Course Companion

A-Level Chemistry

Every topic handout in one volume

全部专题讲义合集

exercises.lol

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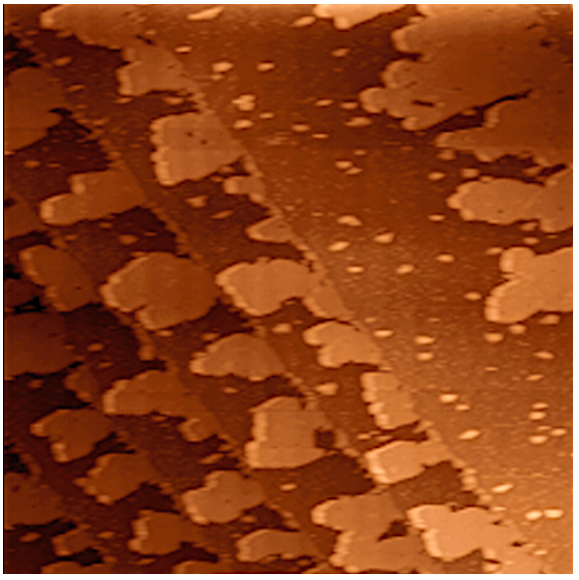
Atomic structure

A-Level Chemistry

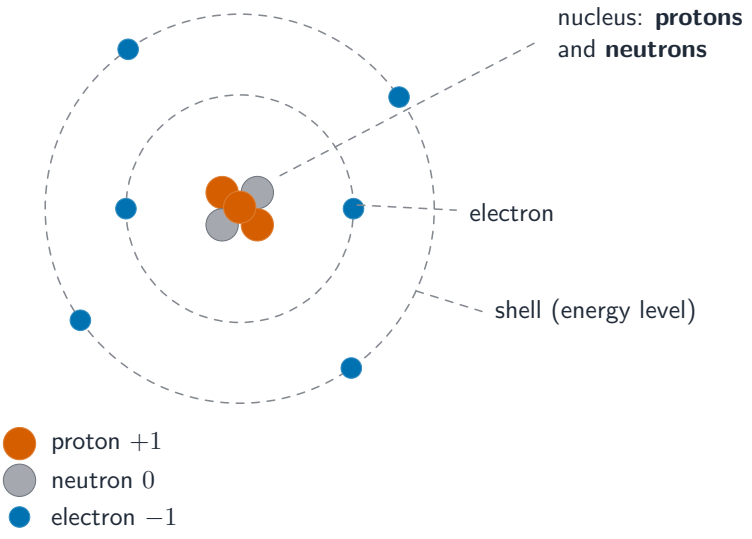
What an atom is made of



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 $A - Z$.

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

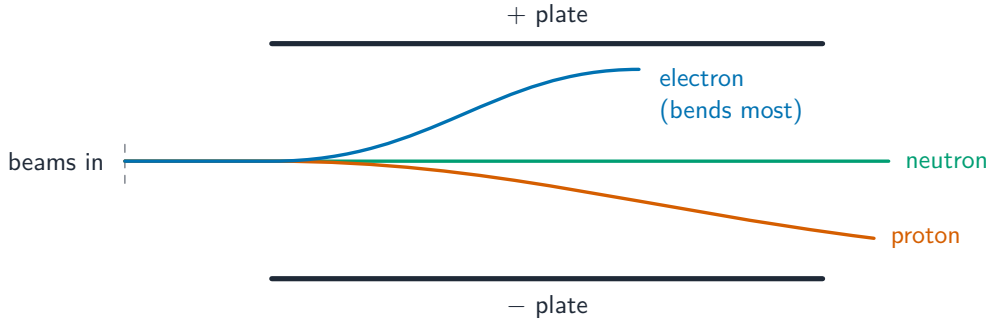
How mass and charge are spread out

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.



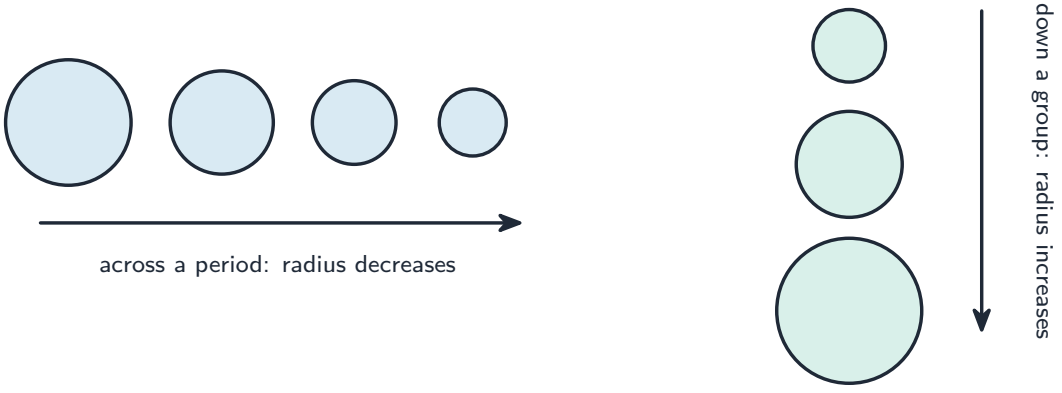
In an electric field the proton bends towards the − plate and the electron bends the opposite way and far more (it is much lighter); the neutron passes straight through

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.



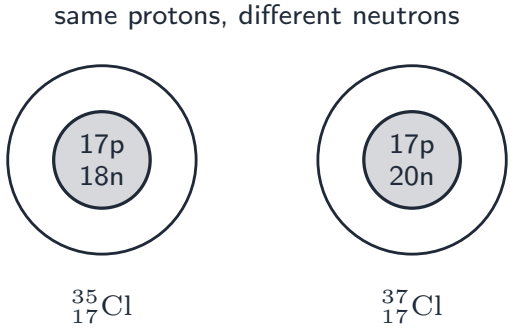
Across a period the atoms shrink (stronger nuclear pull on the same outer shell); down a group they grow (each step adds a shell)

For ions:

- a positive ion (**cation** 阳离子) is smaller than its atom. It has lost its outer shell, and the electrons that remain feel a stronger pull each.
- 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 ${}^{A}_{Z}\mathrm{X}$: the nucleon number A on top, the proton number Z below. For example, chlorine has two main isotopes, ${}^{35}_{17}\mathrm{Cl}$ and ${}^{37}_{17}\mathrm{Cl}$.

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

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

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

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 means a shell that is further from the nucleus and higher in energy.

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

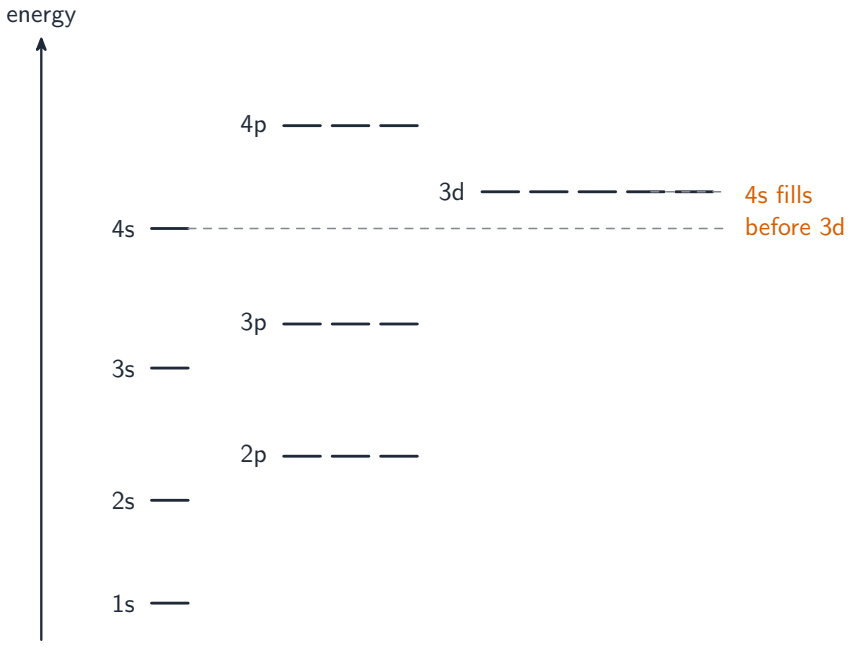
So an s sub-shell holds 2 electrons, a p sub-shell holds 6, and a d sub-shell holds 10.

Order of increasing energy

Electrons fill the lowest-energy sub-shell first. For the first three shells, plus 4s and 4p, the order of rising energy is:

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

Notice the surprise: 4s is slightly lower in energy than 3d, so 4s fills first.



The sub-shells in order of increasing energy. 4s lies just below 3d, so 4s fills first

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:

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

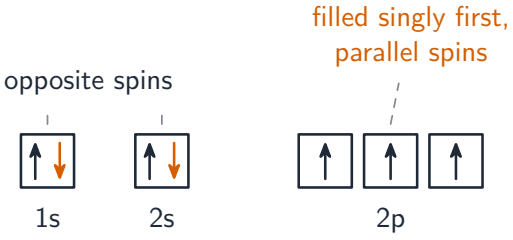
Here [Ar] stands for the full configuration of argon.

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 $[Ar]\,3d^5$.

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.



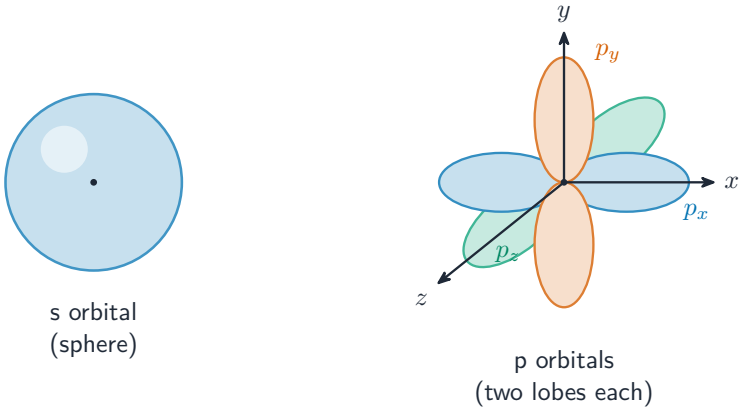
Electrons in boxes for nitrogen ($1s^2\,2s^2\,2p^3$): paired electrons point opposite ways, and the 2p orbitals fill singly with parallel spins

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).



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. Free radicals are very reactive.

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.

We use gaseous atoms so there are no forces between the particles. 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.

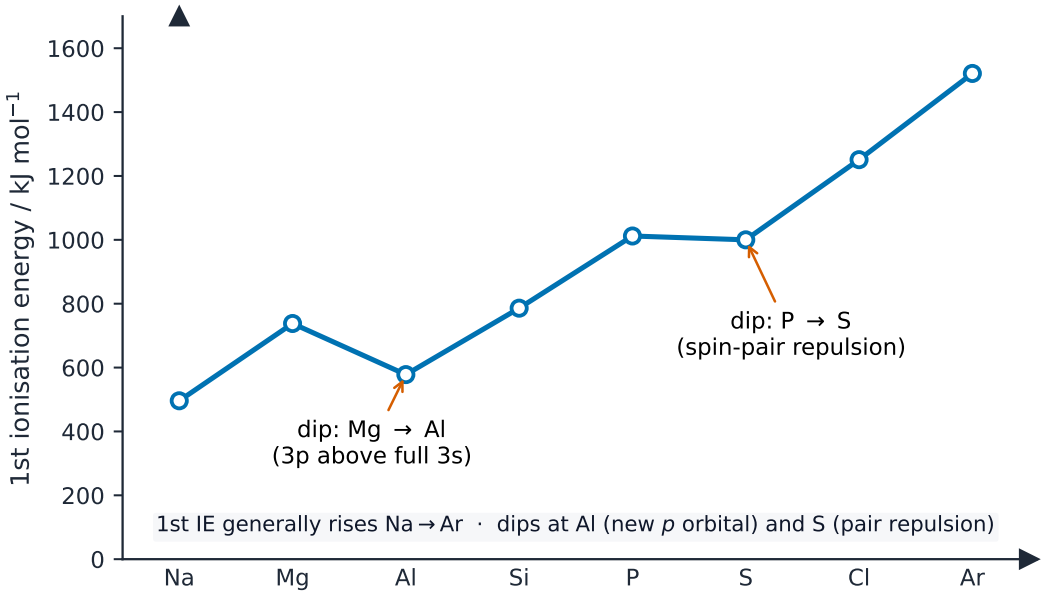
Down a group, the first ionisation energy **falls**. Lower elements have more shells, so more shielding and a larger radius, and the outer electron is easier to remove.

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.

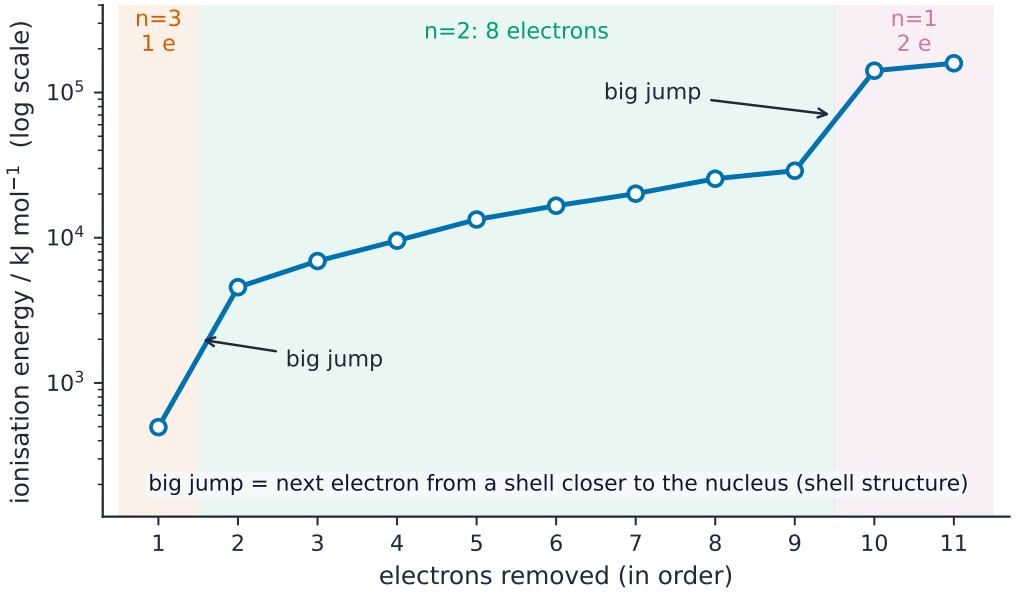


First ionisation energy rises across Period 3 but dips at Al and at S — evidence that sub-shells exist

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.

Count how many electrons come off easily before the first big jump — that is the number of electrons in the outer shell, which tells you the **group** the element is in. You can also use the pattern to work out the electronic configuration and the position of the element in the Periodic Table.



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 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.

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 Fe^{3+} is $[Ar]3d^5$ (not $[Ar]3d^3 4s^2$).
- 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.

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

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 the same number of particles as there are atoms in exactly 12 g of carbon-12. That number is the **Avogadro constant** 阿伏伽德罗常量:

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

So one mole of anything contains 6.02×10^{23} particles. 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:

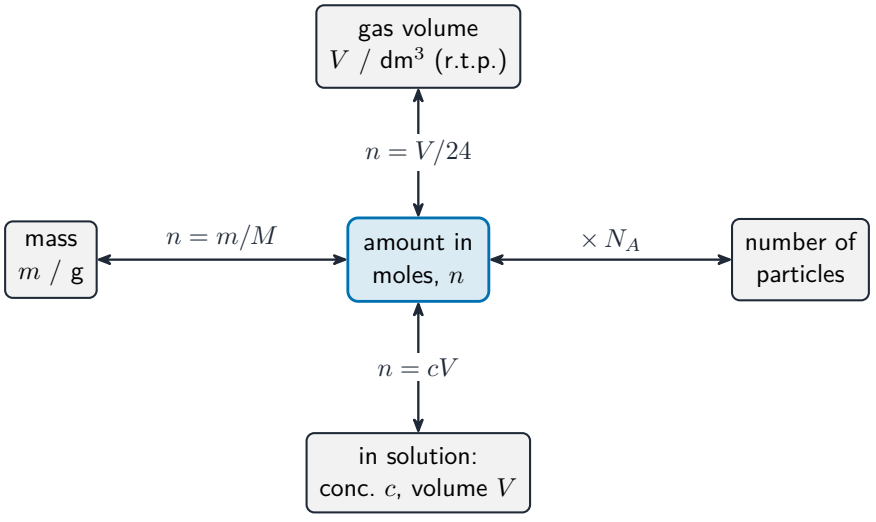
$$n = \frac{m}{M}$$

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^+
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 $CuSO_4$.

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.)

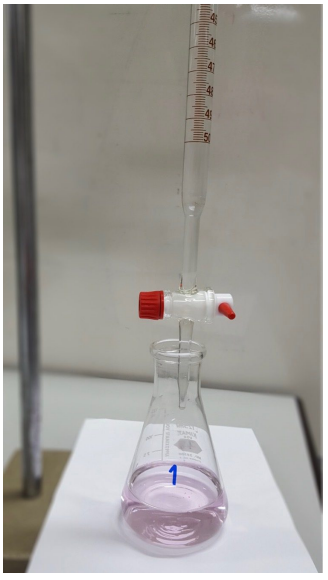
Take 100 g and divide each mass by its A_r to get moles: C = 40.0/12 = 3.33, H = 6.7/1 = 6.7, O = 53.3/16 = 3.33. Dividing through by the smallest (3.33) gives a ratio C : H : O = 1 : 2 : 1, so the empirical formula is CH_2O.

element	% by mass	$\div A_r \rightarrow$ moles	$\div$ 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.

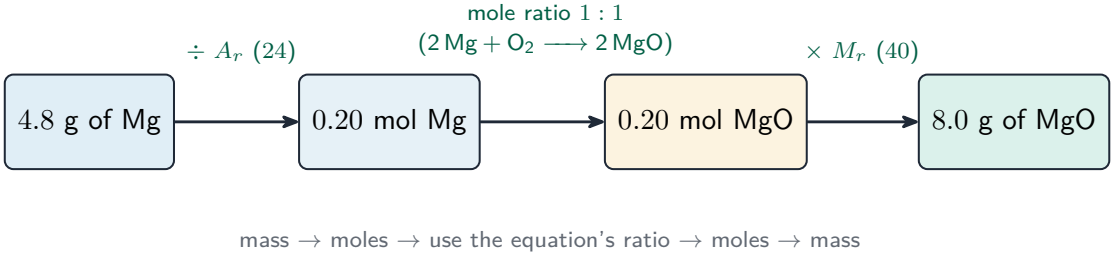
Reacting masses and percentage yield

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? $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$. ($A_r$: 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

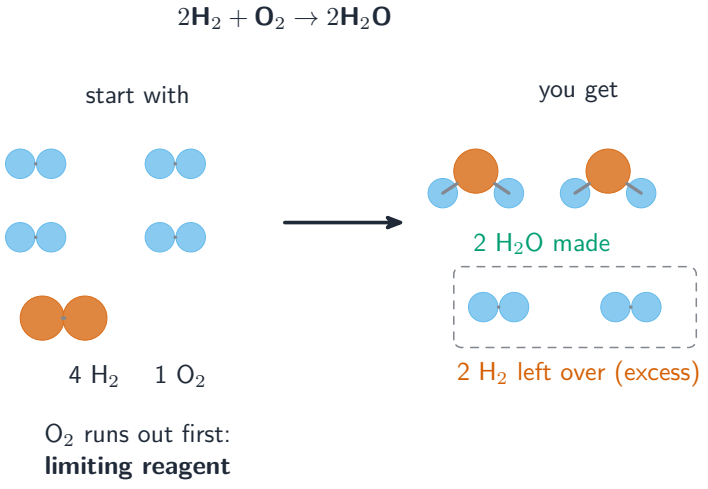
In real reactions you usually get less product than the maximum. The **percentage yield** 产率 compares the amount you actually made with the most you could make:

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

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.



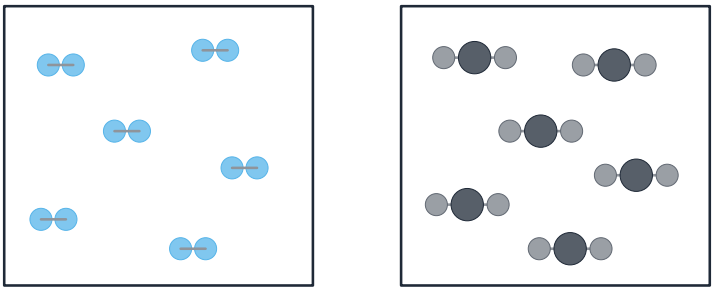
The limiting reagent runs out first and decides how much product forms; the leftover reactant is in excess

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:

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

same volume, same temperature and pressure



hydrogen, H_2 carbon dioxide, CO_2

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.

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}:

$$n = c \times V$$

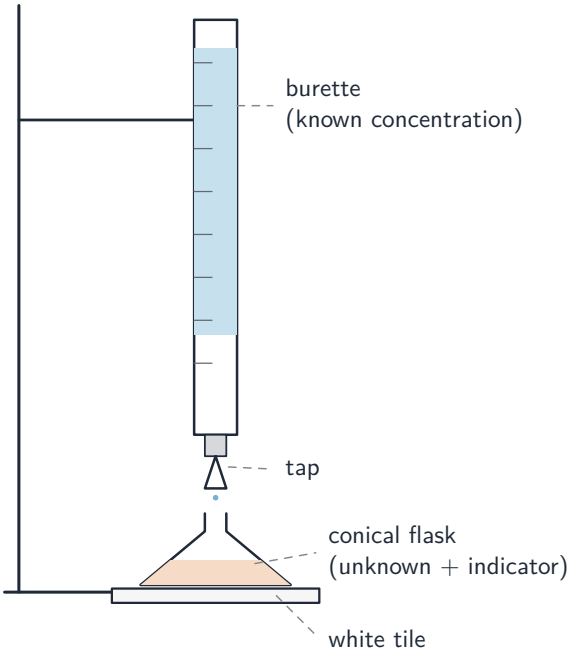
where c is the concentration and V is the volume in dm^3. Remember that 1000 cm^3 = 1 dm^3.

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: $NaOH + HCl \rightarrow NaCl + H_2O$. 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.



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.

Exam tips

- Convert volumes to dm^3 **before** using concentration ($25.0\ cm^3 = 0.0250\ dm^3$); the missing $\div 1000$ 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 $\times$ 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.

Chemical bonding

A-Level Chemistry

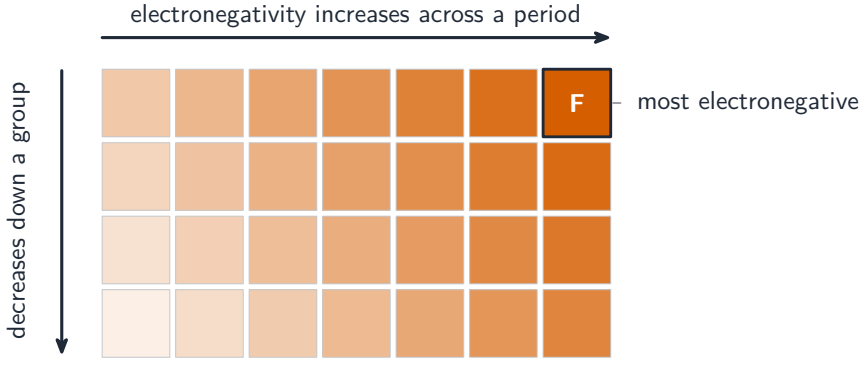
Electronegativity

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.



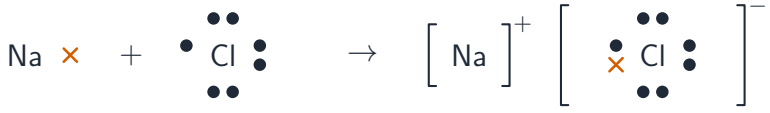
Electronegativity rises across a period and falls down a group, so fluorine is the most electronegative element

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

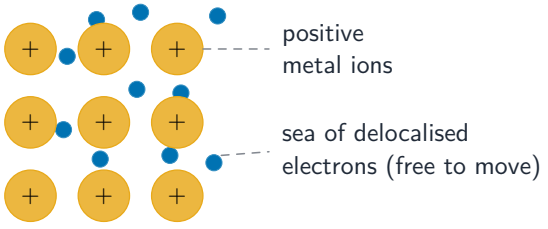
Ionic bonding in NaCl: sodium transfers its single outer electron to chlorine, giving Na^+ and a full-octet Cl^-

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

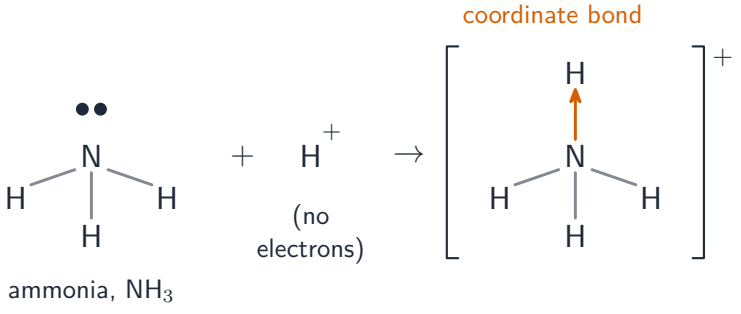
Covalent and coordinate bonding

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.



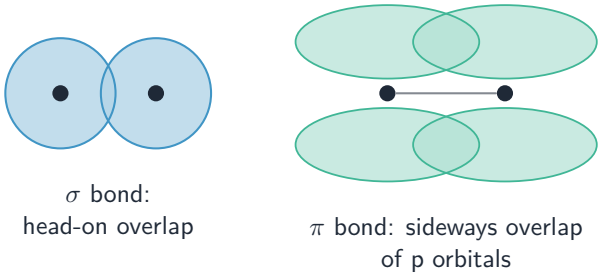
A coordinate (dative) bond: nitrogen's lone pair forms the fourth N–H bond, both electrons coming from N

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:

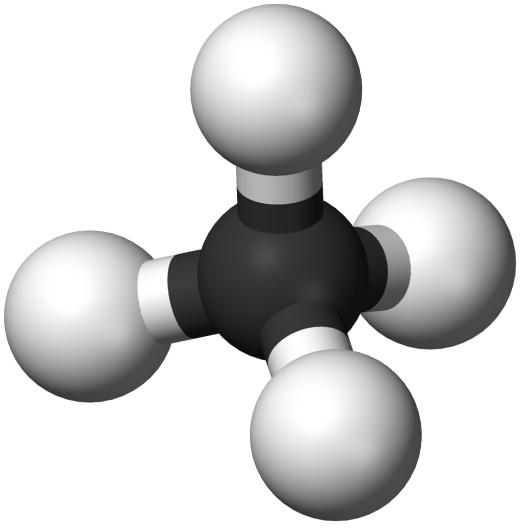
- sp: two equal orbitals, used in a linear molecule.
- sp^2: three equal orbitals, used in a flat molecule like C_2H_4.
- sp^3: four equal orbitals, used in CH_4.

