Course Companion

International Baccalaureate · IB Diploma · Chemistry · HL

Every topic handout in one volume

全部专题讲义合集

exercises.lol

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Introduction to the particulate nature of matter

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Structure 1.1, Introduction to the particulate nature of matter, for the course first assessed in 2025. All of it is SL and HL content.

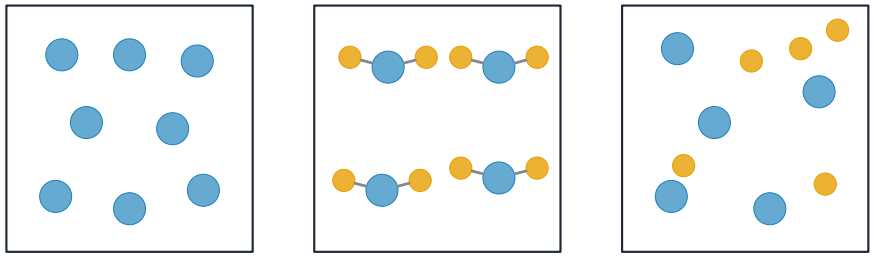
Prerequisites: the idea that matter is made of particles, and reading a temperature–time graph. This is the first unit of the course; the rest of the course builds on it.

Elements, compounds and mixtures

Why is sea water not a pure substance?

A simplified salt-water sample contains water and dissolved salt. Heating can remove water as vapour while non-volatile salt remains; collecting the water requires condensation, not just watching vapour escape. Real sea water contains other substances, so the purity of a collected fraction depends on the method and possible contaminants. Sea water is a mixture: its components do not form a single new substance in a fixed formula, so a physical process can separate them. Water itself cannot be split by boiling; it needs a chemical reaction, such as electrolysis, to give hydrogen and oxygen.

Three kinds of matter



element
only one type of atom

compound
different atoms bonded in a fixed ratio

mixture
different particles, variable proportions

Elements and compounds are pure substances; a mixture is not

- An **element** 元素 contains only one type of atom and cannot be chemically broken down into simpler substances, for example iron, Fe, or oxygen, O_2.
- A **compound** 化合物 contains two or more elements **chemically bonded** in a fixed ratio, for example water, H_2O. Its properties differ from those of its elements: sodium and chlorine are dangerous, sodium chloride is table salt.
- A **mixture** 混合物 contains more than one element or compound in variable proportions, rather than one new compound with a fixed composition. Components retain their chemical identities, although mixing and interactions can change bulk properties such as boiling point. Bonds within component molecules do not disappear.

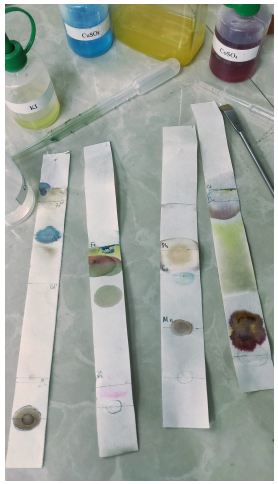
Homogeneous and heterogeneous mixtures

- A **homogeneous** 均匀的 mixture has the same composition throughout, and you cannot see the parts: a uniform salt solution, well-mixed air or a suitable single-phase brass sample. Some alloys contain more than one phase, so "alloy" alone does not guarantee a homogeneous sample.
- A **heterogeneous** 不均匀的 mixture does not have a uniform composition, and the parts can often be seen: sand in water, oil and water, granite.

Separating mixtures

Choosing a method

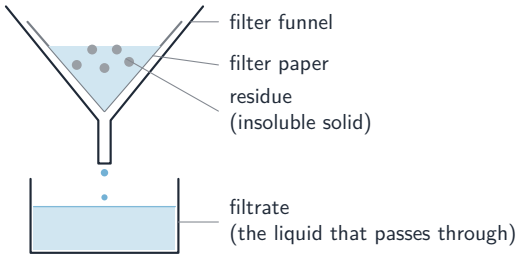
Mixtures are separated by physical methods that use a difference in physical properties: solubility, boiling point, or particle size.



On real chromatograms, each substance in the mixture rises a different distance, leaving a separate coloured spot

Mixture	Method	Property used
insoluble solid in a liquid (sand and water)	**filtration** 过滤	particle size
dissolved solid in a liquid (salt water), solid wanted	**evaporation** 蒸发 or **crystallization** 结晶	the solvent evaporates, the solute does not
dissolved solid in a liquid, liquid wanted	simple **distillation** 蒸馏	different boiling points
two miscible liquids (ethanol and water)	fractional distillation	different boiling points
an insoluble and a soluble solid (sand and salt in water)	dissolve the salt, filter off sand, then crystallize the salt	different solubility; dissolution involves **solvation** 溶剂化
coloured substances in a solution (inks, dyes)	paper chromatography (Structure 2.2)	attraction to two phases

Filtration

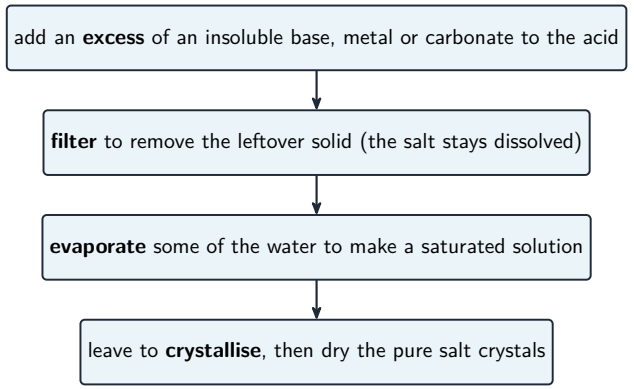


The solid that stays in the paper is the residue; the liquid that passes through is the filtrate

The filter paper has tiny holes. Dissolved particles and the solvent pass through; larger, undissolved particles do not.

