and divide each mass by its own volume.

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Reaction kinetics

A-Level Chemistry

Rate equations and orders

A **rate equation** 速率方程 shows how the rate depends on the **concentrations** 浓度 of the **reactants** 反应物:

$$\text{rate} = k\,[\mathrm{A}]^m[\mathrm{B}]^n$$

- m is the **order of reaction** 反应级数 with respect to A, and n the order with respect to B. Each is 0, 1 or 2.
- the **overall order of reaction** 总反应级数 is $m + n$.
- k is the **rate constant** 速率常数. The rate equation can only be found by experiment, not from the **balanced equation** 配平方程式.



A gas syringe measures the volume of gas made over time, which gives the rate of reaction

Finding the order

- **initial rates method** 初始速率法: change one concentration at a time and see how the starting rate changes. If doubling [A] doubles the rate, the order in A is 1; if it quadruples the rate, the order is 2; if the rate is unchanged, the order is 0.

Worked example. In experiments on A + B → products, doubling [A] (with [B] fixed) doubles the rate, and doubling [B] (with [A] fixed) quadruples the rate. Write the rate equation and give the overall order.

Doubling [A] doubles the rate, so **first order** 一级 in A. Doubling [B] quadruples (2^2) the rate, so **second order** 二级 in B. Hence

$$\text{rate} = k[\text{A}][\text{B}]^2, \qquad \text{overall order} = 1 + 2 = 3.$$

Units of k. Rearrange the rate equation so that k is alone, then put in the units: rate in mol dm^{-3} s^{-1}, each concentration in mol dm^{-3}. For the example above:

$$k = \frac{\text{rate}}{[\text{A}][\text{B}]^2} \Rightarrow \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})^3} = \text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$$

Overall order	Units of k
0	mol dm^{-3} s^{-1}
1	s^{-1}
2	mol^{-1} dm^3 s^{-1}
3	mol^{-2} dm^6 s^{-1}

Each extra order adds one mol^{-1} dm^3. Work the units out each time rather than learning the table: a mistake in the algebra shows up at once.

Exam data usually come as a table, and you must choose the pair of experiments in which **only one** concentration changes:

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	8.0×10^{-4}
3	0.10	0.30	2.0×10^{-4}
4	0.30	0.20	?

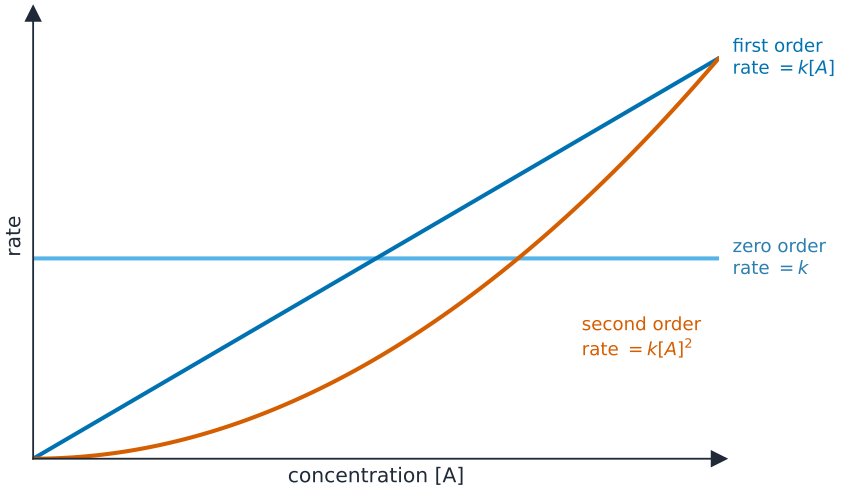
Worked example (initial-rates table). Use the table to find the order with respect to A and to B, the rate equation, the value and units of k, and the rate in experiment 4.

- Experiments 1 and 2: [A] doubles with [B] fixed, and the rate rises four times (2^2), so **second order** in A.
- Experiments 1 and 3: [B] triples with [A] fixed, and the rate does not change, so **zero order** in B.
- Rate $= k[\text{A}]^2$. From experiment 1: $k = 2.0 \times 10^{-4} \div (0.10)^2 = 2.0 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}.
- Experiment 4: rate $= 2.0 \times 10^{-2} \times (0.30)^2 = 1.8 \times 10^{-3}$ mol dm^{-3} s^{-1}. The value of [B] does not matter, because B is zero order.

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A zero-order reactant is still used up in the reaction: it simply does not appear in the rate equation, often because it takes part only **after** the rate-determining step.

- **graphs**: a **concentration–time graph** 浓度 – 时间图 for a first-order reaction has a constant **half-life** 半衰期 (the time for the concentration to halve). A rate–concentration graph is a straight line through the **origin** 原点 for first order, and a curve for second order.
  On a **concentration–time** graph, the shape gives the order: **zero** order is a straight line going down (the rate stays the same until the reactant runs out); **first** order is a curve with a **constant** half-life; **second** order is a curve whose half-life gets **longer** each time (for example 20 s, then 40 s, then 80 s). Measure two successive half-lives from the graph and compare them.

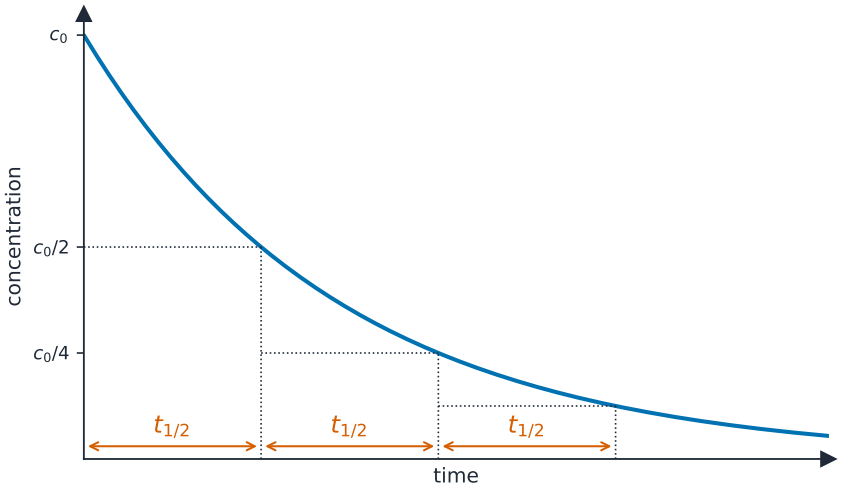


Rate against concentration: zero order is a flat line, first order a straight line through the origin, second order an upward curve

Half-life and the rate constant

For a **first-order** reaction the half-life is **constant** – it does not depend on the concentration. You can find the rate constant from it:

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$



A first-order reaction has a constant half-life: the concentration halves in the same time $t_{1/2}$ again and again, whatever the starting value

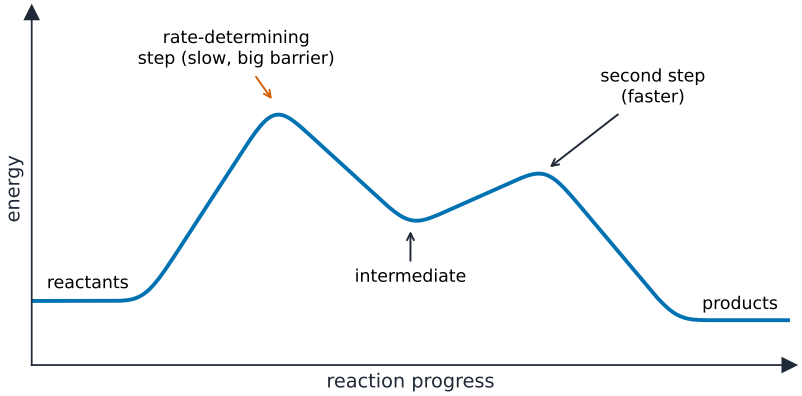
Worked example. A first-order reaction has a half-life of 120 s. Find its rate constant.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.8 \times 10^{-3}\ \text{s}^{-1}.$$

You can also find k by putting initial-rate data into the rate equation.

Reaction mechanisms

Most reactions happen in several **steps** 步骤. The slowest step is the **rate-determining step** 决速步骤, and it controls the overall rate. Only the **species** 微粒 involved up to and including this step appear in the rate equation.



rate-determining step = highest E_a barrier (slowest elementary step)

A two-step profile: the slower step has the bigger barrier and is rate-determining; the dip between the two barriers is an intermediate

- an **intermediate** 中间体 is a species made in one step and then used up in a later step. It is not in the overall equation.
- you can suggest a **mechanism** 反应机理 that fits both the rate equation and the overall equation, predict the order from a given mechanism, or pick out the rate-determining step.

If you compare the initial rate of different mixtures, you can deduce the rate equation, and from that work out the mechanism.

Worked example (mechanism from a rate equation). For $2NO_2 + F_2 \rightarrow 2NO_2F$ the rate equation is rate $= k[NO_2][F_2]$. Suggest a two-step mechanism.

1. The rate equation has one NO_2 and one F_2, so the rate-determining step uses exactly one of each: $NO_2 + F_2 \rightarrow NO_2F + F$ (slow).
2. The second NO_2 must react in a later, fast step, with the F atom made in step 1: $NO_2 + F \rightarrow NO_2F$ (fast).
3. Check: adding the steps and cancelling F gives the overall equation. F is the intermediate.

The same reasoning explains the hydrolysis of 2-bromo-2-methylpropane, rate $= k[(CH_3)_3CBr]$. Hydroxide ions are not in the rate equation, so they react **after** the slow step: the C–Br bond breaks first to give a carbocation, which OH^- then attacks. This is the S_N1 mechanism. A reactant that is zero order is still used up; it just reacts after the rate-determining step.

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Effect of temperature

Raising the temperature increases the rate constant k (more molecules pass the **activation energy** 活化能), so the rate goes up.

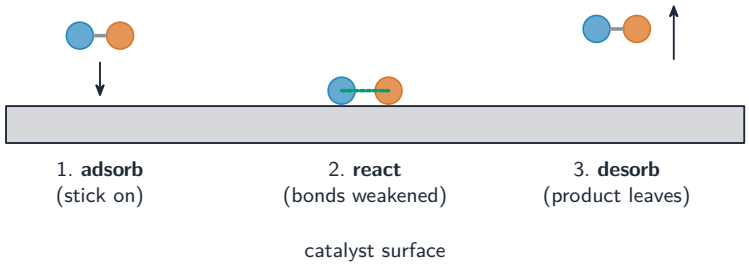
Catalysts

Catalysts 催化剂 can be homogeneous or heterogeneous.

Heterogeneous catalysts

A **heterogeneous catalyst** 多相催化剂 is in a different **physical state** 物态 from the reactants (usually a solid with gases). It works in three stages:

1. **adsorption** 吸附: reactant molecules stick to the catalyst surface.
2. the bonds in the reactants are **weakened** 削弱, so they react more easily.
3. **desorption** 脱附: the product molecules leave the surface.



A heterogeneous catalyst works in three stages: the reactants adsorb onto the surface, their weakened bonds let them react, then the product desorbs

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Real heterogeneous catalysts are made as small shaped pellets, rings and perforated discs, which give a large surface area for the reactants to stick to

Examples are iron in the **Haber process** 哈伯法, and platinum, palladium and rhodium in a **catalytic converter** 催化转化器.

Homogeneous catalysts

A **homogeneous catalyst** 均相催化剂 is in the same physical state as the reactants. It is used up in one step and then **reformed** 再生 in a later step, so it comes back unchanged. Examples are oxides of nitrogen helping to **oxidise** 氧化 **atmospheric** 大气中的 sulfur dioxide, and Fe^{2+} or Fe^{3+} speeding up the reaction between I^- and $S_2O_8^{2-}$.

How the iron ions work. The reaction $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ is slow because both reactants are negative ions, which **repel** 互相排斥 each other, so the activation energy is high. With iron ions it goes in two steps:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

Each step is between a positive and a negative ion, which attract, so each has a lower activation energy. The Fe^{2+} used in the first step is made again in the second, and the steps can run in either order, which is why Fe^{3+} works as well as Fe^{2+}. Iron can do this because it has two stable oxidation states, +2 and +3.

Nitrogen oxides do the same for sulfur dioxide in the air:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2$$

NO_2 is used in the first step and made again in the second; adding the steps gives $SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$.

Common mistakes.

- Taking the orders from the balanced equation. In the NO_2 example above the equation has $2NO_2$, but the order in NO_2 is 1. Orders come only from experiment.
- Saying a zero-order reactant "is not needed" or "does not react". It is used up, but after the rate-determining step.
- Using the half-life to find k for a reaction that is not first order. Only a first-order reaction has a constant half-life.
- Saying k changes when a concentration changes. k changes only with temperature (or a catalyst); a change of concentration changes the rate.
- Mixing up a catalyst and an intermediate. A catalyst is there at the start and made again at the end; an intermediate is made in one step and used up in a later one.

Exam tips

- Find **orders** from initial-rate data: doubling a concentration that doubles the rate is first order, quadruples it is second order, no change is **zero order** 零级.
- Write rate $= k[A]^m[B]^n$ and work out the **units of** k from it.
- The **rate-determining step** contains the species (and orders) in the rate equation – use this to test a mechanism.
- A **constant half-life** means first order.

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Group 2

A-Level Chemistry

Thermal stability of the nitrates and carbonates

The **thermal stability** 热稳定性 of the **Group 2** 第 2 族 **nitrates** 硝酸盐 and **carbonates** 碳酸盐 **increases** down the group. Here is the reason, in terms of how the ions affect each other.



Heating limestone (calcium carbonate) in a kiln decomposes it to calcium oxide – a thermal decomposition

A small **cation** 阳离子 with a small **ionic radius** 离子半径 has a high **charge density** 电荷密度. It pulls on the electrons of the nearby anion and **distorts** 使变形 its shape – this is **polarisation** 极化. Distorting the large **anion** 阴离子 (the carbonate or nitrate ion) weakens a bond inside it, so the compound breaks down more easily.

Going down the group, the cation gets larger. Its charge density drops, so it **polarises** 使极化 the anion **less**. The anion is less distorted, so the compound is harder to break down – it is more **thermally stable** 热稳定的 and needs a higher temperature to **decompose** 分解.



high charge density — **distorts the anion a lot**

less stable: decomposes easily

low charge density — **distorts the anion little**

more stable: needs high heat

A small cation has a high charge density, so it distorts (polarises) the large anion more – weakening it, so the compound is less stable

The equations, with M standing for any Group 2 metal:

$$MCO_3(s) \rightarrow MO(s) + CO_2(g) \qquad 2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g)$$

The data show the trend. Approximate values:

Carbonate	Decomposition temperature / °C	ΔH of decomposition / kJ mol^{-1}
$MgCO_3$	540	+117
$CaCO_3$	900	+178
$SrCO_3$	1290	+235
$BaCO_3$	1360	+267

Decomposition becomes more endothermic down the group, so a higher temperature is needed before $T\Delta S$ outweighs ΔH (topic 23).

Comparing them in the laboratory. Heat equal **amounts in moles** of each carbonate in turn, in identical test tubes over the same Bunsen flame, with a delivery tube dipping into the same volume of limewater. Time how long the limewater takes to turn **cloudy** (milky). The shorter the time, the less stable the carbonate: magnesium carbonate gives cloudiness quickly, barium carbonate only after a long time, or not at all in a Bunsen flame. For the nitrates, watch for the first brown NO_2 gas instead, or test for oxygen with a glowing splint.

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Worked example (predicting). Beryllium is above magnesium in Group 2. Predict how the thermal stability of beryllium carbonate compares with that of magnesium carbonate, and explain. Be^{2+} has the same charge as Mg^{2+} but a much **smaller** ionic radius, so a much **higher charge density**. It polarises the carbonate ion more strongly, weakening its C–O bonds, so beryllium carbonate is **less** stable: it decomposes at a lower temperature. (In fact it is so unstable that it is hard to make at all.)

Worked example. Down Group 2 the **hydroxides** become **more** soluble while the **sulfates** become **less** soluble. Explain why the two trends run in opposite directions. Solubility is a contest between the **lattice energy** holding the solid together and the **hydration energy** rewarding the ions for dissolving. Both get less exothermic as the cation grows, so whichever falls **faster** decides the trend. With the **small** hydroxide ion, the lattice energy depends strongly on the cation's size, so it falls faster than the hydration energy: the lattice gets relatively easier to break and solubility **rises**. With the **large** sulfate ion, the lattice energy is already dominated by that big anion and barely changes down the group, while the cation's hydration energy still falls - so solubility **falls**. Name **both** energies and say which one falls faster; simply restating the trends earns no explanation marks.

Solubility of the hydroxides and sulfates

When an **ionic solid** 离子固体 **dissolves** 溶解, two energy changes compete. The **enthalpy change of solution** 溶解焓变 is the sum of them:

$$\Delta H^{\ominus}_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$$

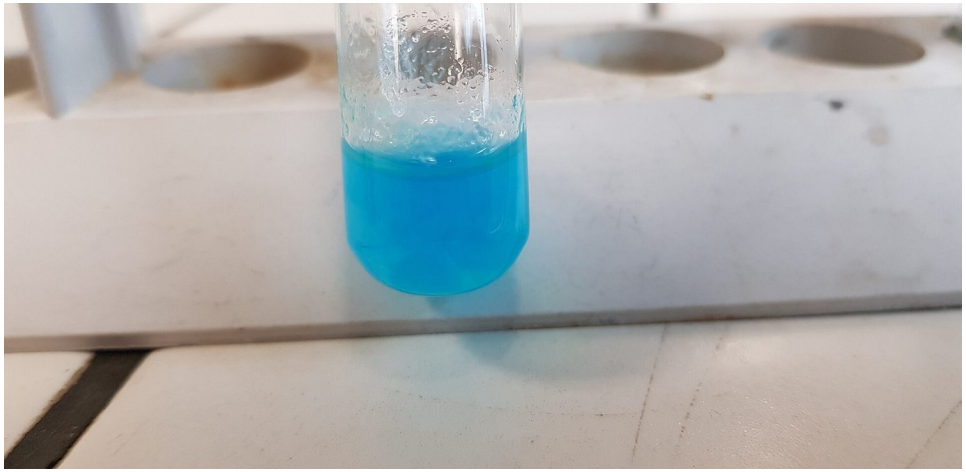
hydroxides
get *more* soluble
down the group

sulfates
get *less* soluble
down the group

Down Group 2 the hydroxides get more soluble but the sulfates less

- you must first pull the **lattice** 晶格 apart (this needs the **lattice energy** 晶格能).
- then water surrounds the **ions** 离子 (this releases the **enthalpy change of hydration** 水合焓变).

If the energy released on hydration roughly matches (or beats) the energy needed to break the lattice, the solid dissolves easily.