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



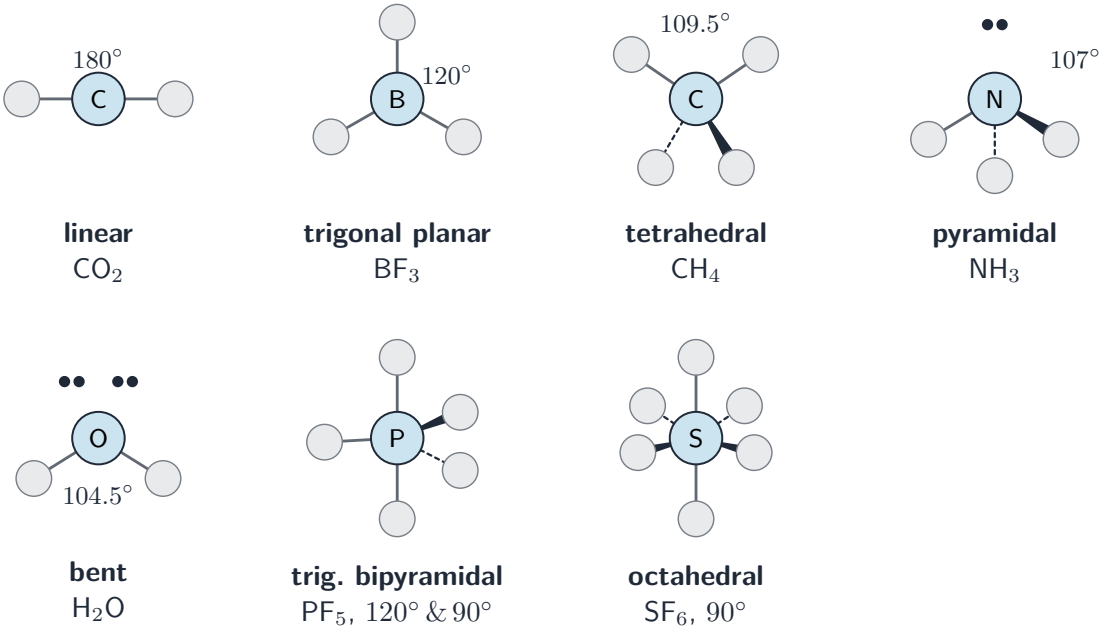
A molecular model shows the three-dimensional shape of a covalent molecule.

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.

A **lone pair** 孤对电子 (not in a bond) pushes more strongly than a **bonding pair** 成键电子对. Each lone pair squeezes the **bond angle** 键角 by about 2.5°.

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, subtract 2.5° for **each** lone pair, and name the shape from the **atoms** - NH_3 has four pairs but is pyramidal, not tetrahedral.

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

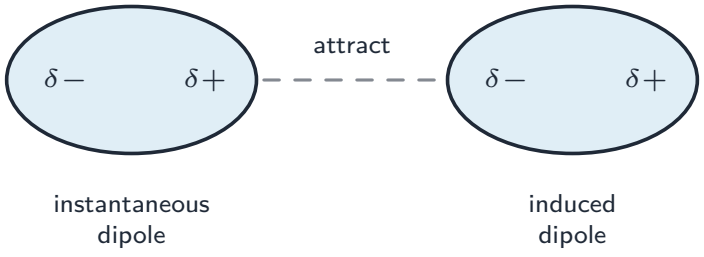
When two atoms with different electronegativity share a bond, the electrons sit closer to the more electronegative atom. The bond then has a **polarity** 极性: one end is slightly negative ($\delta-$) and the other slightly positive ($\delta+$). This separation of charge is a **dipole** 偶极.

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.

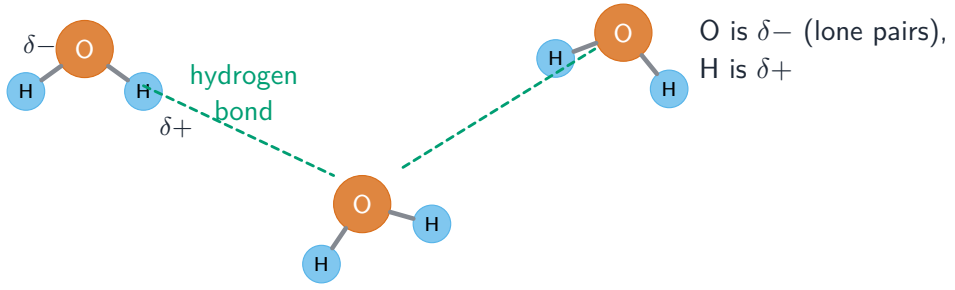


A London force: a momentary dipole in one molecule induces a dipole in its neighbour, so they attract — this acts between all molecules

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.

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.



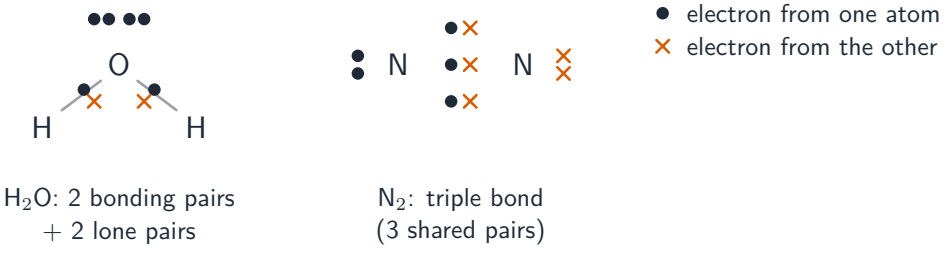
Hydrogen bonding in water: a δ+ hydrogen is attracted to a lone pair on the δ− oxygen of a neighbouring molecule

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.

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)

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".

States of matter

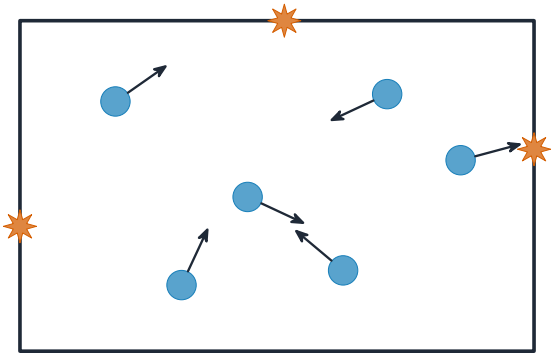
A-Level Chemistry

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**

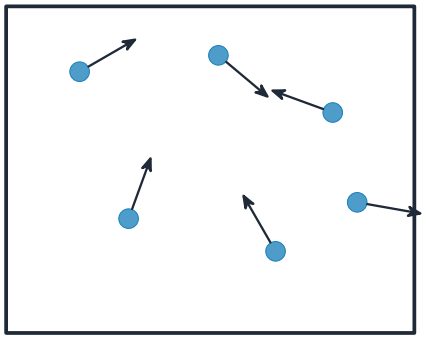
Gas pressure: fast molecules move in all directions and collide with the walls; the many tiny pushes add up to the pressure

Ideal gases

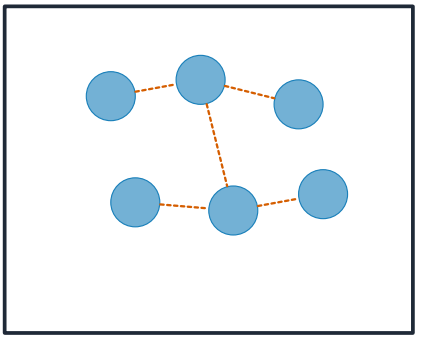
An **ideal gas** 理想气体 is a simple model. We assume two things:

- 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

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

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}.)

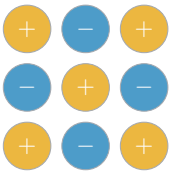
Convert: $V = 6.00 \times 10^{-4}$ m^3, $T = 300$ K. Then

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

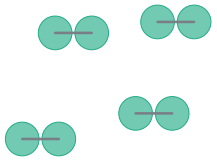
Bonding and structure

Quartz is a giant covalent structure of silicon and oxygen.

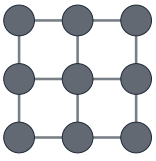
How a substance behaves depends on how its particles are joined. There are four main structures of a **crystalline solid** 晶体.



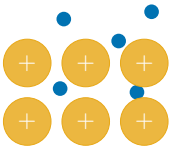
giant ionic
NaCl: high m.p.,
conducts when molten



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

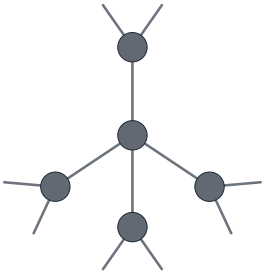
A **giant ionic** 离子晶体 structure is a huge regular **lattice** 晶格 of positive and negative **ions** 离子, held together by strong attraction in every direction. Examples are sodium chloride and magnesium oxide.

Simple molecular

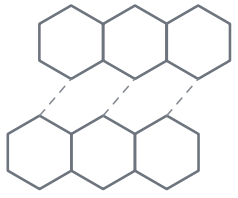
A **simple molecular** 分子晶体 structure is made of small **molecules** 分子. The bonds inside each molecule are strong, but the intermolecular forces between the molecules are weak. Examples are iodine (I_2), **fullerene** 富勒烯 (C_{60}) and ice.

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.



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.

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.

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.

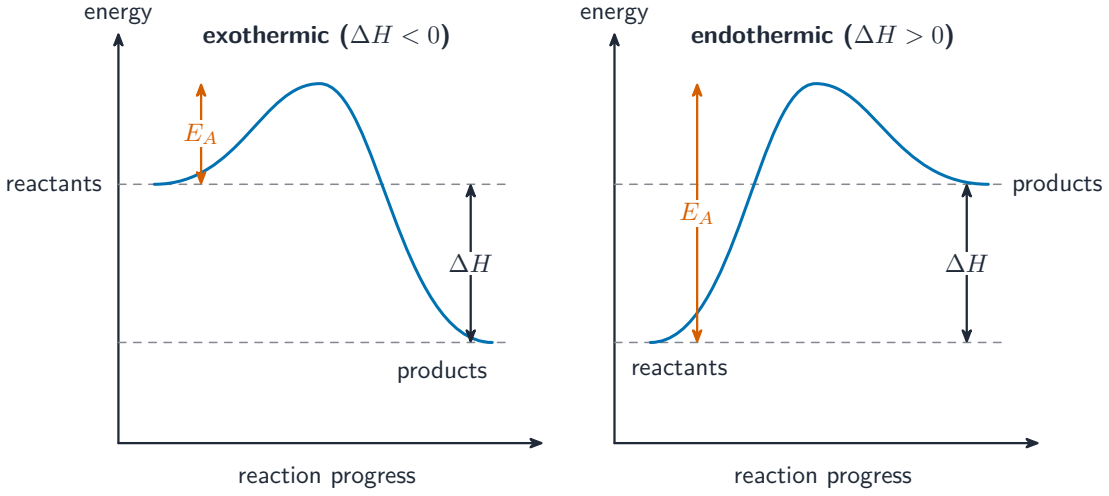
Every chemical reaction takes in or gives out energy. This energy change, measured at constant pressure, is the **enthalpy change** 焓变, with symbol ΔH.

- 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 ($\Delta H > 0$).

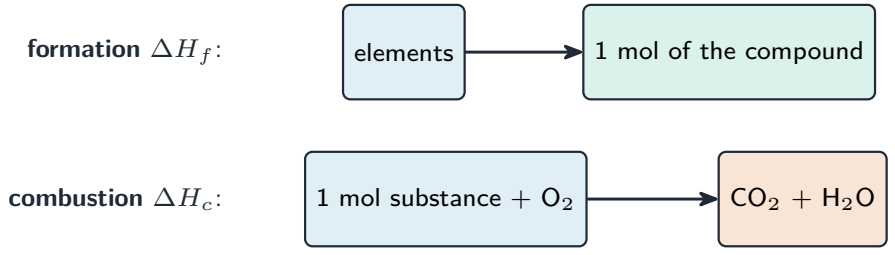


Exothermic reactions end lower than they start ($\Delta H < 0$); endothermic reactions end higher ($\Delta H > 0$)

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.

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

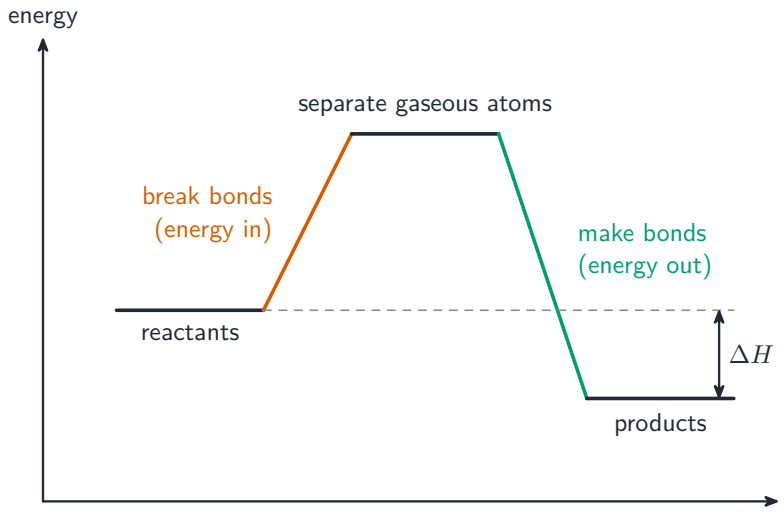
During a reaction, old bonds break and new bonds form. **Breaking** a bond needs energy (endothermic); **making** a bond releases energy (exothermic). The enthalpy change of the reaction is the difference between the two:

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

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.

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



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:

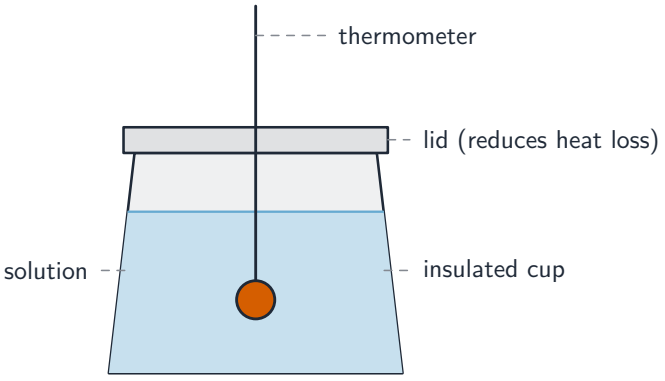
$$\Delta H = -\frac{mc\Delta T}{n}$$

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

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

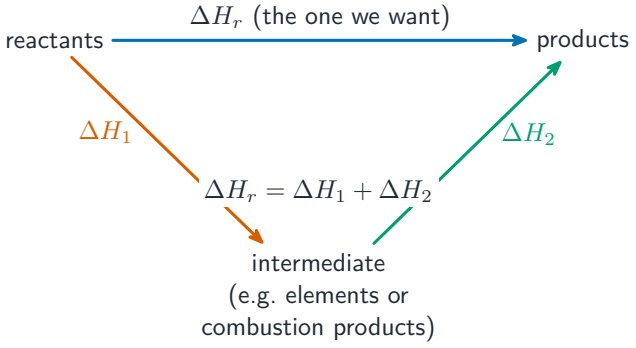


An insulated cup and a thermometer measure the temperature change of a known mass of solution

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.



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.

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.
- 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.

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

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

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

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

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

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

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

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

Redox in terms of electrons

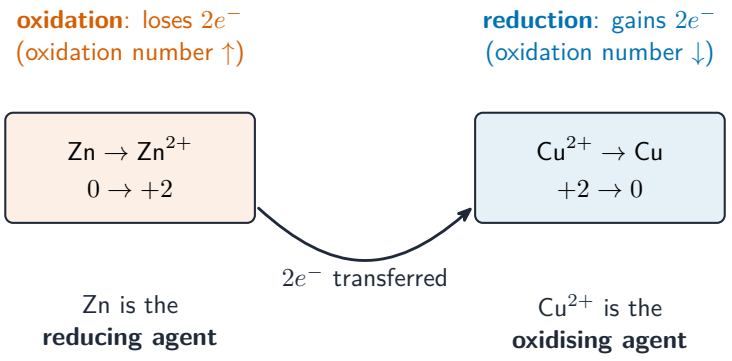
A battery uses redox reactions to push electrons round a circuit.

A **redox** 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.

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

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

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

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

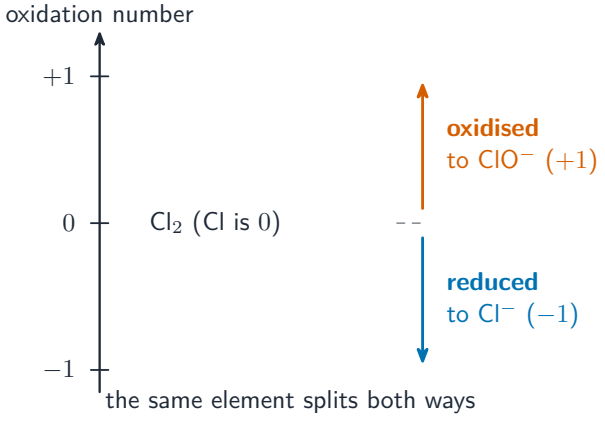
Worked example. Balance the reaction of manganate(VII) with iron(II) in acid: $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$.

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^+ ($8\,H^+$):

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

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^-).



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

Oxidising and reducing agents

Rusting is the oxidation of iron by oxygen.

- an **oxidising agent** 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.

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

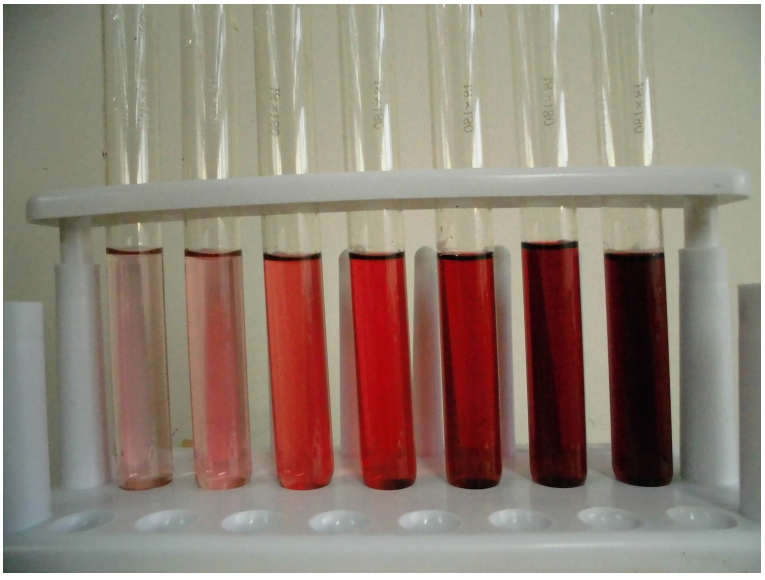
Exam tips

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

Equilibria

A-Level Chemistry

Reversible reactions and dynamic equilibrium



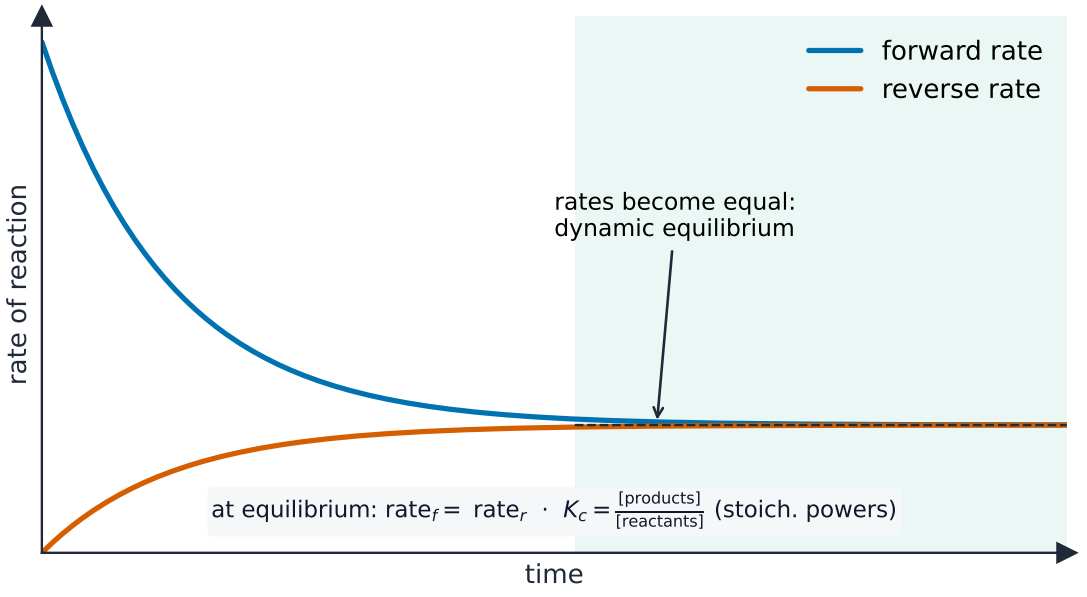
Cobalt chloride changes colour as its equilibrium shifts.

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.



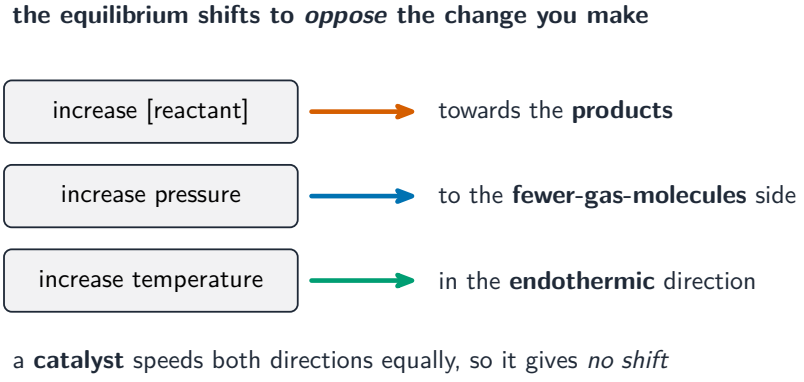
At dynamic equilibrium the forward and reverse rates have become equal, so the concentrations stay constant

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.



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

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):

	$\mathbf{H_2}$	$\mathbf{I_2}$	$2\mathbf{HI}$
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 $K_c = \dfrac{1.60^2}{0.20 \times 0.20} = 64$.

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 $\dfrac{\text{kPa}^2}{\text{kPa} \times \text{kPa}^3} = \text{kPa}^{-2}$.

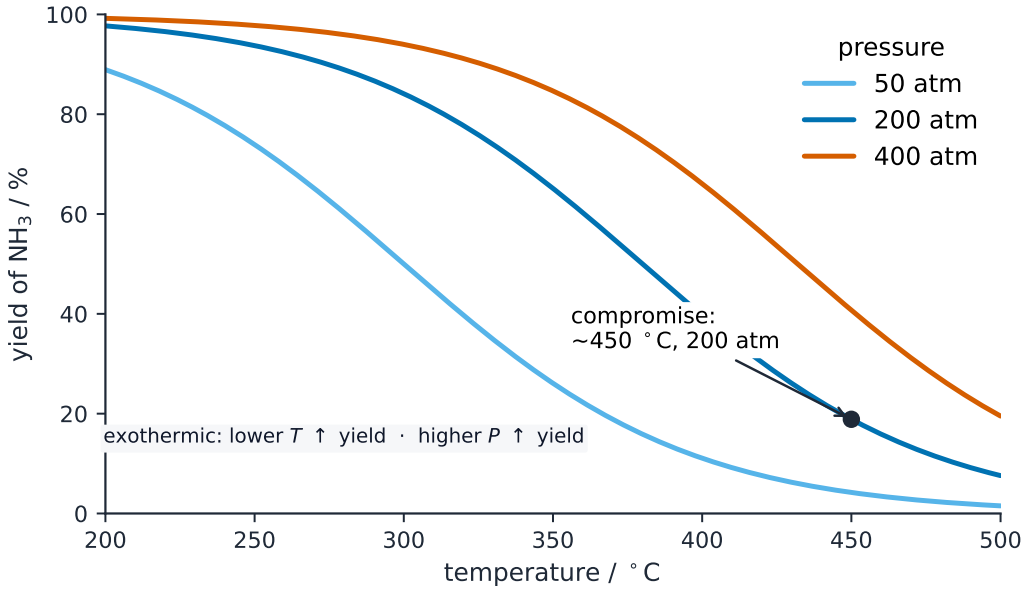
Only **temperature** changes the value of K_c or K_p. Changing concentration or pressure shifts the position of equilibrium but leaves the constant unchanged; adding a catalyst changes **neither** the constant nor the position — it only makes equilibrium arrive faster.

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.

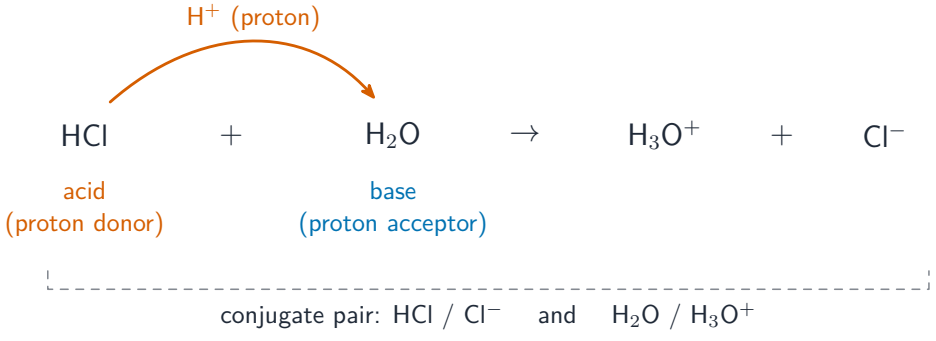


The Haber equilibrium gives more ammonia at lower temperature and higher pressure; about 450 °C and 200 atm is the working compromise

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.



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

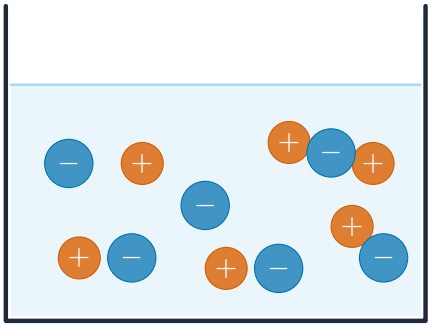
Common acids you must know: hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric

acid (HNO_3) and ethanoic acid (CH_3COOH). Common alkalis: sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonia (NH_3).

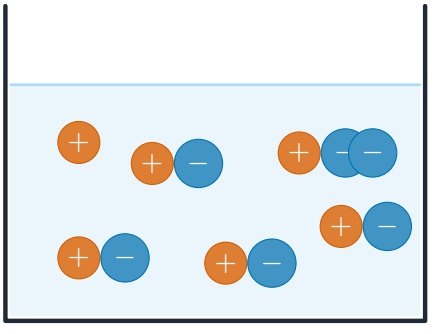
Strong and weak acids and bases

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).