Crystallization

To get crystals of a soluble solid, such as copper(II) sulfate, from its solution:

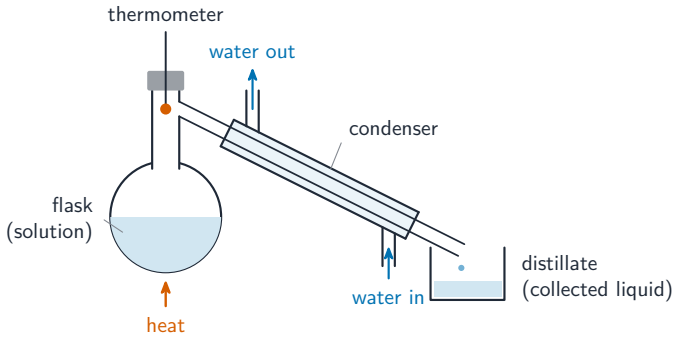


Making a soluble salt from an insoluble solid: react with excess, filter off the excess, evaporate, then crystallise

1. Heat the solution to evaporate some of the water until it is **saturated** 饱和的: a drop on a cold glass rod forms crystals.
2. Leave it to cool slowly. For a solute whose solubility decreases sufficiently on cooling, crystals can form. Choose a suitable solubility curve; not every solute has the same temperature dependence.
3. Filter off the crystals, wash them with a little cold water and dry them.

Evaporation to dryness can leave a solid residue, but may produce small crystals, trap impurities or decompose a heat-sensitive solid. Controlled crystallization and washing are chosen when purer crystals are wanted; neither guarantees complete recovery.

Distillation



The liquid boils off, condenses in the cold condenser and collects as the distillate

- For a solution containing a non-volatile solute, the vapour is mainly solvent; it condenses and is collected. For two volatile liquids, the vapour is commonly enriched in the more volatile component but need not be pure. They do not necessarily wait to boil one at a time.
- Cold water enters the condenser at the bottom and leaves at the top, so the jacket stays full.
- The thermometer bulb sits level with the side arm, so it reads the temperature of the vapour that is leaving.
- A fractionating column provides repeated vaporization and condensation, improving separation of volatile components. Boiling points depend on pressure, and mixtures such as ethanol/water can limit the purity obtainable by ordinary distillation. Use approved apparatus, suitable heating, eye protection and an open vapour path; never heat a sealed improvised vessel or distil to dryness.

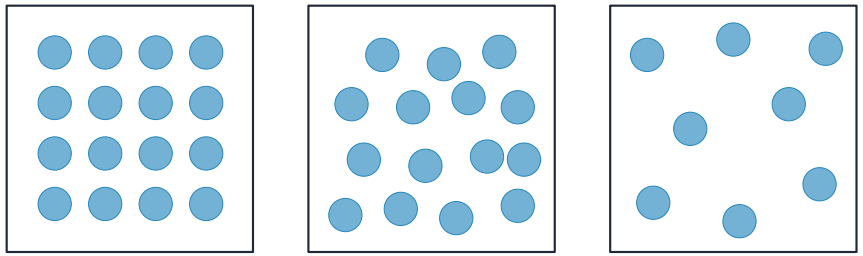
The kinetic molecular theory

■ Particles in the three states

The **kinetic molecular theory** 分子动理论 says that all matter is made of particles that are always moving. How the particles are arranged and how they move decides the state.



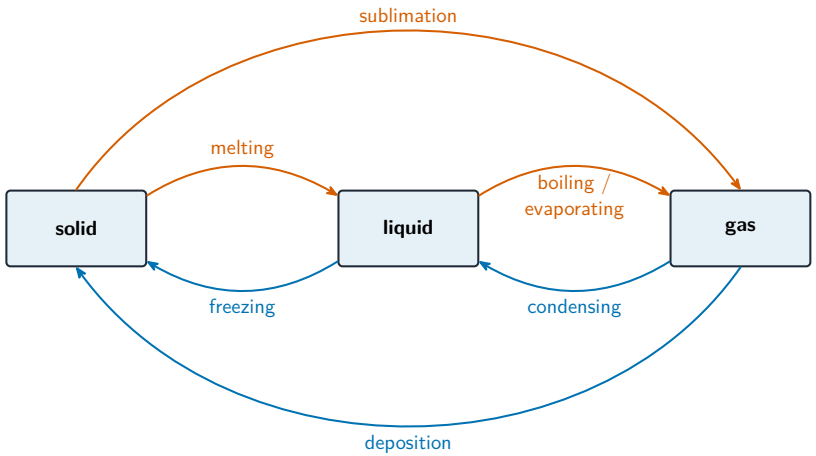
Warmed solid iodine turns straight into a purple gas (sublimation)



The state depends on how close the particles are and how freely they move

	Solid	Liquid	Gas
Arrangement	close together; regular in a crystalline solid	close together, without long-range crystalline order	far apart in the simple gas model
Movement	vibrate about fixed positions	move past each other	move fast in all directions
Attractions and motion	constrain particles around positions	still important while particles rearrange	neglected in an ideal-gas model
Shape	fixed	takes the shape of the container	fills the container
Volume	fixed	fixed	fills the container
Compressible?	only slightly under ordinary conditions	only slightly	much more readily

■ Changes of state



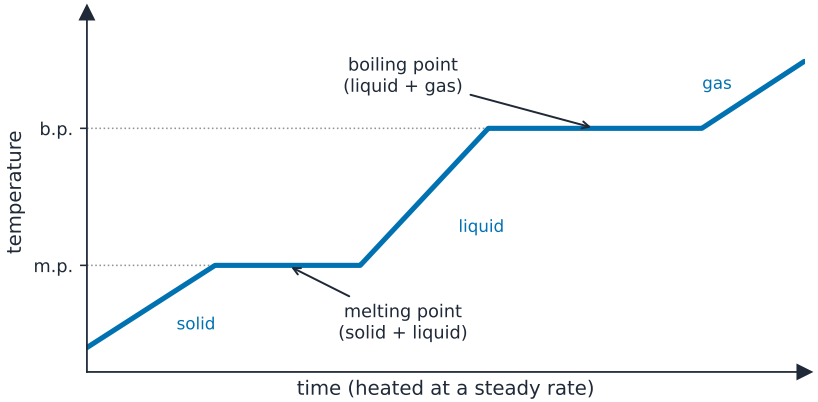
orange: particles gain energy blue: particles lose energy

Orange changes need energy; blue changes release it

- Melting, boiling or evaporating, and **sublimation** 升华 (solid straight to gas) are **endothermic** 吸热的: energy is taken in to overcome the forces between particles.
- Freezing, condensing and **deposition** 凝华 (gas straight to solid) are **exothermic** 放热的: energy is released as forces form.
- Dry ice (solid CO_2) and iodine sublime at atmospheric pressure. Frost forming on a cold window is deposition.