An insoluble metal hydroxide forms as a gelatinous precipitate when its lattice energy is too large to be repaid by hydration

Going down the group, both the lattice energy and the **hydration enthalpy** 水合焓 get **smaller** (less negative), because the cation is larger. But they shrink at different rates, and this explains the opposite **trends** 趋势:

Compound	**Trend in solubility 溶解度 down the group**	**Why**
hydroxides 氢氧化物	increases	the OH^- ion is small, so the lattice energy falls a lot down the group; this change **outweighs** 超过 the fall in hydration energy
sulfates 硫酸盐	decreases	the SO_4^{2-} ion is large, so the lattice energy stays almost the same; the fall in hydration energy then **dominates** 起主导作用, so dissolving becomes less **favourable** 有利的

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$$\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$$

hydroxides (small OH^-):
lattice energy falls *a lot* down the group
⇒ outweighs the smaller hydration fall → **more** soluble

sulfates (large SO_4^{2-}):
lattice energy stays almost constant
⇒ the hydration fall then dominates → **less** soluble

Why the trends are opposite: the small OH^- lattice energy falls a lot down the group (hydroxides dissolve more), but the large SO_4^{2-} lattice energy barely changes (sulfates dissolve less)

Using the trends.

- **Barium sulfate** is so insoluble that it precipitates when barium ions meet sulfate ions. This is the **test for sulfate**: add acidified barium chloride (or nitrate) solution, and a white precipitate forms. Swallowed barium sulfate is safe for X-ray images of the gut because it does not dissolve, so toxic Ba^{2+} ions are not absorbed.
- **Magnesium hydroxide** is only very slightly soluble, so its suspension is a mild alkali: it is used in indigestion remedies ("milk of magnesia"). **Calcium hydroxide** is more soluble, and its solution is limewater; barium hydroxide gives a strongly alkaline solution.
- A saturated solution of each hydroxide, tested with a pH meter, shows the trend: the pH **rises** down the group, because more OH^- ions are in solution.

Common mistakes.

- Saying the **anion** polarises the cation. The small, highly charged **cation** polarises (distorts) the large carbonate or nitrate **anion**.
- Explaining thermal stability by "bigger atoms" or "more shells" alone. Link the size to **charge density**: a larger cation with the same 2+ charge has a lower charge density, so it polarises the anion less.
- Saying a larger lattice energy makes a solid more soluble. A more exothermic lattice energy means **more** energy is needed to break the lattice, so it makes dissolving **less** favourable.
- Explaining the sulfate trend by the lattice energy falling. For the large SO_4^{2-} ion the lattice energy hardly changes; it is the fall in **hydration enthalpy** that makes the sulfates less soluble.
- Forgetting the oxygen when a nitrate decomposes. Group 2 nitrates give the oxide, brown $\mathbf{NO_2}$ and $\mathbf{O_2}$: $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$.

Exam tips

- Thermal stability of carbonates and nitrates **increases down** the group – larger cations polarise the anion less.
- Give the **decomposition products** 分解产物: carbonates → **oxide** 氧化物 + CO_2; nitrates → oxide + NO_2 + O_2 (brown gas).
- Hydroxides get more **soluble** 可溶的 and sulfates less soluble down the group.
- Explain trends with cation charge density (**polarising power** 极化能力), not just size.
- In a practical comparison, use the same **number of moles** of each carbonate and the same heating, and time the limewater turning cloudy.

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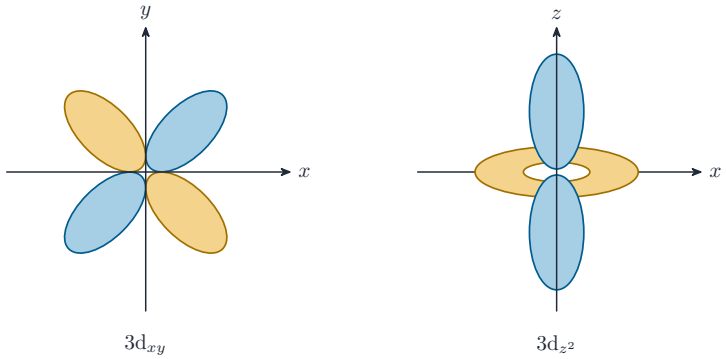
Chemistry of transition elements

A-Level Chemistry

Transition elements

A **transition element** 过渡元素 is a d-block element that forms one or more stable ions with **incomplete d orbitals**. (Scandium and zinc are in the d-block but are not transition elements, because their stable ions have empty or full d orbitals.)

The 3d **orbitals** 轨道 have set shapes: the $3d_{xy}$ orbital has four lobes pointing between the axes, and the $3d_{z^2}$ orbital has two lobes along the z-axis with a ring around the middle.



$3d_{xy}$

four lobes **between** the x and y axes

$3d_{z^2}$

two lobes **along** the z axis, with a ring round the middle

The 3dxy orbital has four lobes between the x and y axes; the 3dz2 orbital has two lobes along the z axis and a ring around the middle

When you sketch them, label the axes. The $3d_{xy}$ lobes point **between** the axes (the $3d_{x^2-y^2}$ orbital is the one whose lobes lie along them), and the $3d_{z^2}$ ring lies in the xy plane.

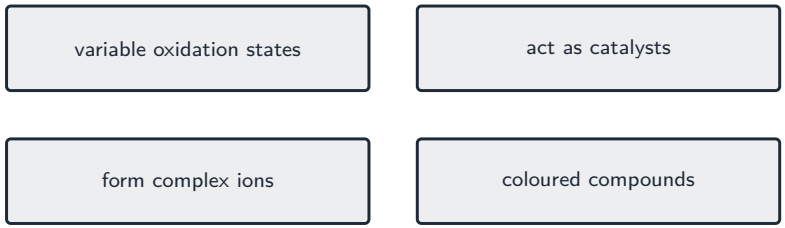
Four key properties (and why)

Property	Reason
variable **oxidation state** 氧化态	the 3d and 4s sub-shells are close in energy, so similar small amounts of energy remove different numbers of electrons
act as a **catalyst** 催化剂	they have more than one stable oxidation state, and vacant d orbitals that can form dative bonds
form complex ions	vacant d orbitals can accept lone pairs
form coloured compounds	electrons move between split d orbitals (see below)

Catalysts at work. Iron is the catalyst in the Haber process (a **heterogeneous catalyst** 多相催化剂: a solid surface that the gases adsorb onto). In solution, Fe^{2+} or Fe^{3+} is a **homogeneous catalyst** 均相催化剂 for the slow reaction between peroxodisulfate and iodide ions, because it can switch between two oxidation states:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}, \qquad 2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2.$$

The direct reaction is slow because two negative ions repel each other; each catalysed step involves oppositely charged ions, so the activation energy is lower. The iron ends as Fe^{2+}, unchanged overall.



The four key properties of the transition elements

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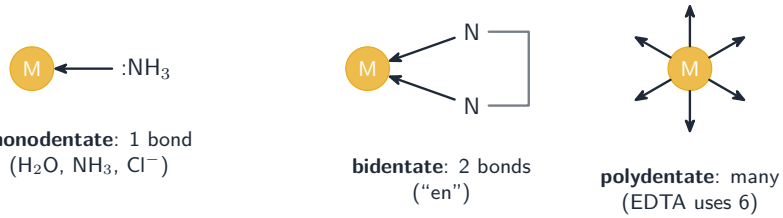
A ruby is red because of transition-metal (chromium) ions held in its crystal lattice

Ligands and complexes

A transition metal ion can be surrounded by molecules or ions called ligands, which bond to it to make **complex ions** 配离子.

A **ligand** 配体 is a species with a lone pair of electrons that forms a **dative covalent bond** 配位键 to the central metal ion. (The **lone pair** 孤对电子 is what it donates.) Ligands are grouped by how many such bonds they can form:

- **monodentate** 单齿: one bond (H_2O, NH_3, Cl^-, CN^-).
- **bidentate** 双齿: two bonds (1,2-diaminoethane "en", and the ethanedioate ion $C_2O_4^{2-}$).
- **polydentate** 多齿: many bonds ($EDTA^{4-}$, which uses six).



Ligands are grouped by how many dative bonds they form: monodentate (one), bidentate (two) or polydentate (many, like EDTA's six)

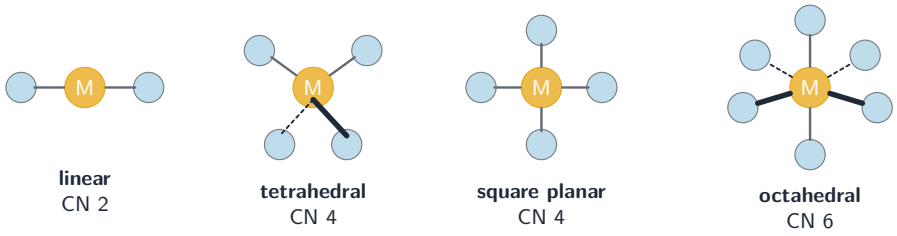
A **complex** 配合物 is a central metal atom or ion surrounded by one or more ligands. Its shape can be **linear** 直线形, **square planar** 平面正方形, **tetrahedral** 四面体形

or **octahedral** 八面体形.

The **coordination number** 配位数 is the number of dative bonds from the ligands to the central ion (6 → octahedral, 4 → tetrahedral or square planar, 2 → linear). To predict the charge of a complex, add the metal's charge and all the ligand charges.

> **Worked example: formula and charge.** Predict the formula of the complex formed by Fe^{3+} with six cyanide ligands, and of the complex of Ni^{2+} with three 1,2-diaminoethane (en) ligands. Give each coordination number and shape.

Fe^{3+} with six CN^-: the charge is $+3 + 6(-1) = -3$, so $[Fe(CN)_6]^{3-}$, coordination number 6, octahedral, bond angles 90°. Each en is neutral and bidentate, so three en give 6 dative bonds: $[Ni(en)_3]^{2+}$, coordination number 6, octahedral. The other bond angles to learn are 180° (linear), 109.5° (tetrahedral) and 90° (square planar).



Complex shapes follow the coordination number: 2 is linear, 4 is tetrahedral or square planar, 6 is octahedral

Ligand exchange

In **ligand exchange** 配体交换 one ligand replaces another, often with a colour change. For copper(II):

$$[Cu(H_2O)_6]^{2+}\ \text{(pale blue)} \xrightarrow{NH_3} [Cu(NH_3)_4(H_2O)_2]^{2+}\ \text{(deep blue)}$$

With concentrated HCl it becomes yellow $[CuCl_4]^{2-}$; cobalt(II) behaves in a similar way. Here the **coordination number** also changes, from 6 to 4, and the shape changes from octahedral to tetrahedral, because the chloride ions are larger than water molecules, so only four fit around the metal ion.

Learn the full set of reactions for both ions. Exams give the reagent and ask for the formula, the colour **and state**, and the type of reaction:

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Start: $[M(H_2O)_6]^{2+}$	**Copper(II): pale blue solution**	**Cobalt(II): pink solution**
a little NaOH(aq) or NH_3(aq)	$Cu(OH)_2$, pale blue **precipitate** (acid–base / precipitation: OH^- removes H^+ from water ligands)	$Co(OH)_2$, blue precipitate (turns pink on standing)
excess NaOH(aq)	the precipitate stays	the precipitate stays
excess NH_3(aq)	$[Cu(NH_3)_4(H_2O)_2]^{2+}$, deep blue solution (ligand exchange)	$[Co(NH_3)_6]^{2+}$, pale brown (straw) solution (ligand exchange); darkens in air as it is oxidised to cobalt(III)
excess concentrated HCl	$[CuCl_4]^{2-}$, yellow solution (green part-way) (ligand exchange)	$[CoCl_4]^{2-}$, blue solution (ligand exchange)

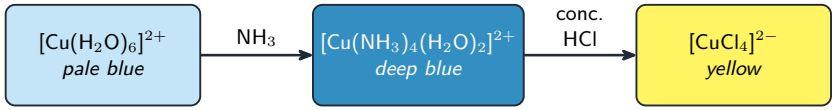
The equations show the change of ligand and the charge:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$$

Ammonia first acts as a **base** (it makes OH^- ions, giving the hydroxide precipitate); only in excess does it act as a **ligand** and dissolve the precipitate.



Ligand exchange changes the colour of copper(II): pale blue with water, deep blue with ammonia, yellow with concentrated HCl

Redox reactions of transition ions

Use $E^\ominus$ values to predict whether a redox reaction is feasible. Write both half-equations as reductions. The one with the **more positive** $E^\ominus$ goes forward as a reduction; the other goes backwards as an oxidation. The reaction is feasible if $E^\ominus_{cell} = E^\ominus(\text{reduced}) - E^\ominus(\text{oxidised})$ is positive.

> **Worked example: feasibility.** Can Fe^{3+} ions oxidise iodide ions? Can they oxidise bromide ions? Use $Fe^{3+}/Fe^{2+} = +0.77$ V, $I_2/I^- = +0.54$ V, $Br_2/Br^- = +1.07$ V.

For iodide, $E^\ominus_{cell} = 0.77 - 0.54 = +0.23$ V, positive, so it is feasible: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$. For bromide, $0.77 - 1.07 = -0.30$ V, negative, so it is not feasible. A feasible reaction may still be too slow to see, because $E^\ominus$ says nothing about rate, and non-standard concentrations can change the result.

Common titrations you should be able to calculate include $MnO_4^-/C_2O_4^{2-}$ and MnO_4^-/Fe^{2+} in acid (the purple MnO_4^- is decolourised as it reacts; the end point is the first permanent pale pink), and Cu^{2+}/I^- (which makes iodine, then titrated with thiosulfate).

> **Worked example.** In acid, MnO_4^- reacts with Fe^{2+} in the ratio 1 : 5: $MnO_4^- + 5Fe^{2+} + 8H^+ \to Mn^{2+} + 5Fe^{3+} + 4H_2O$. A 25.0 cm^3 sample of Fe^{2+} solution needs 22.0 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ to reach the end point. Find the concentration of the Fe^{2+}.

Moles of MnO_4^- used $= 0.0200 \times \dfrac{22.0}{1000} = 4.40 \times 10^{-4}$ mol. Each mole of MnO_4^- reacts with 5 moles of Fe^{2+}, so moles of $Fe^{2+} = 5 \times 4.40 \times 10^{-4} = 2.20 \times 10^{-3}$ mol. This was in 25.0 cm^3, so

$$[Fe^{2+}] = \frac{2.20 \times 10^{-3}}{25.0/1000} = 0.0880 \text{ mol dm}^{-3}.$$

> **Worked example: manganate(VII) and ethanedioate.** The equation is $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \to 2Mn^{2+} + 10CO_2 + 8H_2O$. What volume of 0.0200 mol dm^{-3} $KMnO_4$ reacts with 25.0 cm^3 of 0.0500 mol dm^{-3} sodium ethanedioate?

Moles of $C_2O_4^{2-} = 0.0500 \times 0.0250 = 1.25 \times 10^{-3}$. The ratio is 2 : 5, so moles of $MnO_4^- = \frac{2}{5} \times 1.25 \times 10^{-3} = 5.00 \times 10^{-4}$, and the volume is $\dfrac{5.00 \times 10^{-4}}{0.0200} = 0.0250$ dm^3 $= 25.0$ cm^3. This titration is done warm (about 60°C), because the reaction is slow at first; the Mn^{2+} it makes then catalyses it (**autocatalysis** 自催化).

> **Worked example: copper(II) and iodide.** Excess potassium iodide is added to 25.0 cm^3 of a copper(II) solution. The iodine formed needs 21.6 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate, with starch added near the end point (blue-black to white). Find $[Cu^{2+}]$.

$$2Cu^{2+} + 4I^- \to 2CuI + I_2, \qquad I_2 + 2S_2O_3^{2-} \to 2I^- + S_4O_6^{2-}.$$

2 mol Cu^{2+} give 1 mol I_2, which needs 2 mol $S_2O_3^{2-}$, so the overall ratio $Cu^{2+} : S_2O_3^{2-}$ is 1 : 1. Moles of thiosulfate $= 0.100 \times 0.0216 = 2.16 \times 10^{-3}$, so $[Cu^{2+}] = \dfrac{2.16 \times 10^{-3}}{0.0250} = 0.0864$ mol dm^{-3}. The white precipitate is copper(I) iodide, CuI; the mixture looks off-white or beige because of the iodine.

For any other redox system, the method is the same: write or balance the equation, find the moles of the reagent you know, use the **mole ratio**, then scale to the volume or mass asked for.

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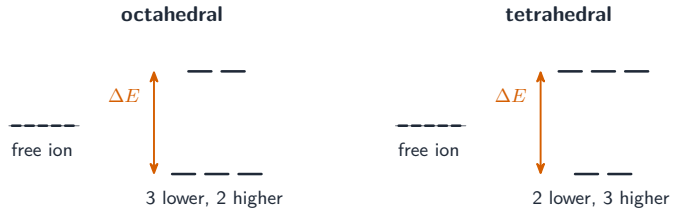
Why complexes are coloured

In a free ion the five d orbitals are **degenerate** 简并 – they have the same energy. When ligands come close, they split the d orbitals into two **non-degenerate** 非简并 sets, separated by an energy gap ΔE:

- **octahedral**: three lower and two higher orbitals.
- **tetrahedral**: two lower and three higher orbitals.

A complex absorbs light whose frequency matches ΔE, promoting an electron from a lower to a higher d orbital. The colour you **see** is the **complementary colour** 互补色 of the light absorbed. Different ligands give a different ΔE, so they change the frequency absorbed and hence the colour – which is why ligand exchange changes the colour.

In qualitative terms, ligands such as NH_3 and CN^- split the d orbitals **more** than H_2O, and Cl^- splits them **less**. A larger ΔE means light of a **higher frequency** (shorter wavelength) is absorbed, so the colour seen changes. For copper(II): $[Cu(H_2O)_6]^{2+}$ absorbs mostly red and orange light and looks pale blue; $[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a larger ΔE, absorbs higher-frequency yellow-orange light, and looks deep blue-violet. A tetrahedral complex has a smaller ΔE than an octahedral one of the same ion.



the complex absorbs light of energy ΔE, so we see the **complementary colour**

Ligands split the five d orbitals into two sets separated by a gap ΔE; the complex absorbs light of that energy, so we see the complementary colour



Different metals and oxidation states give different colours: cobalt(II) (red), dichromate (orange), chromate (yellow), nickel(II) (green), copper(II) (blue) and permanganate (violet)

Stereoisomerism in complexes

- **geometrical isomerism** 几何异构 (**cis** 顺式 / **trans** 反式) appears in square planar complexes such as $[Pt(NH_3)_2Cl_2]$, and in octahedral complexes such as $[Co(NH_3)_4(H_2O)_2]^{2+}$.

square planar $[Pt(NH_3)_2Cl_2]$



cis (same side) **trans** (opposite)

Geometrical isomerism in a square planar complex: the two identical ligands are adjacent (cis) or opposite (trans)

- **optical isomerism** 旋光异构 appears in octahedral complexes with bidentate ligands, such as $[Ni(en)_3]^{2+}$, which has two non-superimposable mirror images.