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

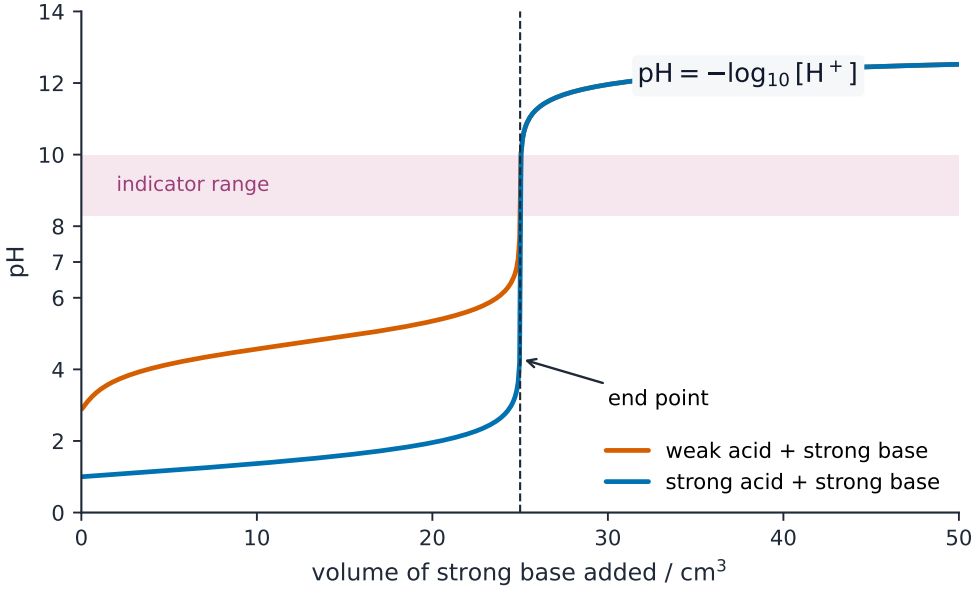
Neutralisation 中和 happens when the hydrogen ions from an acid react with the hydroxide ions from an alkali:

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

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.



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

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^+.

Reaction kinetics

A-Level Chemistry

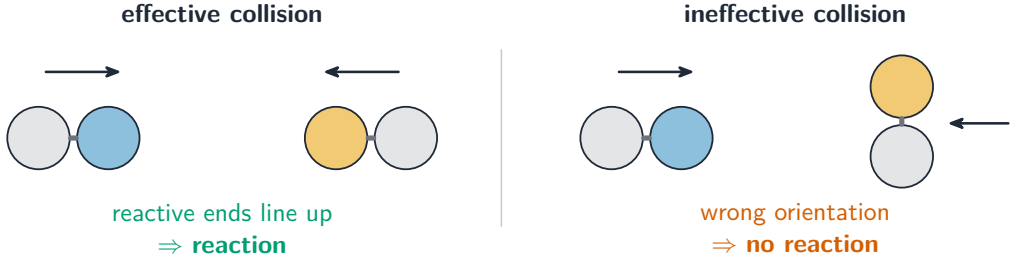
Rate of reaction

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.

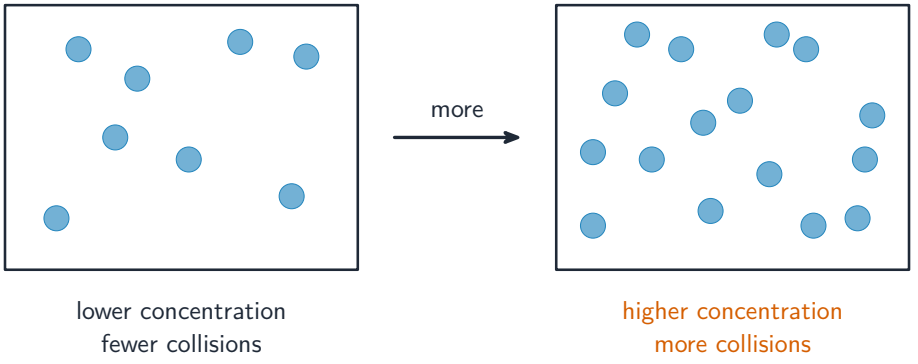
So the rate depends on the **frequency of effective collisions** — how many useful collisions happen each second.



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.

Temperature and activation energy

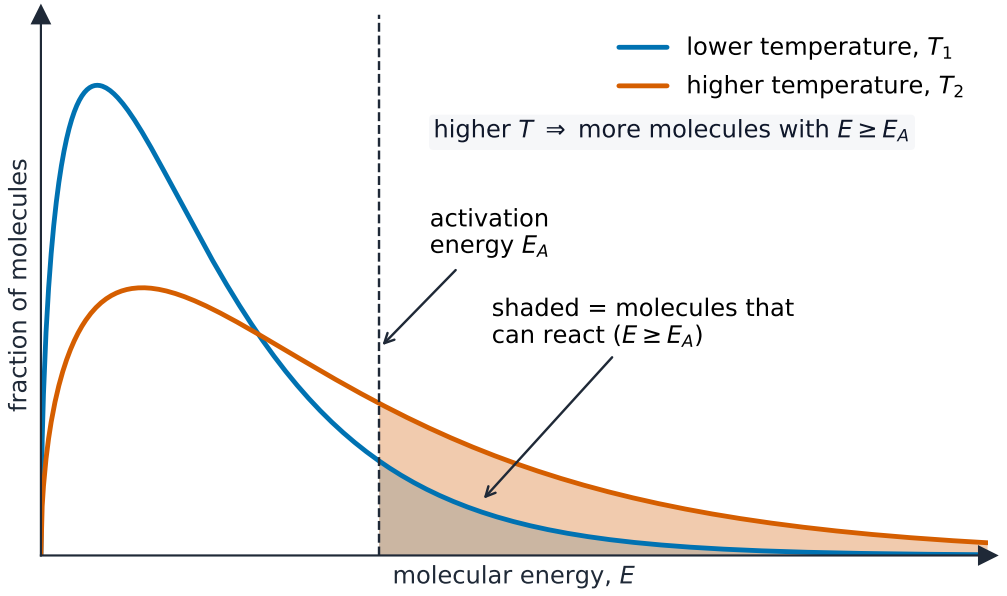
The **activation energy** 活化能 (E_A) is the minimum energy a collision needs in order to be effective.

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.



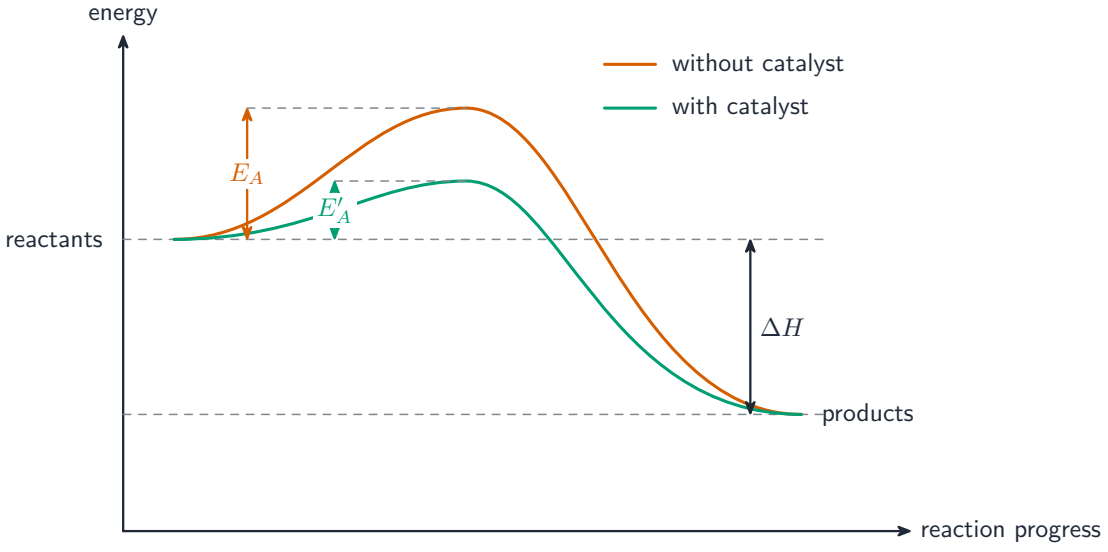
At higher temperature the curve spreads to the right, so a larger fraction of molecules can react

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.

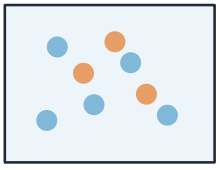
On a **reaction pathway diagram** 反应路径图, the catalysed route has a lower energy "hill". The enthalpy change of the reaction, ΔH, is **not** changed by the catalyst.



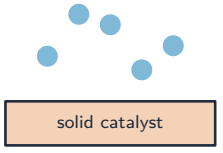
A catalyst gives a route with lower activation energy; the enthalpy change is unchanged

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.

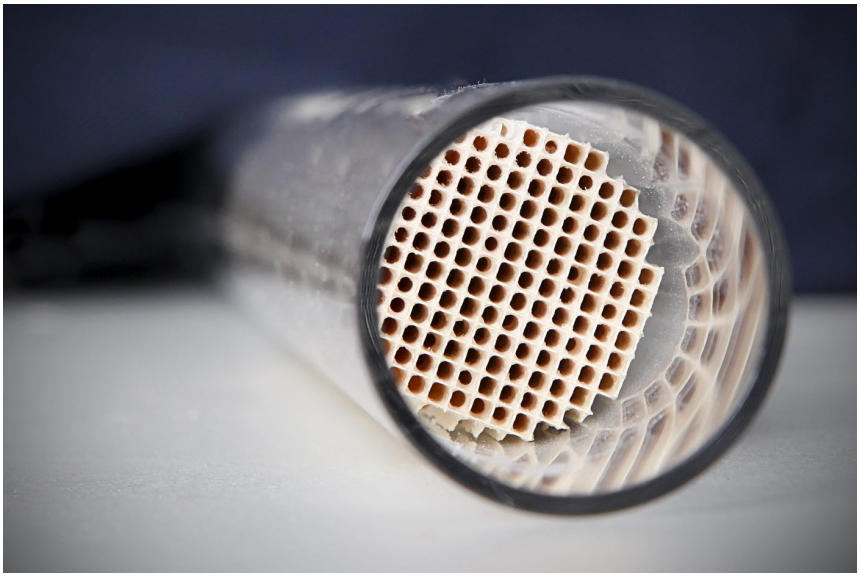


homogeneous
(same state, mixed in)



heterogeneous
(different state, a surface)

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



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

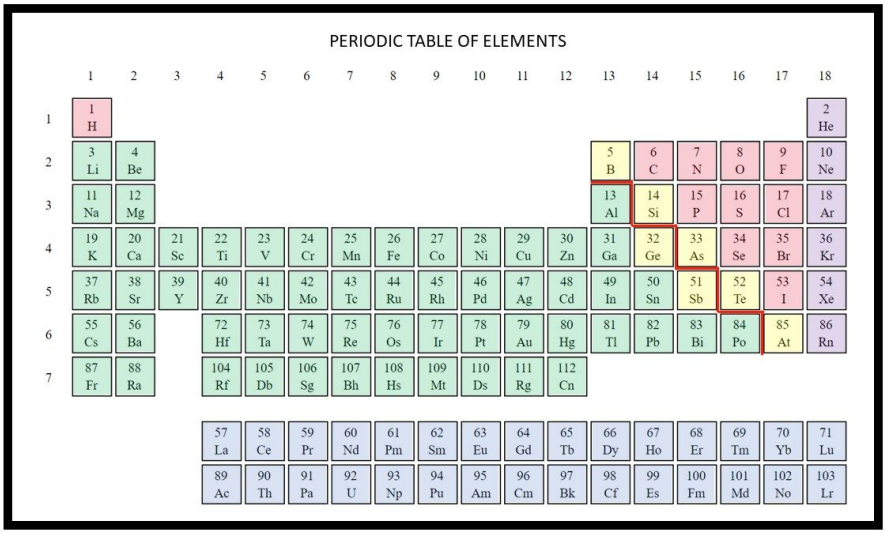
Exam tips

- 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 never touches the 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).

The Periodic Table: chemical periodicity

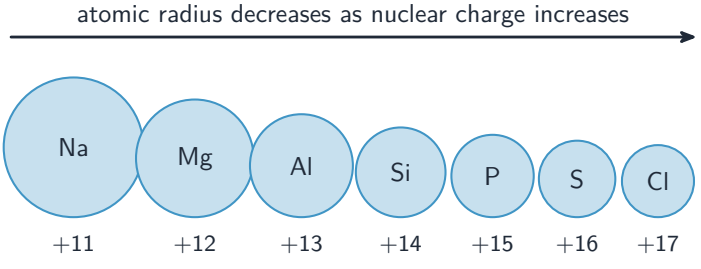
A-Level Chemistry

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.



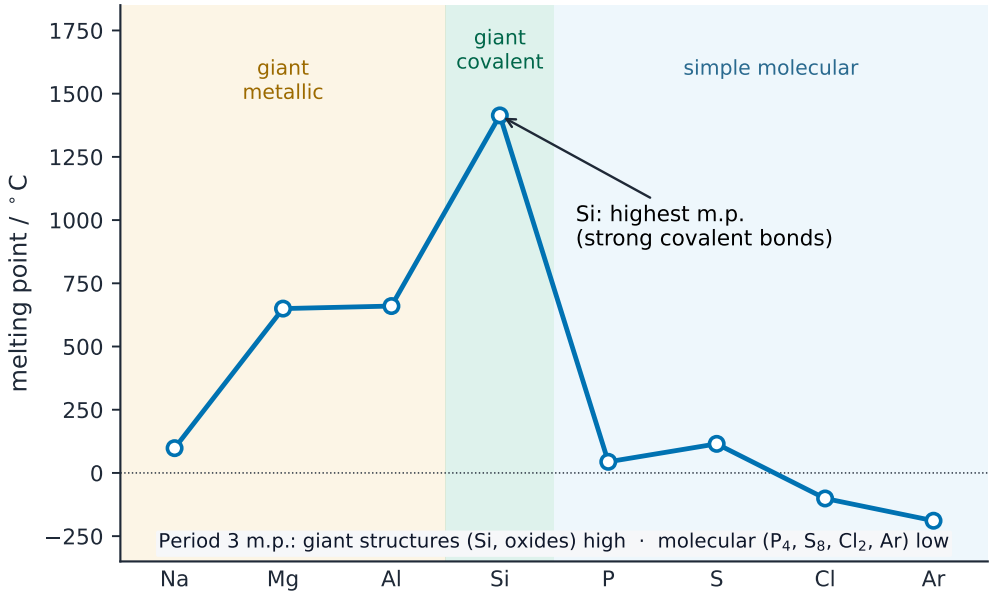
Atomic radius decreases across Period 3: the rising nuclear charge pulls the same outer shell inwards

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

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.

Oxidation number of the oxides and chlorides

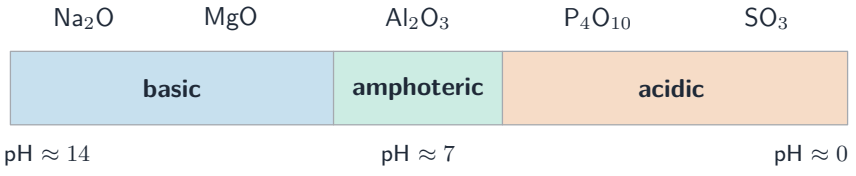
The **oxidation number** 氧化数 of the Period 3 element in its oxide or chloride rises across the period, because it equals the number of outer-shell (**valence shell** 价层) **electrons** 电子 the atom uses in bonding:

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:



metal oxides (left) are basic; non-metal oxides (right) are acidic

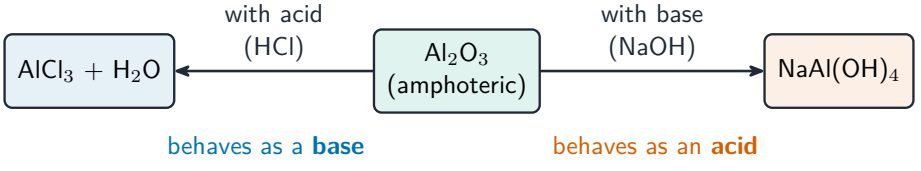
The Period 3 oxides change from basic (the metals) through amphoteric (Al_2O_3) to acidic (the non-metals)

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

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:

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

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

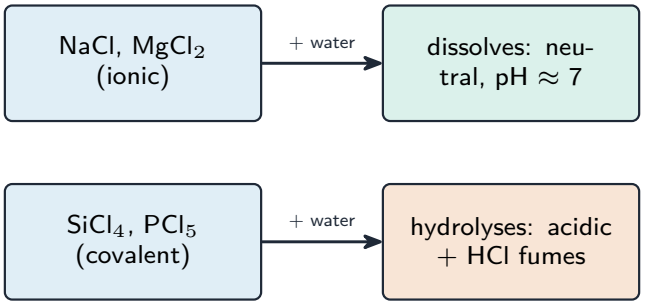


Aluminium oxide is amphoteric — it reacts with acids (behaving as a base) and with bases (behaving as an acid)

Chlorides with water

- $NaCl$ and $MgCl_2$ are ionic. They simply dissolve, giving a near-neutral solution.
- $SiCl_4$ 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.

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.

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**.

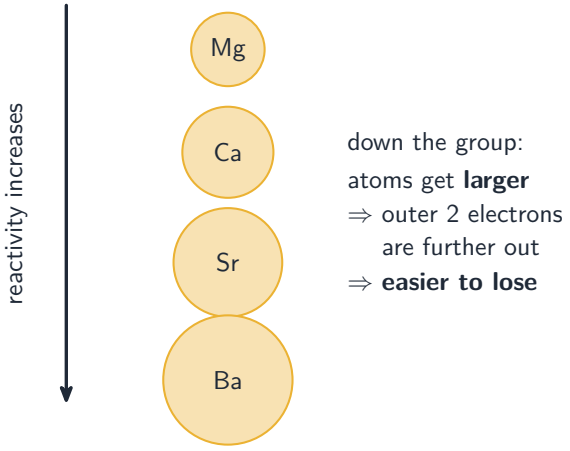
Group 2

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

Reactions of the elements

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

$$2\mathrm{Mg} + \mathrm{O_2} \rightarrow 2\mathrm{MgO}$$

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:

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

Magnesium is slow with cold water but reacts fast with steam, giving MgO and H_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:

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

Thermal decomposition

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

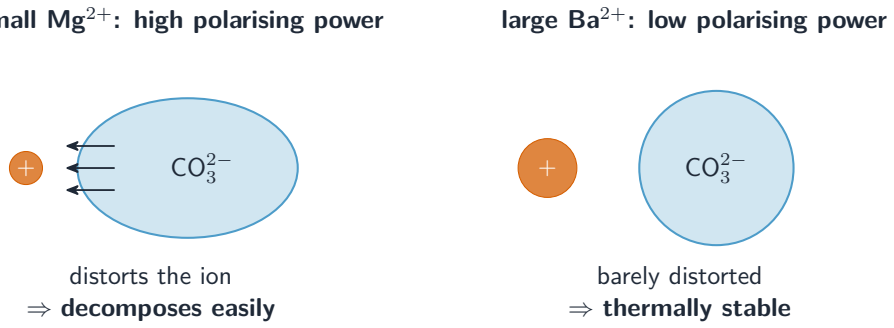
- the carbonates break into the oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

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

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

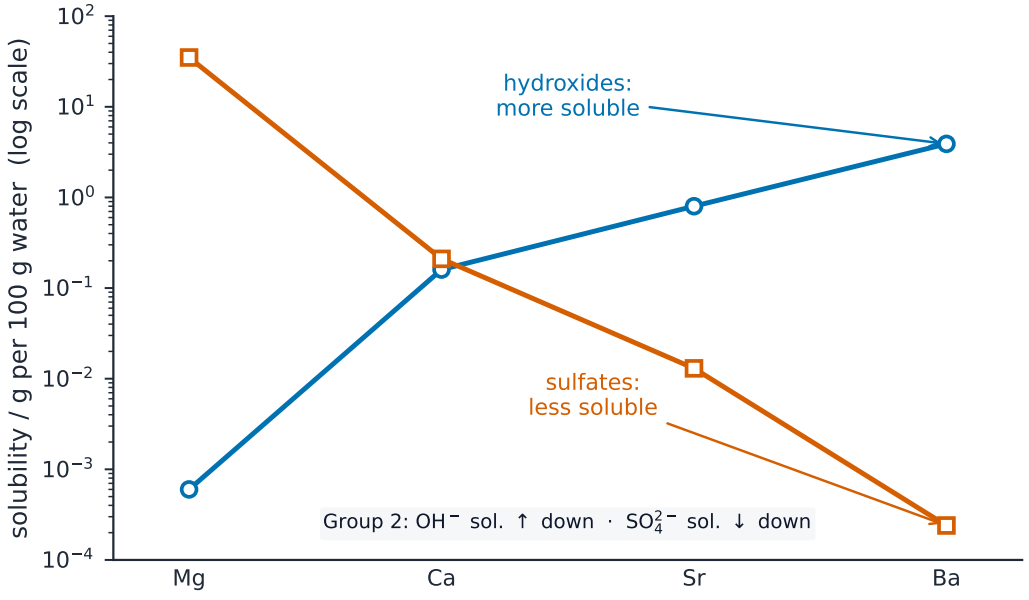
The **thermal stability** 热稳定性 of both the carbonates and the nitrates **increases** down the group. A larger metal ion pulls less on the carbonate or nitrate ion, so the compound is harder to break apart — it needs a higher temperature. So magnesium carbonate decomposes most easily, and barium carbonate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



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.

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.

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).

Group 17

A-Level Chemistry

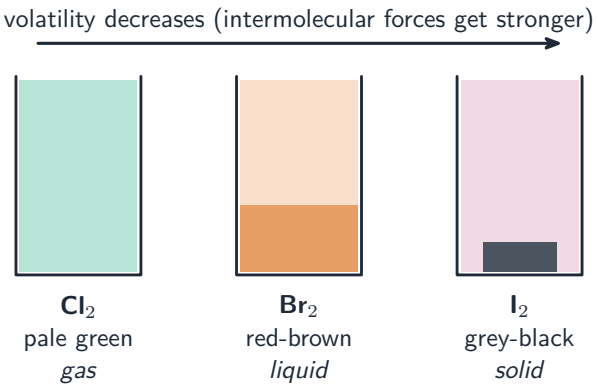
Physical properties of the halogens

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.



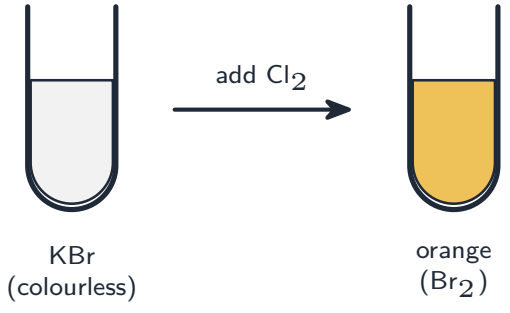
Down Group 17 the halogens change from a pale green gas to a red-brown liquid to a grey-black solid as volatility falls

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.

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:



Chlorine displaces bromine: the solution turns orange

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

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.

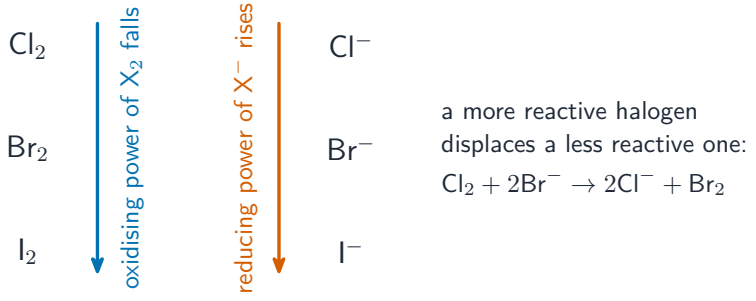
Thermal stability of the hydrogen halides

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.

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.

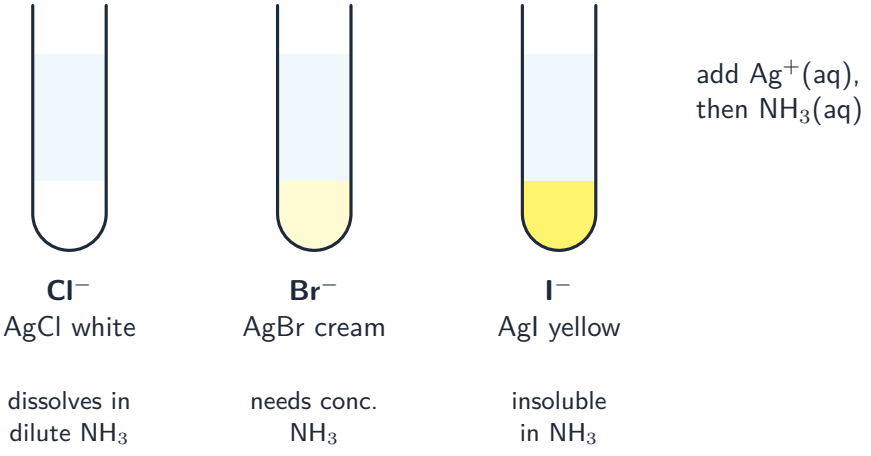


Two opposite trends: the oxidising power of the halogens falls down the group, while the reducing power of the halide ions rises

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



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

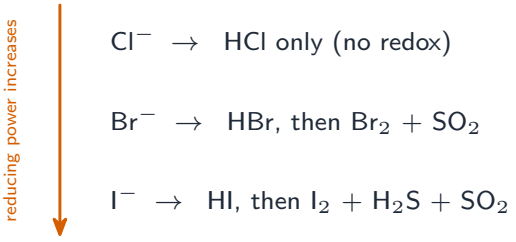
The silver halide test: AgCl is white, AgBr cream and AgI yellow

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.



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.

Chlorine in water purification

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

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

The active species HOCl and ClO^- kill **bacteria** 细菌, making the water safe to drink.

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.

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.
- 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 nothing pulls other molecules towards it.