Evaporation and boiling are different. Evaporation occurs at a liquid surface over a range of temperatures: sufficiently energetic particles can escape. Boiling involves vapour bubbles throughout the liquid when conditions allow them to persist. A pure substance has a defined boiling temperature at a specified pressure; changing pressure changes that temperature. Melting and boiling water overcome intermolecular attractions rather than breaking each water molecule into hydrogen and oxygen. Some solids, such as glass, lack a regular crystalline arrangement: the simple ordered-particle drawing is a model, not every solid's structure.

The heating curve



plateau: attractions overcome; temperature constant

On each flat part the energy separates particles instead of making them move faster

- On the sloping parts the energy increases the kinetic energy of the particles, so the temperature rises.
- On the flat parts (the melting point and the boiling point) the energy is used to overcome the attractions between particles. The kinetic energy, and so the temperature, stays the same.
- Plateau duration depends on sample mass, latent energy, heating power and heat losses. The longer boiling plateau in this schematic is illustrative, not a universal timing rule or measured data.
- For an appropriate pure crystalline substance at fixed pressure, a sharp melting point supports a **purity** 纯度 assessment. Many impurities depress/broaden melting, but a range alone is not conclusive: heating rate, instrument error or decomposition may also matter. Pure-substance phase plateaus assume suitable pressure and near-equilibrium conditions.

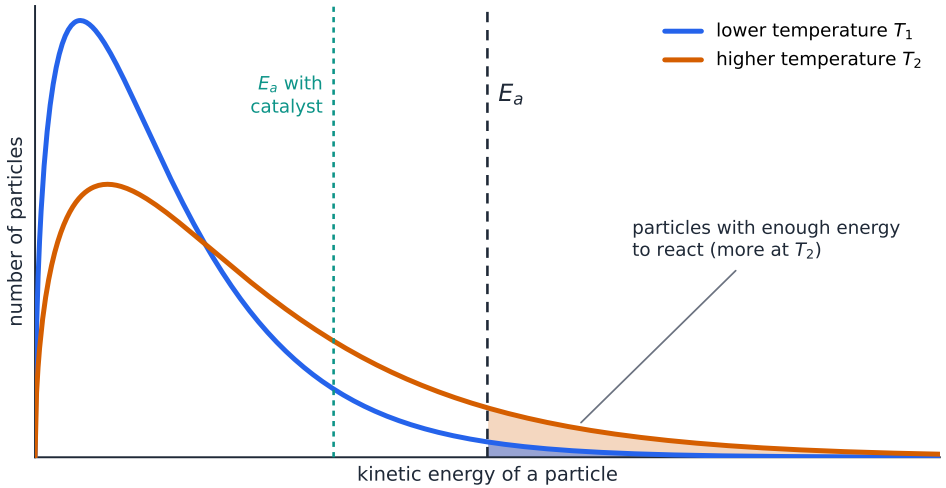
State symbols describe the sample

Use **(s)** for solid, **(l)** for liquid, **(g)** for gas and **(aq)** for dissolved in water. Aqueous does not mean a pure liquid. Water boiling is $H_2O(l) \rightarrow H_2O(g)$, a physical change with the same molecular identity. Sodium chloride dissolving can be represented $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$: the dissolved particles are ions, not lumps of solid salt small enough to see.

Temperature and kinetic energy

The kelvin scale

In the course's kinetic model, temperature relates to **average kinetic energy** 平均动能 rather than the energy of every individual particle. For an ideal gas, mean translational kinetic energy is proportional to kelvin temperature: doubling T doubles that mean. A distribution of particle energies remains. Do not identify temperature with total internal energy in every material: phase changes also involve potential-energy changes.



At a higher temperature the curve flattens and spreads out, and the shaded fraction of particles above Ea grows much larger; a catalyst moves Ea to the left instead

$$T/\mathrm{K} = \theta/^\circ\mathrm{C} + 273.15$$

The exact offset is **273.15** (NIST temperature conversion); use **273** for the whole-kelvin course estimates below, keeping one convention consistent.

- 0 K, **absolute zero** 绝对零度 (−273.15 °C), is the zero of the thermodynamic scale. The simple classical gas model approaches zero mean translational kinetic energy there; it does not describe all quantum motion in real matter.
- For the ordinary thermal systems and classical model considered here, T is non-negative, and no degree sign: write 298 K, not 298 °K.
- A temperature change of 1 K is the same as a change of 1 °C.

Worked example: converting temperatures

- 25 °C: $25 + 273 = 298$ K.
- 77 K (liquid nitrogen boils): $77 - 273 = -196$ °C.
- Warming a gas from 27 °C to 327 °C, the temperature goes from 300 K to 600 K, so the average kinetic energy doubles. In degrees Celsius it looks like a twelve-fold rise, which is wrong.