You can also deduce the polarity of a complex: a *cis* form may be polar, while the matching *trans* form is often non-polar because its dipoles cancel.

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Worked example: polarity. Which isomers of $[Pt(NH_3)_2Cl_2]$ and $[Co(NH_3)_4(H_2O)_2]^{2+}$ are polar? In *trans*-$[Pt(NH_3)_2Cl_2]$ the two Pt–Cl dipoles point in opposite directions and cancel, so it is **non-polar**; in the *cis* isomer they do not cancel, so it is **polar**. The same reasoning gives polar *cis* and non-polar *trans* for $[Co(NH_3)_4(H_2O)_2]^{2+}$. *Cis*-$[Pt(NH_3)_2Cl_2]$ is the anticancer drug **cisplatin** 顺铂; the *trans* isomer does not work, because its shape cannot bind to DNA in the same way.

Complexes with **two or three bidentate** ligands can show both types. *Cis*-$[Co(en)_2Cl_2]^+$ is chiral, so it has two optical isomers; *trans*-$[Co(en)_2Cl_2]^+$ has a plane of symmetry and is not chiral. So this complex has **three** stereoisomers in total.

Stability constants

The **stability constant** 稳定常数 (K_{stab}) is the equilibrium constant for forming a complex ion from the metal ion and its ligands in solution (water is left out of the expression).

For the copper–ammonia exchange:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2^{2+}]}{[Cu(H_2O)_6^{2+}]\,[NH_3]^4}, \qquad \text{units: } \mathrm{mol^{-4}\,dm^{12}}.$$

Water is the solvent, so its concentration is effectively constant and it is left out. Work out the units from the powers: here $\dfrac{\mathrm{mol\ dm^{-3}}}{(\mathrm{mol\ dm^{-3}})^5} = \mathrm{mol^{-4}\,dm^{12}}$.

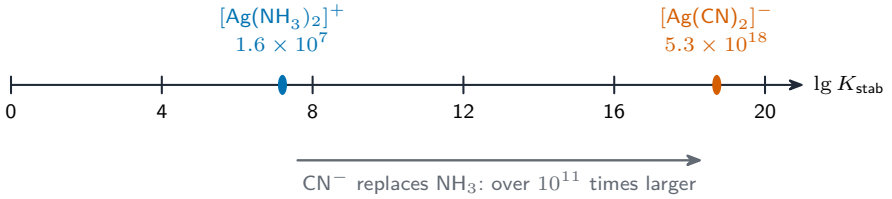
Worked example: combining equilibrium constants. Silver chloride dissolves in aqueous ammonia: $AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$. Given $K_{sp}(AgCl) = 1.8 \times 10^{-10}\ \mathrm{mol^2\,dm^{-6}}$ and $K_{stab}([Ag(NH_3)_2]^+) = 1.6 \times 10^{7}\ \mathrm{mol^{-2}\,dm^{6}}$, find K_c.

$$K_c = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = [Ag^+][Cl^-] \times \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = K_{sp} \times K_{stab}.$$

So $K_c = 1.8 \times 10^{-10} \times 1.6 \times 10^{7} = 2.9 \times 10^{-3}$, with **no units** (they cancel). The trick is to multiply top and bottom by $[Ag^+]$ so that the two known expressions appear.

A **large** K_{stab} means a very stable complex. In a ligand exchange, the position moves towards the complex with the larger K_{stab} – that is why a ligand that forms a more stable complex can push out a weaker one.

Worked example: comparing K_{stab}. Silver(I) ions are added to a solution with equal concentrations of CN^- and NH_3. K_{stab} is 5.3×10^{18} for $[Ag(CN)_2]^-$ and 1.6×10^{7} for $[Ag(NH_3)_2]^+$ (same units). Which complex forms? The one with the larger K_{stab}, $[Ag(CN)_2]^-$: its equilibrium lies much further to the right, so it is the more stable complex, and adding cyanide to $[Ag(NH_3)_2]^+$ would replace the ammonia. Bidentate and polydentate ligands usually give larger K_{stab} values than monodentate ones, so en or EDTA replaces water or ammonia easily.



The complex with the larger stability constant wins the ligand exchange.

Common mistakes.

- Taking electrons from 3d first when you write the ion's configuration. The **4s** electrons are lost first: Fe is $[Ar]\,3d^6 4s^2$, so Fe^{2+} is $[Ar]\,3d^6$, not $[Ar]\,3d^4 4s^2$.
- Saying a complex gives out the colour you see. It **absorbs** some frequencies; you see the remaining light, the complementary colour.
- Saying the electron jumps from 3d to 4s. In a d–d transition it moves between the two sets of **split 3d** orbitals.
- Saying the coordination number is the number of ligands. It is the number of **dative bonds**: $[Ni(en)_3]^{2+}$ has three ligands but a coordination number of 6.
- Forgetting the ligand charges when you work out the charge on a complex: Cu^{2+} with four Cl^- gives $[CuCl_4]^{2-}$.
- Expecting Zn^{2+} or Sc^{3+} compounds to be coloured. With a full ($3d^{10}$) or empty ($3d^0$) d sub-shell there is no d–d transition, so they are white.

Exam tips

- Define a **transition element**: it forms at least one ion with a **partially filled d sub-shell** – so Sc and Zn are excluded.
- Colour comes from **d-d transitions** (ligands split the d orbitals); the colour seen is the complement of the light absorbed.
- State the **ligand and coordination number** and predict the shape (6 = octahedral, 4 = tetrahedral or square planar).

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- **Ligand exchange** can change colour and coordination number; a larger stability constant = a more stable complex.
- For copper(II) and cobalt(II), learn formula, colour **and state** with OH^-, NH_3 (a little and excess) and concentrated HCl; a hydroxide product is a **precipitate**.
- Write K_{stab} without $[H_2O]$ and give its units from the powers.
- In a redox titration, the **mole ratio** from the balanced equation is the key step: $MnO_4^- : Fe^{2+} = 1:5$, $MnO_4^- : C_2O_4^{2-} = 2:5$, $Cu^{2+} : S_2O_3^{2-} = 1:1$.
- Sketch $3d_{xy}$ (lobes between the axes) and $3d_{z^2}$ (lobes along z plus a ring), with labelled axes.

An introduction to A Level organic chemistry

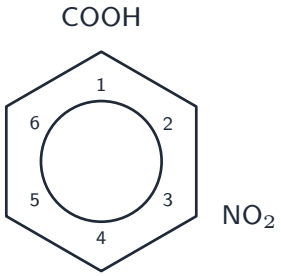
A-Level Chemistry

New functional groups and naming

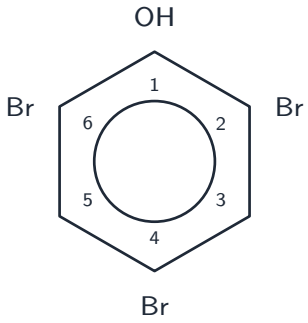
At A Level you meet more **functional group** 官能团 families, including the **amide** 酰胺 group and **aromatic** 芳香 compounds (those built on a benzene ring). As before, the functional group decides the properties, and you read it from the general, structural, displayed or skeletal formula.

Naming aromatic compounds

A **benzene** 苯 molecule is a ring of six carbons. When you name an aromatic compound, use the **benzene ring** 苯环 as the parent and number the positions of the substituents. For example, 3-nitrobenzoic acid has a $-NO_2$ group on carbon 3, and 2,4,6-tribromophenol has three bromine atoms on a phenol ring. You can also name cyclic compounds with a single ring of up to six carbons.



3-nitrobenzoic acid



2,4,6-tribromophenol

Number the ring from the principal group (carbon 1); the substituent positions then give the name

Systematic names: suffixes and prefixes

The **principal** functional group gives the **suffix** 后缀 (the end of the name); other groups are written as **prefixes** 前缀 in alphabetical order, each with a number.

Group	As the suffix	As a prefix	Example
carboxylic acid –COOH	-oic acid	–	butanoic acid
ester –COO–	alkyl ...-oate	–	ethyl propanoate
acyl chloride –COCl	-oyl chloride	–	ethanoyl chloride
amide $-CONH_2$	-amide	–	propanamide
nitrile $-C \equiv N$	-nitrile (the C counts in the chain)	cyano-	propanenitrile
aldehyde –CHO	-al	–	butanal
ketone C=O	-one	oxo-	pentan-2-one
alcohol –OH	-ol	hydroxy-	propan-2-ol
amine $-NH_2$	-amine	amino-	ethylamine
halogen	–	chloro-, bromo-, iodo-	chloroethane
on a benzene ring	–	nitro-, methyl-, phenyl-	methylbenzene; phenylamine

The groups higher in the table take priority for the suffix: in $CH_3CH(OH)COOH$ the acid wins, so the name is 2-hydroxypropanoic acid. For an **ester**, the part from the alcohol comes first as an alkyl word and the part from the acid gives the "-oate": $CH_3COOCH_2CH_3$ is ethyl ethanoate. In an amide, an alkyl group on the nitrogen is shown with *N*-, as in *N*-methylethanamide, $CH_3CONHCH_3$; an amino acid such as $CH_3CH(NH_2)COOH$ is 2-aminopropanoic acid. A ring of carbons takes **cyclo-**: cyclohexane, cyclohexanol, cyclopentene.

> **Worked example.** Name $CH_3CHBrCH_2COOH$ and $HOCH_2CH_2COCH_3$. In the first, the acid is the principal group, so its carbon is C1; the chain has four carbons with Br on C3: **3-bromobutanoic acid**. In the second, the ketone is the principal group and the chain is numbered from the end that gives it the lowest number: C=O on C2, OH on C4: **4-hydroxybutan-2-one**.

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Reading skeletal formulas

In a **skeletal formula** 骨架式, each line end and each corner is a carbon atom; hydrogens on carbon are not drawn, but every other atom (and the H on O or N) is. Each carbon has four bonds, so count the lines at a corner and add hydrogens to make four. A hexagon with a circle inside is a benzene ring. To find a molecular formula from a skeletal one, count the carbons, then work out each carbon's hydrogens in turn.

Two new types of mechanism

- **electrophilic substitution** 亲电取代: an electrophile replaces a hydrogen atom on a benzene ring (this is how benzene reacts).
- **addition–elimination** 加成消去: a molecule first adds on, then a small molecule is removed (seen with 2,4-DNPH and with acyl chlorides).

electrophilic substitution
an electrophile replaces an H
on a benzene ring

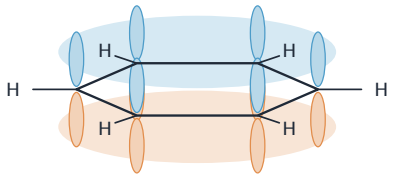
addition–elimination
a molecule adds on, then
a small molecule is removed

Two aromatic mechanisms: electrophilic substitution and addition-elimination

The shape of benzene

Benzene is a flat, regular hexagon. Each carbon is $\mathbf{sp^2}$ hybridised: **hybridisation** 杂化 mixes its 2s orbital and two of its 2p orbitals into three equal hybrid orbitals. The carbon uses these three orbitals to make **sigma bonds** σ 键 to two neighbouring carbons and one hydrogen. This gives the ring of σ bonds.

Each carbon also has one electron left in a p orbital, standing up at right angles to the ring. These p orbitals overlap sideways all the way round, making a single **delocalised** 离域 **pi bond** π 键 system – a ring of electrons above and below the plane. Because the electrons are shared evenly, all six C–C bonds are the same length, and benzene is very stable.



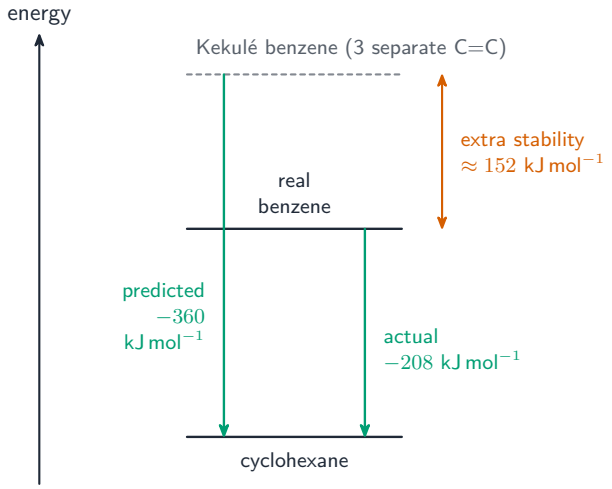
one **delocalised** π system
above and below the ring

sp^2 σ framework;
all six C–C bonds equal

Benzene's bonding: an sp^2 σ framework makes the flat hexagon, while the p orbitals overlap into one delocalised π system above and below the ring

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How do we know benzene really is delocalised? One strong piece of evidence is its **enthalpy change of hydrogenation** 氢化焓变. Adding hydrogen to one C=C double bond (as in cyclohexene) releases about 120 kJ mol^{-1}, so a Kekulé ring of three separate double bonds should release about $3 \times 120 = 360$ kJ mol^{-1}. Real benzene releases only 208 kJ mol^{-1} – it is about 152 kJ mol^{-1} **more stable** than the model predicts.



Evidence for delocalisation: real benzene releases far less on hydrogenation (-208 kJ mol^{-1}) than the Kekulé model predicts ($-360 = 3\times$ cyclohexene), so it is about 152 kJ mol^{-1} more stable than expected

Optical isomerism

Two **enantiomers** 对映体 (mirror-image isomers) have **identical** physical and chemical properties, with two exceptions:

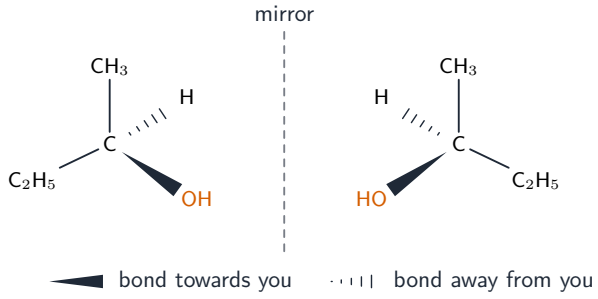
- they rotate **plane polarised light** 平面偏振光 in opposite directions. A substance that does this is **optically active** 旋光活性.
- they may have different effects in living things (biological activity).

A **racemic mixture** 外消旋混合物 is a 50:50 mix of the two enantiomers. It does **not** rotate plane polarised light, because the two opposite rotations cancel out.

Measuring it. Plane polarised light has its vibrations in one plane only. Pass it through a solution of one enantiomer, and the plane is turned through an angle, for example +12° (clockwise). The same concentration of the other enantiomer turns it by the same angle the other way, −12°. A racemic mixture gives 0°.

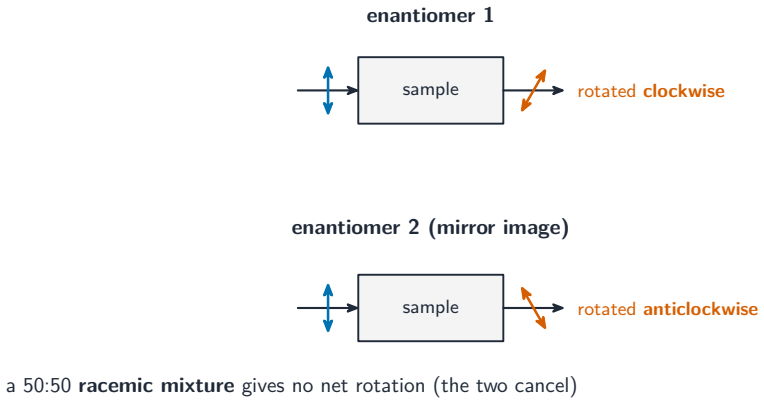
Drawing enantiomers. Draw the chiral carbon with two bonds in the plane of the

page (plain lines), one **coming towards** you (a solid wedge) and one **going away** (a hashed wedge). Then draw its mirror image beside a dashed mirror line: the groups are swapped left to right. Check: no rotation of one molecule can make it fit exactly on top of the other – they are **non-superimposable**.



The two enantiomers of butan-2-ol are mirror images that cannot be superimposed

More than one chiral centre. A molecule can have several chiral carbons. Each one can have two arrangements, so a molecule with n chiral centres can have up to 2^n optical isomers. For example 3-chlorobutan-2-ol, $CH_3CH(OH)CHClCH_3$, has chiral centres at C2 and C3, so it has up to $2^2 = 4$ optical isomers. Mark each chiral centre with an asterisk (*) when asked to identify them.



a 50:50 **racemic mixture** gives no net rotation (the two cancel)

The two enantiomers rotate plane-polarised light in opposite directions; a 50:50 racemic mixture gives no net rotation

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Why chirality matters for drugs

Chirality 手性 is important when making medicines. A molecule with a **chiral centre** 手性中心 has two enantiomers, and they can behave very differently in the body – one may cure while the other does harm. So drug makers either:

- separate a racemic mixture into the two pure enantiomers, or
- use a **chiral catalyst** 手性催化剂 to make just the single enantiomer they want.

Why the two enantiomers behave differently: drug molecules act by fitting into **receptors** 受体 and enzymes in the body, which are made of chiral amino acids. Like a right hand in a right-hand glove, only one enantiomer has the right shape to fit. The other may do nothing, or bind somewhere else and cause side effects. The famous case is **thalidomide**, given to pregnant women in the 1950s: one enantiomer eased morning sickness, but the other caused serious birth defects. Making a single enantiomer is better for patients and for cost: the dose is halved, no money is spent making a useless or harmful isomer, and there are fewer side effects. Separating a racemic mixture is slow and expensive, and half of the product is wasted, which is why chiral catalysts (and enzymes, which are naturally chiral) are preferred.

> **Worked example.** Which of butan-1-ol, butan-2-ol and 2-methylpropan-2-ol is **chiral**? A molecule is chiral if it has a carbon carrying **four different** groups. In butan-2-ol, $CH_3CH(OH)CH_2CH_3$, carbon 2 carries OH, H, CH_3 and C_2H_5 - four different groups, so it is a **chiral centre** and butan-2-ol exists as two optical isomers. Butan-1-ol's carbon 1 carries **two hydrogens**, and the central carbon of 2-methylpropan-2-ol carries **two identical methyl** groups, so neither is chiral. It takes only **one** repeated group on a carbon to destroy the chirality there - and compare groups properly: CH_3 and C_2H_5 differ only beyond the first atom.

Common mistakes.

- Drawing benzene as three fixed C=C double bonds and explaining its reactions that way. The six p electrons are **delocalised** round the ring, so all C–C bonds are the same length and benzene resists addition.
- Getting the stability sign wrong. Benzene releases **less** energy on hydrogenation (208 against the Kekulé 360 kJ mol^{-1}), so it is **more** stable than the Kekulé model.
- Calling a carbon chiral when two of its groups are the same element. The four **groups** must be different as whole groups: CH_3 and C_2H_5 count as different.
- Saying enantiomers have different boiling points or react differently with ordinary reagents. Their physical and chemical properties are **identical**; only the direction they rotate plane-polarised light and their effect in the body differ.
- Saying a racemic mixture is optically inactive because it has no chiral centre. Each molecule **is** chiral; the 50:50 mixture shows no rotation because the two opposite rotations **cancel**.