N≡N

strong triple bond: very high bond energy ⇒ hard to break

symmetrical molecule ⇒ no polarity ⇒ nothing pulls it into a reaction

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

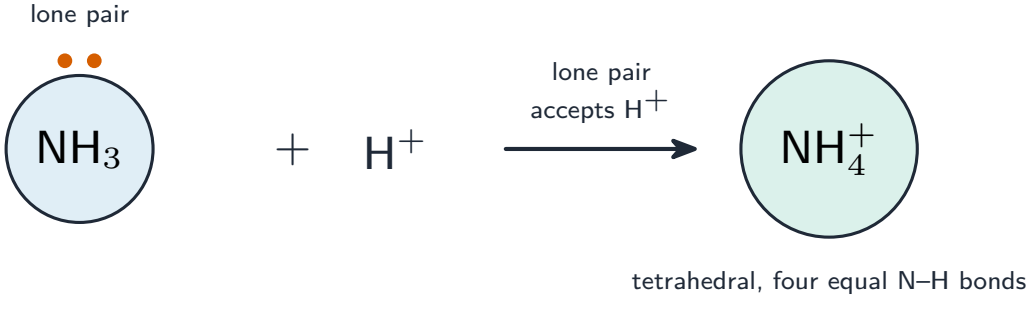
Ammonia and the ammonium ion

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

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:

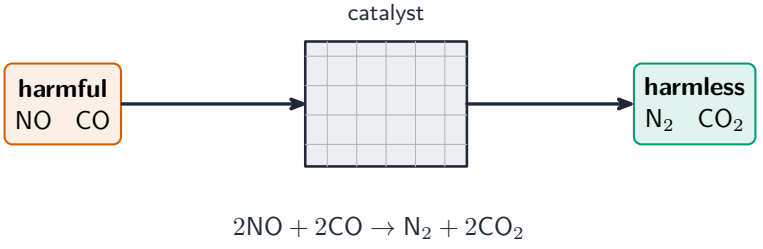
- **natural**: lightning gives enough energy for nitrogen and oxygen in the air to combine.
- **man-made**: the high temperature inside an **internal combustion engine** 内燃机 makes nitrogen and oxygen react:

$$N_2 + O_2 \rightarrow 2NO$$

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:

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



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

Photochemical smog

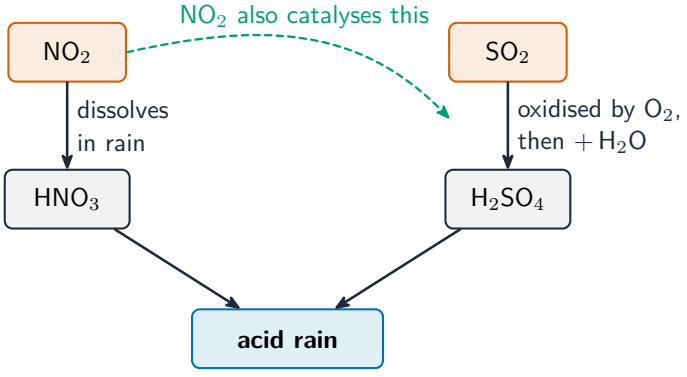
In sunlight, NO and NO_2 react with unburned **hydrocarbons** to form peroxyacetyl nitrate (PAN). PAN is a harmful part of **photochemical smog** 光化学烟雾, the brown haze seen over busy cities.

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

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.



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.

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

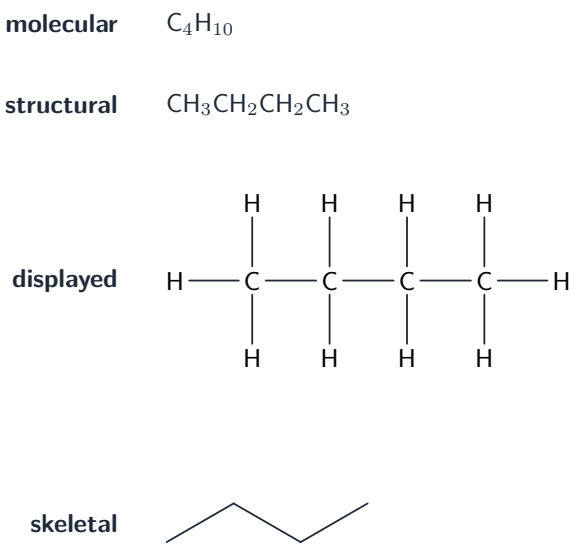
Crude oil is a complex mixture of hydrocarbons — the feedstock for organic chemistry.

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).

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



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.

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.

Characteristic organic reactions

Some key terms

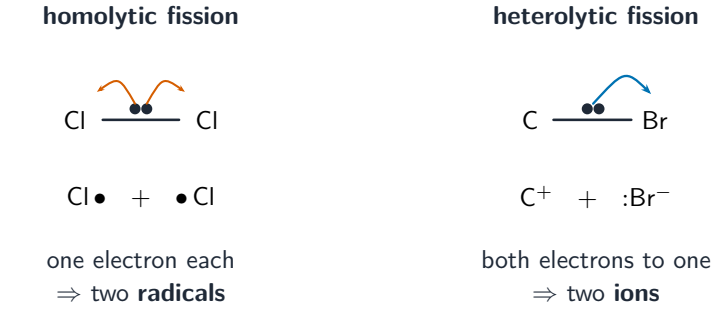
- a **homologous series** 同系列 is a family of compounds with the same functional group and general formula, where each member differs by CH_2.

- 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:

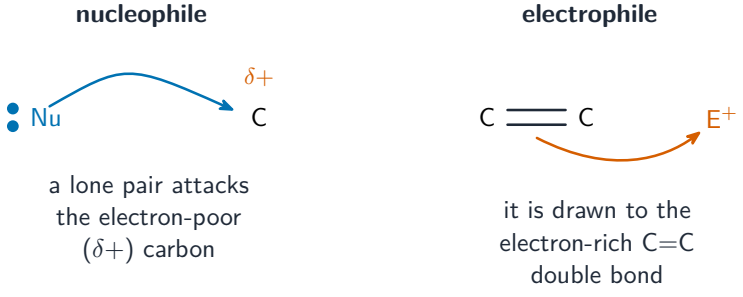
- **homolytic fission** 均裂: the bond splits evenly, one electron to each atom. This makes two **free radicals** 自由基 (species with an unpaired electron).
- **heterolytic fission** 异裂: the bond splits unevenly, both electrons going to one atom. This makes two ions.



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 a species with a lone pair that is attracted to a positive (electron-poor) centre.
- an **electrophile** 亲电试剂 is a species attracted to a negative (electron-rich) centre, such as a C=C double bond.



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

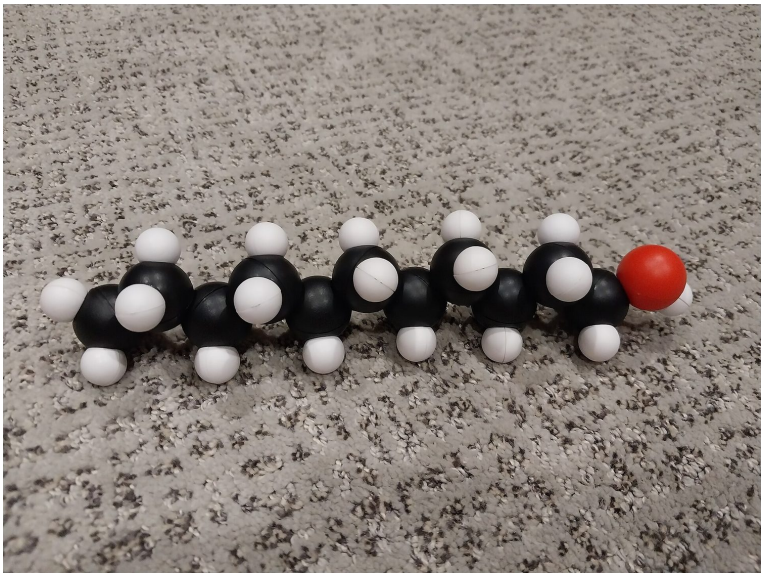
For organic redox, the symbol [O] stands for one oxygen atom from an oxidising agent, and [H] for one hydrogen atom from a reducing agent.

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 **curly arrow** 弯箭头 shows a pair of electrons moving; it starts at a bond or a **lone pair** 孤对电子.

Shapes of organic molecules



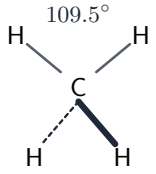
Organic molecules have definite three-dimensional shapes.

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

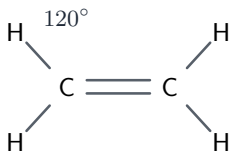
The shape around a carbon depends on its **hybridisation** 杂化:

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°

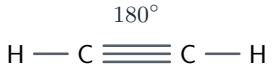
Every single bond is a **sigma bond** σ 键, made by direct overlap. A double bond is one sigma bond plus one **pi bond** π 键, made by sideways overlap of p orbitals. Ethene is planar because of its sp^2 carbons.



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°)

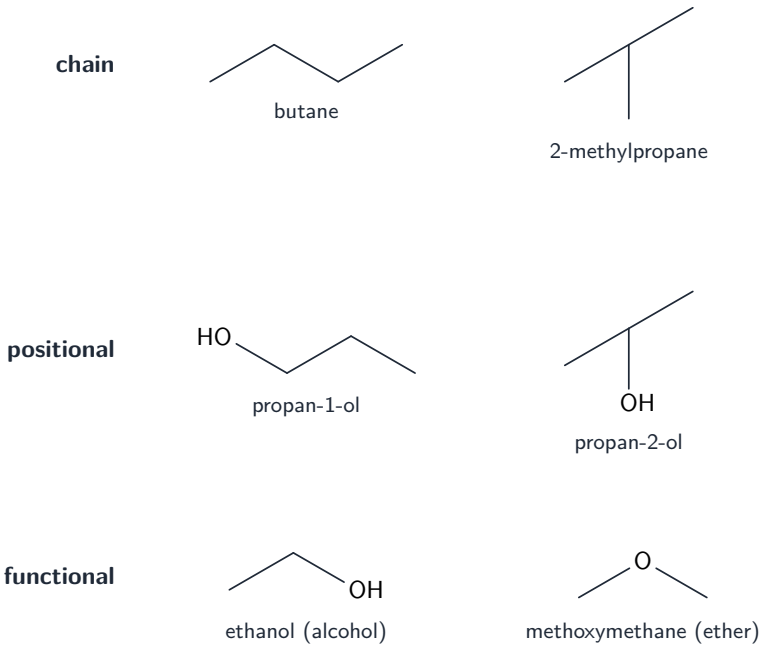
Isomerism

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).

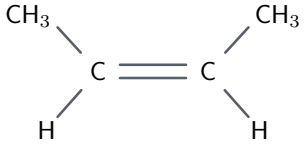


The three kinds of structural isomerism — chain, positional and functional-group — each pair sharing the same molecular formula

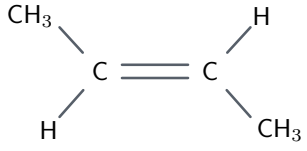
Stereoisomerism

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).



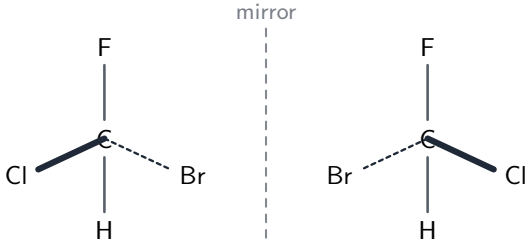
cis: both CH_3 on the same side



trans: CH_3 on opposite sides

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

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

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.

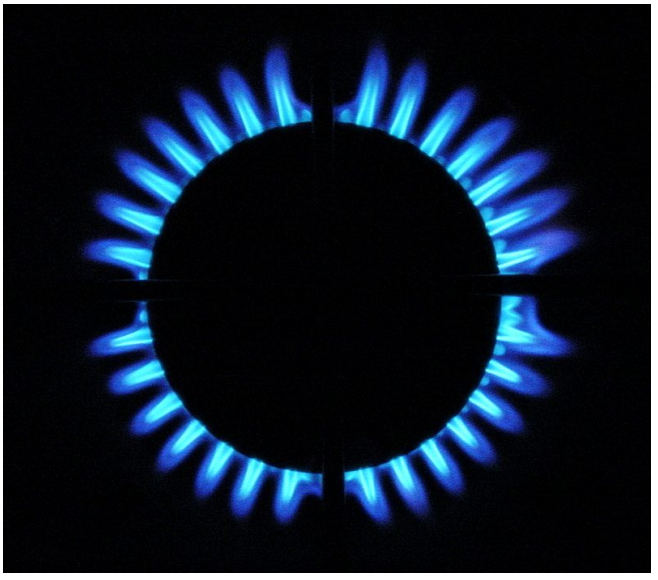
Exam tips

- 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.

Combustion

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

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

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

Complete combustion gives CO2 and water; incomplete also gives CO and soot

- **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).

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: $Cl\cdot + C_2H_5\cdot \rightarrow C_2H_5Cl$

1. initiation

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

UV light splits Cl–Cl into two radicals

2. propagation

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

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

each radical makes a new radical, so the chain continues

3. termination

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

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.)

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.

Alkenes

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

Alkenes have a C=C double bond (general formula 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 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

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.

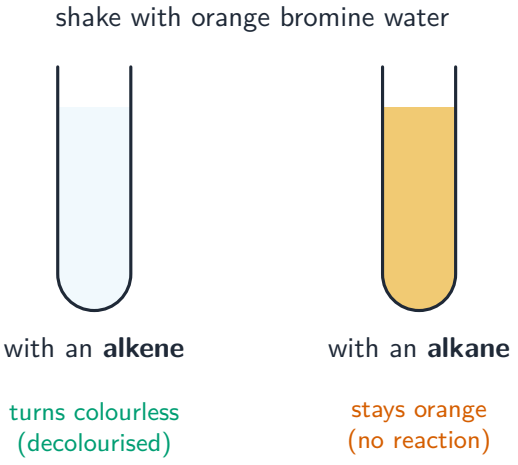
Worked example. Give the products when $(CH_3)_2C{=}CHCH_3$ is heated with hot concentrated acidified $KMnO_4$. Cut at the C=C and take each carbon separately. The **left** carbon carries **two methyl groups** and no hydrogen, so it stops at a **ketone**: $(CH_3)_2C{=}O$, which is propanone. The **right**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

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

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

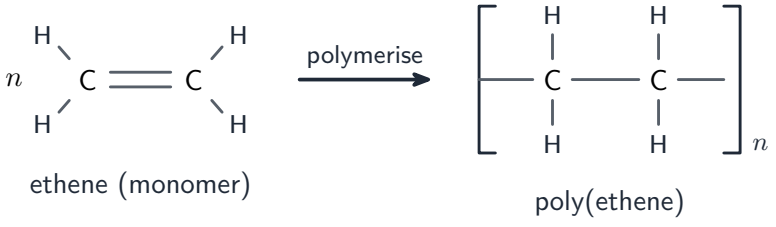
Shake the compound with orange **bromine water** 溴水. An alkene **decolourises** it (turns it colourless) by electrophilic addition. An alkane does not.



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

Addition polymerisation

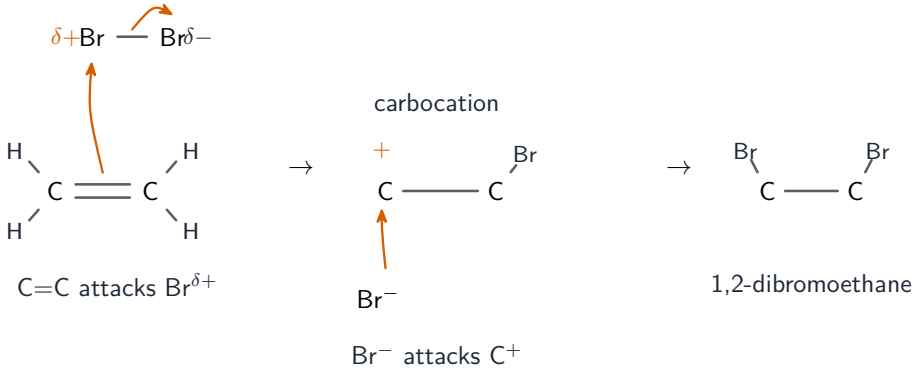
In **addition polymerisation** 加成聚合, many alkene molecules join into one long chain, with no other product. Ethene gives poly(ethene). The long-chain product is a **polymer** 聚合物.



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

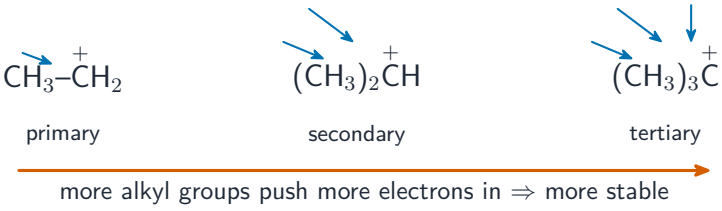
The mechanism and Markovnikov's rule

In electrophilic addition (for example bromine with ethene), the electron-rich C=C attracts the electrophile. This forms a positive intermediate called a **carbocation** 碳正离子, which the negative part then attacks.



Electrophilic addition of bromine to ethene: the C=C attacks $Br^{\delta+}$, a carbocation forms, then Br^- attacks it

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).
- Test for C = C: **bromine water decolourises** (orange → colourless) — state the observation.

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).

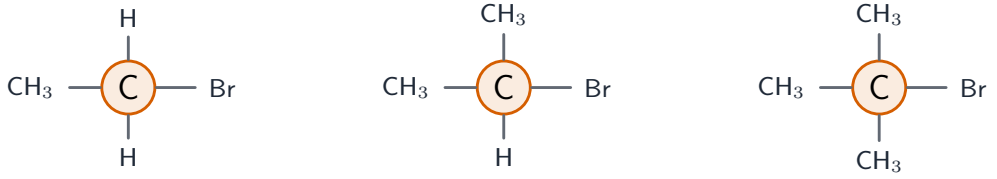
Volatile halogenoalkanes were once widely used as refrigerants and aerosol propellants

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 $SOCl_2$.

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
1 C on the C–Br carbon

secondary
2 C

tertiary
3 C

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

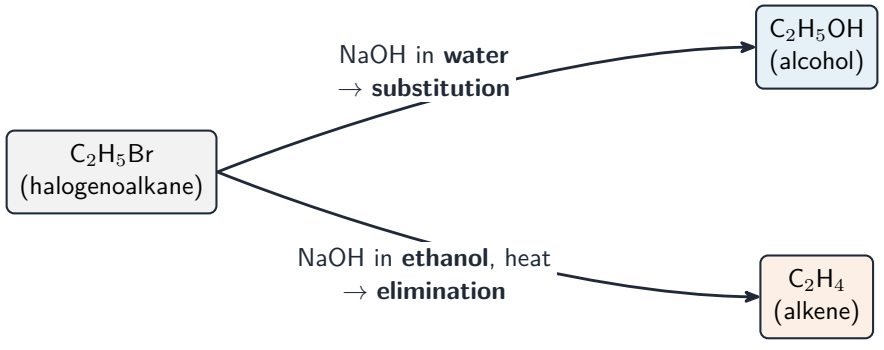
To **identify the halogen**, warm the halogenoalkane with **silver nitrate** 硝酸银 in ethanol. A silver halide **precipitate** 沉淀 forms, and its colour shows which halogen is present (white AgCl, cream AgBr, yellow AgI).

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.

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



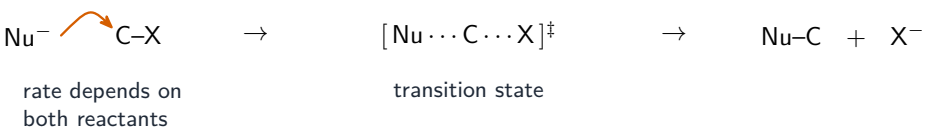
The same halogenoalkane: NaOH in water substitutes to an alcohol, while NaOH in ethanol (with heat) eliminates to an alkene

The S_N1 and S_N2 mechanisms

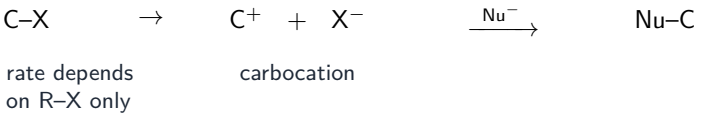
Nucleophilic substitution can follow two routes:

- **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: one step



S_N1: two steps



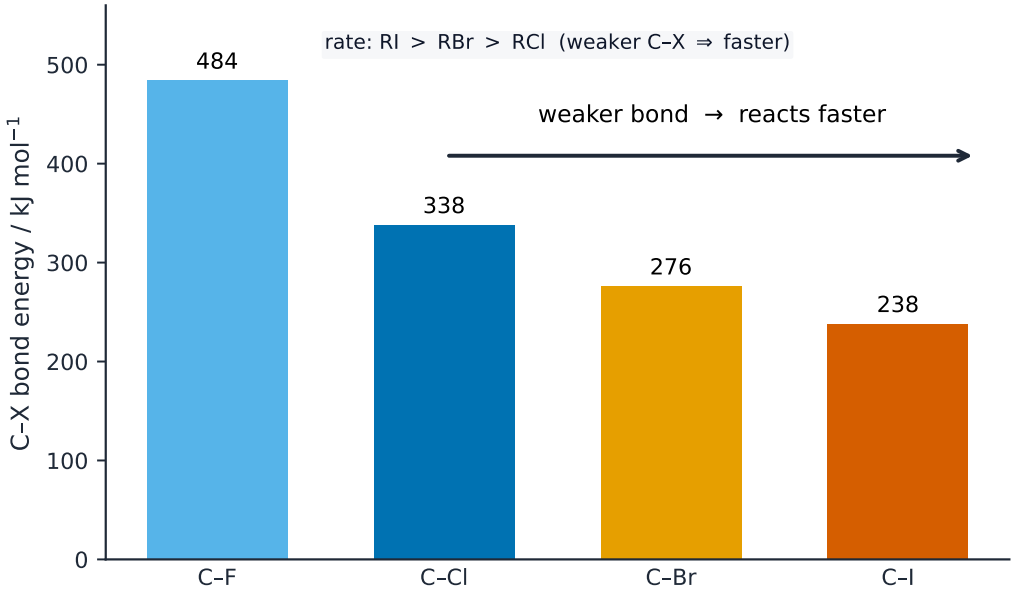
S_N2 is a single step through a crowded transition state; S_N1 is two steps via a carbocation

Alkyl groups push electrons towards the positive carbon (the **inductive effect** 诱导效应), so they stabilise the carbocation. 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.



The weaker the C–X bond, the faster the halogenoalkane reacts — so iodoalkanes react fastest and chloroalkanes slowest

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

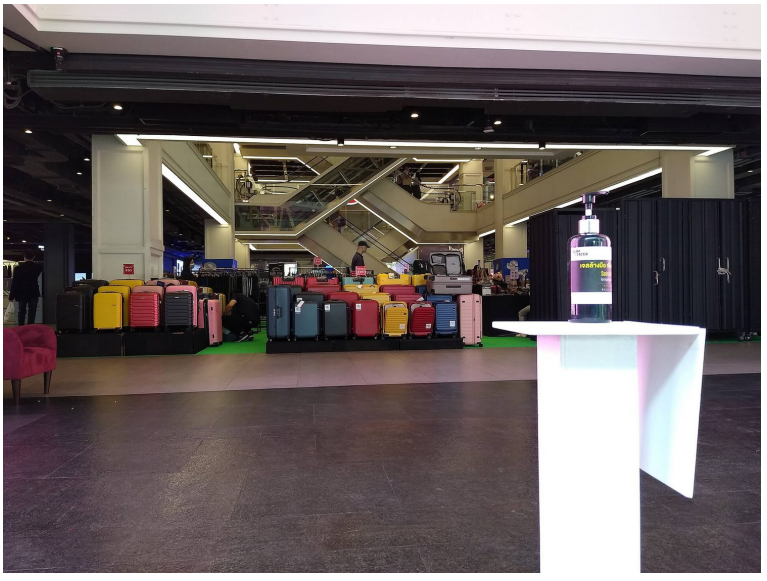
- Draw **nucleophilic substitution** with a curly arrow from the nucleophile's lone pair to the $\delta+$ carbon and one from the C-X bond.
- Match mechanism to class: $S_{\mathbf{N}}1$ (tertiary, carbocation, two steps) vs $S_{\mathbf{N}}2$ (primary, one step, transition state).
- Reactivity is set 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.

Hydroxy compounds

A-Level Chemistry

Alcohols

An **alcohol** 醇 has the –OH (hydroxyl) functional group.



Ethanol, the alcohol in hand sanitiser, kills microbes

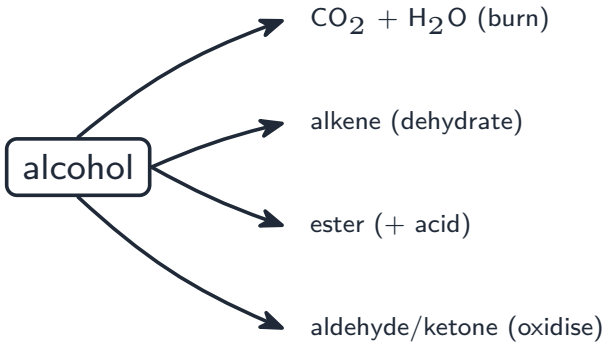
Making alcohols

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

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.

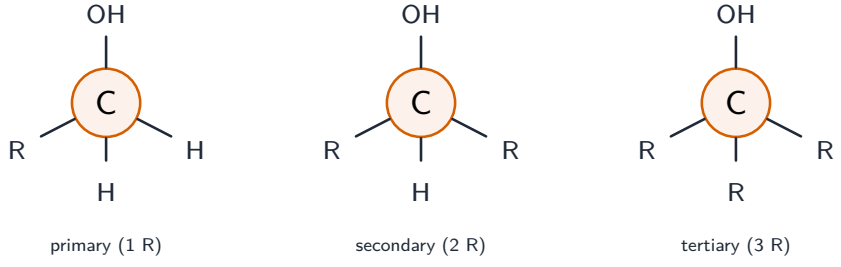
- **oxidation** 氧化 with acidified $K_2Cr_2O_7$ (or $KMnO_4$). The product depends on the class of alcohol (see below).
- **dehydration** 脱水 to an alkene, using a hot Al_2O_3 catalyst or concentrated acid.
- **ester formation**: an alcohol reacts with a carboxylic acid (with concentrated H_2SO_4 catalyst) to make an ester.



An alcohol can burn, dehydrate, esterify or be oxidised

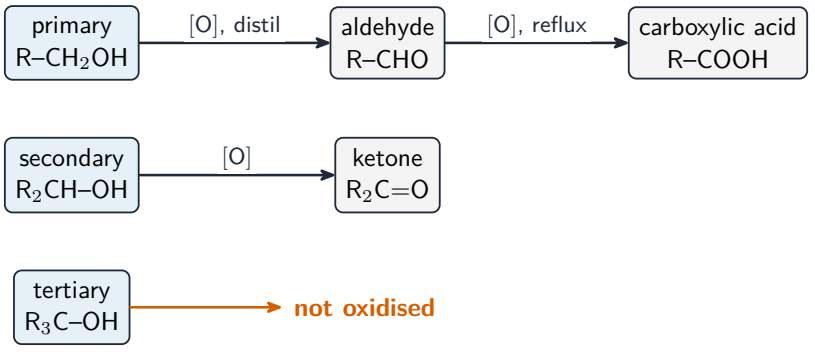
Three classes and how oxidation tells them apart

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.