Practice

1. Classify each as an element, a compound or a mixture: (a) carbon dioxide, (b) air, (c) copper, (d) sea water, (e) sodium chloride.
2. Classify each mixture as homogeneous or heterogeneous: (a) clear vinegar, (b) muddy water, (c) single-phase brass, (d) a fruit salad.
3. Describe how to get pure, dry crystals of copper(II) sulfate from a mixture of the solid with sand.
4. Explain why the thermometer bulb in a distillation is placed at the side arm, not in the liquid.
5. Explain how water can be collected from salty water by distillation.
6. Describe the arrangement and movement of particles in a liquid.
7. Explain why gases are easy to compress but liquids are not.
8. Name the change of state when (a) solid iodine turns to a purple vapour, (b) water vapour forms ice on a freezer wall.
9. Explain why the temperature stays constant while ice melts, although it is being heated.
10. A sample melts between 112 °C and 117 °C. The pure substance melts at 122 °C. What does this show?
11. Convert (a) −40 °C to K, (b) 373 K to °C.
12. A gas is heated from 200 K to 400 K. State how its average kinetic energy changes. Explain why heating from 20 °C to 40 °C does not double it.
13. Give state symbols for pure liquid water, water vapour, solid sodium chloride and sodium ions dissolved in water. Explain why (aq) and (l) are not synonyms.
14. An invented 12.0 g sand/salt mixture contains 7.50 g salt. After dissolving, filtration and crystallization, 6.60 g dry salt is recovered. Find the initial sand mass and percentage salt recovery. Give two reasons why incomplete recovery does not by itself establish a chemical reaction.

Answers.

1. (a) compound, (b) mixture, (c) element, (d) mixture, (e) compound.
2. (a) homogeneous, (b) heterogeneous, (c) homogeneous, (d) heterogeneous.

3. Add water and stir (copper sulfate dissolves, sand does not). Filter: sand stays as the residue. Heat the filtrate until saturated, cool so crystals form, filter them off, wash with a little cold water and dry.
4. The thermometer must measure the temperature of the vapour that is distilling over, which helps identify the collected fraction; temperature alone does not prove it is a pure single substance.
5. Heat the salty water: the water boils and its vapour passes into the condenser, cools and condenses, and drips into the beaker. The salt has a very high boiling point and stays in the flask.
6. Particles are close together in a random arrangement; they move and slide past each other.
7. Gas particles are far apart, with a lot of empty space between them; liquid particles are already close together.
8. (a) sublimation, (b) deposition.
9. The energy is used to overcome the forces between particles in the solid, not to increase their kinetic energy, so the temperature does not change until all the ice has melted.
10. The depressed and broadened range is consistent with impurity for an appropriate crystalline substance. Check heating rate, calibration and possible decomposition before treating it as conclusive proof.
11. (a) $-40 + 273 = 233$ K, (b) $373 - 273 = 100$ °C.
12. It doubles, because kinetic energy is proportional to the temperature in K. 20 °C to 40 °C is 293 K to 313 K, an increase of only about 7%.
13. $H_2O(l)$, $H_2O(g)$, $NaCl(s)$, $Na^+(aq)$. Aqueous means dissolved in water, whereas liquid states a physical state without implying a solvent. $H_2O(l) \rightarrow H_2O(g)$ keeps the molecular identity; boiling does not split water into its elements.
14. Initial sand $\mathbf{12.0 - 7.50 = 4.50\ g}$. Salt recovery $\mathbf{6.60/7.50 \times 100 = 88.0\ \%}$. Salt may remain dissolved in the mother liquor or be lost during transfer/washing. Check dryness and contamination too; less recovered mass alone does not demonstrate a new substance formed.

Exam tips

- Distinguish variable-composition mixtures from fixed-composition compounds. Identify atoms, molecules or ions and use (s), (l), (g) and (aq) appropriately.
- Name the property a separation uses: solubility, particle size or boiling point.
- On a heating curve, say that energy overcomes the forces between particles; the kinetic energy and temperature stay constant.
- Always convert to kelvin before comparing kinetic energies or using a gas law; write K without a degree sign.
- Evaporation is a surface process; boiling involves persistent vapour bubbles. Specify pressure when discussing a boiling temperature and distinguish a fraction from proof of purity.

The nuclear atom

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

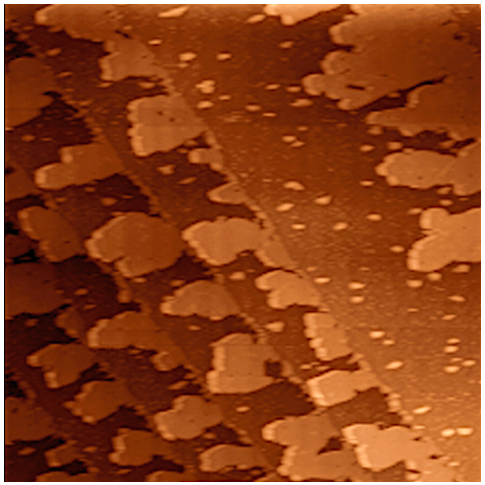
This handout teaches Structure 1.2, The nuclear atom, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: the particle model of matter from Structure 1.1, and positive and negative charge. Use the data booklet for relative atomic masses.

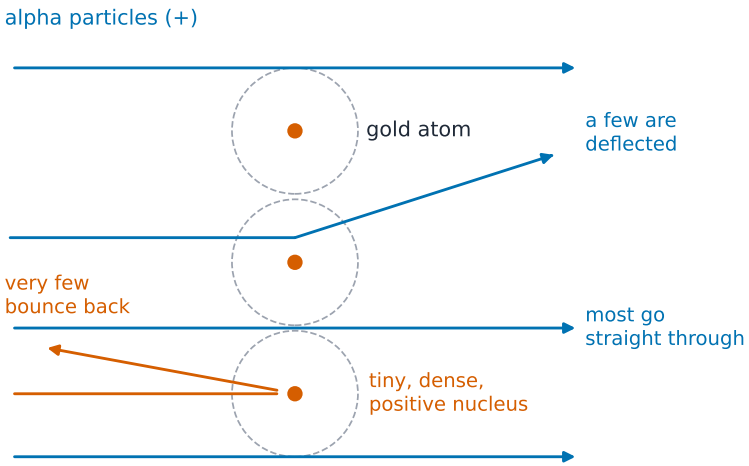
Inside the atom

What did Rutherford see?

Geiger and Marsden investigated the scattering of positively charged alpha particles by metals; Rutherford used the large deflections to develop the nuclear model in 1911. With a sufficiently thin foil most particles pass through with little deflection, but a small fraction undergo large deflections. The fraction depends on the material, foil thickness, particle energy and angle counted: it is not one universal gold-foil number. Rutherford's original paper distinguishes gold-foil results from the often-quoted 1-in-8000 estimate for platinum.