- Numbering a substituted benzene ring to give large locants. Number from the parent group (for example the –COOH of benzoic acid, carbon 1) and give the other substituents the **lowest** numbers.

Exam tips

- **Optical isomers** need a **chiral carbon** (four different groups); they are non-superimposable mirror images that rotate plane-polarised light oppositely.
- A **racemic mixture** forms when a **planar intermediate** (carbocation or C = O) is attacked equally from both sides.
- Benzene's **delocalised** ring (equal bond lengths, planar) explains its stability versus the Kekulé model.
- New mechanisms: electrophilic substitution and nucleophilic addition–elimination.
- In a name, the highest-priority group gives the suffix and carbon 1; the rest are prefixes in alphabetical order.
- A molecule with n chiral centres can have up to 2^n optical isomers; mark each with an asterisk.
- For drug synthesis, give the reasons for one enantiomer: only one fits the receptor, the other may be harmful, and a single isomer halves the dose and avoids separation costs.

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Hydrocarbons

A-Level Chemistry

Arenes

Arenes 芳烃 are aromatic hydrocarbons, built on the **benzene** 苯 ring. The delocalised ring of electrons is stable and electron-rich, so benzene mostly reacts by **electrophilic substitution** 亲电取代 – keeping the ring – rather than by addition.



Naphthalene, used in mothballs, is a simple arene – two benzene rings fused together

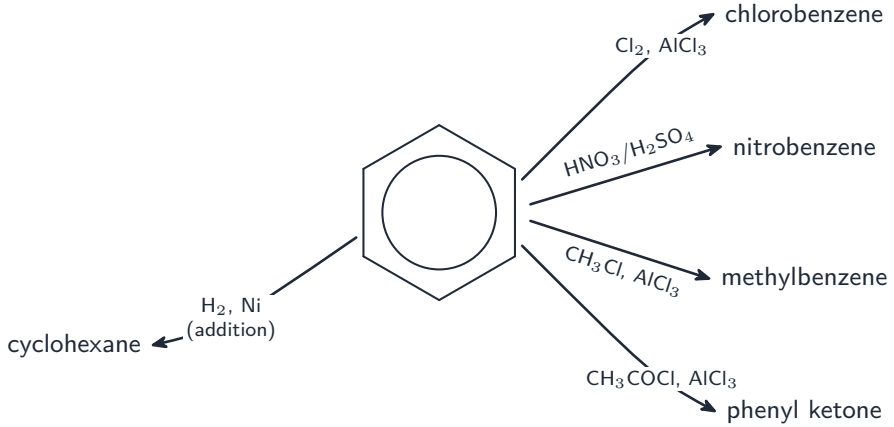
Reactions of benzene and methylbenzene

Reaction	Reagents and conditions	Product
halogenation	Cl_2 or Br_2, with $AlCl_3$ or $AlBr_3$ as a **catalyst** 催化剂	a **halogenoarene** 卤代芳烃 (aryl halide)
nitration 硝化	concentrated HNO_3 + concentrated H_2SO_4, 25–60 °C	nitrobenzene
Friedel–Crafts alkylation 傅克烷基化	CH_3Cl + $AlCl_3$, heat	methylbenzene (adds an alkyl group)
Friedel–Crafts acylation 傅克酰基化	CH_3COCl + $AlCl_3$, heat	a phenyl ketone (adds an acyl group)
side-chain oxidation	hot alkaline $KMnO_4$, then dilute acid	**benzoic acid** 苯甲酸
hydrogenation 氢化	H_2, Pt/Ni catalyst, heat	cyclohexane



Friedel-Crafts: alkylation adds an alkyl group, acylation an acyl group

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Benzene keeps its stable ring, reacting mostly by electrophilic substitution (and by addition only with hydrogen)

In the side-chain oxidation, the whole **side-chain** 侧链 (such as the $-CH_3$ on methylbenzene) is turned into a –COOH group, giving benzoic acid. In the hydrogenation, three molecules of H_2 add to the **benzene ring** 苯环 to make a saturated cyclohexane ring.

Equations to learn. Write benzene as C_6H_6 and a phenyl group as C_6H_5-:

$$C_6H_6 + Br_2 \xrightarrow{AlBr_3} C_6H_5Br + HBr$$

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

$$C_6H_5CH_3 + 3[O] \rightarrow C_6H_5COOH + H_2O \qquad C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

The acylation product, $C_6H_5COCH_3$, is phenylethanone. Side-chain oxidation turns **any** alkyl side-chain into a single –COOH on the ring, however long it was: ethylbenzene also gives benzoic acid (the other carbons leave as CO_2). In alkaline $KMnO_4$ the product is first the benzoate ion, so dilute acid is added afterwards to give benzoic acid, which then crystallises out. The purple manganate(VII) is reduced to a brown precipitate of MnO_2.

Methylbenzene reacts faster than benzene and gives a mixture of products, because the methyl group directs to positions 2 and 4: nitration gives 2-nitromethylbenzene and 4-nitromethylbenzene. Nitration of methylbenzene needs only about 30 °C. Above about 60 °C benzene gives 1,3-dinitrobenzene, and methylbenzene can go as far as 2,4,6-trinitromethylbenzene (TNT).

The mechanism: electrophilic substitution

The ring is rich in electrons, but it is also very stable, so it needs a **strong** electrophile. A catalyst makes one first:

- nitration: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$. The electrophile is the **nitronium ion** 硝鎓离子, NO_2^+.
- bromination: $Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$. The **halogen carrier** 卤素载体 $AlBr_3$ pulls a Br^- away and leaves Br^+.
- Friedel–Crafts alkylation: $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$ (the electrophile is a **carbocation** 碳正离子).
- Friedel–Crafts acylation: $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$ (an acylium ion).

$AlCl_3$ can accept a pair of electrons because the aluminium has only six electrons in its outer shell, so it pulls the chlorine (with both bonding electrons) off the reagent.

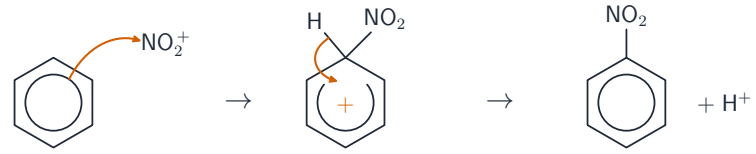
Then the same two steps happen with either electrophile:

1. a pair of the delocalised electrons forms a bond to the electrophile. The intermediate has a + charge spread over five carbons, and the ring's delocalisation is partly lost.
2. the C–H bond on the carbon that gained the electrophile breaks, and its electron pair goes back into the ring. An H^+ leaves and the stable ring is restored.

In bromination the H^+ meets $AlBr_4^-$: $H^+ + AlBr_4^- \rightarrow HBr + AlBr_3$. So the $AlBr_3$ is given back, which shows it is a catalyst.

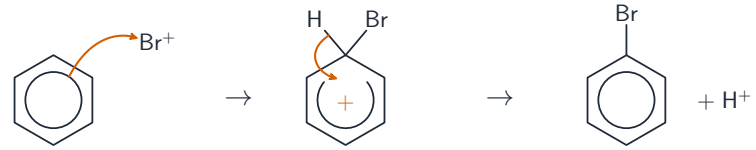
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Nitration electrophile: $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$



delocalised electrons attack the electrophile | intermediate: the C–H bond pair goes back into the ring | nitrobenzene: the stable delocalised ring is restored

Bromination electrophile: $Br_2 + AlBr_3 \longrightarrow Br^+ + AlBr_4^-$



catalyst regenerated: $H^+ + AlBr_4^- \longrightarrow HBr + AlBr_3$

Electrophilic substitution: the ring attacks the electrophile, the intermediate loses H^+, and the delocalised ring comes back. Nitration and bromination use the same two steps

Substitution wins over addition because the **delocalisation** 离域 (aromatic stabilisation) of the ring is kept. Addition would destroy this stable system, so it is not favoured.

Evidence for the stability. Adding H_2 to cyclohexene (one C=C) releases 120 kJ mol^{-1}. If benzene were "cyclohexa-1,3,5-triene" with three separate C=C bonds, hydrogenating it would release $3 \times 120 = 360$ kJ mol^{-1}. The measured value is only about 208 kJ mol^{-1}. So real benzene is about 152 kJ mol^{-1} **lower in energy** (more stable) than the triene structure: this is the stabilisation energy from delocalisation. Also, all six C–C bonds in benzene have the same length (0.139 nm), between a C–C single bond (0.154 nm) and a C=C double bond (0.134 nm).

Drawing it for full marks.

- the equation that makes the electrophile (NO_2^+ or Br^+).
- a curly arrow from **inside the ring** (the circle) to the electrophile.
- the intermediate: a **horseshoe** 马蹄形 that is open at the carbon carrying H and the new group, with + inside it. The horseshoe covers five carbons, not six.
- a curly arrow from the **C–H bond** back into the ring, and the products, including H^+.

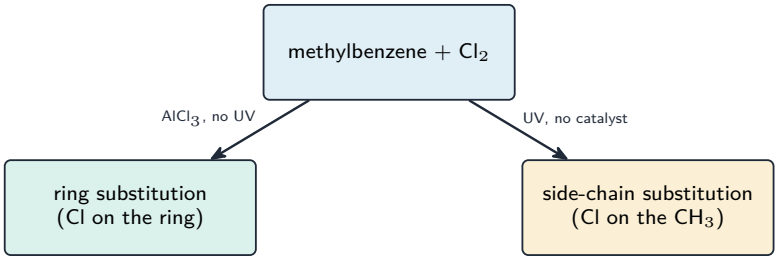
Common mistakes.

- Drawing a full circle in the intermediate. The top carbon has four single bonds, so it is not part of the delocalised system.
- Starting the first arrow at a single carbon atom or from outside the ring.
- Giving NO_2 (no charge) or HNO_3 as the electrophile.
- Thinking benzene decolourises bromine water like an alkene. It does **not**: without a halogen carrier, Br_2 is not a strong enough electrophile to react with the ring.

Side-chain or ring?

Where a halogen reacts depends on the conditions:

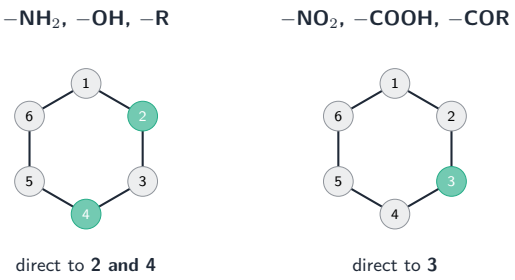
- with a halogen-carrier catalyst (such as $AlCl_3$) and **no** UV light → substitution in the **ring**.
- with UV light and **no** catalyst → free-radical substitution in the **side-chain**.



The conditions decide: a halogen carrier ($AlCl_3$) substitutes the ring; UV light substitutes the side-chain

Directing effects

A group already on the ring decides where the next group goes – its **directing effect** 定位效应:



A group already on the ring directs the next one: –NH_2/–OH/–R send it to positions 2 and 4; –NO_2/–COOH/–COR send it to position 3

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Group already present	Directs the new group to
–NH_2, –OH, –R	positions 2 and 4
–NO_2, –COOH, –COR	position 3

Worked example. Methylbenzene and nitrobenzene are each nitrated. Predict where the new NO_2 group goes, and which compound reacts faster. Look at the group **already on the ring**. In methylbenzene the –CH_3 is an alkyl group: it directs the new group to positions **2 and 4**, and it **releases** electrons into the ring, making the ring more attractive to an electrophile - so methylbenzene nitrates **faster** than benzene. In nitrobenzene the –NO_2 directs to position **3**, and it **withdraws** electrons from the ring - so nitrobenzene nitrates **more slowly** than benzene. The group already present controls **both** the position **and** the rate, and the two always travel together: 2,4-directors activate the ring, 3-directors deactivate it.

Worked example (order of steps). Plan a two-step synthesis of 3-nitrobenzoic acid and of 4-nitrobenzoic acid from methylbenzene. The order matters, because the group on the ring at the time of nitration decides where NO_2 goes.

- **3-nitrobenzoic acid:** first oxidise the side-chain with hot alkaline $KMnO_4$ then dilute acid, giving benzoic acid. Then nitrate (concentrated HNO_3/H_2SO_4): the –COOH directs to position **3**.
- **4-nitrobenzoic acid:** first nitrate methylbenzene: the –CH_3 directs to positions 2 and 4, so separate the 4-isomer. Then oxidise the –CH_3 to –COOH.

Positions are counted from the group already present, carbon 1: positions 2 and 6 are next to it, 3 and 5 are one further round, and 4 is opposite.

Exam tips

- Benzene undergoes **electrophilic substitution**, not addition, because addition would destroy the stable delocalised ring.
- Learn **nitration** (concentrated HNO_3/H_2SO_4, 25–60 °C; hotter gives more than one NO_2 group) and **halogenation** (halogen + $AlCl_3$) with the electrophile-generating step.
- Compare reactivity: benzene resists addition far more than an alkene because of delocalisation.
- Give the electrophile-forming equation for every substitution: NO_2^+, Br^+ or Cl^+, CH_3^+, CH_3CO^+.
- Side-chain oxidation leaves one –COOH for any length of alkyl chain.
- In a synthesis, choose the order of steps so that the group present at the time of substitution directs the new group where you want it.
- Hydrogenation data: about 208 kJ mol^{-1} released instead of 360, so benzene is about 152 kJ mol^{-1} more stable than three separate C=C.

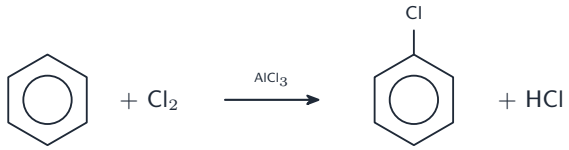
Halogen compounds

A-Level Chemistry

Making halogenoarenes

A **halogenoarene** 卤代芳烃 (also called an **aryl halide** 芳基卤化物) is formed when an **arene** 芳烃 reacts with Cl_2 or Br_2, using $AlCl_3$ or $AlBr_3$ as a **catalyst** 催化剂. This is the **electrophilic substitution** 亲电取代 from the arenes topic – the halogen replaces a hydrogen on the **benzene ring** 苯环.

- benzene gives chlorobenzene.
- **methylbenzene** 甲苯 gives 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene (the **methyl group** 甲基 **directs** 定位 the chlorine to positions 2 and 4).



Making a halogenoarene by electrophilic substitution: with an $AlCl_3$ catalyst, a chlorine replaces a hydrogen on the ring (giving HCl)

The catalyst makes the **electrophile** 亲电试剂, and is then re-formed:

$$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$$

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

The conditions are **room temperature**, with the catalyst and no water (water would react with $AlCl_3$). Iron filings also work, because iron reacts with the chlorine to make $FeCl_3$, which acts in the same way.

> **Worked example (ring or side chain?).** Methylbenzene reacts with chlorine under two different sets of conditions: (1) with $AlCl_3$ at room temperature; (2) in **ultraviolet light** 紫外线, with no catalyst. Name the type of reaction and give a product for each.

- (1) **Electrophilic substitution** on the **ring**: 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene (the halogenoarenes), with HCl.
- (2) **Free-radical substitution** on the **side chain**, as in alkanes: (chloromethyl)benzene, $C_6H_5CH_2Cl$, with HCl. The ring is not attacked.

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The product in (2) is **not** a halogenoarene: its chlorine is on an sp^3 carbon, so it reacts with nucleophiles like a halogenoalkane. A common mark is lost by giving the right product with the wrong conditions, so learn the pairs: **catalyst → ring**, **UV light → side chain**.



Many pesticides and herbicides are halogenoarenes – chlorine atoms bonded to a benzene ring

Why a halogenoarene is less reactive than a halogenoalkane

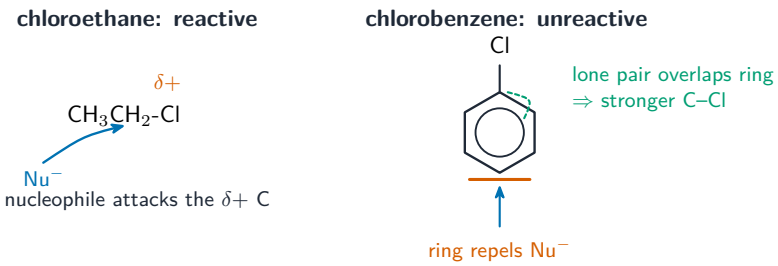
Compare chloroethane (a **halogenoalkane** 卤代烷) with chlorobenzene (a halogenoarene).

A halogenoalkane reacts easily by **nucleophilic substitution** 亲核取代: its C–Cl bond is **polar** 极性的, so a nucleophile can attack the slightly positive carbon and push the halogen out.

A halogenoarene is very **unreactive** 不活泼的 towards nucleophilic substitution. There are two reasons:

- a **lone pair** 孤对电子 on the chlorine **overlaps sideways** 侧面重叠 with the **delocalised** 离域 ring of electrons. This gives the C–Cl bond **partial double-bond character** 部分双键性质, making it shorter and stronger, so it is much harder to break.
- the **electron-rich** 富电子的 ring **repels** 排斥 an approaching **nucleophile** 亲核试剂.

So chlorobenzene does **not** react with nucleophiles such as OH^- under normal conditions, while chloroethane does.



Chloroethane reacts (a nucleophile attacks the δ+ carbon), but chlorobenzene does not: the Cl lone pair strengthens the C–Cl bond and the ring repels nucleophiles

Seeing the difference in the lab

Warm each compound with aqueous silver nitrate in ethanol. Any halide ions released by **hydrolysis** 水解 form a silver halide precipitate:

Compound	Result with $AgNO_3(aq)$, warmed
ethanoyl chloride (an acyl chloride)	white precipitate at once, even in the cold
chloroethane (a halogenoalkane)	white precipitate slowly forms on warming
chlorobenzene (a halogenoarene)	no precipitate

So the ease of hydrolysis is acyl chloride > halogenoalkane > halogenoarene.

Worked example. (a) Explain why chlorobenzene gives no precipitate with warm aqueous silver nitrate, while chloroethane does. (b) Predict what happens with (chloromethyl)benzene, $C_6H_5CH_2Cl$. (a) In chloroethane the C–Cl bond breaks by nucleophilic substitution, releasing Cl^-, which gives white AgCl. In chlorobenzene, a lone pair on Cl overlaps with the delocalised ring, so the C–Cl bond is stronger, and the ring's electrons repel the nucleophile. No Cl^- is released, so there is no precipitate. (b) Here the Cl is on the **side chain**, joined to an sp^3 carbon, not to the ring. It behaves like a halogenoalkane, so a white precipitate forms on warming.