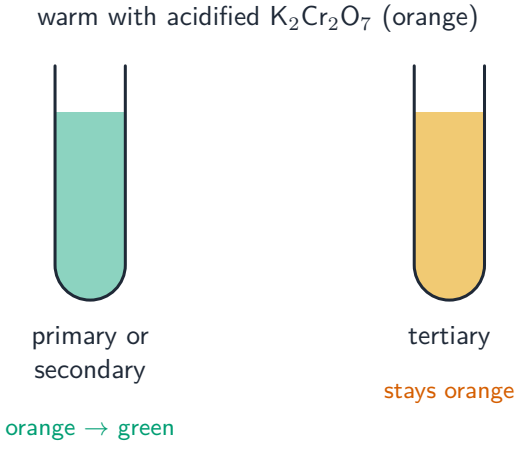
The class is set by the carbon holding the –OH: one R group makes it primary, two secondary, three tertiary — which decides how it oxidises

Class	Oxidation product
primary	**aldehyde** (by **distillation** 蒸馏), then **carboxylic acid** (by **reflux** 回流)
secondary	a **ketone**
tertiary	not oxidised



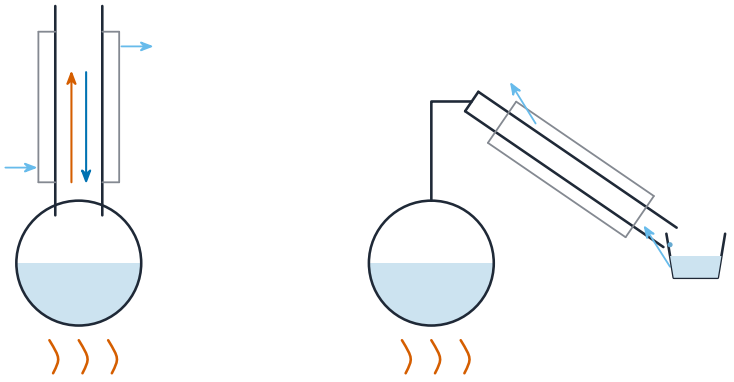
Oxidation by class: a primary alcohol gives an aldehyde then a carboxylic acid, a secondary gives a ketone, a tertiary is not oxidised

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

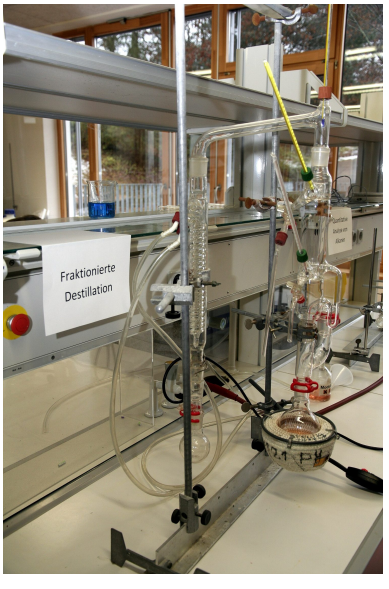
- **distillation** removes the aldehyde as it forms, before it can be oxidised further.
- **reflux** keeps boiling the mixture and returning the vapour, so the alcohol is fully oxidised to the carboxylic acid.



reflux
vapour returns: fully oxidised to the acid

distillation
product distils off as it forms (the aldehyde)

Distillation removes the aldehyde as it forms; reflux keeps boiling and returning the vapour, fully oxidising to the acid



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.

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.

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).

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

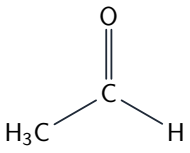
Aldehydes and ketones

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.

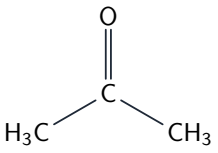
Propanone (acetone), the simplest ketone, is the solvent in nail-polish remover

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

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.

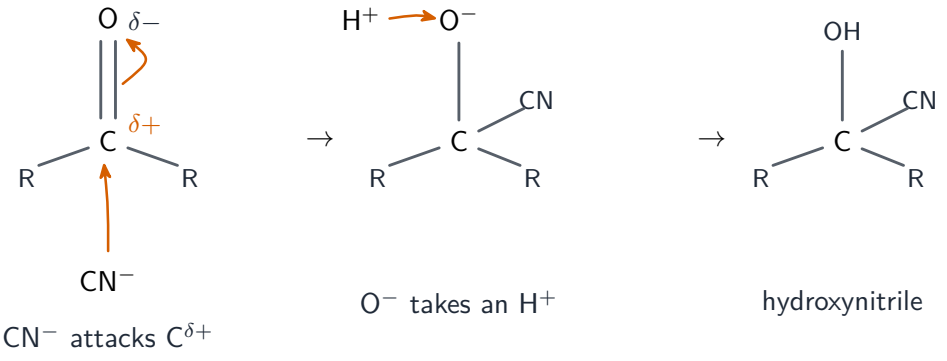
Reactions

- **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 and heat, adds H and CN across the C=O to make a **hydroxynitrile** 羟基腈. This adds one carbon to the chain.

The mechanism: nucleophilic addition

The reaction with HCN is a **nucleophilic addition** 亲核加成. The carbonyl carbon is slightly positive (oxygen pulls the electrons away). So:

1. the CN^- ion (a nucleophile) attacks the slightly positive carbon.
2. this breaks the C=O double bond, leaving a negative oxygen (O^-).
3. the O^- takes an H^+ (from HCN) to finish the hydroxynitrile.



Nucleophilic addition of HCN: CN^- attacks the $\delta+$ carbonyl carbon, the C=O breaks to O^-, then O^- takes an H^+

Tests for carbonyl compounds

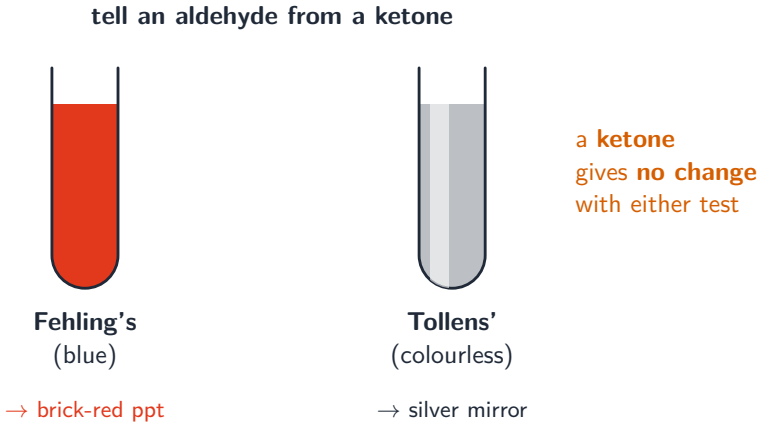
Detecting any carbonyl

Add **2,4-DNPH** reagent (2,4-dinitrophenylhydrazine). An orange precipitate confirms that the compound is an aldehyde or a ketone.

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

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^-.

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 next to the carbonyl. 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.

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** ($\rightarrow$ hydroxynitrile); show the curly arrows.
- The **iodoform (tri-iodomethane)** test is positive for CH_3CO- groups.

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.

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.

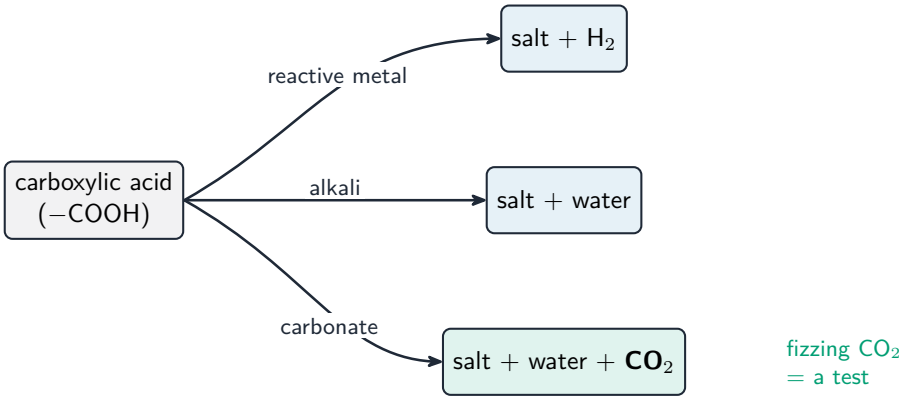
$$2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$$

- **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.

Esters

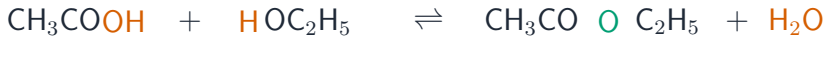
An ester has the –COO– group. It often smells sweet or fruity.

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:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$



the –OH (acid) and –H (alcohol) leave as water; the C–O–C ester link forms

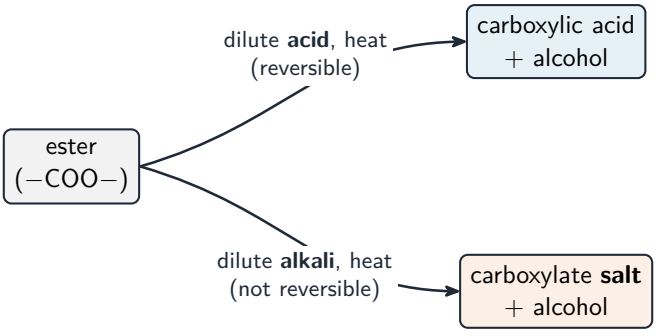
(concentrated H_2SO_4 catalyst; reversible)

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).



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.

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).

Nitrogen compounds

A-Level Chemistry

Primary amines

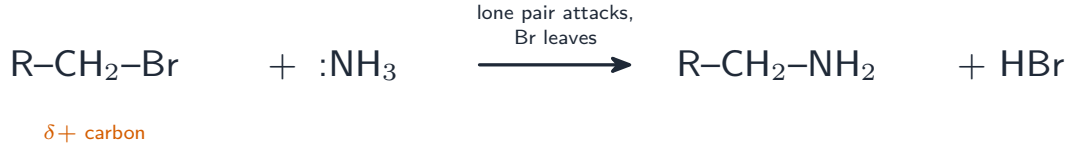
An **amine** 胺 has an –NH_2 group (the nitrogen replaces a hydrogen of ammonia).

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

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.

$$R\text{–}CH_2\text{–}Br + CN^- \longrightarrow R\text{–}CH_2\text{–}CN$$

nucleophilic **substitution** (nitrile)

$$R_2C{=}O + HCN \longrightarrow R_2C(OH)(CN)$$

nucleophilic **addition** (hydroxynitrile)

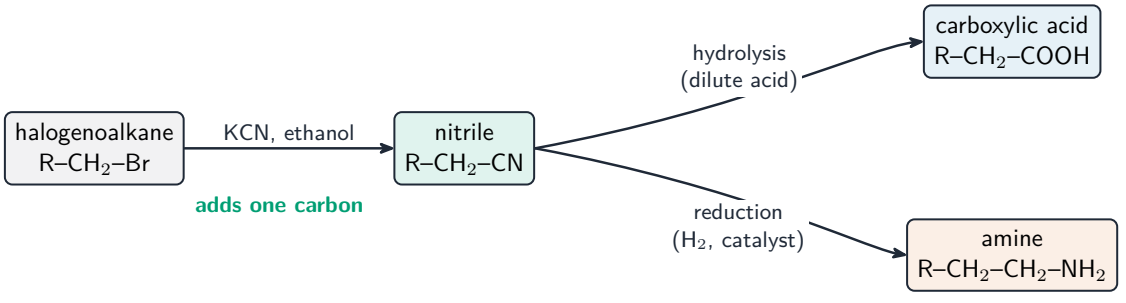
Two ways cyanide adds a carbon: KCN with a halogenoalkane substitutes to a nitrile; HCN with a carbonyl adds to a hydroxynitrile

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:

$$CH_3CN + 2H_2O + HCl \rightarrow CH_3COOH + NH_4Cl$$

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

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, 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.

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.

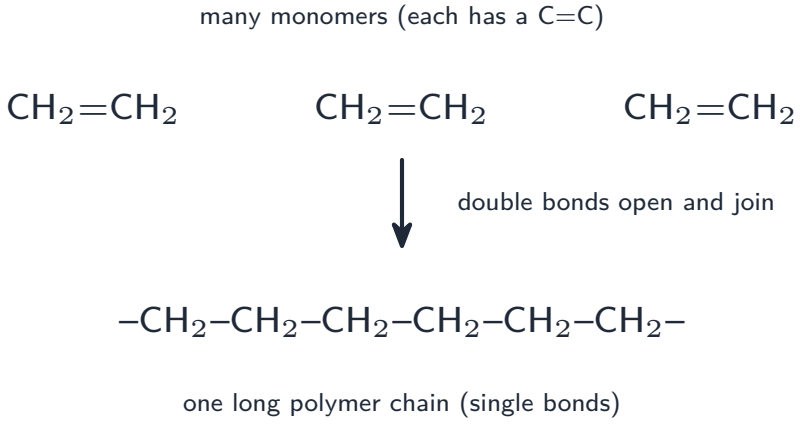
Polymerisation

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

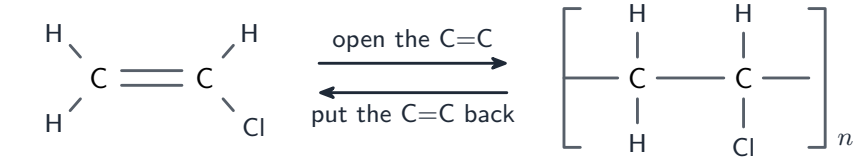
The **repeat unit** 重复单元 is the small part that is copied again and again along the chain. To find it, take the monomer, change the C=C to a single C–C, and draw bonds going out at each end.

- **poly(ethene)** 聚乙烯 is made from ethene:

$$n\,\mathrm{CH_2{=}CH_2} \rightarrow -(\mathrm{CH_2{-}CH_2})_n-$$

- **poly(chloroethene)** 聚氯乙烯 (PVC) is made from chloroethene:

$$n\,\mathrm{CH_2{=}CHCl} \rightarrow -(\mathrm{CH_2{-}CHCl})_n-$$



chloroethene (monomer) poly(chloroethene), PVC

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

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.

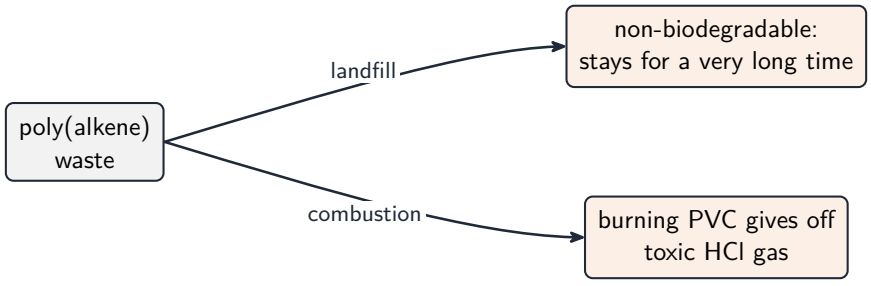
Worked example. A polymer has the repeat unit $-(CH_2-CH(CH_3))_n-$. Identify the monomer and name the polymer. Reverse the rule you used to build it: rub out the bonds sticking out at each end, and turn the single C-C **in the backbone** back into a **C=C**. That gives $CH_2=CH(CH_3)$, which is propene - 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.

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.

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

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

Organic synthesis

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).
- 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.

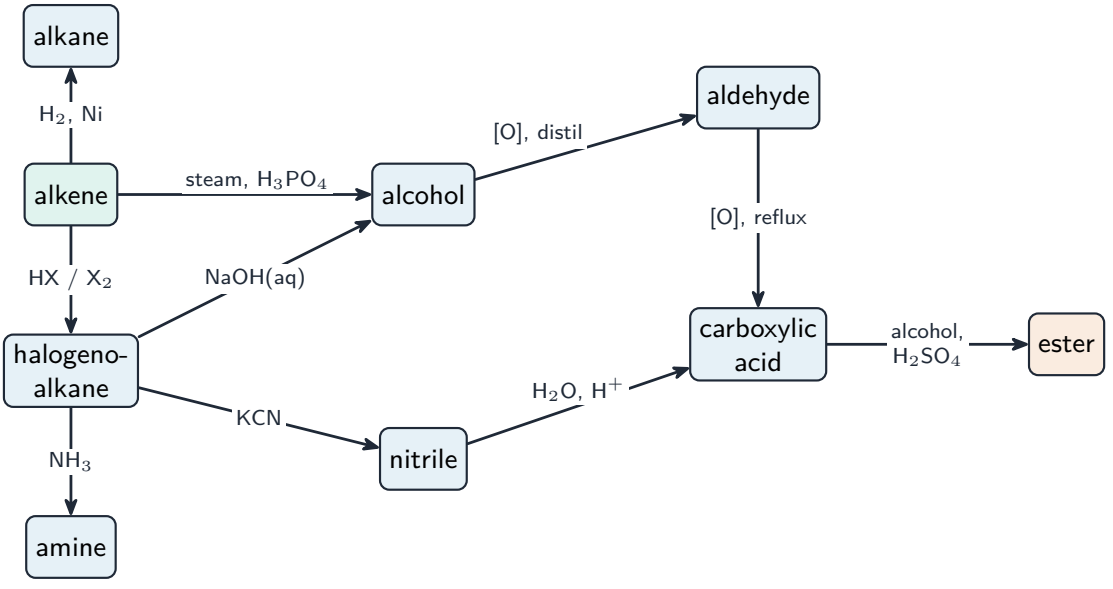
add this	you see	functional group
bromine water	orange → colourless	**C=C (alkene)**
silver nitrate	a precipitate forms	**halogenoalkane**
acidified $K_2Cr_2O_7$	orange → green	**1°/2° alcohol**
2,4-DNPH	orange precipitate	**aldehyde / ketone**
a carbonate	fizzes (CO_2 given off)	**carboxylic acid**

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
nitrile	dilute acid, heat	carboxylic acid
carboxylic acid + alcohol	concentrated H_2SO_4	an **ester** 酯



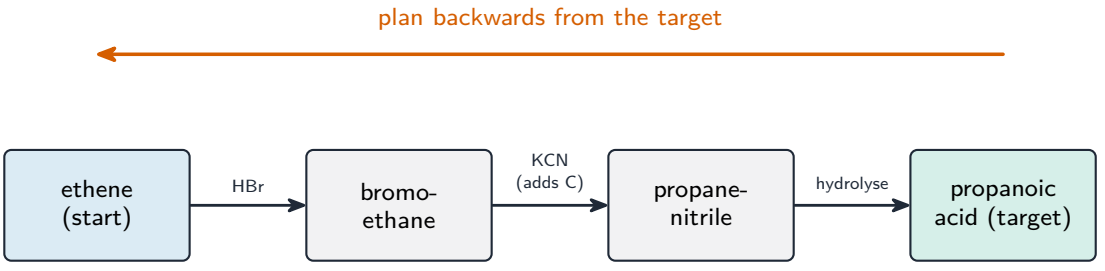
A map of the AS reactions: each arrow turns one functional group into another. Work backwards from your target to plan a route

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.

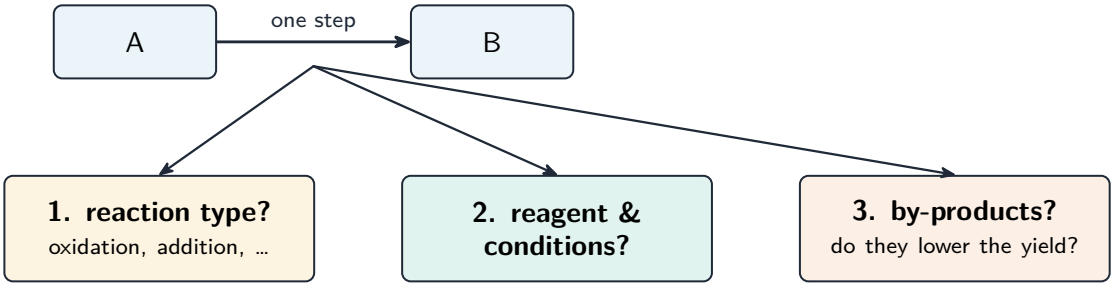
If you need to add a carbon, the KCN step is the key — it is the only AS reaction that lengthens the chain.



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.



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.

Exam tips

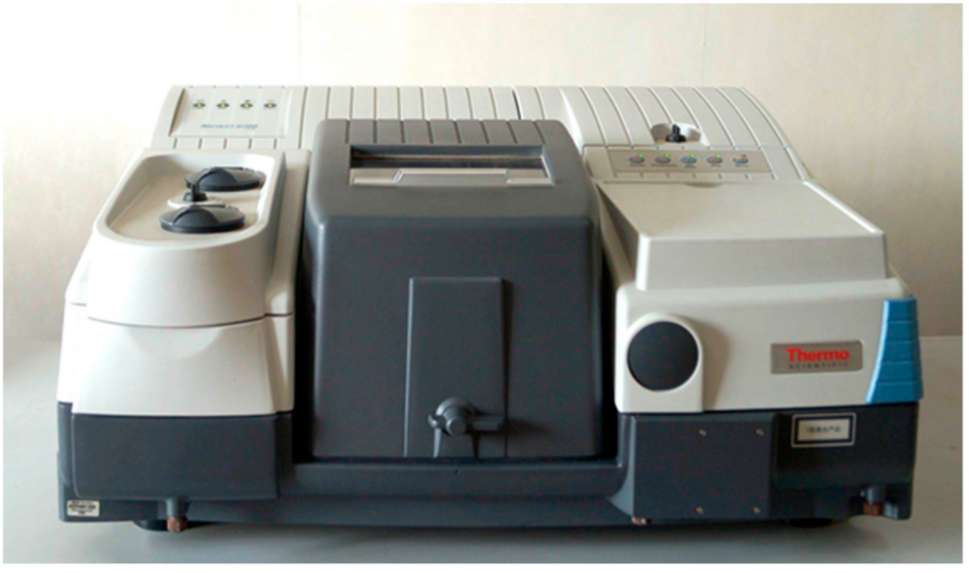
- Learn the **reagents and conditions** for each conversion — that is exactly what synthesis questions test.
- Plan multi-step routes by functional group and watch the **carbon count** (KCN adds one carbon).
- Choose the **shortest valid route** and state every reagent and condition.

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.

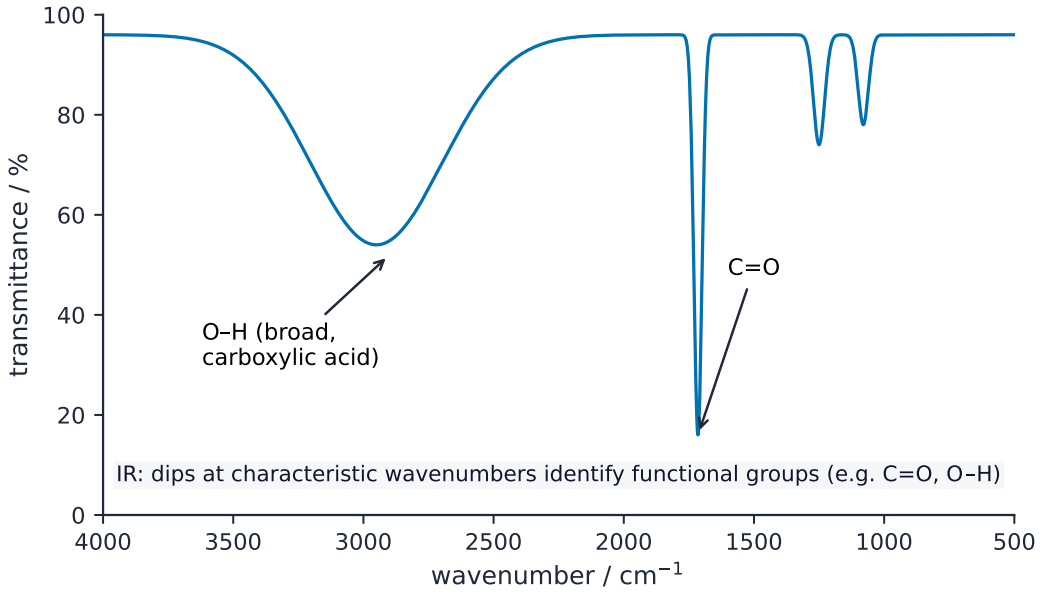


An infrared spectrometer shines infrared through a sample and records which wavenumbers its bonds absorb

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.



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

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:

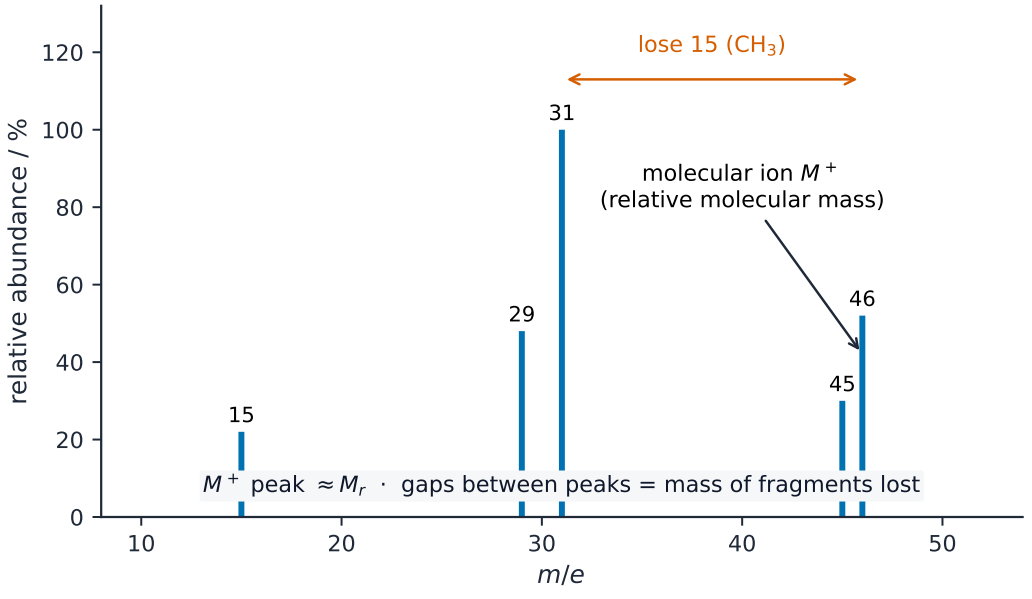
$$A_r = \frac{\sum(\text{isotope mass} \times \text{abundance})}{\sum \text{abundance}}$$

For example, chlorine is 75% ^{35}Cl and 25% ^{37}Cl, giving $A_r = \dfrac{35 \times 75 + 37 \times 25}{100} = 35.5$.

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.



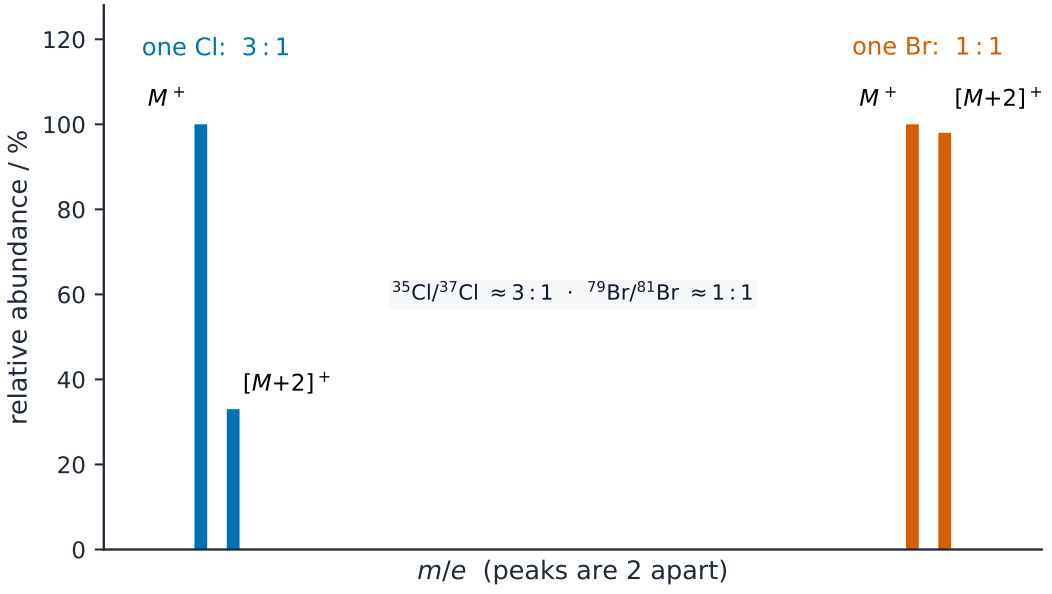
A mass spectrum: the highest-m/e peak is the molecular ion (M^+, the M_r); the gaps between peaks give the masses of the lost fragments

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. 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.