A scanning tunnelling microscope image: islands of silver only one atom thick on a surface 250 nm across. The microscope feels the surface atom by atom

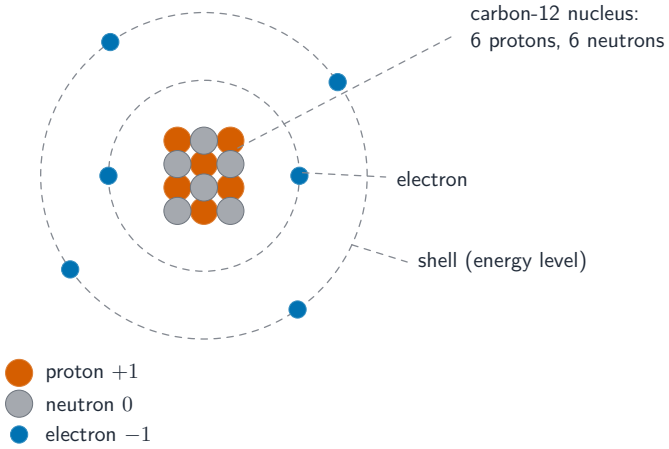


Most of an atom is empty space; its mass and positive charge sit in a tiny nucleus

- Most alpha particles pass straight through, so an atom is mostly empty space.
- A few are deflected, so there is a region of concentrated positive charge that repels them.
- Very few bounce back, so that region, the **nucleus** 原子核, is tiny and holds almost all the mass.

Atomic radii are of order 10^{-10} m and nuclear radii of order 10^{-15}–10^{-14} m, depending on the atom. The sizes are orders of magnitude apart. A classroom drawing enlarges the nucleus so it is visible; it cannot show both scales faithfully. Large-angle scattering supports a compact nucleus, but does not by itself establish the later neutron model or literal electron orbits.

Protons, neutrons and electrons



Neutral carbon-12 has six protons and six electrons. The enlarged nucleus contains six neutrons as well; circles are a simplified energy-level model, not literal trajectories.

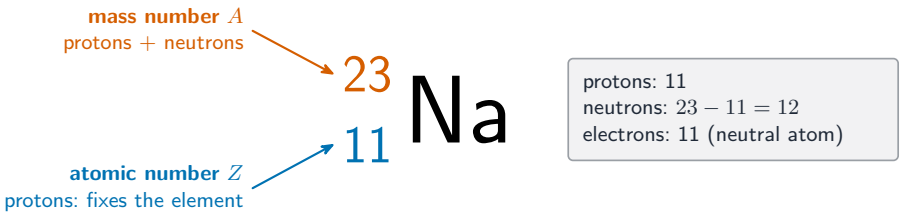
Particle	Relative mass	Relative charge	Where
proton 质子	1	+1	nucleus
neutron 中子	1	0	nucleus
electron 电子	1/1836 (about 0.0005)	−1	outside the nucleus

Protons and neutrons together are called **nucleons** 核子. A neutral atom has equal numbers of protons and electrons, so it has no overall charge. Each proton/electron has equal-magnitude opposite charge; the neutron is uncharged. Hydrogen-1 is the important reminder that an atomic nucleus need not contain any neutrons.

Atomic number and mass number

Nuclear symbols

- The **atomic number** 原子序数 Z is the number of protons. It decides which element the atom is.
- The **mass number** 质量数 A is the number of protons plus neutrons.
- Number of neutrons $= A - Z$.

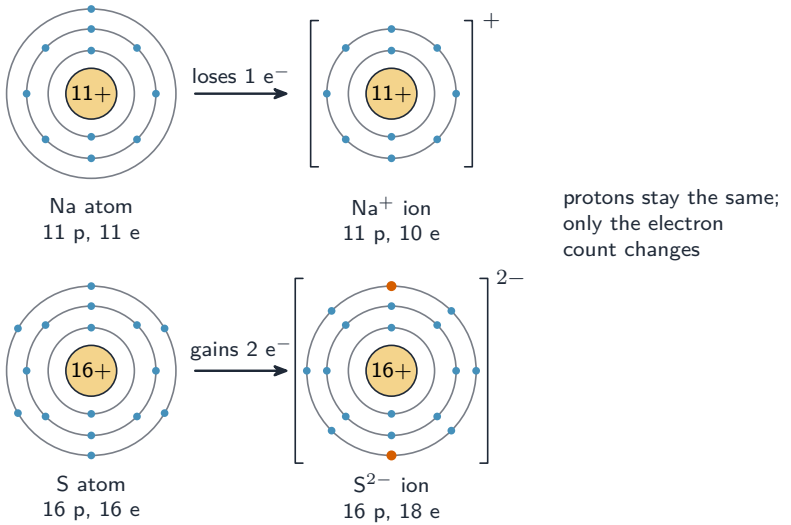


Reading a nuclear symbol: A at the top, Z at the bottom, neutrons $= A - Z$

The **nuclear symbol** 核素符号 writes A at the top left and Z at the bottom left: $^{23}_{11}$Na has 11 protons, $23 - 11 = 12$ neutrons and 11 electrons.

Ions

An **ion** 离子 has gained or lost electrons. The number of protons does not change.



Forming an ion changes only the number of electrons; the protons, and so the element, stay the same.