Common mistakes

- "The C–Cl bond in chlorobenzene is not polar." It is still polar; the bond is unreactive because it is **stronger** (partial double-bond character) and the ring repels nucleophiles.
- Giving only one reason. Mark schemes usually want both: the stronger C–Cl bond **and** the repulsion by the ring's electrons.
- Treating every Cl in an aromatic compound as unreactive. Only a halogen bonded **directly to the ring** is.

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- Giving UV light as the condition for making chlorobenzene. UV light substitutes the **side chain** of methylbenzene; ring substitution needs a halogen carrier such as $AlCl_3$.

Exam tips

- A **halogenoarene** is **less reactive** than a halogenoalkane: the lone pair delocalises into the ring, giving the C-X bond partial double-bond character.
- Distinguish a halogen **on the ring** (needs a catalyst, unreactive to substitution) from one on a **side chain** 侧链 (reacts like a halogenoalkane).

Hydroxy compounds

A-Level Chemistry

Alcohols with acyl chlorides

At A Level you meet one more reaction of an **alcohol** 醇: it reacts with an **acyl chloride** 酰氯 to make an **ester** 酯. This works faster and more completely than using a **carboxylic acid** 羧酸. For example, ethanol and **ethanoyl chloride** 乙酰氯 give **ethyl ethanoate** 乙酸乙酯, plus **fumes** 烟雾 of HCl.



An acyl chloride reacts with an alcohol faster and more completely than a carboxylic acid does, giving the ester and HCl fumes

The reaction happens at room temperature, needs no catalyst and is **not reversible**, unlike the acid-catalysed reaction of a carboxylic acid with an alcohol. Phenol reacts in the same way to give a phenyl ester, for example **phenyl ethanoate** 乙酸苯酯:

$$CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$$

Phenol

Phenol 苯酚 has an –OH group joined directly to a **benzene** 苯 ring. This changes the chemistry of both the –OH group and the ring.



Phenol is a low-melting solid; it slowly turns pink as it oxidises in air

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Making phenol

Cool **phenylamine** 苯胺 with $NaNO_2$ and dilute acid below 10 °C to make a **diazonium salt** 重氮盐. Warming this salt with water then gives phenol (and **nitrogen gas** 氮气).

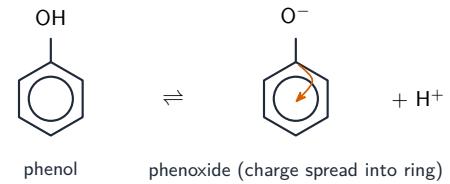
Reactions of phenol

- with a base such as NaOH(aq): phenol reacts to give **sodium phenoxide** 苯酚钠 and water. (Ordinary alcohols do **not** react with NaOH – this shows phenol is more **acidic** 酸性的.) Phenol is only slightly soluble in water, but it dissolves in NaOH(aq), because the ionic salt is soluble: $C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$.
- with sodium metal: gives sodium phenoxide and hydrogen, $2C_6H_5OH + 2Na \rightarrow 2C_6H_5O^-Na^+ + H_2$ (fizzing).
- with a diazonium salt in NaOH(aq): forms a coloured **azo compound** 偶氮化合物 (used in **dyes** 染料).
- **nitration** 硝化 with **dilute** HNO_3 at room temperature: gives a mixture of 2-nitrophenol and 4-nitrophenol.
- **bromination** 溴化 with bromine water at room temperature (no catalyst): the orange bromine water is decolourised and a white **precipitate** 沉淀 of 2,4,6-tribromophenol forms: $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$.

Acidity of phenol

Phenol loses its H^+ to form a **phenoxide ion** 苯氧负离子. This ion is **stabilised** 被稳定 because its negative charge is spread (delocalised) into the ring. So phenol's **acidity** 酸性 is higher than that of water or ethanol:

$$\text{ethanol} < \text{water} < \text{phenol}$$



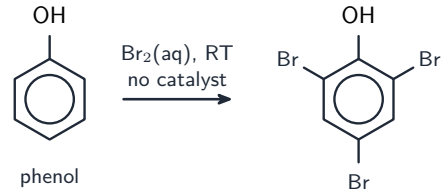
acidity: ethanol < water < phenol

Phenol is more acidic than water or an alcohol: losing H^+ gives a phenoxide ion whose negative charge spreads into the ring, stabilising it

(Phenol is still a **weak acid** 弱酸 – weaker than a carboxylic acid.)

Why the conditions are milder than for benzene

A lone pair on the phenol oxygen is partly **delocalised** 离域 into the ring. This makes the ring more electron-rich, so it attracts **electrophiles** 亲电试剂 more strongly. Phenol therefore reacts faster and under much milder conditions than benzene – no **catalyst** 催化剂 is needed, and dilute **reagents** 试剂 work at room temperature.



the ring is activated, so milder conditions than benzene

Phenol's ring is activated, so bromine water brominates positions 2, 4 and 6 at room temperature with no catalyst, giving a white precipitate

The –OH group directs new **substituents** 取代基 to the 2-, 4- and 6-positions. The same ideas apply to other phenolic compounds, such as **naphthol** 萘酚.



Carbolic soap contains phenol, which was one of the first antiseptics

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Worked example. Phenol, ethanol and ethanoic acid are each shaken with aqueous NaOH and then with aqueous Na_2CO_3. Predict what happens, and order the three by acidity. Acidity depends on how well the **anion left behind** is stabilised. Ethanol's ethoxide keeps its charge stuck on one oxygen, so ethanol is weakest and reacts with **neither**. Phenol's phenoxide spreads the charge **into the ring**, making phenol acidic enough to react with the strong base NaOH but **not** with the weaker Na_2CO_3 - so no fizzing. Ethanoate spreads the charge over **two oxygens**, the most effective of the three, so ethanoic acid reacts with **both** and **fizzes** with the carbonate. Order: **ethanol < phenol < ethanoic acid**. The carbonate is the discriminating test - only a carboxylic acid fizzes, which is exactly how you tell phenol from an acid.

Worked example (a substituted phenol). 4-methylphenol has a methyl group opposite the –OH group. (a) Predict the product with excess bromine water. (b) Is 4-methylphenol a stronger or weaker acid than phenol? (c) Give a test that tells 4-methylphenol from phenylmethanol, $C_6H_5CH_2OH$.

(a) The –OH group directs bromine to positions 2, 4 and 6, but position 4 already carries the methyl group, so only two bromine atoms go on: the product is **2,6-dibromo-4-methylphenol**, with 2HBr. (b) **Weaker**. An alkyl group donates electrons to the ring (a positive **inductive effect** 诱导效应), so the negative charge of the anion is spread less well and the anion is less stable. (c) Add bromine water: 4-methylphenol decolourises it at once and gives a white precipitate. In phenylmethanol the –OH group is on a CH_2, not on the ring, so the ring is not activated and there is no reaction. Phenylmethanol is an ordinary alcohol: it does not react with NaOH(aq) either.

Common mistakes.

- Saying phenol reacts with Na_2CO_3 to give carbon dioxide. Phenol is too weak an acid: it reacts with NaOH but gives **no fizzing** with carbonates. Only carboxylic acids do.
- Explaining phenol's acidity by the O–H bond being "weaker". The key is the **anion**: the negative charge of the phenoxide ion is delocalised into the ring, so the ion is stabilised.
- Brominating phenol with $FeBr_3$, or getting a single substitution. Phenol needs **no catalyst**, and bromine water gives **2,4,6-tribromophenol** at once.
- Nitrating phenol with concentrated acids. **Dilute** HNO_3 at room temperature is enough and gives 2- and 4-nitrophenol; concentrated acid gives multiple substitution and oxidation.
- Making a phenyl ester from phenol and a carboxylic acid. Phenol reacts too slowly with carboxylic acids; use an **acyl chloride**.

- Saying the –OH group activates the ring by withdrawing electrons. A lone pair on oxygen is **donated** into the ring, making it more electron-rich and more attractive to electrophiles.

Exam tips

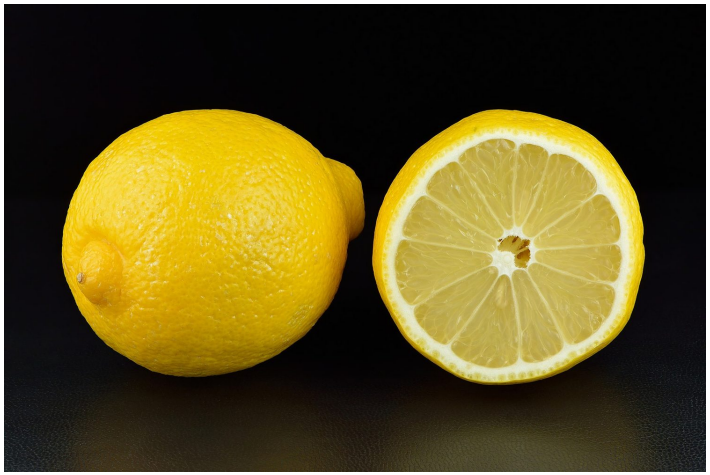
- **Phenol** is a stronger acid than alcohols (its anion is stabilised by delocalisation) but weaker than carboxylic acids – it does **not** react with **carbonates** 碳酸盐.
- Phenol **decolourises** 使褪色 **bromine water** 溴水 and gives a white precipitate **without a catalyst** (the ring is **activated** 活化 by oxygen).
- Count the free 2-, 4- and 6-positions before writing a bromination product of a substituted phenol: each free one gains a Br, and each gives one HBr.
- Electron-donating groups (such as alkyl) on the ring make a phenol **less** acidic; electron-withdrawing groups (such as $–NO_2$ or Cl) make it **more** acidic.
- **Acyl chlorides** react with alcohols/phenols to give esters readily (better than the **reversible** 可逆的 acid route); misty HCl fumes are the **observation** 现象.

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Carboxylic acids and derivatives

A-Level Chemistry

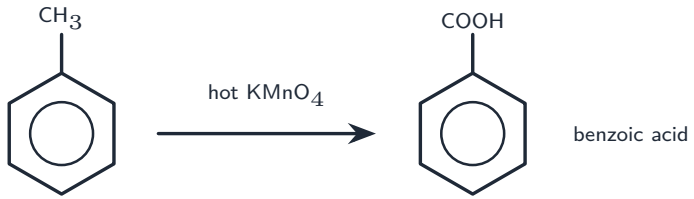
Carboxylic acids



Citrus fruits taste sour because they contain citric acid, a carboxylic acid

Making and reacting

- an **alkylbenzene** 烷基苯 (such as methylbenzene) is oxidised by hot alkaline $KMnO_4$, then dilute acid, to give **benzoic acid** 苯甲酸. The whole side-chain becomes a –COOH group.
- a carboxylic acid reacts with PCl_3 and heat, PCl_5, or $SOCl_2$ to form an **acyl chloride** 酰氯.



Hot KMnO4 oxidises a methyl side-chain to a COOH group

Making acyl chlorides: three reagents. Each replaces the –OH of the acid with –Cl; learn the by-products:

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3 \quad \text{(heat)}$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl \quad \text{(room temperature)}$$

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

Sulfur dichloride oxide, $SOCl_2$, is often the best choice: both by-products are **gases**, which escape, leaving the acyl chloride easy to purify. With PCl_5 the steamy white fumes of HCl are also a test for an –OH group. All three must be used in dry conditions, because acyl chlorides react with water.

Acids that can be oxidised further

Two **carboxylic acids** 羧酸 are special because they can still be oxidised:

- methanoic acid (HCOOH) is oxidised by Fehling's or Tollens' reagent, or acidified $KMnO_4$ / $K_2Cr_2O_7$, to carbon dioxide and water.
- ethanedioic acid (HOOCCOOH) is oxidised by warm acidified $KMnO_4$ to carbon dioxide.

Methanoic acid can be oxidised because it still has a hydrogen on its carbonyl carbon: HCOOH is like an aldehyde, so it gives a silver mirror with Tollens' reagent. Ethanedioic acid has a C–C bond between two oxidised carbons, which breaks easily:

$$HCOOH + [O] \rightarrow CO_2 + H_2O$$

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

The second reaction is used in titrations: warm the ethanedioic acid to about 60 °C, then add manganate(VII) from a burette until a permanent pale pink colour appears (no indicator needed). Each C rises from +3 to +4; each Mn falls from +7 to +2, so the mole ratio is $H_2C_2O_4 : MnO_4^- = 5 : 2$.

Relative acidities

The **acidity** 酸性 order is:

$$\text{alcohol} < \text{phenol} < \text{carboxylic acid}$$

A carboxylic acid is the strongest because, when it loses H^+, the negative charge is spread over **two** oxygen atoms, making the ion very stable. In a **phenol** 苯酚 the charge spreads only into the ring, and in an **alcohol** 醇 (giving RO^-) it is not spread at all.

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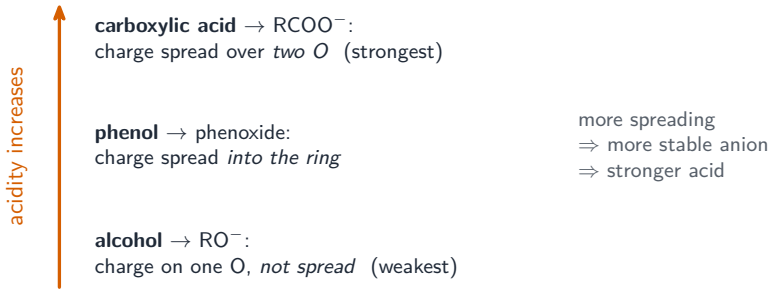
In an alcohol, the alkyl group even **pushes** electrons towards the O, which makes RO^- less stable still; ethanol is a weaker acid than water.

Telling them apart in the laboratory.

Reagent	Carboxylic acid	Phenol	Alcohol
sodium metal	fizzes, H_2	fizzes, H_2	fizzes slowly, H_2
aqueous NaOH	reacts (salt + water)	reacts (sodium phenoxide)	no reaction
aqueous Na_2CO_3	**fizzes**, CO_2	no reaction	no reaction

Only a carboxylic acid is strong enough to release CO_2 from a carbonate:

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$



Acidity rises from alcohol to phenol to carboxylic acid: the more the negative charge on the conjugate base is spread out, the more stable the ion and the stronger the acid

Chlorine atoms make a carboxylic acid **more** acidic. Chlorine is **electron-withdrawing** 吸电子: through the **inductive effect** 诱导效应 it pulls electron density away, helping to spread the negative charge and stabilise the ion. So more chlorine atoms (closer to the –COOH) give a stronger acid.

Acid	pK_a
ethanoic acid, CH_3COOH	4.76
chloroethanoic acid, $CH_2ClCOOH$	2.86
dichloroethanoic acid, $CHCl_2COOH$	1.29
trichloroethanoic acid, CCl_3COOH	0.65

A **lower** pK_a means a **stronger** acid. Each extra Cl withdraws more electron density from the $-COO^-$ group, spreading its negative charge further, so the ion is more stable and the acid gives up H^+ more easily. The effect weakens quickly with distance: 2-

chlorobutanoic acid (Cl next to the COOH) is much stronger than 4-chlorobutanoic acid (Cl three carbons away).

> **Worked example.** Put these in order of acidity, weakest first, and explain: ethanol, phenol, ethanoic acid, chloroethanoic acid. Ethanol < phenol < ethanoic acid < chloroethanoic acid. Ethanol's ion $CH_3CH_2O^-$ has the charge on one O, made worse by the electron-pushing ethyl group. In phenoxide the charge is partly delocalised into the benzene ring. In ethanoate it is delocalised equally over two O atoms. In chloroethanoate, the electron-withdrawing Cl spreads it further still. The more spread out (delocalised) the charge, the more stable the anion and the stronger the acid.

Esters

An alcohol (or phenol) reacts with an acyl chloride at room temperature to give an **ester** 酯 and HCl. Examples are ethyl ethanoate (from ethanol) and phenyl benzoate (from phenol).

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$$

$$C_6H_5COCl + C_6H_5OH \rightarrow C_6H_5COOC_6H_5 + HCl$$

Phenols do **not** form esters by heating with a carboxylic acid and an acid catalyst, as alcohols do: the lone pair on phenol's O is partly delocalised into the ring, so it is a weaker nucleophile. The far more reactive acyl chloride is needed. Making an ester from an acyl chloride is also faster and goes to completion, rather than reaching an equilibrium.



Aspirin is an ester, made from salicylic acid

Acyl chlorides

Acyl chlorides are made from carboxylic acids (with PCl_3, PCl_5 or $SOCl_2$). They are very reactive. At room temperature they react with:

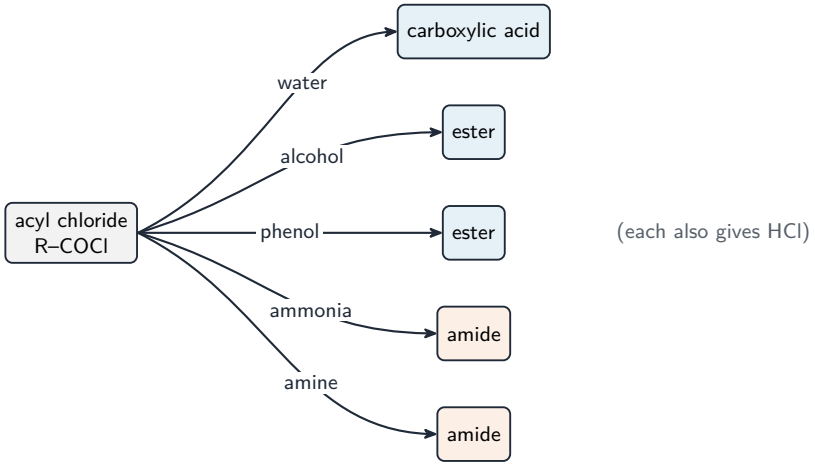
Reactant	Product (plus HCl)
water	the carboxylic acid
an alcohol	an ester
phenol	an ester
ammonia 氨	an **amide** 酰胺
a primary or secondary **amine** 胺	an amide

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

$$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$$

$$CH_3COCl + 2CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3NH_3^+Cl^-$$

With water you see **steamy white fumes** of HCl. With ammonia, the second molecule of ammonia takes up the HCl as white ammonium chloride. The product with methylamine is *N*-methylethanamide.