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).

Chemical energetics

A-Level Chemistry

Lattice energy and Born–Haber cycles

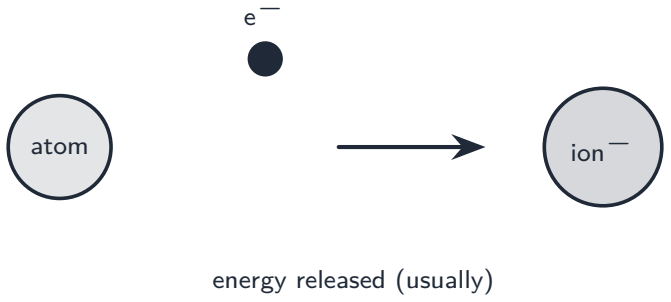
These cycles use several **enthalpy changes** 焓变 (ΔH). Two new ones are:

- 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.

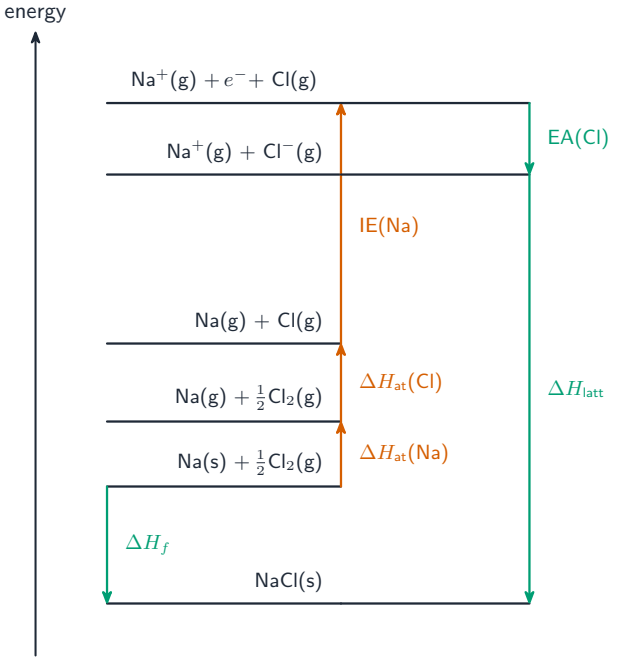


A gaseous atom gains an electron, usually releasing energy

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)

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 $= -349$.

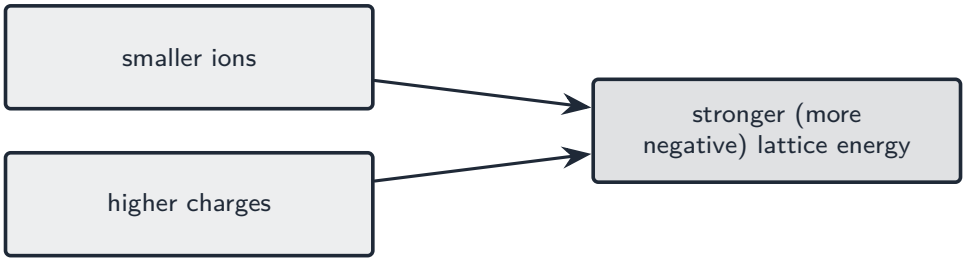
By Hess's law the direct formation route equals the route up and round the cycle:

$$\Delta H_f = \Delta H_{\text{at}}(\text{Na}) + \Delta H_{\text{at}}(\text{Cl}) + \text{IE}_1 + \text{EA} + \Delta H_{\text{latt}},$$

so $\Delta H_{\text{latt}} = -411 - (107 + 122 + 496 - 349) = -787$ kJ mol^{-1}.

What controls the size of a lattice energy

The lattice energy is more negative (stronger) when:



Smaller ions and higher charges give a stronger lattice energy

- the **ionic charge** is higher (e.g. Mg^{2+} beats Na^{+}).
- the **ionic radius** is smaller.

Both make the attraction between the ions stronger.

Enthalpies of solution and hydration

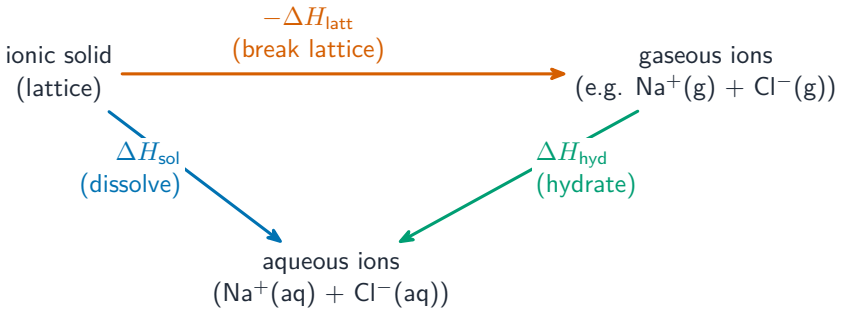
- the **enthalpy change of hydration** 水合焓変, ΔH_{hyd} — the energy change when one mole of gaseous ions is surrounded by water to form aqueous ions. It is exothermic.
- the **enthalpy change of solution** 溶解焓変, ΔH_{sol} — the energy change when one mole of solute dissolves fully in water.

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.

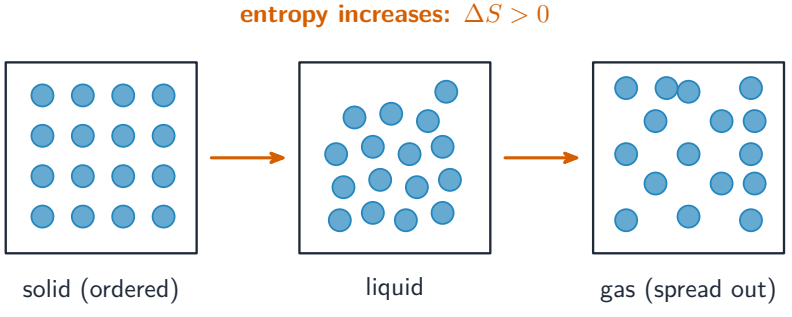


$$\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$$

Dissolving energy cycle: pull the lattice apart (reverse lattice energy), then hydrate the gaseous ions, so $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$

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:

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:

$$\Delta S^{\ominus} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$

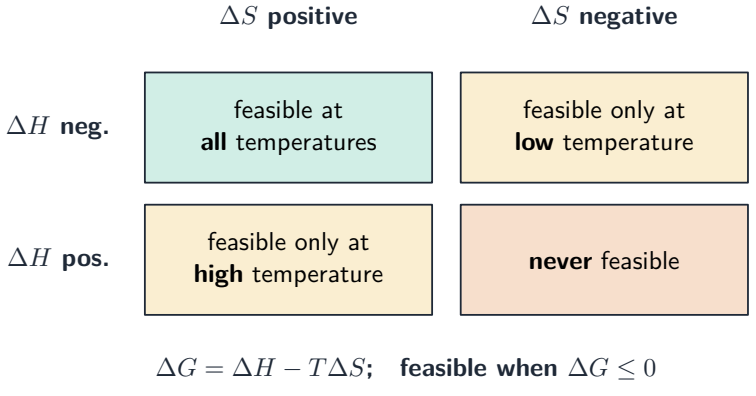
Gibbs free energy change, ΔG

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

$\Delta G = \Delta H - T\Delta S = 120 - 298 \times 0.200 = +60$ kJ mol^{-1} (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.

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.
- **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

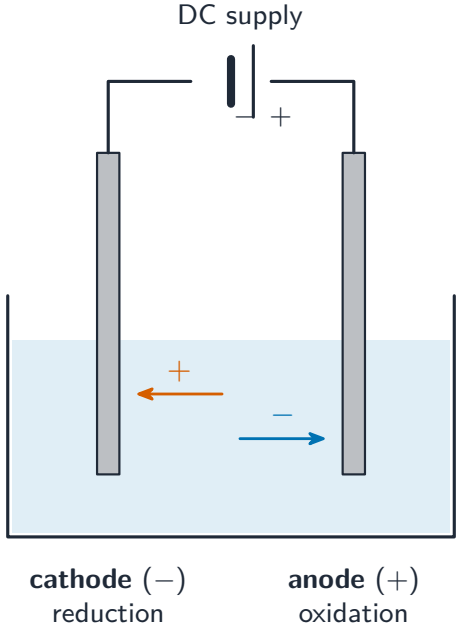
A-Level Chemistry

Electrolysis

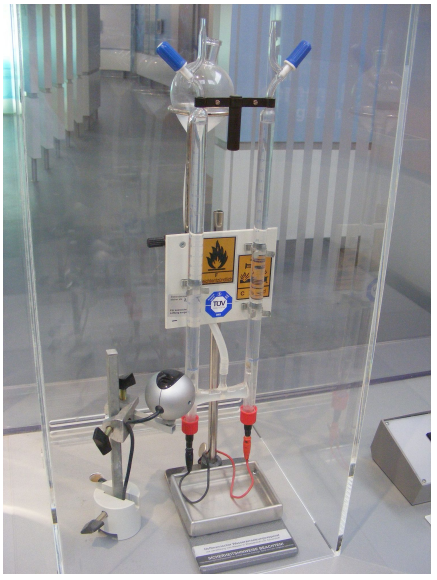
Electrolysis 电解 uses electricity to break down a molten or aqueous **electrolyte** 电解质. Positive ions move to the negative electrode and negative ions move to the positive electrode.

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)



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
metal at cathode
non-metal at anode

aqueous
also contains water,
so H_2 or O_2 may form

A molten electrolyte gives the metal and non-metal; aqueous also has water

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 $\times$ time). Then:

1. moles of electrons $= Q/F$.

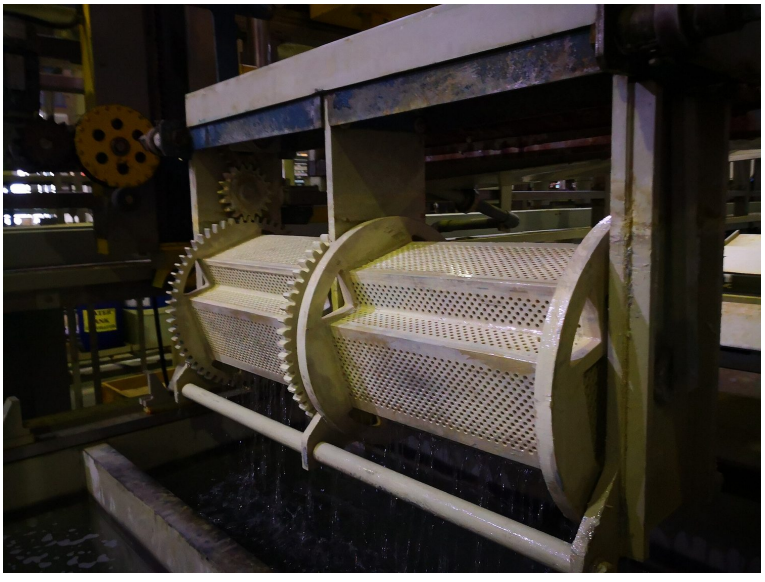
2. use the half-equation to find moles of product.
3. find the mass ($\times M_r$) or the gas volume.

Measuring the mass deposited for a known charge lets you work back to a value of the Avogadro constant.

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate solution, depositing copper at the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. 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 $n(\text{Cu}) = 0.0187$ mol and

$$m = nM = 0.0187 \times 64 \approx 1.2 \text{ g}.$$

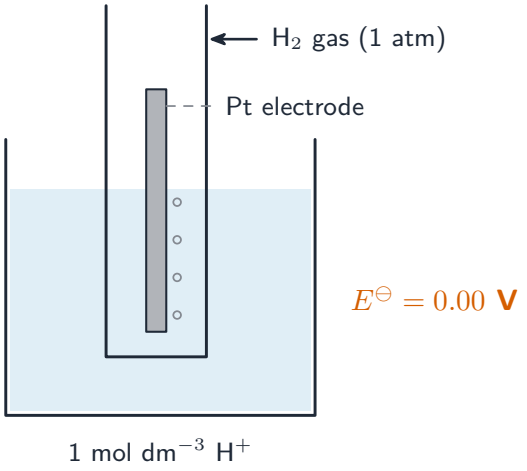


Electrolysis is used to electroplate an object with a thin, shiny layer of metal such as chromium

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 1 atm over platinum in 1 mol dm^{-3} H^+, defined as exactly 0.00 V.



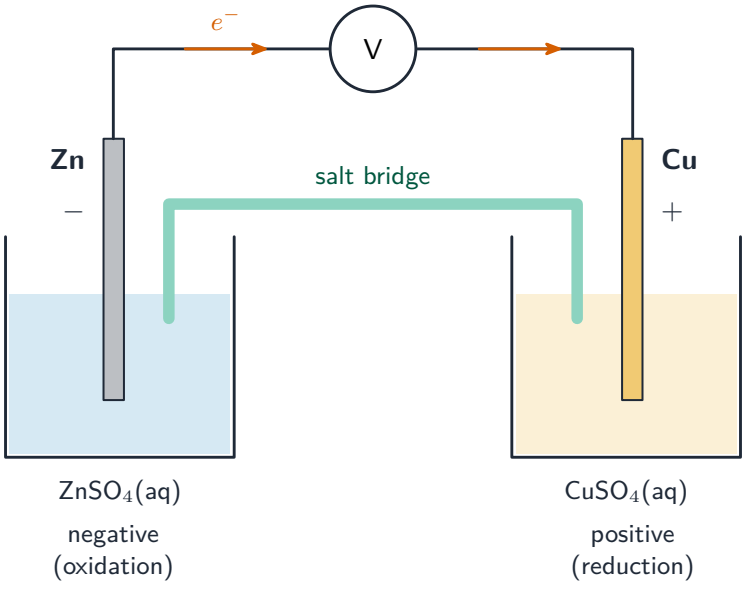
The standard hydrogen electrode: H_2 at 1 atm over platinum in 1 mol dm^{-3} H^+, the 0.00 V reference for every electrode potential

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.

Combining half-cells

The **standard cell potential** 标准电池电势 is the difference between the two standard electrode potentials:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{more positive}) - E^{\ominus}(\text{less positive})$$



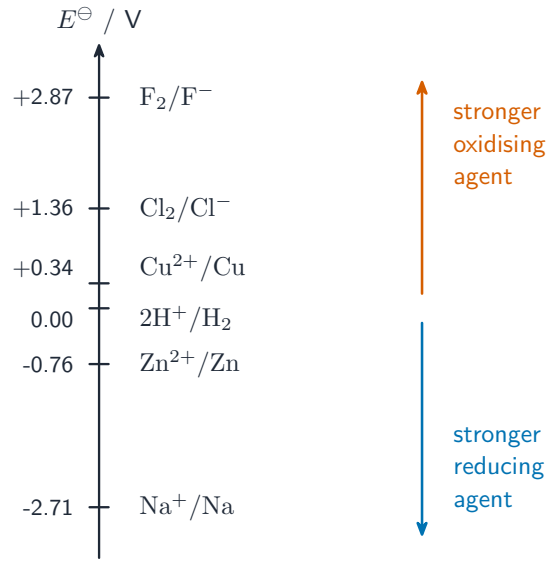
A simple cell: two half-cells joined by a salt bridge, with a voltmeter. Electrons flow from the negative (Zn) electrode to the positive (Cu)

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.



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.

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.

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.
- Standard conditions for $E^{\ominus}$: **298 K,** 1 **mol dm^{-3}, 100 kPa**, platinum electrode — state them if asked.
- 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 $= Q/F$.

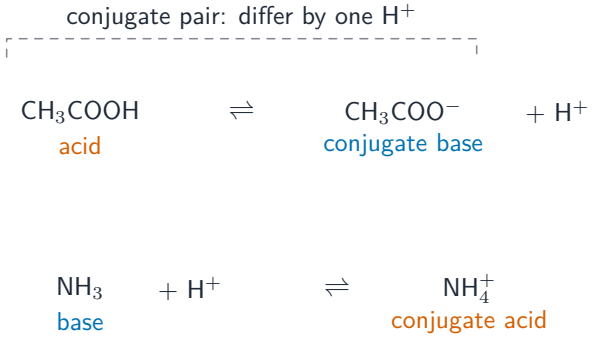
Equilibria

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.

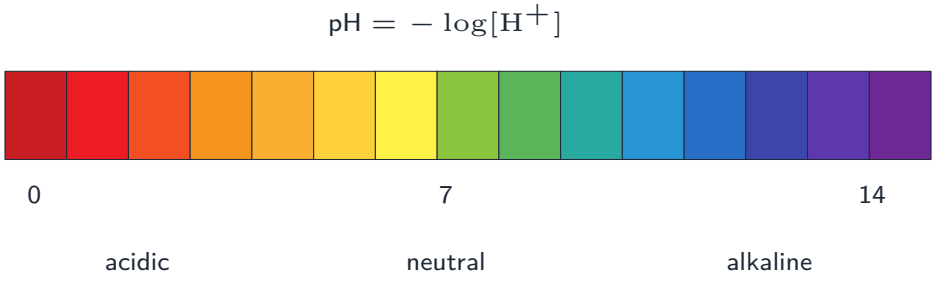
For example, in $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, the pair is CH_3COOH (acid) and CH_3COO^- (its conjugate base).



Conjugate pairs differ by one proton: an acid loses H^+ to give its conjugate base; a base gains H^+ to give its conjugate acid

pH and the equilibrium constants

- **pH** measures acidity: $\mathrm{pH} = -\log[\mathrm{H}^+]$, so $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$.
- the **acid dissociation constant** 酸解离常数 of a weak acid HA is $K_a = \dfrac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$, and $\mathrm{p}K_a = -\log K_a$. A larger K_a (smaller $\mathrm{p}K_a$) means a stronger acid.
- the **ionic product of water** 水的离子积 is $K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 1.0 \times 10^{-14}$ 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 $pH = -\log(0.050) = 1.30$.

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 $pH = 13.0$.

Worked example. Find the pH of 0.10 mol dm^{-3} ethanoic acid (a weak acid). ($K_a = 1.8 \times 10^{-5}$.)

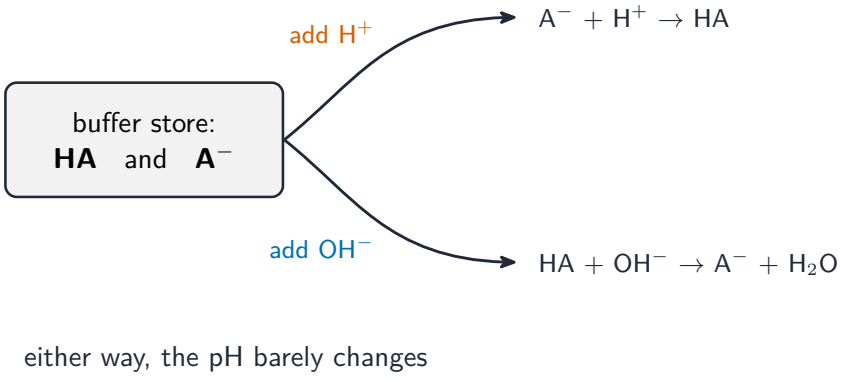
$$[H^+] = \sqrt{K_a \times [HA]} = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3}, \qquad pH = -\log(1.3 \times 10^{-3}) = 2.87.$$

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: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$.



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.

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}.

Stalactites grow as dissolved calcium carbonate slowly comes back out of solution — a real solubility equilibrium

The common ion effect

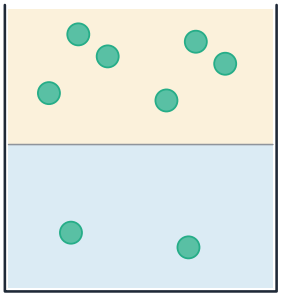
The **common ion effect** 同离子效应 is the way a salt becomes **less** soluble in a solution that already contains one of its ions. The extra ion pushes the dissolving equilibrium back (Le Chatelier), so less salt dissolves. You can calculate the new solubility using K_{sp} and the concentration of the common ion.

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):

$$K_{\text{pc}} = \frac{[\text{solute in solvent 1}]}{[\text{solute in solvent 2}]}$$

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.



A solute shaken with two immiscible solvents spreads between them; the partition coefficient is the ratio of its concentrations in the two layers

Exam tips

- pH $= -\log[\text{H}^+]$; for a **strong acid** $[\text{H}^+]$ = concentration, for a **weak acid** use $[\text{H}^+] = \sqrt{K_a[\text{HA}]}$.
- For a base, get $[\text{H}^+]$ from $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$.
- For a **buffer** use $[\text{H}^+] = K_a \times [\text{acid}]/[\text{salt}]$ and explain how it removes added H^+/OH^-.
- Write the K_{sp} expression with the correct powers; the number of decimal places in a pH equals the significant figures of $[\text{H}^+]$.

Reaction kinetics

A-Level Chemistry

Rate equations and orders

A **rate equation** 速率方程 shows how the rate depends on the concentrations of the reactants:

$$\text{rate} = k\,[\text{A}]^m[\text{B}]^n$$

- 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.

A gas syringe measures the volume of gas made over time, which gives the rate of reaction

Finding the order

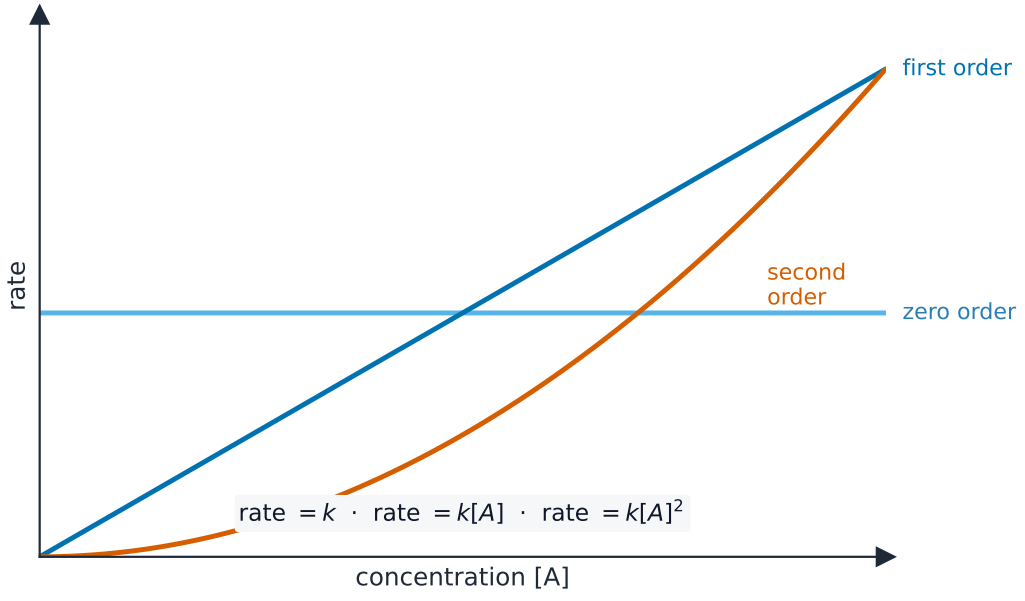
- **initial rates method**: change one concentration at a time and see how the starting rate changes. If doubling [A] doubles the rate, the order in A is 1; if it quadruples the rate, the order is 2; if the rate is unchanged, the order is 0.

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 in A. Doubling [B] quadruples (2^2) the rate, so second order in B. Hence

$$\text{rate} = k[\text{A}][\text{B}]^2, \qquad \text{overall order} = 1 + 2 = 3.$$

- **graphs**: a concentration–time graph 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 for first order, and a curve for second order.

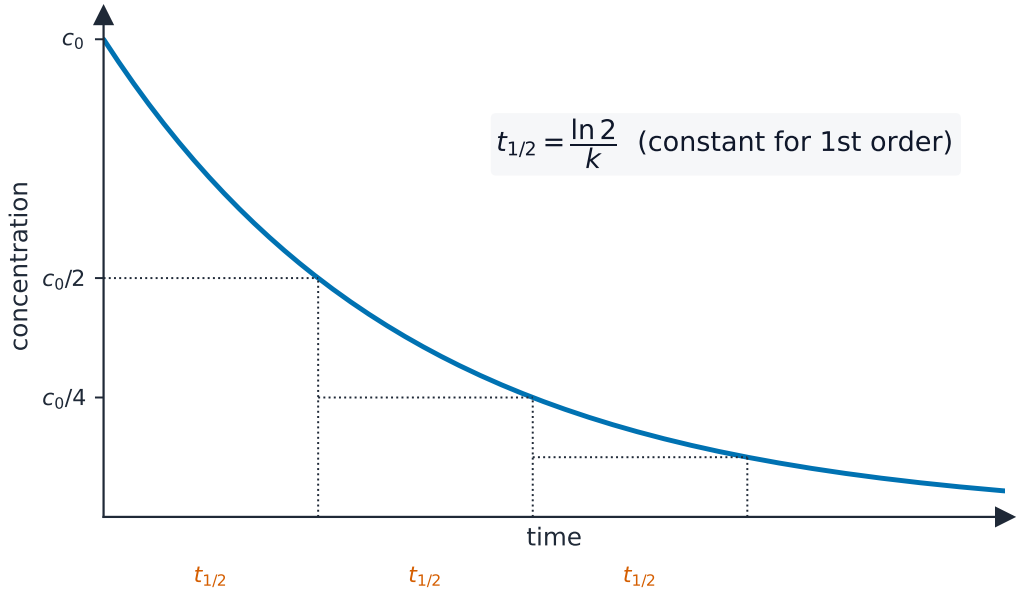


Rate against concentration: zero order is a flat line, first order a straight line through the origin, second order an upward curve

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

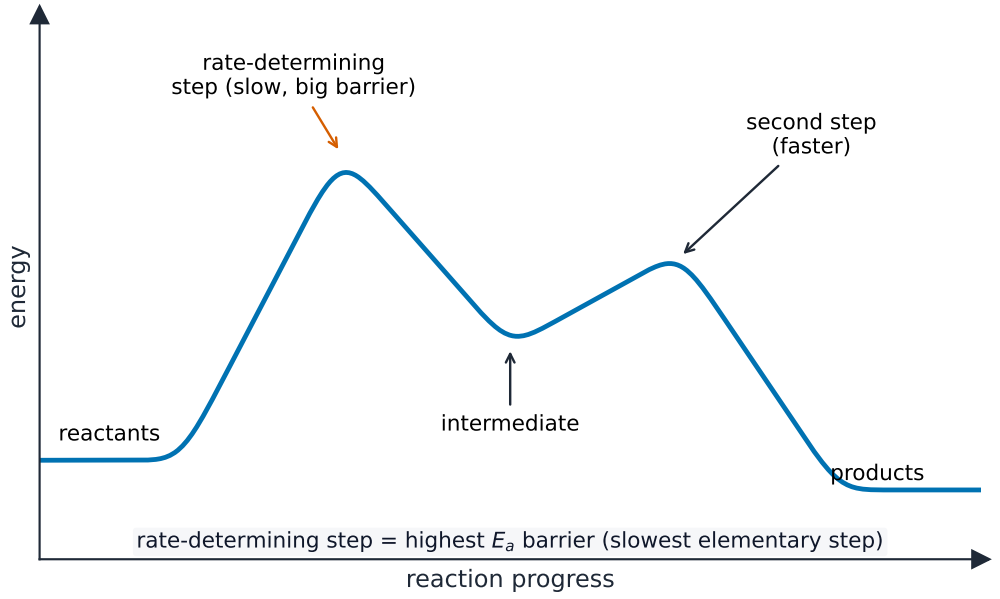
Worked example. A first-order reaction has a half-life of 120 s. Find its rate constant.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.8 \times 10^{-3}\ \text{s}^{-1}.$$

You can also find k by putting initial-rate data into the rate equation.