Species	Protons	Neutrons	Electrons
$^{23}_{11}$Na	11	12	11
$^{23}_{11}$Na^{+}	11	12	10
$^{32}_{16}$S^{2-}	16	16	18
$^{27}_{13}$Al^{3+}	13	14	10

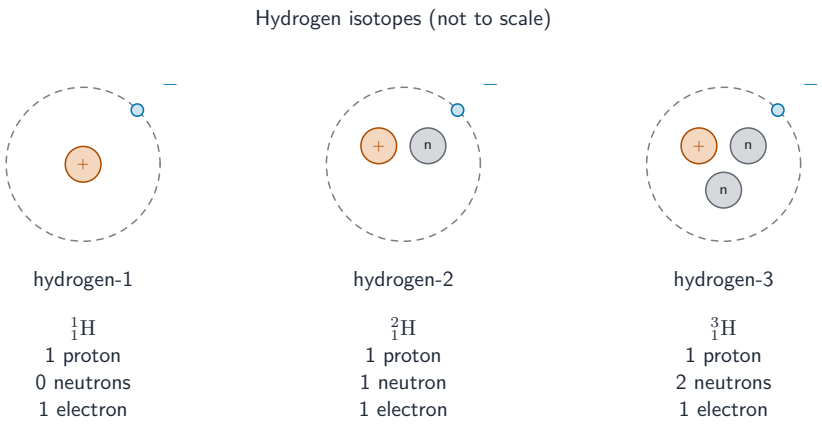
A positive ion has fewer electrons than protons; a negative ion has more. In elementary-charge units, q = number of protons − number of electrons. Thus electrons = Z − q, with the sign retained: for q = −2, electrons = Z + 2. A species with 17 protons, 20 neutrons and 18 electrons is chlorine-37 with charge −1. Its mass number is 37, not 35 or 36.

Ion formation changes the electron count, not A or Z; changing neutron count changes the isotope, while changing proton count changes the element. Never obtain a mass number by rounding an element's periodic-table relative atomic mass. A nuclear symbol refers to one nuclide, whereas the table value generally averages an isotopic mixture.

Isotopes

Same element, different mass

Isotopes 同位素 are atoms of the same element with different numbers of neutrons: the same Z, a different A.



$^{1}_{1}\mathrm{H}$	$^{2}_{1}\mathrm{H}$	$^{3}_{1}\mathrm{H}$
1 proton	1 proton	1 proton
0 neutrons	1 neutron	2 neutrons
1 electron	1 electron	1 electron

Isotopes differ only in the number of neutrons

- Neutral isotopes of the same element have the same electron configuration, so they have **very similar chemical behaviour**. Isotope mass can affect reaction rates and equilibria; identical electronic structure does not make every measured chemical rate exactly identical. Compare like charge states before comparing electron counts.
- They have different masses, so their **physical properties** differ slightly: density, rate of diffusion, and melting and boiling points. Heavy water, D_2O, boils at 101.4 °C.
- Some isotopes are radioactive. Carbon-14 is used to date old wood and bone; cobalt-60 is used in radiotherapy; iodine-131 is used to treat thyroid disease.

Relative atomic mass from abundances

The relative atomic mass A_r of an element is the weighted mean mass of its atoms relative to one-twelfth of the mass of a carbon-12 atom. It has **no unit**. Weight each isotope's relative mass by its **abundance** 丰度 in the stated sample; proportions can differ between samples. Mass number is a whole-number nucleon count and is not an exact measured isotope mass.

$$A_r = \frac{\sum(\text{isotope mass} \times \text{abundance})}{100}$$

Worked example: chlorine

Use supplied approximate chlorine abundances 75.8% ^{35}Cl and 24.2% ^{37}Cl, and the stated whole-number isotope-mass approximation. These are calculation inputs, not exact masses or universal sample proportions.

$$A_r = \frac{35 \times 75.8 + 37 \times 24.2}{100} = \frac{2653 + 895.4}{100} = 35.5$$

The unrounded result is 35.484, reported 35.5 here. It lies nearer 35 because ^{35}Cl is more abundant. It does not mean an individual atom contains 35.484 nucleons or that an isotope with that mass number exists.

Worked example: finding an abundance

For a simplified two-isotope copper calculation, use masses 63 and 65 and A_r = 63.55. Let the abundance of ^{63}Cu be x%.

$$63x + 65(100 - x) = 63.55 \times 100$$

$$6500 - 2x = 6355 \quad \Rightarrow \quad x = 72.5$$

So ^{63}Cu is 72.5% and ^{65}Cu is 27.5%. Using the more accurate but still rounded isotope masses 62.93 and 64.93 with the same supplied mean gives 69.0% instead. These are calculation inputs, not exact isotope masses or a new measurement of natural abundance. State which mass approximation the question supplies.

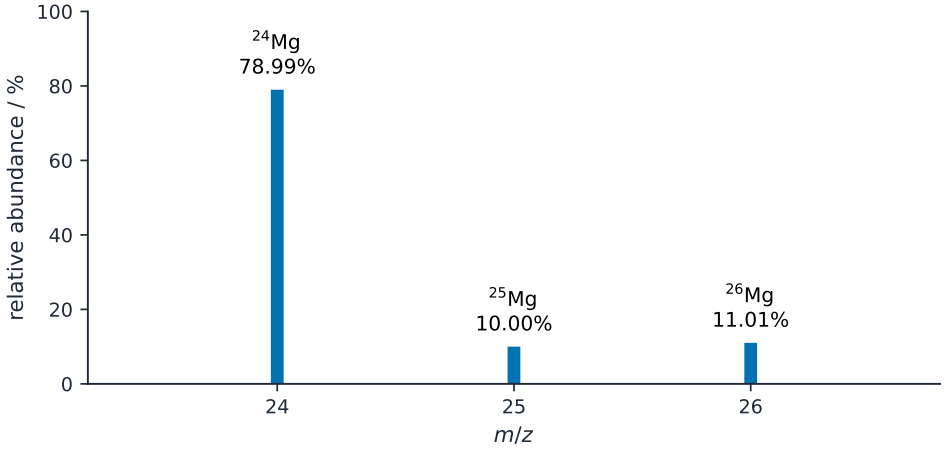
AHL: Mass spectra of elements

How a mass spectrum is read

A **mass spectrometer** 质谱仪 turns atoms into positive ions and separates them by their mass-to-charge ratio, m/z. For singly charged atomic ions, m/z numerically matches the isotope's relative mass to the precision used here. A doubly charged atomic ion has half that m/z; do not read a peak position as mass without knowing the charge. Instrument operating details are outside this unit's assessed scope.



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



Each line is one isotope; its height is the isotope's relative abundance

- For a resolved elemental spectrum assigned to singly charged atomic ions, each isotope gives an assigned peak. Undetected low-abundance isotopes may not be visible.
- Peak position gives mass-to-charge ratio; supplied charge and peak identity determine the mass interpretation.
- Relative height represents relative abundance under the question's stated measurement assumptions. Molecular ions, fragments and other charge states must not be counted as extra isotopes automatically.