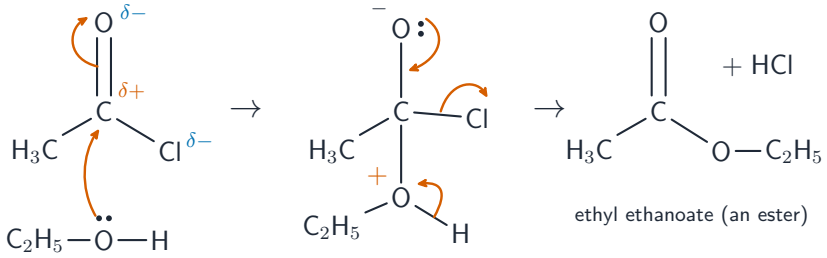


Acyl chlorides are very reactive: with water, an alcohol, phenol, ammonia or an amine they give the labelled product plus HCl

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The addition–elimination mechanism

All these reactions follow an **addition–elimination** 加成消去 mechanism: a nucleophile first **adds** to the slightly positive carbonyl carbon, then HCl is **eliminated**. The carbonyl carbon is very $\delta+$ because **two** electronegative atoms, O and Cl, pull electrons away from it. Water, alcohols, ammonia and amines are neutral, but each has a lone pair on its O or N, so each can act as a nucleophile.



1. addition: a lone pair on the alcohol O attacks the $\delta+$ C

2. elimination: C=O re-forms, Cl^- leaves and O loses H^+

Ethanoyl chloride + ethanol: the alcohol's lone pair adds to the $\delta+$ carbon (addition), then C=O re-forms, Cl^- leaves and H^+ is lost (elimination)

1. **Addition.** A lone pair on the O of ethanol attacks the $\delta+$ carbon. One pair of the C=O bond moves onto the O, which becomes O^-. The ethanol O now has three bonds and a + charge. The carbon is **tetrahedral** 四面体形 for a moment, with four groups around it.
2. **Elimination.** A lone pair on the O^- moves back to re-form C=O. The C–Cl bond pair goes onto the Cl, which leaves as Cl^-. The O^+ loses H^+, and $H^+ + Cl^-$ make HCl.

Swap the nucleophile and the same arrows give the other products: water gives ethanoic acid, ammonia gives ethanamide, and an amine gives an N-substituted amide. With ammonia or an amine, the HCl then reacts with a second molecule of the base to form an ammonium salt.

Common mistakes.

- Drawing Cl^- leaving in the **first** step, as if this were S_N1. The nucleophile adds first; Cl only leaves when the C=O re-forms.
- Starting the attacking arrow at the H of water or the alcohol. It must start at a lone pair on the **O** (or the **N** of ammonia).
- Missing the arrow that re-forms C=O, or the + charge on the O (or N) of the intermediate.

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Ease of hydrolysis

Compare how easily three chlorides react with water (**hydrolysis** 水解):

$$\text{acyl chloride} \gg \text{alkyl chloride} \gg \text{aryl chloride}$$

An acyl chloride reacts violently with cold water; an alkyl chloride reacts slowly; an aryl chloride (halogenoarene) does not react, because its C–Cl bond is strengthened by the ring.

Chloride	Conditions to hydrolyse	Why
acyl chloride	cold water, at once	the carbon is attached to O and Cl, so it is very $\delta+$; the C=O lets the nucleophile **add** first, and the carbon is planar and open to attack
alkyl chloride	heat under reflux with aqueous NaOH	the carbon is only bonded to one Cl, so it is less $\delta+$, and the nucleophile must push the Cl out as it attacks
aryl chloride	no reaction, even on heating with NaOH	a lone pair on Cl overlaps with the ring's delocalised π system, giving the C–Cl bond some double-bond character, so it is **stronger**; the electron-rich ring also repels nucleophiles

To show the difference, add a few drops of each to aqueous silver nitrate in ethanol: the acyl chloride gives an immediate white precipitate of AgCl, the alkyl chloride a slow one on warming, and the aryl chloride none.

> **Worked example.** Ethanoyl chloride reacts violently with cold water, while ethyl ethanoate needs prolonged reflux with acid or alkali. Explain the difference. Both are attacked at the **carbonyl carbon**, so compare how open that carbon is to attack and how good the leaving group is. In ethanoyl chloride the chlorine is strongly **electronegative** and withdraws electrons, making the carbonyl carbon much more $\delta+$ and so far more open to a nucleophile; and Cl^-, the anion of a strong acid, is a **good leaving group**. In the ester the –OR oxygen **donates** a lone pair into the carbonyl, reducing that $\delta+$ charge, and RO^- is a **poor** leaving group. So the acyl chloride hydrolyses far more easily. Argue from **both** the $\delta+$ on the carbon **and** the leaving group: either one alone is usually only half the marks.

Exam tips

- **Acyl chlorides** are very reactive – learn their products with water (HCl), alcohols (esters), ammonia (amides) and amines.
- Reactivity order of derivatives: **acyl chloride > ester > amide**.
- Acid strength: electron-withdrawing groups (e.g. Cl) **increase** it – explain via the carboxylate ion.
- Know the by-products: $PCl_3 \rightarrow H_3PO_3$; $PCl_5 \rightarrow POCl_3 + HCl$; $SOCl_2 \rightarrow SO_2 + HCl$ (both gases, easy to purify).
- Only carboxylic acids fizz with sodium carbonate; phenol reacts with NaOH but not Na_2CO_3; alcohols react with neither.
- Methanoic acid and ethanedioic acid are oxidised further, to CO_2; ethanedioate : manganate(VII) = 5 : 2.
- Ease of hydrolysis: acyl chloride (cold water) > alkyl chloride (hot NaOH) > aryl chloride (none); explain with the $\delta+$ carbon and the C–Cl bond strength.

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Nitrogen compounds

A-Level Chemistry

Primary and secondary amines

An **amine** 胺 has an $-NH_2$ (primary) or –NH (secondary) group.



A primary amine has -NH2; a secondary amine has -NH-

Making amines

- a **halogenoalkane** 卤代烷 with NH_3 in ethanol, heated under pressure → a primary amine.
- a halogenoalkane with a primary amine, heated under pressure → a secondary amine.
- **reduction** 还原 of an **amide** 酰胺 with $LiAlH_4$.
- reduction of a **nitrile** 腈 with $LiAlH_4$ or H_2/Ni.

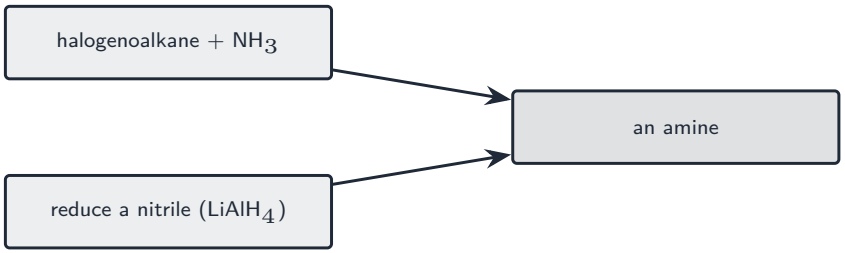
The equations, using ethyl compounds:

$$CH_3CH_2Br + CH_3NH_2 \rightarrow CH_3CH_2NHCH_3 + HBr \qquad \text{(a secondary amine)}$$

$$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O \qquad (LiAlH_4 \text{ in dry ether})$$

$$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2 \qquad (LiAlH_4, \text{ or } H_2 \text{ with a Ni catalyst})$$

Reducing an amide keeps the number of carbons: the C=O simply becomes CH_2. Reducing a nitrile also keeps it, so a nitrile made from a halogenoalkane and KCN gives an amine with **one more** carbon than the halogenoalkane.



Two routes to an amine: from a halogenoalkane, or by reducing a nitrile

An amine (or **ammonia** 氨) reacts with an acyl chloride in a **condensation** 缩合 reaction to give an amide. The reagent is an **acyl chloride** 酰氯. It is fast at room temperature, and HCl is the small molecule lost:

$$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$$

The product is *N*-methylethanamide. With ammonia instead, the product is ethanamide, CH_3CONH_2. If excess amine is used, the HCl reacts with it to form a salt, $CH_3NH_3^+Cl^-$.

Basicity of amines

The **basicity** 碱性 of an amine comes from the lone pair on its nitrogen, which can accept an H^+ from water. Amines are weak bases, so the reaction is an equilibrium, and the OH^- formed makes the solution alkaline:

$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

With an acid, an amine forms a salt: $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$ (ethylammonium chloride). Adding NaOH to the salt gives back the free amine.

Phenylamine and azo compounds

Making phenylamine

Make **phenylamine** 苯胺 from benzene in two steps: nitrate benzene to nitrobenzene, then reduce it with hot Sn and concentrated HCl, followed by NaOH(aq).

$$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$$

In the acid, phenylamine is made as its salt, $C_6H_5NH_3^+$. The NaOH is added to remove the H^+ and set the free phenylamine loose.

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Reactions

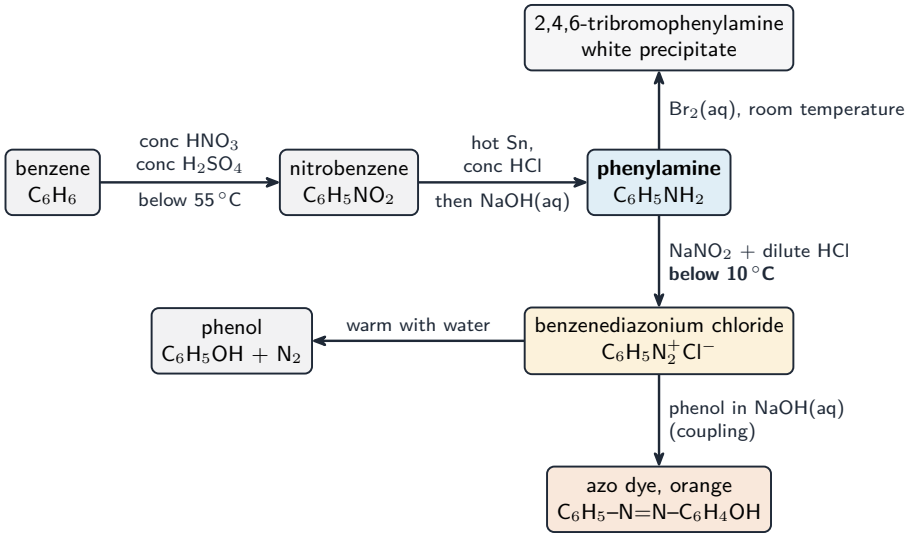
- with bromine water at room temperature → 2,4,6-tribromophenylamine (a white precipitate). The ring is activated, like phenol.
- with HNO_2 (from $NaNO_2$ and dilute acid) below 10 °C → a diazonium salt; warming this with water gives phenol.

$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3HBr$$

$$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$$

$$C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$$

With bromine water, the orange colour disappears at once and a white precipitate forms, with no catalyst needed: the nitrogen lone pair is delocalised into the ring, so the ring is much richer in electrons than benzene. Nitrous acid is unstable, so it is made **in the flask** from sodium nitrite and dilute HCl. The bubbles of nitrogen gas on warming are a sign that the diazonium salt is decomposing.

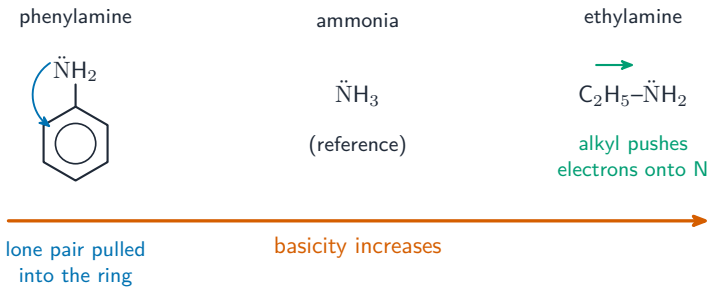


From benzene to phenylamine, and on to the diazonium salt: warming it with water gives phenol, coupling it with alkaline phenol gives an azo dye

Relative basicity

$$\text{phenylamine} < \text{ammonia} < \text{ethylamine}$$

Ethylamine is the strongest base: its alkyl group pushes electron density onto the nitrogen, making the lone pair more available. Phenylamine is the weakest, because its lone pair is **delocalised** 离域 into the benzene ring, so it is less available to accept an H^+.



Basicity depends on the nitrogen lone pair: an alkyl group makes it more available (ethylamine strongest), a benzene ring pulls it away (phenylamine weakest)

Azo compounds

A **diazonium salt** 重氮盐 (benzenediazonium chloride) couples with **phenol** 苯酚 in NaOH(aq) to form an **azo compound** 偶氮化合物. The azo group is –N=N–. Azo compounds are brightly coloured and are often used as **dyes** 染料; many other azo dyes are made the same way.

$$C_6H_5N_2^+Cl^- + C_6H_5OH + NaOH \rightarrow C_6H_5\text{–}N{=}N\text{–}C_6H_4OH + NaCl + H_2O$$

The diazonium ion joins the phenol ring at the carbon **opposite** the OH group (the 4-position), and the product is a yellow-orange solid. To make a different azo dye, change either partner: start from a different arylamine (for example 4-methylphenylamine) to change one ring, or couple with a different phenol or arylamine to change the other. The –N=N– bridge links two benzene rings, which gives a long delocalised system that absorbs visible light; that is why azo compounds are coloured.

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Methyl orange, a bright orange azo dye; the strong colour comes from the –N=N– azo group, which is why azo compounds are so widely used as dyes

Amides

An amide is made from ammonia or a primary amine with an acyl chloride at room temperature.



Paracetamol is a common painkiller that contains the amide group (–CONH–)

Its reactions:

- **hydrolysis** with aqueous acid or alkali, giving the carboxylic acid (or its salt) and the amine (or ammonium).
- **reduction** of the C=O group with $LiAlH_4$ to give an amine.

Hydrolysis needs heating under reflux. The products depend on the conditions:

$$CH_3CONH_2 + H_2O + HCl \rightarrow CH_3COOH + NH_4Cl \qquad \text{(acid)}$$

$$CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3 \qquad \text{(alkali)}$$

With alkali, ammonia gas is given off; it turns damp red litmus paper blue, which is a test for an amide. For an *N*-substituted amide such as $CH_3CONHCH_3$, hydrolysis breaks the C–N bond to give the acid and **methylamine** (as $CH_3NH_3^+$ in acid).

An amide is a **much weaker base** than an amine, because the nitrogen lone pair is delocalised onto the neighbouring C=O group, so it is not available to accept an H^+.

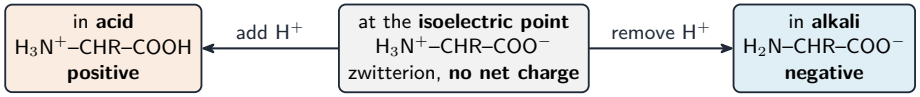
Amino acids

An **amino acid** 氨基酸 has both a basic $–NH_2$ group and an acidic –COOH group.

Zwitterions and the isoelectric point

The –COOH can give its H^+ to the $–NH_2$ in the same molecule, forming a **zwitterion** 两性离子 (H_3N^+–CHR–COO^-) – an ion with both a positive and a negative end but no overall charge.

- in acid (low pH), the amino acid gains H^+ and becomes **positive**.
- in alkali (high pH), it loses H^+ and becomes **negative**.
- at one special pH, the **isoelectric point** 等电点, it is mostly the zwitterion with no net charge.

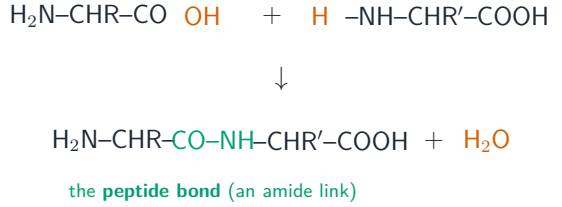


An amino acid's charge depends on pH: positive in acid, the neutral zwitterion at the isoelectric point, negative in alkali

Peptide bonds

Two amino acids join in a condensation reaction: the –COOH of one and the $–NH_2$ of the other react, losing water and forming a **peptide bond** 肽键 (an amide link). Two amino acids give a **dipeptide** 二肽, three give a tripeptide.

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Two amino acids condense: the –OH from one –COOH and the –H from the other $–NH_2$ leave as water, forming the peptide (amide) bond

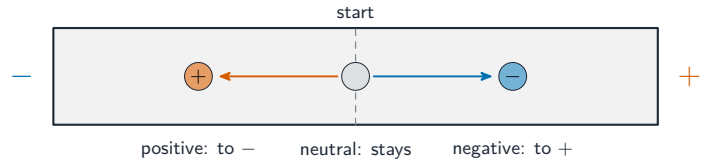
> **Worked example.** Glycine is H_2NCH_2COOH and alanine is $H_2NCH(CH_3)COOH$. Draw the dipeptides they can form with each other. There are **two**, because either amino acid can provide the –COOH:
>
> - Gly–Ala: $H_2NCH_2CONHCH(CH_3)COOH$
> - Ala–Gly: $H_2NCH(CH_3)CONHCH_2COOH$

Each dipeptide still has a free $–NH_2$ at one end and a free –COOH at the other, so it can join to a third amino acid. Three **different** amino acids, each used once, can give $3 \times 2 \times 1 = 6$ tripeptides. Hydrolysis (with hot aqueous acid or alkali) breaks the peptide bonds and gives back the amino acids.

Electrophoresis

In **electrophoresis** 电泳, a mixture is placed in an electric field at a chosen pH:

- above its isoelectric point, an amino acid is negative and moves to the positive electrode.
- below its isoelectric point, it is positive and moves to the negative electrode.
- at its isoelectric point, it does not move. So different amino acids separate.



Electrophoresis at a chosen pH: a positive amino acid moves to the negative electrode, a negative one to the positive, and a neutral one stays – so they separate

Worked example. An amino acid has an isoelectric point of pH 6.0. Give its charge, and the electrode it moves towards in electrophoresis, at pH 2, at pH 6.0 and at pH 11. Compare the solution's pH with the **isoelectric point** each time. At **pH 2**, well below it, the solution is acidic, so the $-NH_2$ gains an H^+: the amino acid is **positive** and moves to the **cathode** (negative electrode). At **pH 6.0**, exactly its isoelectric point, it is the **zwitterion** with no net charge, so it does **not** move. At **pH 11**, well above it, the –COOH loses its H^+: the amino acid is **negative** and moves to the **anode**. Compare the pH with the **isoelectric point**, never with 7 - and note the zwitterion still carries both charges, it simply has no **net** charge.

Worked example: a mixture. A mixture of three amino acids is put in the middle of a gel at pH 6.0: aspartic acid (isoelectric point 2.8), glycine (6.0) and lysine (9.7). Predict the result. Aspartic acid is **above** its isoelectric point, so it is negative and moves to the **anode**. Glycine is at its isoelectric point and stays at the start. Lysine is **below** its isoelectric point, so it is positive and moves to the **cathode**. Three separate spots form. The **further** the pH is from an amino acid's isoelectric point, the larger its charge and the faster it moves; a small ion also moves faster than a large one with the same charge, which is why a dipeptide moves more slowly than a single amino acid.

Common mistakes.