Reaction mechanisms

Most reactions happen in several steps. The slowest step is the **rate-determining step** 決速歩骤, and it controls the overall rate. Only the species involved up to and including this step appear in the rate equation.



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 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** 初始速率 of different mixtures, you can deduce the rate equation, and from that work out the mechanism.

Effect of temperature

Raising the temperature increases the rate constant k (more molecules pass the activation energy), so the rate goes up.

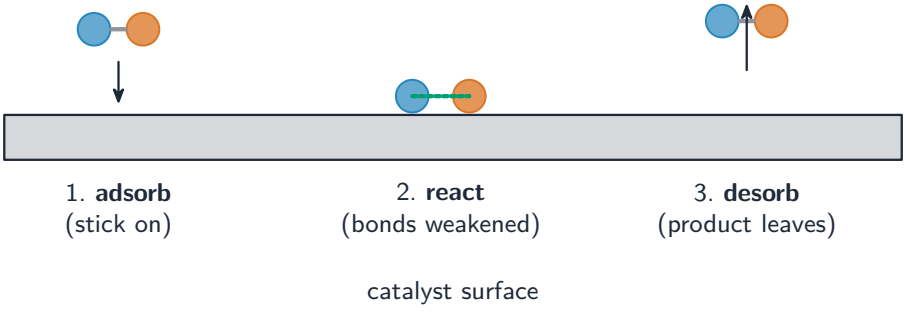
Catalysts

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 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, 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

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, and platinum, palladium and rhodium in a catalytic converter.

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 in a later step, so it comes back unchanged. Examples are oxides of nitrogen helping to oxidise atmospheric sulfur dioxide, and Fe^{2+} or Fe^{3+} speeding up the reaction between I^- and $S_2O_8^{2-}$.

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.
- 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.

Group 2

A-Level Chemistry

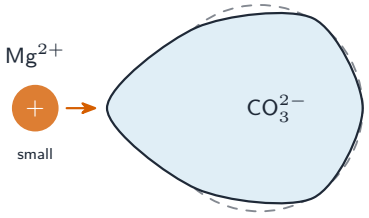
Thermal stability of the nitrates and carbonates

The **thermal stability** 热稳定性 of the Group 2 **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

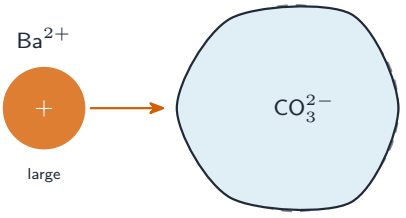
A small **cation** 阳离子 with a small **ionic radius** 离子半径 has a high charge density. It pulls on the electrons of the nearby anion and distorts its shape — this is **polarisation** 极化. Distorting the large **anion** 阴离子 (the carbonate or nitrate ion) weakens a bond inside it, so the compound breaks down more easily.

Going down the group, the cation gets larger. Its charge density drops, so it polarises the anion **less**. The anion is less distorted, so the compound is harder to break down — it is more thermally stable and needs a higher temperature to decompose.



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

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 dissolves, two energy changes compete. The **enthalpy change of solution** 溶解焓变 is the sum of them:

hydroxides
get *more* soluble
down the group

sulfates
get *less* soluble
down the group

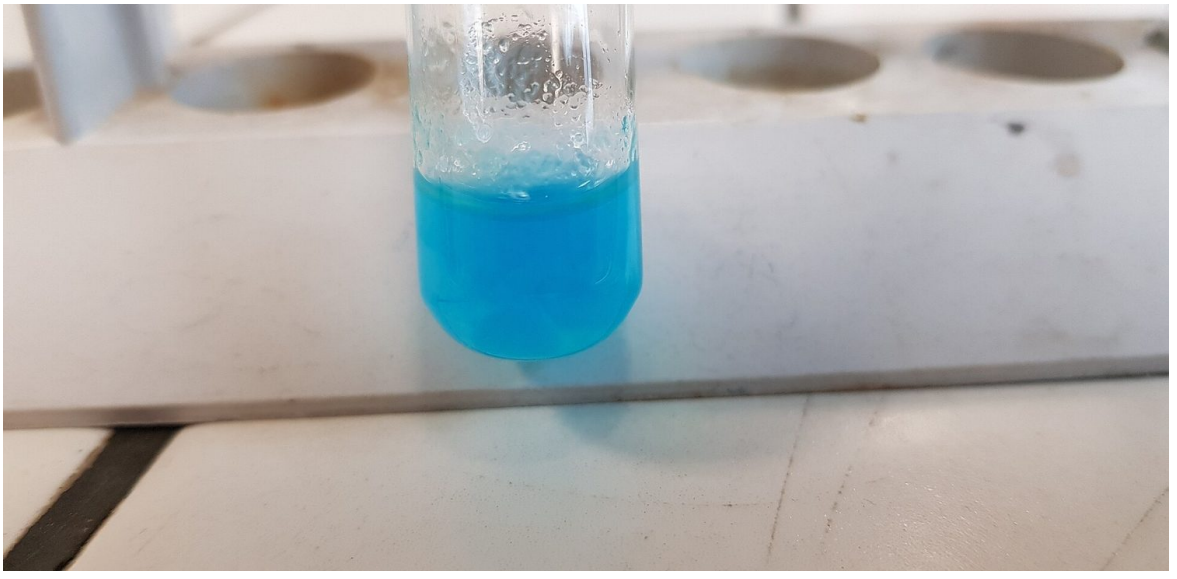
Down Group 2 the hydroxides get more soluble but the sulfates less

$$\Delta H_{\text{sol}}^{\ominus} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

- you must first pull the lattice apart (this needs the **lattice energy** 晶格能).

- then water surrounds the ions (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 get **smaller** (less negative), because the cation is larger. But they shrink at different rates, and this explains the opposite trends:

$$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

hydroxides (small OH^-):
lattice energy falls *a lot* down the group
$\Rightarrow$ outweighs the smaller hydration fall
→ **more** soluble

sulfates (large SO_4^{2-}):
lattice energy stays almost constant
$\Rightarrow$ 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)

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 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, so dissolving becomes less favourable

Exam tips

- Thermal stability of carbonates and nitrates **increases down** the group — larger cations polarise the anion less.
- Give the **decomposition products**: carbonates → oxide + CO_2; nitrates → oxide + NO_2 + O_2 (brown gas).
- Hydroxides get **more soluble** and sulfates **less soluble** down the group.
- Explain trends with **cation charge density (polarising power)**, not just size.

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.

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)

The four key properties of the transition elements

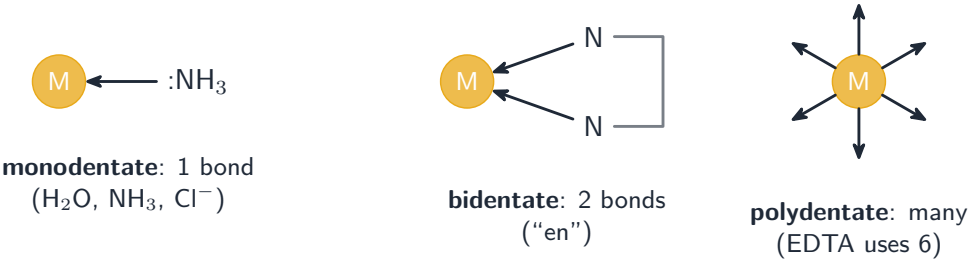
A ruby is red because of transition-metal (chromium) ions held in its crystal lattice

Ligands and complexes

A transition metal ion can be surrounded by **complex ions** 配离子. The species attached are ligands.

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:

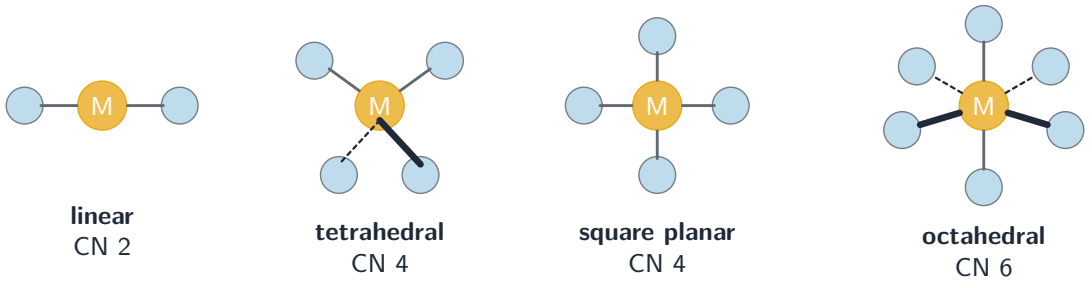
- **monodentate** 单齿: one bond (H_2O, NH_3, Cl^-, CN^-).
- **bidentate** 双齿: two bonds (1,2-diaminoethane "en", and the ethanedioate ion $C_2O_4^{2-}$).
- **polydentate** 多齿: many bonds ($EDTA^{4-}$, which uses six).



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.



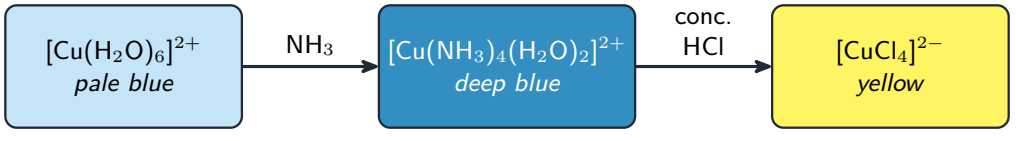
Complex shapes follow the coordination number: 2 is linear, 4 is tetrahedral or square planar, 6 is octahedral

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.



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. Common titrations you should be able to calculate include $MnO_4^-/C_2O_4^{2-}$ and MnO_4^-/Fe^{2+} in acid (purple to colourless), 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 (see the balanced equation above). 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

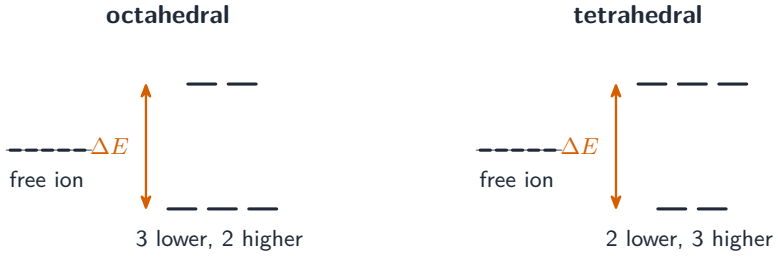
$$[Fe^{2+}] = \frac{2.20 \times 10^{-3}}{25.0/1000} = 0.0880 \text{ mol dm}^{-3}.$$

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.



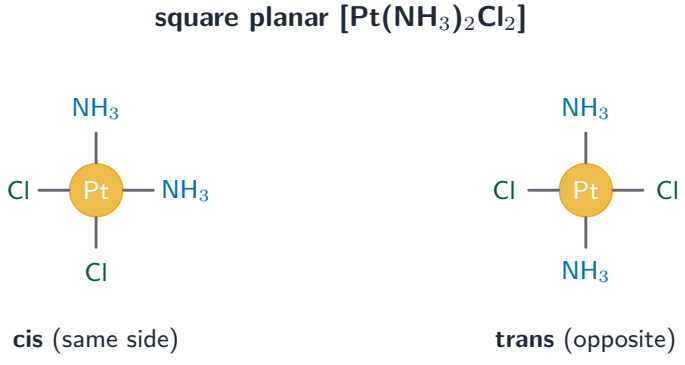
the complex absorbs light of energy ΔE, so we see the **complementary colour**

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 $[Co(NH_3)_4(H_2O)_2]^{2+}$.



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.

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).

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.

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).
- **Ligand exchange** can change colour and coordination number; a larger stability constant = a more stable complex.

An introduction to A Level organic chemistry

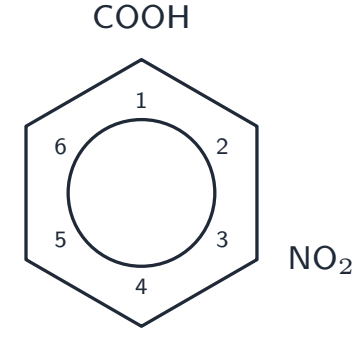
A-Level Chemistry

New functional groups and naming

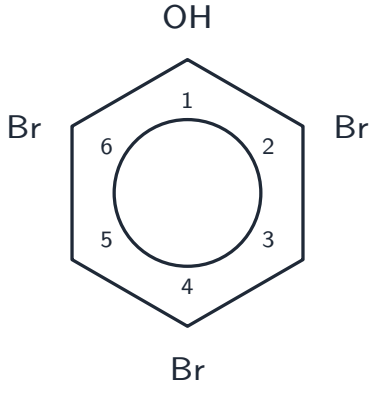
At A Level you meet more **functional group** 官能团 families, including the **amide** 酰胺 group and **aromatic** 芳香 compounds (those built on a benzene ring). As before, the functional group decides the properties, and you read it from the general, structural, displayed or skeletal formula.

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

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

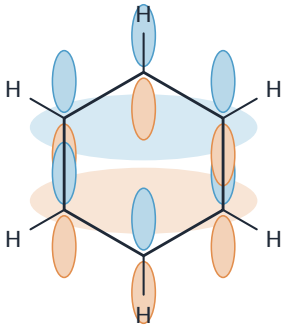
addition–elimination
a molecule adds on, then
a small molecule is removed

Two aromatic mechanisms: electrophilic substitution and addition-elimination

The shape of benzene

Benzene is a flat, regular hexagon. Each carbon is **sp**^{2} hybridised, using its three **hybridisation** 杂化 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.



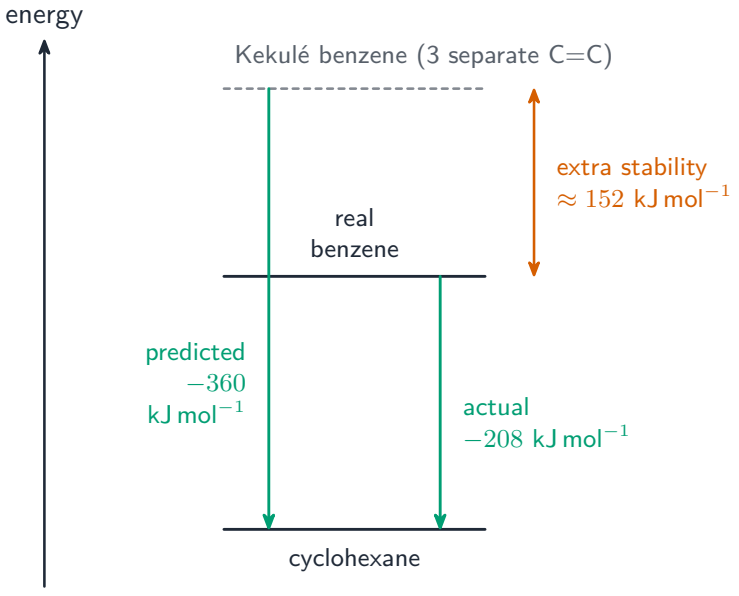
one **delocalised** π system
above and below the ring

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

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.



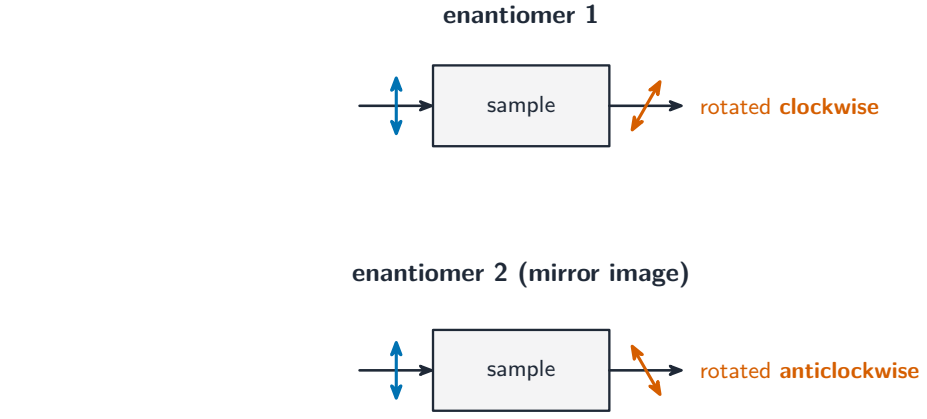
Evidence for delocalisation: real benzene releases far less on hydrogenation (-208 kJ mol^{-1}) than the Kekulé model predicts ($-360 = 3\times$ cyclohexene), so it is about 152 kJ mol^{-1} more stable than expected

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.



The two enantiomers rotate plane-polarised light in opposite directions; a 50:50 racemic mixture gives no net rotation

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.

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. Take the carbons one at a time. 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, but only once you look past the first atom.

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.
- Learn the two new mechanisms — electrophilic substitution of arenes, and nucleophilic addition-elimination.

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

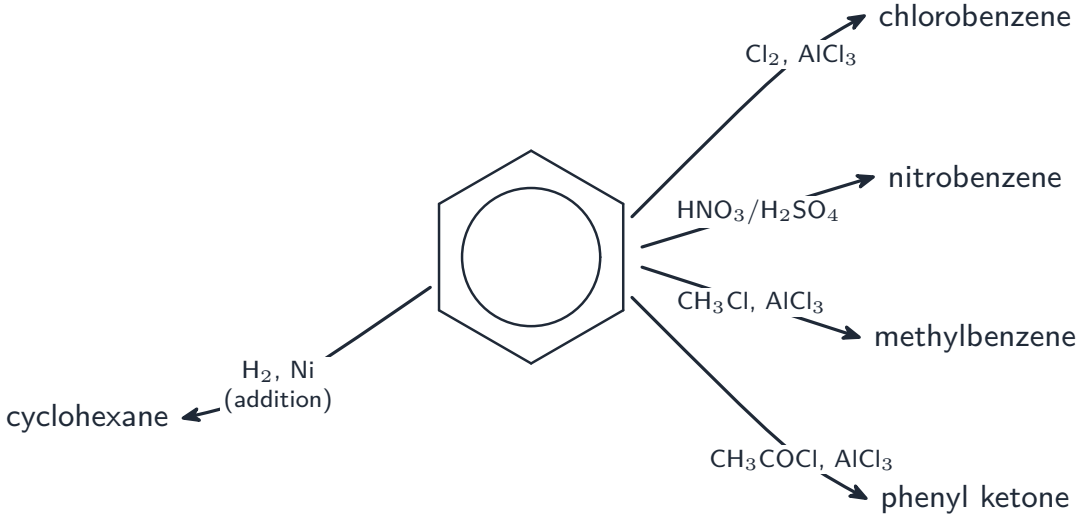
Reactions of benzene and methylbenzene

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

alkylation
adds an alkyl group
(CH_3Cl + $AlCl_3$)

acylation
adds an acyl group
(CH_3COCl + $AlCl_3$)

Friedel-Crafts: alkylation adds an alkyl group, acylation an acyl group



Benzene keeps its stable ring, reacting mostly by electrophilic substitution (and by addition only with hydrogen)

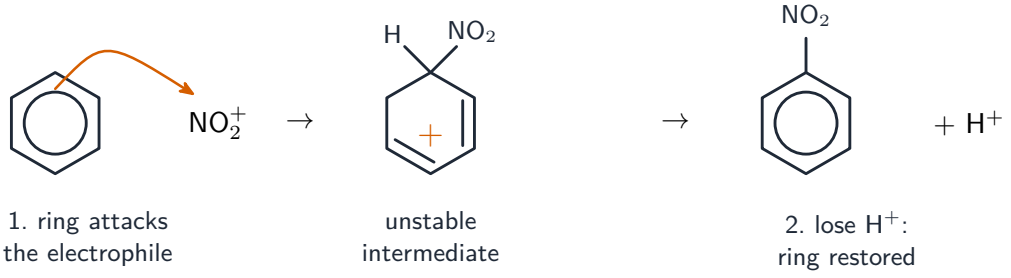
In the side-chain oxidation, the whole **side-chain** 侧链 (such as the –CH_3 on methylbenzene) is turned into a –COOH group, giving benzoic acid. In the hydrogenation, three molecules of H_2 add to the **benzene ring** 苯环 to make a saturated cyclohexane ring.

The mechanism: electrophilic substitution

Take nitration as the example. The acid mix makes the electrophile NO_2^+. Then:

1. the delocalised electrons of the ring form a bond to the electrophile, giving an unstable intermediate.
2. an H^+ is lost from that carbon, which restores the stable ring.

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.

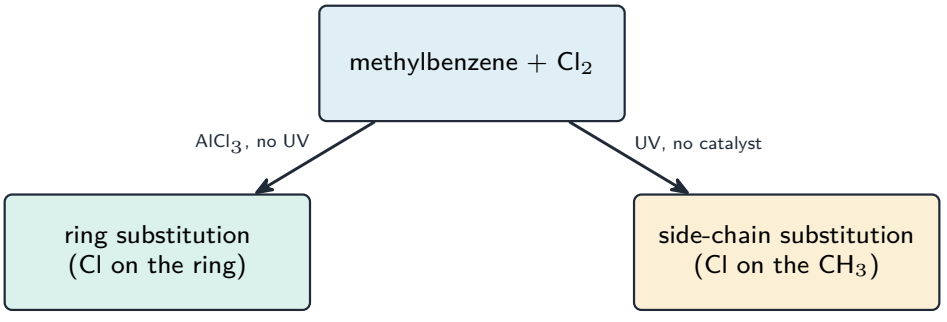


Electrophilic substitution (nitration): the ring attacks the electrophile NO_2^+ to give an unstable intermediate, then loses H^+ to restore the ring

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**.

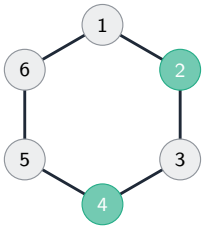


The conditions decide: a halogen carrier ($AlCl_3$) substitutes the ring; UV light substitutes the side-chain

Directing effects

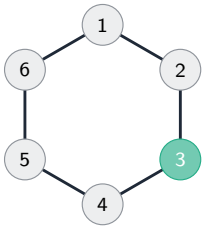
A group already on the ring decides where the next group goes — its **directing effect** 定位效应:

–NH_2, –OH, –R



direct to **2 and 4**

–NO_2, –COOH, –COR



direct to **3**

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

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.

Exam tips

- Benzene undergoes **electrophilic substitution**, not addition, because addition would destroy the stable delocalised ring.
- Learn **nitration** (concentrated HNO_3/H_2SO_4, $50-60$ °C) and **halogenation** (halogen + $AlCl_3$) with the electrophile-generating step.
- Compare reactivity: benzene resists addition far more than an alkene because of delocalisation.

Halogen compounds

A-Level Chemistry

Making halogenoarenes

A **halogenoarene** 卤代芳烃 (also called an aryl halide) 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 from the arenes topic — the halogen replaces a hydrogen on the ring.

- benzene gives chlorobenzene.
- methylbenzene gives 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene (the methyl group directs 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)

Many pesticides and herbicides are halogenoarenes — chlorine atoms bonded to a benzene ring

Why a halogenoarene is less reactive than a halogenoalkane

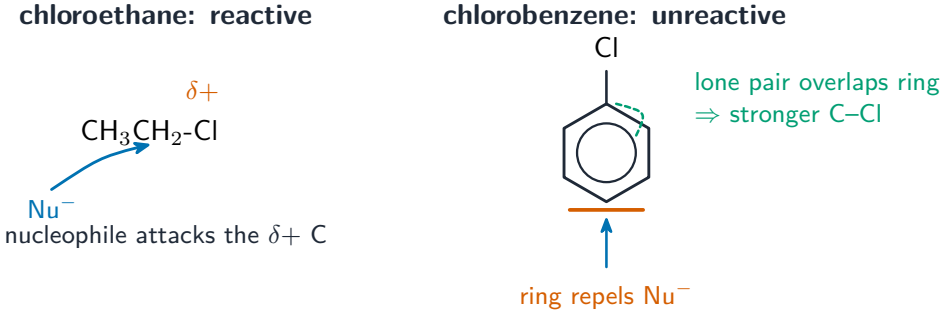
Compare chloroethane (a **halogenoalkane** 卤代烷) with chlorobenzene (a halogenoarene).

A halogenoalkane reacts easily by **nucleophilic substitution** 亲核取代: its C–Cl bond is polar, so a nucleophile can attack the slightly positive carbon and push the halogen out.

A halogenoarene is **very unreactive** towards nucleophilic substitution. There are two reasons:

- a **lone pair** 孤对电子 on the chlorine overlaps sideways with the **delocalised** 离域 ring of electrons. This gives the C–Cl bond partial double-bond character, making it shorter and stronger, so it is much harder to break.
- the electron-rich ring repels 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

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** (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. For example, ethanol and ethanoyl chloride give ethyl ethanoate, plus fumes of HCl.

An acyl chloride reacts with an alcohol faster and more completely than a carboxylic acid does, giving the ester and HCl fumes

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

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).

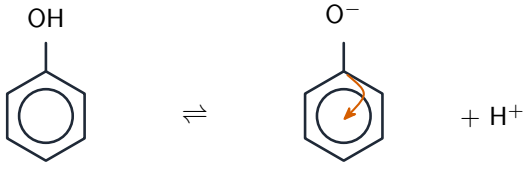
Reactions of phenol

- with a base such as NaOH(aq): phenol reacts to give sodium phenoxide and water. (Ordinary alcohols do **not** react with NaOH — this shows phenol is more acidic.)
- with sodium metal: gives sodium phenoxide and hydrogen.
- with a diazonium salt in NaOH(aq): forms a coloured **azo compound** 偶氮化合物 (used in dyes).
- **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): gives a white precipitate of 2,4,6-tribromophenol.