Worked example: magnesium

$$A_r = \frac{24 \times 78.99 + 25 \times 10.00 + 26 \times 11.01}{100} = \frac{1895.8 + 250.0 + 286.3}{100} = 24.32$$

The data booklet value is 24.31.

When heights are not percentages

Sometimes the heights are given as relative intensities that do not add up to 100. Then divide by their total instead of by 100. For a spectrum with lines at m/z 10 (height 23) and 11 (height 100):

$$A_r = \frac{10 \times 23 + 11 \times 100}{23 + 100} = \frac{1330}{123} = 10.8$$

The result is consistent with boron given these assigned elemental peaks; the calculation is 10.813008… before rounding. A mass estimate alone is not proof of sample purity or unique identity.

Practice

1. State the relative mass, relative charge and position of a proton, a neutron and an electron.
2. Explain what the gold-foil experiment showed about the structure of the atom.
3. Give the numbers of protons, neutrons and electrons in $^{40}_{20}\mathrm{Ca}^{2+}$ and in $^{19}_{9}\mathrm{F}^{-}$.
4. A species has 26 protons, 30 neutrons and 23 electrons. Write its nuclear symbol with its charge.
5. Explain why neutral ^{35}Cl and ^{37}Cl have very similar chemical behaviour. Why should this not imply exactly identical reaction rates?
6. State one physical property that differs between isotopes, and explain why.
7. Neon is 90.5% ^{20}Ne, 0.3% ^{21}Ne and 9.2% ^{22}Ne. Calculate its A_r to 2 decimal places.
8. Gallium has isotopes ^{69}Ga and ^{71}Ga, and $A_r = 69.8$. Calculate the abundance of each.
9. An invented two-isotope sample has relative isotope masses 64.00 and 66.00 and mean relative atomic mass 64.60. Find both percentage abundances and check the result.
10. A species has 17 protons, 20 neutrons and 18 electrons. Identify its element, mass number and charge. What changes if it loses one electron?
11. Does relative atomic mass 35.5 mean each atom has 35.5 nucleons? State its unit and distinguish it from mass number.
12. **AHL.** A spectrum of an element has lines at m/z 79 (50.7%) and 81 (49.3%). Calculate A_r and identify the element.

13. **AHL.** Lines at m/z 28, 29 and 30 have heights 92.2, 4.7 and 3.1. Calculate A_r and identify the element.
14. **AHL.** Explain why the mass spectrum of chlorine gas, Cl_2, has lines at m/z 70, 72 and 74.

Answers.

1. Proton: 1, +1, nucleus. Neutron: 1, 0, nucleus. Electron: 1/1836, −1, outside the nucleus.
2. Most alpha particles passed straight through, so the atom is mostly empty space. A few were deflected or bounced back, so the positive charge and most of the mass are in a tiny, dense nucleus.
3. Ca^{2+}: 20 protons, 20 neutrons, 18 electrons. F^-: 9 protons, 10 neutrons, 10 electrons.
4. $^{56}_{26}Fe^{3+}$.
5. Neutral atoms have the same electron configuration, giving very similar bonding behaviour. Their different masses can still affect reaction rates or equilibria.
6. For example, different masses affect diffusion rates under comparable conditions. A measured isotope effect depends on the substance, phase and conditions.
7. $(20 \times 90.5 + 21 \times 0.3 + 22 \times 9.2)/100 = (1810 + 6.3 + 202.4)/100 = 20.19$.
8. $69x + 71(100 - x) = 6980$, so $7100 - 2x = 6980$ and $x = 60$: ^{69}Ga 60%, ^{71}Ga 40%.
9. Let f be the fraction with mass 64.00: 64f + 66(1−f) =64.60, so f=0.700. Abundances are **70.0% and 30.0%**. Check: 64×0.70 +66×0.30 =64.60, nearer the more abundant isotope.
10. Z=17 identifies chlorine; A=17+20=37 and q=17−18=−1. Losing one electron gives neutral chlorine-37 with 17 electrons; the nucleus is unchanged.
11. No: relative atomic mass is a weighted mean relative to the carbon-12 reference and has no unit. An individual nuclide's mass number is an integer count of protons plus neutrons.
12. **AHL.** $(79\times50.7+81\times49.3)/100 = 79.99$, about 80: bromine (data booklet 79.90).
13. **AHL.** $(28 \times 92.2 + 29 \times 4.7 + 30 \times 3.1)/(92.2 + 4.7 + 3.1) = 2810.9/100 = 28.11$: silicon.
14. **AHL.** Each Cl_2 molecule holds two atoms, each ^{35}Cl or ^{37}Cl: ^{35}Cl–^{35}Cl is 70, ^{35}Cl–^{37}Cl is 72 and ^{37}Cl–^{37}Cl is 74.

Exam tips

- The atomic number is the number of protons; never say "the number of electrons", which changes in an ion.
- In an ion, change only the electrons: add for a negative charge, subtract for a positive one.
- Isotopes: same proton count, different neutron count. Explain similar chemistry through electron configuration; distinguish mass effects on rates.
- Give A_r to the precision the data allows, and check that it lies between the lightest and heaviest isotope, nearer the more abundant one.
- **AHL.** If the line heights do not add up to 100, divide by their sum.

Structure 1.3 · Electron configurations

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Structure 1.3, Electron configurations, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: protons, neutrons and electrons from Structure 1.2, the atomic number Z, and arithmetic with powers of ten. You will use three relations from the data booklet: $c = f\lambda$, $E = hf$ and the Avogadro constant N_A.

Light, energy and emission spectra

Why do atoms give out coloured light?

Put a little sodium salt in a flame and the flame turns orange-yellow. Pass a high voltage through hydrogen gas in a tube and it glows pink. Each element gives its own colours. The colours tell us how the electrons in the atom are arranged.