- Saying phenylamine is a stronger base than ethylamine because "the ring donates electrons". The opposite is true: the nitrogen lone pair is **delocalised into the ring**, so it is less available for H^+, and phenylamine is the weakest of the three.
- Calling an amide basic like an amine. In an amide the lone pair is delocalised onto the **C=O** group, so amides are essentially neutral.
- Making the diazonium salt above 10 °C. The diazonium ion decomposes on warming, giving phenol and nitrogen gas, so keep it **below** 10 °C until it is coupled.
- Coupling with phenol in acid. The coupling is done in **alkaline** solution (NaOH(aq)), where the phenoxide ion is more strongly activated.
- Using ammonia alone to make a pure primary amine. The primary amine formed is itself a nucleophile and reacts further, so a **large excess of ammonia** is needed to favour the primary amine.
- Sending an amino acid the wrong way in electrophoresis. **Below** its isoelectric point it is positive and moves to the **cathode**; **above** it, negative, it moves to the **anode**.
- Forgetting to add NaOH after the Sn/HCl reduction. Without it, the product is the salt $C_6H_5NH_3^+Cl^-$, not phenylamine.
- Drawing only one dipeptide from two different amino acids. Gly–Ala and Ala–Gly are **different** molecules.
- Drawing a zwitterion as an uncharged amino acid. The zwitterion is H_3N^+–CHR–COO^-: both groups are ionised, but the **overall** charge is zero.

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Exam tips

- **Phenylamine** is a **weaker base** than aliphatic amines because the N lone pair delocalises into the ring.
- **Diazotisation** ($NaNO_2$/HCl, below 10 °C) then coupling gives **azo dyes** – learn the conditions and the coloured product.
- **Amino acids** are **zwitterions** (both $-NH_2$ and $-COOH$), so they are amphoteric; describe behaviour either side of the isoelectric point.

Polymerisation

A-Level Chemistry

Condensation polymerisation

In **condensation polymerisation** 缩合聚合, monomers join into a long **chain** 链 **and** a **small molecule** 小分子 (such as water or HCl) is lost each time a new bond forms. Each monomer needs **two reactive groups** 反应基团, so the chain can grow at both ends.

polyester: -C(=O)-OH + H-O- → -C(=O)-O- + H_2O

polyamide: -C(=O)-OH + H-N(H)- → -C(=O)-NH- + H_2O

every new ester or amide link loses a small molecule (condensation)

Condensation links: a polyester forms ester links and a polyamide forms amide links; each new link releases a small molecule (here water)

Polyesters

A **polyester** 聚酯 has many **ester links** 酯键 along its chain. You can make one from:

- a **diol** 二醇 (two –OH groups) and a **dicarboxylic acid** 二羧酸 (two –COOH groups), or a **dioyl chloride** 二酰氯.
- a single **hydroxycarboxylic acid** 羟基羧酸, which has both an –OH and a –COOH.

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PET drinks bottles are made of a polyester – a condensation polymer, collected here for recycling

Worked example (PET). PET is made from **benzene-1,4-dicarboxylic acid**, HOOC–C_6H_4–COOH, and **ethane-1,2-diol**, HO–CH_2CH_2–OH. Draw the repeat unit and state what is lost. At each link, the –OH of a –COOH group and the H of an –OH group leave as water, and the C=O carbon bonds to the oxygen of the diol. The repeat unit holds one of each monomer:

$$\left[\text{–OC–}C_6H_4\text{–CO–O–}CH_2CH_2\text{–O–}\right]_n$$

Each repeat unit has **two** ester links, so **two** water molecules are lost for each repeat unit.

Worked example (one monomer). Poly(lactic acid) 聚乳酸 is made from 2-hydroxypropanoic acid (lactic acid), $CH_3CH(OH)COOH$, which has both groups in one molecule. The –OH of one molecule reacts with the –COOH of the next, so the repeat unit is a single monomer minus water: $\left[\text{–O–CH}(CH_3)\text{–CO–}\right]_n$. It is used for food packaging and dissolving stitches, because its ester links hydrolyse slowly in the body and in compost.

Polyamides

A **polyamide** 聚酰胺 has many **amide links** 酰胺键. You can make one from:

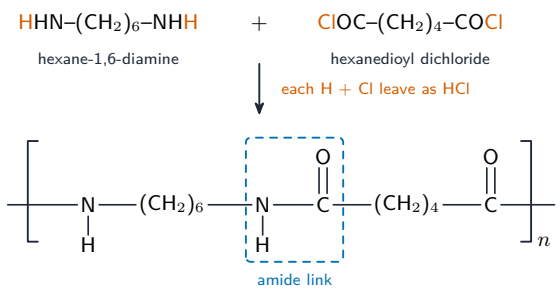
- a **diamine** 二胺 (two $–NH_2$ groups) and a dicarboxylic acid or a dioyl chloride.
- a single **aminocarboxylic acid** 氨基羧酸, or from **amino acids** 氨基酸 joining together (**proteins** 蛋白质 are natural polyamides).



The "nylon rope trick": nylon (a polyamide) forms where two reactant solutions meet, so a single long thread can be pulled out (it is pink here from an added indicator)

Worked example (nylon-6,6). Nylon-6,6 尼龙-66 is made from **hexane-1,6-diamine**, $H_2N(CH_2)_6NH_2$, and **hexanedioyl dichloride**, $ClOC(CH_2)_4COCl$. Give the repeat unit and the small molecule lost. The H of each $–NH_2$ and the Cl of each –COCl leave together as HCl, and an amide link –CO–NH– forms:

$$\left[–NH–(CH_2)_6–NH–CO–(CH_2)_4–CO–\right]_n$$



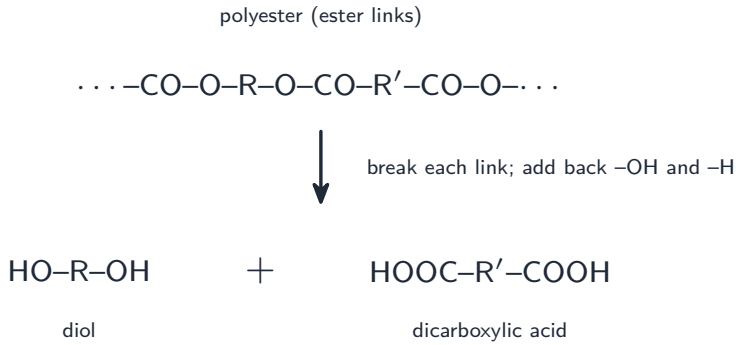
Nylon-6,6: the H of each –NH2 and the Cl of each –COCl leave as HCl, and the repeat unit holds one of each monomer joined by an amide link

The "6,6" counts the carbon atoms in each monomer: six in the diamine and six in the diacid. With hexanedioic acid instead of the dichloride, the small molecule is water, and the reaction needs heating; the dichloride reacts at room temperature, which is why the rope trick works.

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Repeat units and monomers

The **repeat unit** 重复单元 of a condensation polymer contains parts of **both** monomers, minus the atoms lost as the small molecule. To find the **monomers** 单体 from a section of polymer, break the chain at each ester or amide link, then add back –OH and –H (or –Cl).



To find the monomers, break the chain at each link and add back –OH and –H to the cut ends – here giving the diol and the dicarboxylic acid

Worked example. A polymer chain contains repeating –CONH– links. Name the type of polymer, identify the monomers, and give the small molecule lost. A –CONH– link is an **amide**, so this is a **polyamide** made by **condensation** polymerisation. To find the monomers, break the chain at **each** amide link and give the cut ends their atoms back: the carbon side takes –OH, making a **dicarboxylic acid**, and the nitrogen side takes –H, making a **diamine**. The small molecule lost at each link is **water** (or HCl, if an acyl dichloride was used in place of the acid). Each monomer must have **two** functional groups, or the chain could never keep growing - if the monomer you propose has only one, you have broken the chain in the wrong place.

Predicting the type of polymerisation

Clue	Type
the monomer has a **C=C double bond** 碳碳双键, and **nothing** else is lost	**addition polymerisation** 加成聚合
each monomer has **two functional groups** 官能团, and a small molecule is lost; the chain has ester or amide links	condensation polymerisation

addition polymerisation
- monomer has a **C=C**
- the double bond opens and the monomers join
- **nothing else** is lost

e.g. ethene → poly(ethene)

condensation polymerisation
- each monomer has **two** functional groups
- a **small molecule** (H_2O or HCl) is lost
- ester or amide links form

e.g. a polyester or polyamide

The two kinds of polymerisation: addition opens a C=C and loses nothing; condensation joins two-group monomers and loses a small molecule

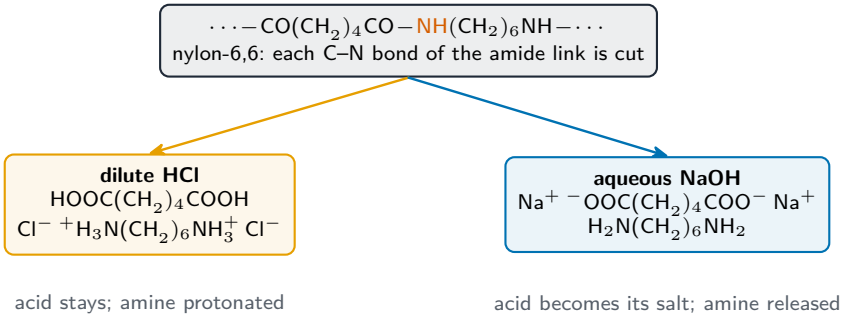
Degradable polymers

- **poly(alkene)s** 聚烯烃 are chemically **inert** 惰性的 – they have only strong, **non-polar** 非极性的 C–C and C–H bonds, so they are hard to **biodegrade** 生物降解 and last a long time.
- some polymers are made so that light can break them down (they are **photodegradable** 可光降解的).
- polyesters and polyamides are **biodegradable** 可生物降解, because their ester and amide links can be broken by acidic or **alkaline** 碱性的 **hydrolysis** 水解.

Worked example (hydrolysis products). Give the products when nylon-6,6 is heated with (a) dilute hydrochloric acid, (b) aqueous sodium hydroxide. Hydrolysis breaks each C–N bond of the amide link, giving back the acid and amine parts; then the conditions decide their form.

- (a) In acid, the carboxylic acid stays as **hexanedioic acid**, $HOOC(CH_2)_4COOH$, and the basic amine groups are protonated: the **diammonium salt** $Cl^- {}^+H_3N(CH_2)_6NH_3^+ Cl^-$.
- (b) In alkali, the acid groups become the **sodium salt**, $Na^+ {}^-OOC(CH_2)_4COO^- Na^+$, and the amine is released as **hexane-1,6-diamine**.

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One cut, two outcomes: the conditions decide which part is a salt.

A polyester behaves in the same way: in alkali it gives the diol and the sodium salt of the diacid.

Common mistakes.

- Drawing a condensation polymer's repeat unit with the full monomers. Remove the atoms lost as water or HCl at **each** link, and show the bonds at both ends as **continuation bonds** across the brackets.
- Losing water when a dioyl chloride is used. A dioyl chloride loses **HCl**, not water.
- Breaking the chain in the wrong place to find the monomers. Cut through the **C–O** of the ester or the **C–N** of the amide (between C=O and O/N), not next to it.
- Calling a polymer with a C=C monomer a condensation polymer because the backbone looks long. If nothing is lost, it is **addition** polymerisation.
- Saying poly(alkene)s are biodegradable because they are "organic". Their non-polar C–C and C–H bonds give **no** site for hydrolysis, so they persist; only the ester and amide links of condensation polymers hydrolyse.

Exam tips

- **Condensation polymers** (polyesters, polyamides) form with **loss of a small molecule** (H_2O or HCl) – draw the repeat unit and the lost molecule.
- Identify the **monomers from the polymer** by breaking the ester or amide link – a common question.
- **Predict the type** from the monomers: a C = C gives addition; two functional groups give condensation.
- Polyesters and polyamides are **hydrolysable** (more degradable); addition polymers are not.
- For hydrolysis products, write the **salt** that the conditions give: an ammonium salt of the amine in acid, a sodium carboxylate in alkali.

- Count the links in one repeat unit: two monomers per repeat unit means two small molecules lost per repeat unit.

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Organic synthesis

A-Level Chemistry

Like the AS synthesis topic, this asks you to **join up** known reactions to build a target molecule. Now you also have the A Level reactions of arenes, phenol, amines, amides and acyl chlorides.

Identifying functional groups

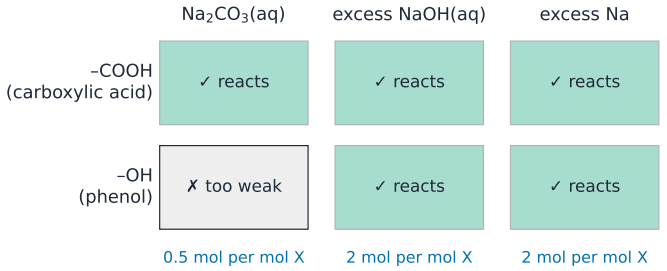
A molecule may carry several **functional group** 官能团 types. Use the test reactions to spot each one, then predict its behaviour. For example:

- decolourises bromine water with **no** catalyst, giving a white precipitate → a phenol or a phenylamine (the ring is activated).
- reacts violently with cold water, giving fumes of HCl → an **acyl chloride** 酰氯.
- gives a purple colour with neutral $FeCl_3$ → a **phenol** 苯酚.

> **Worked example (several groups in one molecule).** Compound **X** is 4-hydroxybenzoic acid, HO–C_6H_4–COOH. Predict what happens when X reacts with (a) Na_2CO_3(aq); (b) excess NaOH(aq); (c) excess sodium metal. Give the number of moles of reagent used per mole of X.

- (a) Only the **carboxylic acid** is acidic enough to react with a carbonate: fizzing (CO_2), giving HO–C_6H_4–COO^-Na^+. The phenol is too weak an acid. **0.5 mol** Na_2CO_3 (1 mol of H^+ needs half a mole of carbonate).
- (b) Both the –COOH and the phenol –OH react with NaOH: $Na^+\ ^-O$–C_6H_4–$COO^-\ Na^+$. **2 mol** NaOH.
- (c) Sodium reacts with **both** O–H groups, giving the same disodium salt and hydrogen: 2 mol Na per mole of X, releasing **1 mol** H_2.

The pattern to learn: carbonate reacts with **carboxylic acids only**; NaOH with carboxylic acids **and** phenols; sodium with every O–H, including alcohols.



Which O–H reacts: carbonate needs a carboxylic acid; NaOH and Na take the phenol too

add this	you see	functional group
bromine water (no catalyst)	white precipitate	**phenol or phenylamine**
cold water	violent, HCl fumes	**acyl chloride**
neutral $FeCl_3$	purple colour	**phenol**

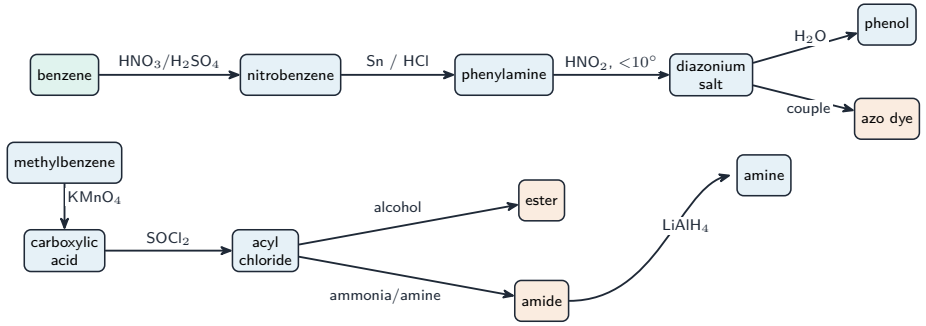
Identification tests added at A Level: each reagent gives a characteristic result that points to a functional group

A map of the A Level reactions

Start	Reagent and conditions	Product
benzene (an **arene** 芳烃)	HNO_3 / H_2SO_4 (**electrophilic substitution** 亲电取代)	nitrobenzene
nitrobenzene	Sn / conc HCl, then NaOH (**reduction** 还原)	phenylamine
phenylamine	HNO_2, below 10 °C	a diazonium salt
diazonium salt	warm water	phenol; or couple with phenol → azo dye
benzene	CH_3Cl / $AlCl_3$, heat (Friedel–Crafts alkylation)	methylbenzene (adds a carbon)
benzene	CH_3COCl / $AlCl_3$, heat (Friedel–Crafts acylation)	phenylethanone, a ketone

Start	Reagent and conditions	Product
methylbenzene	hot $KMnO_4$ (**oxidation** 氧化)	benzoic acid
carboxylic acid 羧酸	$SOCl_2$ or PCl_5	acyl chloride
acyl chloride	alcohol / phenol	an **ester** 酯
acyl chloride	ammonia / **amine** 胺	an **amide** 酰胺
amide or **nitrile** 腈	$LiAlH_4$	an amine
halogenoalkane	KCN	a nitrile (adds one carbon)

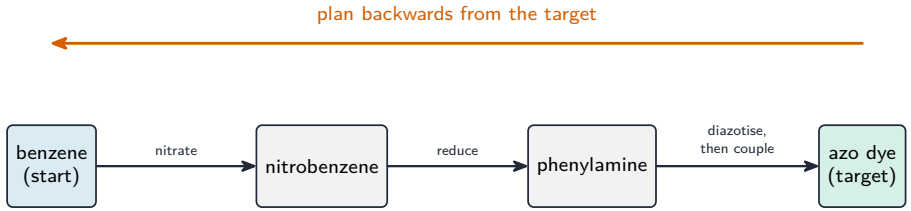
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A map of the A Level reactions: the aromatic chain (top) and the acyl-chloride chain (bottom), with their feed-ins. Work backwards from your target

Planning and analysing a route

To devise a **synthetic route** 合成路线, work **backwards** from the target: which single reaction makes it, and from what? Repeat until you reach the starting material, then write each step with its **reagent** 试剂 and conditions.



Plan a route by working backwards from the target, one reaction at a time, until you reach the starting material

When you **analyse** a route, state the type of reaction for each step (for example electrophilic substitution, **addition–elimination** 加成消去, oxidation or reduction) and watch for likely **by-products** 副产物 – for example, making an amine from a halogenoalkane also gives over-substituted amines, lowering the yield.

Worked example. Devise a route from benzene to phenylamine, $C_6H_5NH_2$. Work **backwards**: phenylamine comes from **reducing** nitrobenzene, and nitrobenzene comes from **nitrating** benzene - so the route is two steps. Step 1: benzene with concentrated HNO_3 and concentrated H_2SO_4 at 55 °C; electrophilic substitution gives nitrobenzene (keep below 55 °C, or further substitution follows). Step 2: reduce the nitrobenzene with **tin and concentrated HCl**, then add NaOH to free the amine from its salt. There is no direct route - you cannot put an $-NH_2$ straight onto a ring, which is exactly why this nitrate-then-reduce pair is worth knowing by heart.