Acidity of phenol

Phenol loses its H^+ to form a phenoxide ion. This ion is stabilised because its negative charge is spread (delocalised) into the ring. So phenol's **acidity** 酸性 is higher than that of water or ethanol:

$$\text{ethanol} < \text{water} < \text{phenol}$$



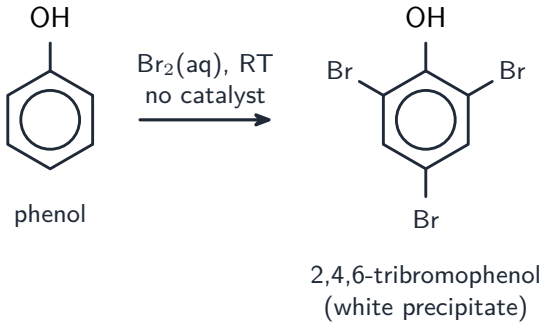
acidity: ethanol < water < phenol

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 — 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 more strongly. Phenol therefore reacts faster and under much milder conditions than benzene — no catalyst is needed, and dilute reagents 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 to the 2-, 4- and 6-positions. The same ideas apply to other phenolic compounds, such as naphthol.

Carbolic soap contains phenol, which was one of the first antiseptics

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.

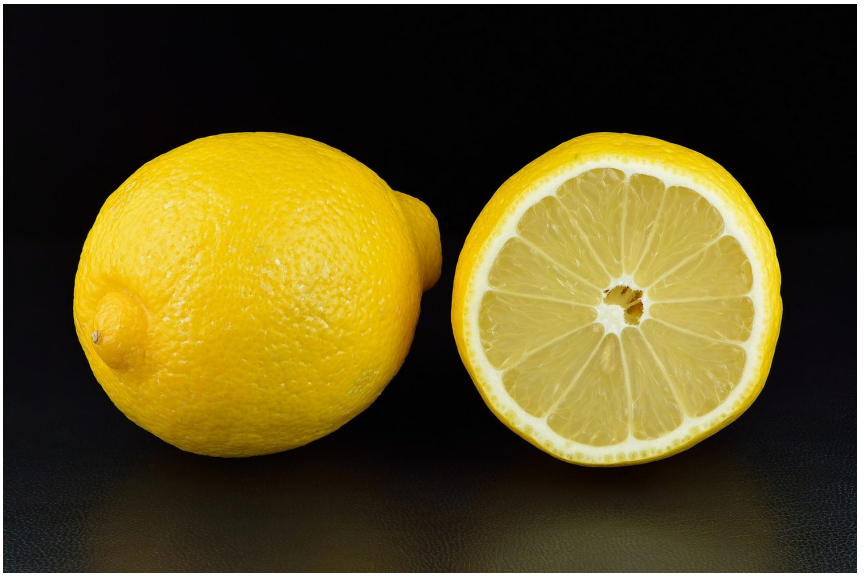
Exam tips

- **Phenol** is a stronger acid than alcohols (its anion is stabilised by delocalisation) but weaker than carboxylic acids — it does **not** react with carbonates.
- Phenol decolourises **bromine water** and gives a white precipitate **without a catalyst** (the ring is activated by oxygen).
- **Acyl chlorides** react with alcohols/phenols to give esters readily (better than the reversible acid route); misty HCl fumes are the observation.

Carboxylic acids and derivatives

A-Level Chemistry

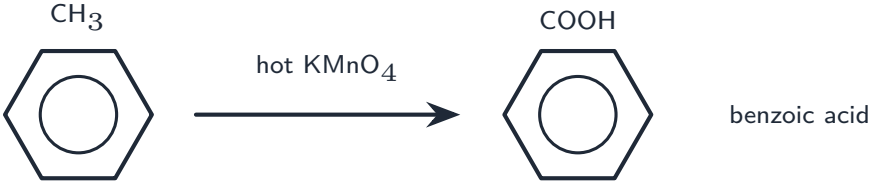
Carboxylic acids



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

Acids that can be oxidised further

Two **carboxylic acids** 羧酸 are special because they can still be oxidised:

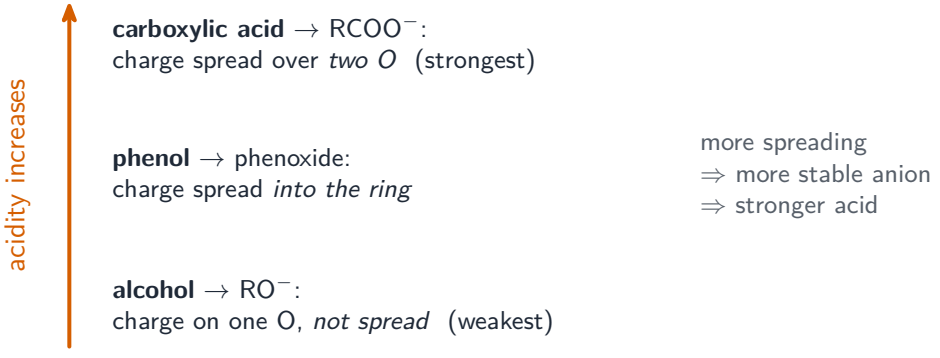
- methanoic acid (HCOOH) is oxidised by Fehling's or Tollens' reagent, or acidified $KMnO_4$ / $K_2Cr_2O_7$, to carbon dioxide and water.
- ethanedioic acid (HOOCCOOH) is oxidised by warm acidified $KMnO_4$ to carbon dioxide.

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.



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.

Esters

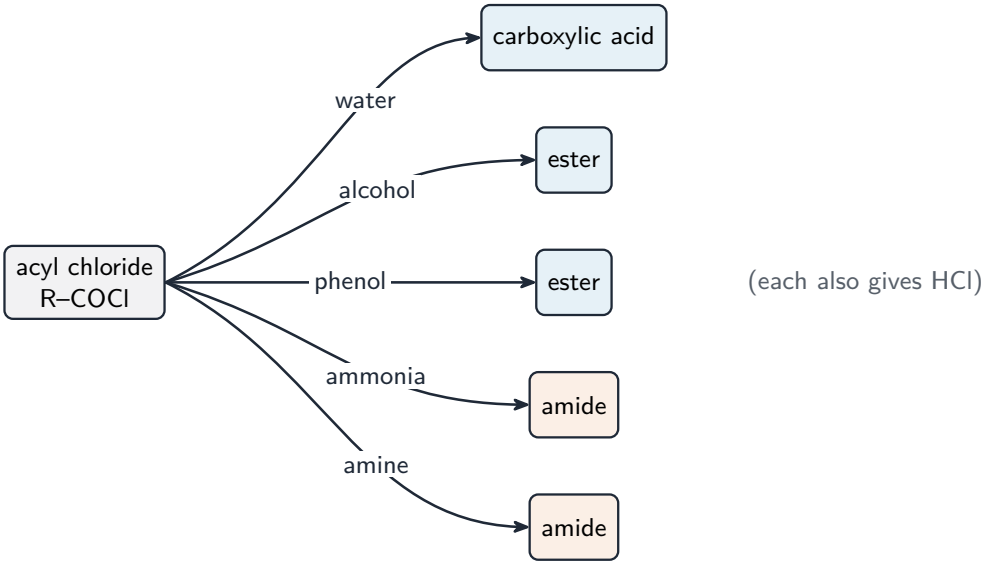
An alcohol (or phenol) reacts with an acyl chloride at room temperature to give an **ester** 酯 and HCl. Examples are ethyl ethanoate (from ethanol) and phenyl benzoate (from phenol).

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:

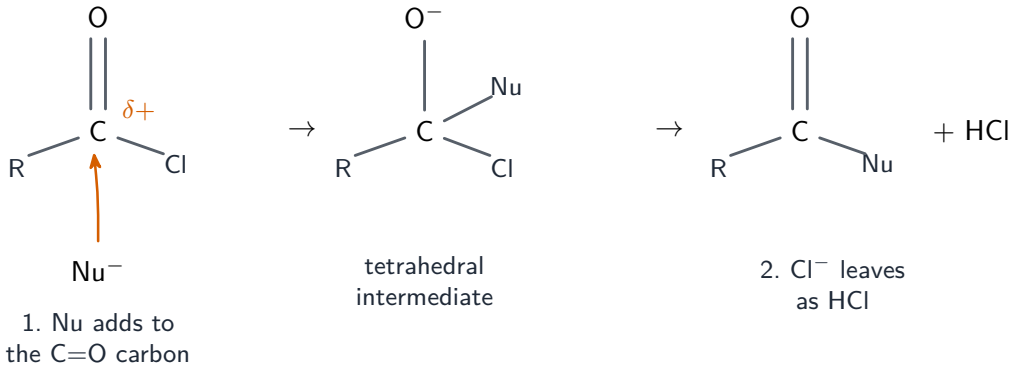
Reactant	**Product (plus HCl)**
water	the carboxylic acid
an alcohol	an ester
phenol	an ester
ammonia 氨	an **amide** 酰胺
a primary or secondary **amine** 胺	an amide



Acyl chlorides are very reactive: with water, an alcohol, phenol, ammonia or an amine they give the labelled product plus HCl

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**.



Addition–elimination: the nucleophile adds to the δ+ carbonyl carbon, then the C=O reforms and Cl^- leaves as HCl

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.

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.

Nitrogen compounds

A-Level Chemistry

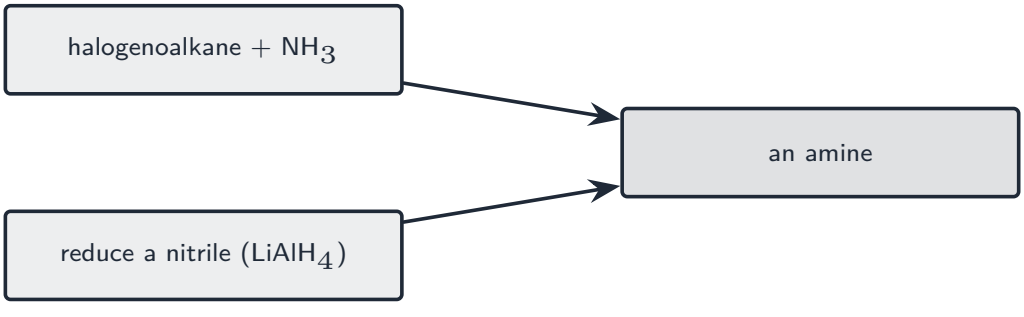
Primary and secondary amines

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.



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.

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.

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).

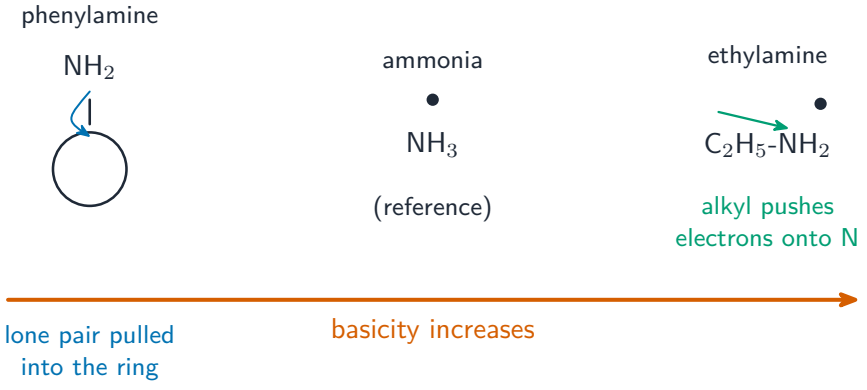
Reactions

- 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.

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

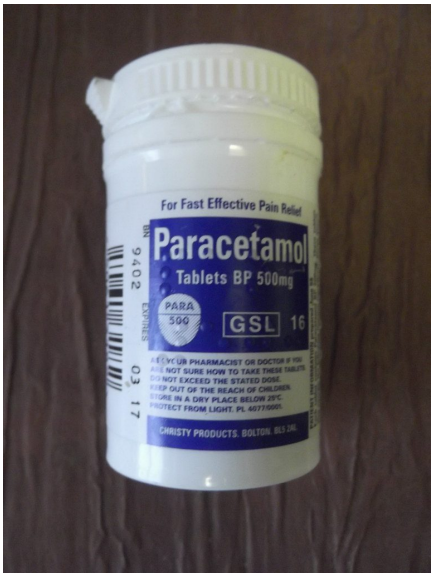
A **diazonium salt** 重氮盐 (benzenediazonium chloride) couples with **phenol** 苯酚 in NaOH(aq) to form an **azo compound** 偶氮化合物. The azo group is –N=N–. Azo compounds are brightly coloured and are often used as **dye** 染料 s; many other azo dyes are made the same way.

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

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.

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.

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

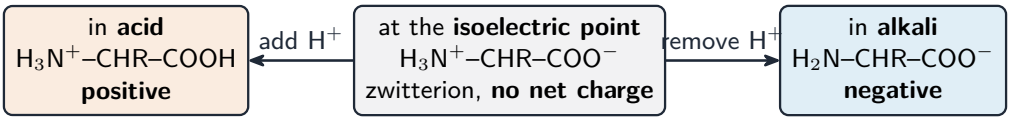
An **amino acid** 氨基酸 has both a basic $–NH_2$ group and an acidic –COOH group.

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.

$$H_2N–CHR–CO\,OH \;+\; H\,–NH–CHR'–COOH \;\downarrow\; H_2N–CHR–CO–NH–CHR'–COOH + H_2O$$

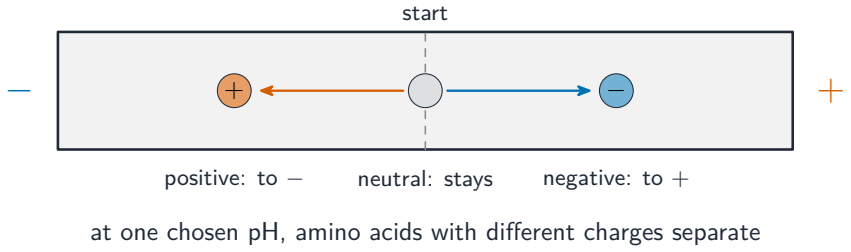
the **peptide bond** (an amide link)

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

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

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 **and** a small molecule (such as water or HCl) is lost each time a new bond forms. Each monomer needs **two** reactive groups, 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 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.
- a single hydroxycarboxylic acid, which has both an –OH and a –COOH.

PET drinks bottles are made of a polyester — a condensation polymer, collected here for recycling

Polyamides

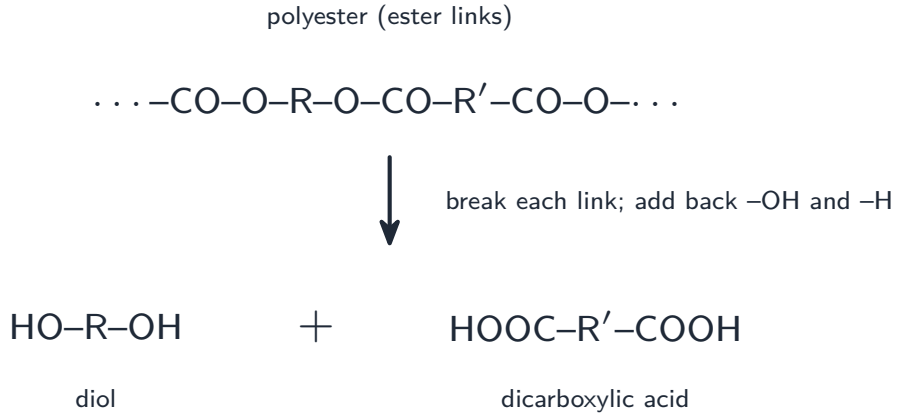
A **polyamide** 聚酰胺 has many amide links. You can make one from:

- a **diamine** 二胺 (two $-NH_2$ groups) and a dicarboxylic acid or a dioyl chloride.
- a single aminocarboxylic acid, or from **amino acids** 氨基酸 joining together (proteins 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)

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, and **nothing** else is lost	**addition polymerisation** 加成聚合
each monomer has **two** functional groups, 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 — they have only strong, non-polar C–C and C–H bonds, so they are hard to **biodegrade** 可生物降解 and last a long time.
- some polymers are made so that light can break them down (they are photodegradable).
- polyesters and polyamides **are** biodegradable, because their ester and amide links can be broken by acidic or alkaline **hydrolysis** 水解.

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.

Organic synthesis

A-Level Chemistry

Organic synthesis

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:

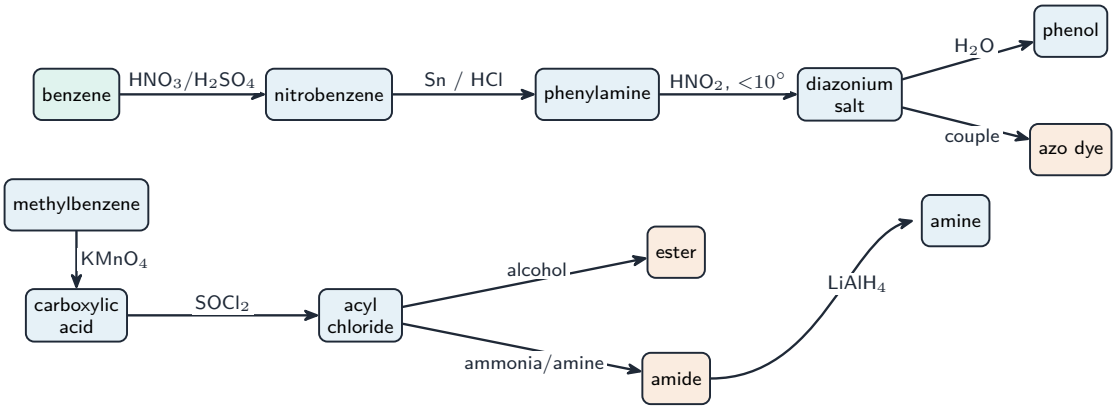
- decolourises bromine water with **no** catalyst, giving a white precipitate → a phenol or a phenylamine (the ring is activated).
- reacts violently with cold water, giving fumes of HCl → an **acyl chloride** 酰氯.
- gives a purple colour with neutral $FeCl_3$ → a **phenol** 苯酚.

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

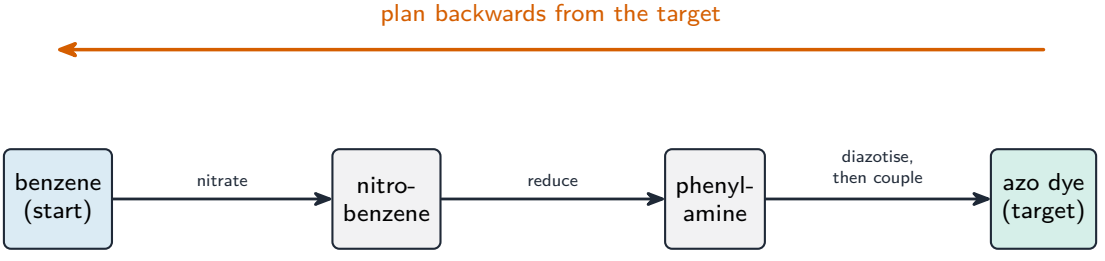
Start	Reagent and conditions	Product
benzene (an **arene** 芳烃)	HNO_3 / H_2SO_4 (**electrophilic substitution** 亲电取代)	nitrobenzene
nitrobenzene	Sn / conc HCl, then NaOH (**reduction** 还原)	phenylamine
phenylamine	HNO_2, below 10 °C	a diazonium salt
diazonium salt	warm water	phenol; or couple with phenol → azo dye
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)



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.

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

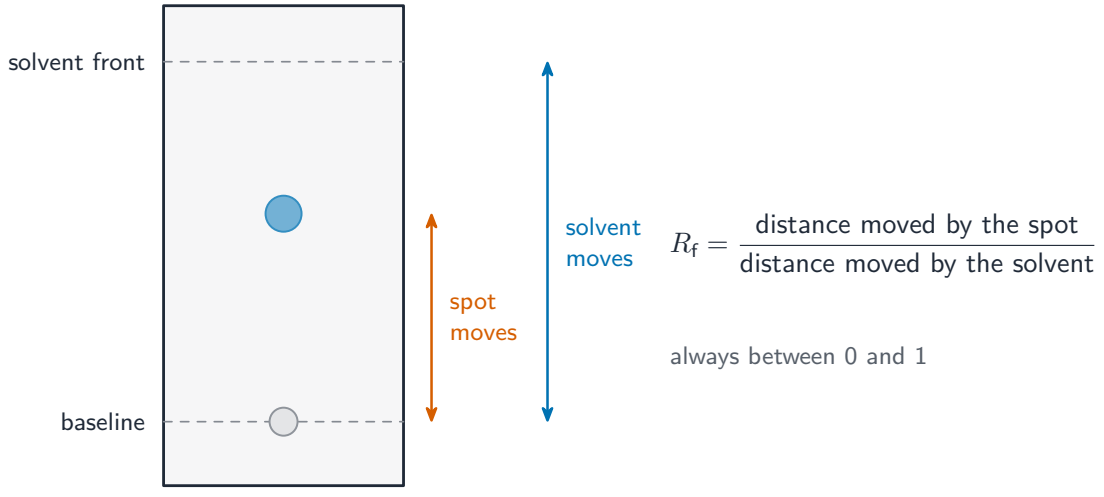
Chromatography 色谱 separates a mixture using two "phases" — one that stays still and one that moves. In **thin-layer chromatography** 薄层色谱 (TLC):

- 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.

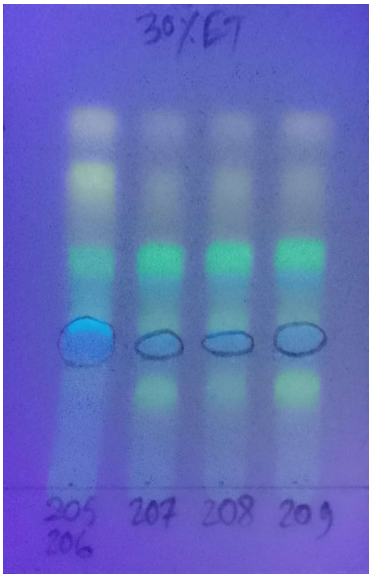
The R_f value compares how far a spot moves with how far the solvent moves:

$$R_\mathrm{f} = \frac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$$

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



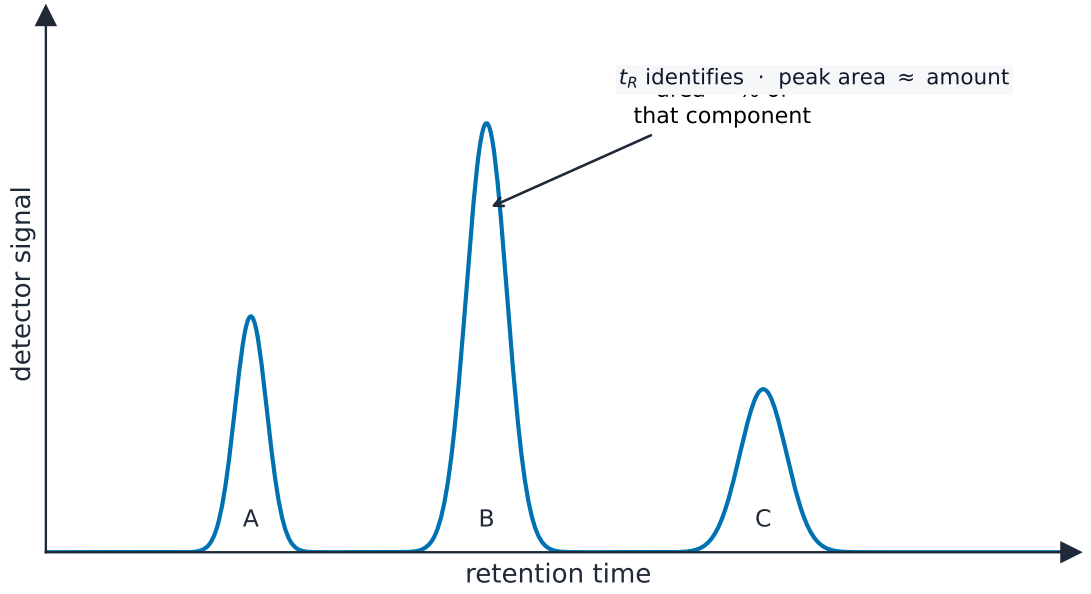
A real TLC plate under UV light: each glowing spot is a separated component of the mixture

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.



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:

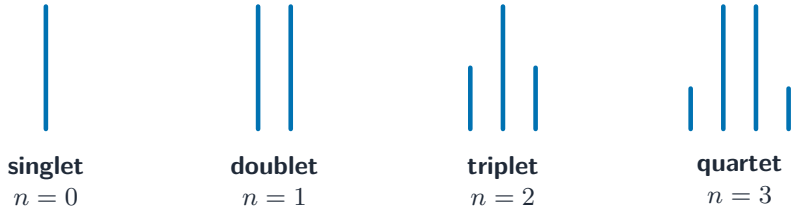
- the **number of peaks** tells you how many different carbon environments there are (equivalent carbons share a peak).
- the position of each peak (its chemical shift) suggests the type of carbon, which helps you deduce possible structures.

Proton (^{1}H) NMR spectroscopy

Proton NMR looks at the hydrogen atoms (**proton** 质子 nuclei). From the spectrum you read off:

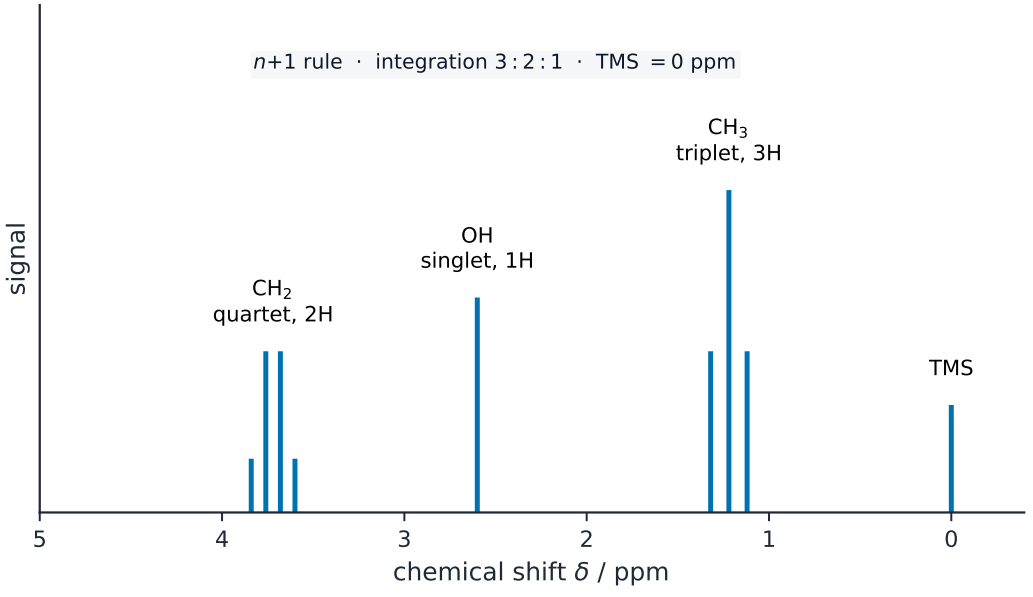
- **chemical environments**: protons in different environments appear at different **chemical shift** 化学位移 values.
- **relative numbers**: the relative peak **areas** give the ratio of each type of proton.
- **splitting** 裂分: a peak is split by the protons on the neighbouring carbon, following the $n + 1$ **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



n equivalent neighbours split a peak into $n + 1$ lines

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

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.

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.