Worked example (a three-step route). Devise a route from methylbenzene to *N*-ethylbenzamide, $C_6H_5CONHCH_2CH_3$. Working **backwards**: an amide comes from an acyl chloride and an amine, so the last step is benzoyl chloride + ethylamine; benzoyl chloride comes from benzoic acid; benzoic acid comes from oxidising the side chain of methylbenzene.

1. Methylbenzene, heat under reflux with alkaline $KMnO_4$, then acidify (**oxidation**): benzoic acid, C_6H_5COOH.
2. Benzoic acid with $SOCl_2$ (or PCl_5), at room temperature: benzoyl chloride, C_6H_5COCl, with SO_2 and HCl.
3. Benzoyl chloride with ethylamine, $CH_3CH_2NH_2$, at room temperature (**addition–elimination**): *N*-ethylbenzamide and HCl.

The HCl formed in step 3 reacts with more ethylamine to give ethylammonium chloride, so two moles of amine are used per mole of acyl chloride. Check the carbons: 7 in methylbenzene are kept, and the amine brings the 2 extra.

Worked example (analysing a route). A student makes phenylamine from benzene by nitration, then reduction with Sn/conc HCl. The yield is low, and the product contains 1,3-dinitrobenzene derivatives. Identify the type of each reaction and explain the by-product. Step 1 is **electrophilic substitution** (NO_2^+ is the electrophile); step 2 is **reduction**. If the nitration mixture is heated above about 55 °C, a second $-NO_2$ group adds to the ring, giving 1,3-dinitrobenzene, which is reduced in step 2 to a diamine: this lowers the yield of phenylamine. Keeping the temperature below 55 °C prevents it.

Common mistakes.

- Writing "add $KMnO_4$" with no conditions. Every step needs its **reagent and conditions**: hot, acidified or alkaline $KMnO_4$, under reflux, for methylbenzene → benzoic acid.
- Forgetting the NaOH after the Sn/HCl reduction. In acid the product is the phenylammonium salt; the **base** frees the amine.
- Using $NaBH_4$ to reduce an amide or a nitrile. $NaBH_4$ is too weak; use **$LiAlH_4$** (or H_2/Ni for a nitrile).

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- Losing count of carbons. KCN adds **one** carbon to the chain; most other steps keep the count the same, so check it at every step.
- Warming the diazonium salt before the coupling step. Above 10 °C it gives phenol and N_2 instead of the azo dye.
- Reaching for $AlCl_3$ to brominate a phenol or phenylamine. These rings are **activated**, so bromine water alone works, and gives substitution at all three of the 2-, 4- and 6-positions.

Exam tips

- Combine AS and A-level steps and watch for **benzene-ring reactions** and **carbon-count changes**.
- State every **reagent and condition**, and note when a step produces a **racemic mixture**.
- Choose the shortest route that reaches the target functional group.

Analytical techniques

A-Level Chemistry

Thin-layer chromatography

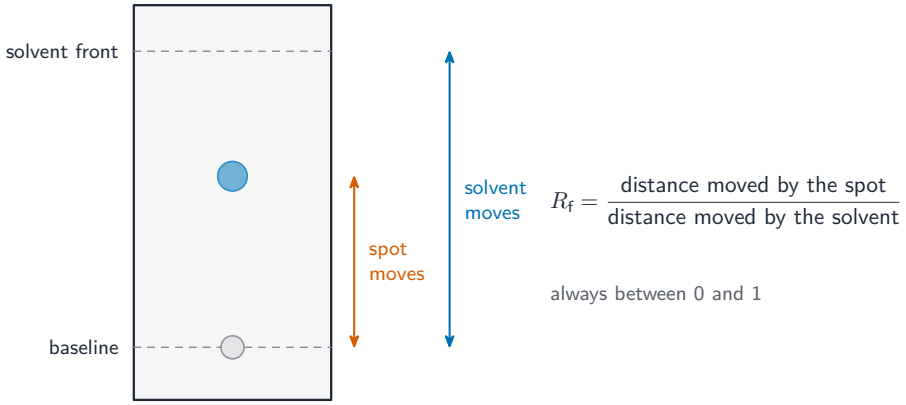
Chromatography 色谱 separates a mixture using two "phases" – one that stays still and one that moves. In **thin-layer chromatography** 薄层色谱 (TLC):

- the **stationary phase** 固定相 stays still (for example aluminium oxide on a plate).
- the **mobile phase** 流动相 moves (a polar or non-polar solvent that travels up the plate).
- the **baseline** 基线 is the starting line where the spots are placed; the **solvent front** 溶剂前沿 is the highest level the solvent reaches.

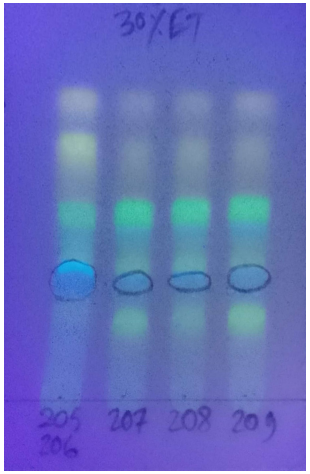
The R_f value compares how far a spot moves with how far the solvent moves:

$$R_f = \frac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$$

It is always between 0 and 1. A substance that sticks more strongly to the stationary phase, or is less soluble in the mobile phase, moves less and has a **smaller** R_f.



Thin-layer chromatography: the R_f value is how far the spot moved divided by how far the solvent front moved



A real TLC plate under UV light: each glowing spot is a separated component of the mixture

Why spots move different distances. As the solvent rises, each compound is shared between the two phases. It is **adsorbed** onto the polar surface of the aluminium oxide (or silica), held by hydrogen bonds or dipole forces, and it **dissolves** in the moving solvent. A compound that is adsorbed strongly spends more time stuck to the plate and moves a short distance. A compound that is very soluble in the solvent spends more time moving and travels far. Changing the solvent changes the R_f values, so always state the solvent with an R_f.

Method points. Draw the baseline in **pencil** (ink would run), above the level of the solvent in the tank (or the spots would dissolve away). Put a lid on the tank so the air is saturated with solvent vapour and the solvent does not evaporate from the plate. Remove the plate before the solvent reaches the top, and mark the solvent front at once. Colourless spots are made visible by shining **ultraviolet light** on a plate containing a fluorescent dye, or by spraying with a locating agent such as **ninhydrin** (for amino acids) or exposing to iodine vapour.

> **Worked example.** On a plate the solvent front is 8.0 cm above the baseline. A mixture gives spots at 2.0 cm and 5.6 cm. A pure sample of compound P, run alongside, gives one spot at 5.6 cm. Find the R_f values and decide whether P is in the mixture. $R_f = 2.0 \div 8.0 = 0.25$ and $5.6 \div 8.0 = 0.70$. P also has $R_f = 0.70$ in the same solvent on the same plate, so P is **probably** present. Running the reference on the same plate (**co-spotting**) is fairer than comparing with a table, because the temperature and solvent are identical. The spot at 0.25 is the more polar component: it is held more strongly by the polar stationary phase.

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Gas/liquid chromatography

In **gas/liquid chromatography** 气液色谱 (GLC):

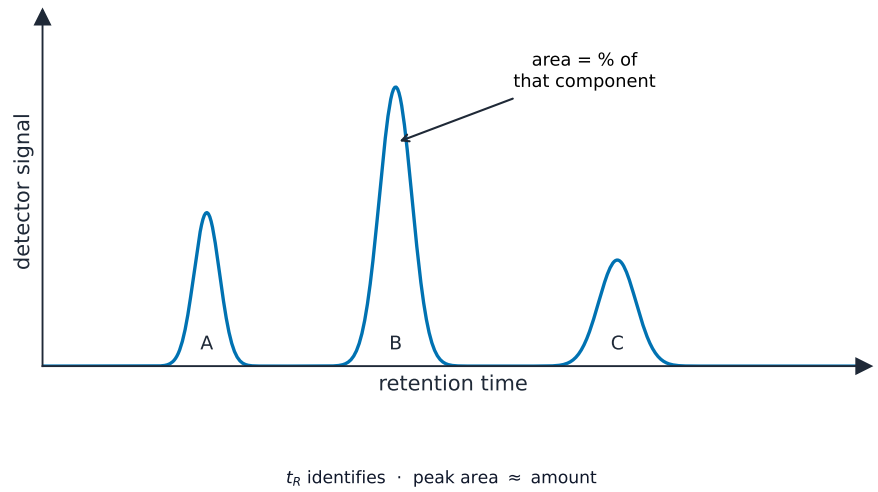
- the stationary phase is a high-boiling-point non-polar liquid on a solid support.
- the mobile phase is an unreactive carrier gas.
- the **retention time** 保留时间 is how long a component takes to pass through.

The area of each peak gives the percentage of that component in the mixture. A component that interacts more with the stationary phase has a longer retention time.

Components that are more **soluble** in the non-polar liquid stationary phase (because they have stronger intermolecular forces with it, such as larger non-polar molecules with stronger London forces), or that have **higher boiling points**, spend more time in the liquid and less in the moving gas, so they have **longer** retention times. Retention time also depends on the column temperature, its length, and the gas flow rate, so these are kept the same when comparing samples.

> **Worked example (percentage composition).** A GLC of a mixture of three esters gives peak areas of 45, 30 and 75 (arbitrary units). Find the percentage of each. Total area $= 45 + 30 + 75 = 150$. The percentages are $45/150 \times 100 = 30\%$, $30/150 \times 100 = 20\%$ and $75/150 \times 100 = 50\%$. This assumes the detector responds equally to each component; for accurate work, the instrument is first calibrated with known mixtures. If the peaks are triangles, find each area as $\frac{1}{2} \times$ base $\times$ height.

GLC is used, for example, to measure the alcohol in a blood sample, or to check the purity of a product: a pure substance gives a single peak.



A gas–liquid chromatogram: each component gives a peak at its own retention time, and the peak area is its percentage in the mixture

Carbon-13 NMR spectroscopy

NMR 核磁共振 (nuclear magnetic resonance) studies how certain nuclei behave in a strong magnetic field.



An NMR spectrometer: the large cylinder holds a superconducting magnet that makes the very strong magnetic field the technique needs

In carbon-13 NMR, each different **chemical environment** 化学环境 of carbon gives one peak. So:

- the **number of peaks** tells you how many different carbon environments there are (equivalent carbons share a peak).
- the position of each peak (its chemical shift) suggests the type of carbon, which helps you deduce possible structures.

Carbon environment	Chemical shift δ / ppm (typical)
C–C (alkyl)	5–40
C–Cl or C–Br	10–70
C–N (amine)	25–60
C–O (alcohol, ether, ester)	50–90
C=C (alkene) and aromatic C	110–160
C=O (ester, acid, amide)	160–185
C=O (aldehyde, ketone)	190–220

Use the data booklet for the exact ranges in an exam. Peak heights in ^{13}C NMR do **not** give the numbers of carbons; only the **number** and **positions** of the peaks are used.

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Worked example (counting environments). How many peaks does each isomer of $C_4H_{10}O$ give: butan-1-ol, butan-2-ol, 2-methylpropan-2-ol? Butan-1-ol, $CH_3CH_2CH_2CH_2OH$: all four carbons are different → **4** peaks. Butan-2-ol, $CH_3CH(OH)CH_2CH_3$: the two CH_3 groups are different (one is next to the C–OH, the other is not) → **4** peaks. 2-methylpropan-2-ol, $(CH_3)_3COH$: the three CH_3 groups are equivalent by symmetry → **2** peaks. So ^{13}C NMR picks out the third isomer at once; the other two are told apart by the positions of their C–O peaks or by proton NMR.

Worked example (from a spectrum). A ketone $C_5H_{10}O$ gives three ^{13}C peaks, one at δ 211. Is it pentan-2-one or pentan-3-one? Pentan-2-one, $CH_3COCH_2CH_2CH_3$, has five different carbons (5 peaks). Pentan-3-one, $CH_3CH_2COCH_2CH_3$, is symmetrical: the two CH_3 are equivalent, the two CH_2 are equivalent, plus the C=O → **3** peaks. So it is **pentan-3-one**; the peak at 211 is its C=O.

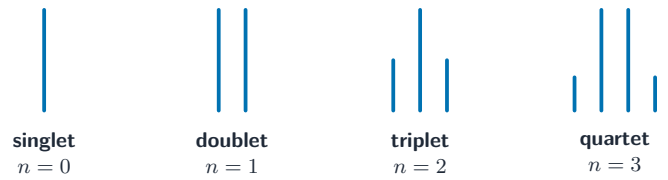
Proton (^{1}H) NMR spectroscopy

Proton NMR looks at the hydrogen atoms (**proton** 质子 nuclei). From the spectrum you read off:

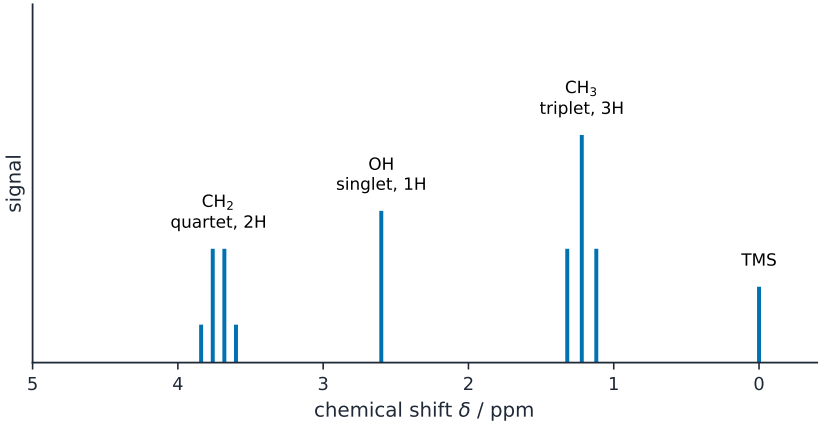
- **chemical environments**: protons in different environments appear at different **chemical shift** 化学位移 values.
- **relative numbers**: the relative peak **areas** give the ratio of each type of proton.
- **splitting** 裂分: a peak is split by the protons on the neighbouring carbon, following the $n+1$ **rule** – n equivalent neighbours split a peak into $n+1$ lines:

Neighbours (n)	Pattern
0	**singlet** 单峰
1	**doublet** 双峰
2	**triplet** 三峰
3	**quartet** 四峰
many	**multiplet** 多重峰

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The $n+1$ rule: n equivalent neighbouring protons split a peak into $n+1$ lines (singlet, doublet, triplet, quartet)



Proton NMR of ethanol: three environments give a CH_3 triplet, a CH_2 quartet and an OH singlet, with areas in the ratio 3 : 2 : 1

Proton chemical shifts. The more electronegative the atom near a proton, the further **downfield** (higher δ) its peak:

Proton environment	δ / ppm (typical)
alkyl, CH_3, CH_2 (R–CH)	0.9–1.7
next to C=O, $CH_3C{=}O$	2.0–2.5
next to a benzene ring	2.2–3.0
on C bonded to O, CH–O (alcohol, ester)	3.3–4.3
O–H in an alcohol	1.0–5.5 (variable)
on a benzene ring	6.5–8.0

Proton environment	δ / ppm (typical)
aldehyde CHO	9.5–10
O–H in a carboxylic acid	10–12

Worked example (predicting a spectrum). Predict the proton NMR spectrum of propan-2-ol, $(CH_3)_2CHOH$. There are three environments. The six CH_3 protons are equivalent: area 6, at about δ 1.2, split by the one CH proton into a **doublet**. The CH proton: area 1, at about δ 4.0 (on C–O), split by six neighbours into a **multiplet** (seven lines). The OH proton: area 1, a **singlet** (it does not split, and it disappears with a D_2O shake). Area ratio 6 : 1 : 1.

Practical points

- **tetramethylsilane** 四甲基硅烷 (TMS) is the standard, set at a chemical shift of 0.
- a **deuterated solvent** 氘代溶剂 (such as $CDCl_3$) is used so that the solvent itself gives no proton signal.
- shaking the sample with D_2O makes the O–H and N–H peaks disappear (their hydrogen is swapped for deuterium), which identifies those protons.

Worked example. A compound $C_4H_8O_2$ gives three proton NMR peaks: a **triplet** at δ 1.2 (area 3), a **quartet** at δ 4.1 (area 2), and a **singlet** at δ 2.0 (area 3). Deduce the structure. Read the areas first, then the splitting. Areas 3 : 2 : 3 give three proton environments holding 3, 2 and 3 hydrogens. Apply the $n+1$ rule **in reverse**: a **triplet** (area 3) is a CH_3 with **2** neighbours, and a **quartet** (area 2) is a CH_2 with **3** neighbours - each splitting the other, which is the classic **ethyl group**, CH_3CH_2-. That CH_2 lies far downfield at δ 4.1, so it is attached to an **oxygen**. The remaining **singlet** (area 3) is a CH_3 with **no** neighbours at δ 2.0, so it sits next to the C=O. Together: $CH_3COOCH_2CH_3$, **ethyl ethanoate**. A triplet-and-quartet pair is almost always an ethyl group - spot it first and the rest follows.

Common mistakes.

- Counting the protons **in** a group to predict its splitting. The splitting comes from the n equivalent protons on the **neighbouring** carbon: a CH_3 next to a CH_2 is a **triplet**, not a quartet.
- Splitting an O–H peak. An O–H proton usually appears as a **singlet** and does not split its neighbours, because it exchanges quickly; the D_2O shake removes it.
- Reading peak heights as the proton ratio. The ratio comes from the peak **areas** (integration).
- Counting every carbon as a separate ^{13}C peak. Carbons related by **symmetry** share a peak: propanone has two carbon environments, not three.

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- Saying TMS is used because it is "a reference". Say why it suits: all 12 of its protons are in one environment, giving a single strong peak, and it is inert and volatile.
- Using an ordinary $CHCl_3$ solvent. Its own proton would show on the spectrum; use a **deuterated** solvent such as $CDCl_3$.
- Calling the spot nearest the baseline in TLC the least polar. With a polar stationary phase (aluminium oxide or silica), the **more polar** compound sticks more and moves **less**, giving a smaller R_f.

Exam tips

- In **^{13}C NMR** the number of peaks equals the number of **carbon environments** – use symmetry to count them.
- In **^{1}H NMR** use **chemical shift** (data booklet), **integration** (ratio of H's) and **splitting** (the $n+1$ rule): a triplet + quartet means an ethyl group.
- **TMS** is the reference ($\delta = 0$); a **D_2O shake** removes O-H and N-H peaks.
- Combine IR, mass spectrum and NMR to deduce a structure, stating which evidence gives which feature.
- R_f = spot distance ÷ solvent-front distance, both from the baseline; a more polar compound has a smaller R_f on a polar plate.
- GLC percentage = peak area ÷ total area × 100; longer retention time = more soluble in (more attracted to) the liquid stationary phase.
- To predict a proton spectrum, list each environment with its area, its δ from the table, and its splitting from the neighbours.