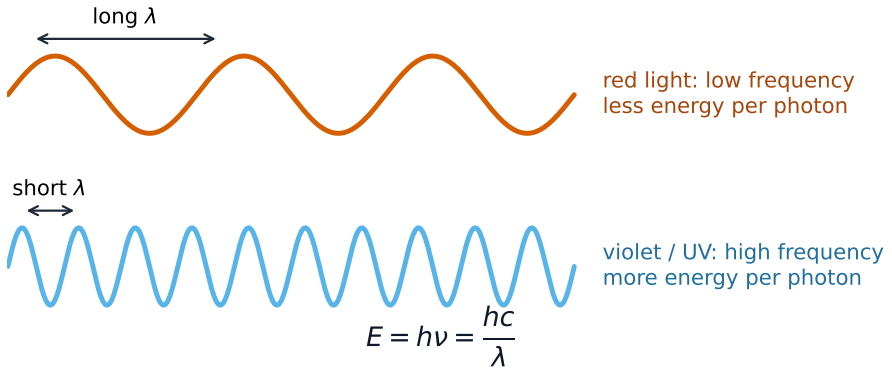
Flame tests: each metal ion gives its own colour because heat excites its electrons and, as they drop back down, they emit light of specific wavelengths



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

Light carries energy in packets

Light is part of the **electromagnetic spectrum** 电磁波谱. In vacuum it travels at the same speed $c = 3.00 \times 10^8$ m s^{-1}, and its frequency f and wavelength λ are linked by



Shorter wavelength means higher frequency and more energy per photon

$$c = f\lambda$$

Light is given out and taken in as packets of energy called **photons** 光子. The energy of one photon depends only on its frequency:

$$E = hf$$

Here $h = 6.63 \times 10^{-34}$ J s is the Planck constant. So **higher frequency means higher energy and shorter wavelength**.

Region	Wavelength	Frequency and photon energy
infrared	longer than about 700 nm	lowest of the three
visible: red → violet	about 700 nm → 400 nm	rising
ultraviolet	shorter than about 400 nm	highest of the three

In the visible region, red light has the longest wavelength and the lowest energy; violet light has the shortest wavelength and the highest energy.

Continuous and line spectra

White light from a hot solid, such as a lamp filament, contains every visible wavelength. A prism spreads it into a **continuous spectrum** 连续光谱: a smooth band of colour with no gaps.

Light from excited gas atoms is different. A prism spreads it into a few sharp coloured lines on a dark background. This is a **line emission spectrum** 线状发射光谱. Every element has its own pattern of lines, so the spectrum works like a fingerprint for the element.

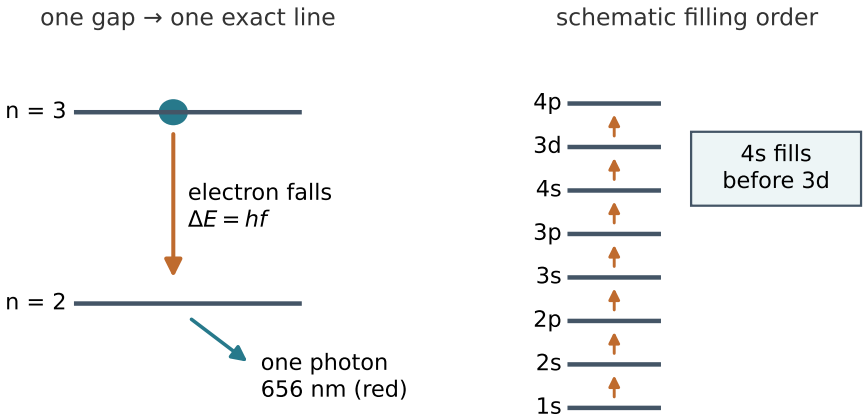
Where the lines come from

An electron in an atom can only have certain fixed energies, called **energy levels** 能级. When the atom absorbs energy (from a flame or an electric current), an electron moves up to a higher level. The atom is now in an **excited state** 激发态.

The electron then falls back to a lower level. It gives out the energy difference as **one photon**:

$$\Delta E = E_{\text{upper}} - E_{\text{lower}} = hf$$

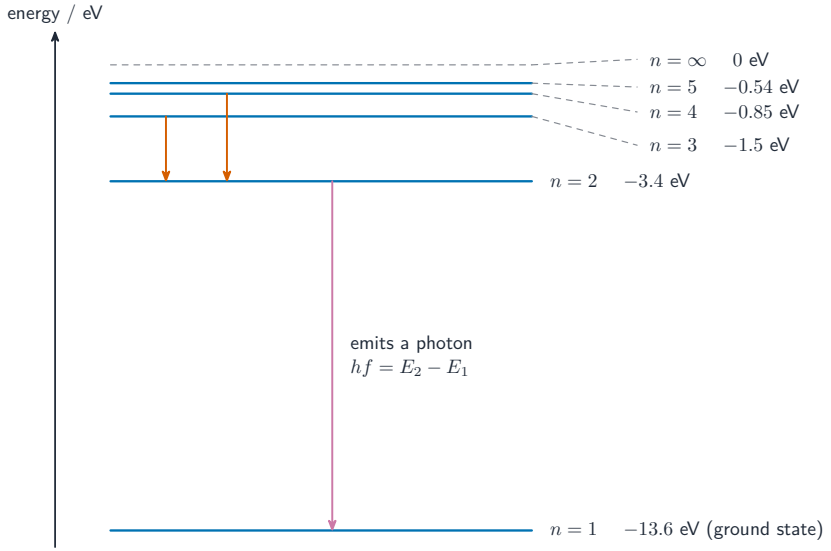
Only certain gaps exist, so only certain photon energies, and therefore only certain frequencies, appear. That is why we see separate lines and not a continuous band.



A fixed hydrogen energy gap gives a photon; the right panel is a schematic filling-order guide, not one universal measured energy scale. Chromium, copper and ion formation need the qualifications taught below.

The hydrogen spectrum is evidence for energy levels

Hydrogen has one electron, so its spectrum is the simplest. Two features matter:



The discrete energy levels of hydrogen produce a line spectrum

- **The lines are separate.** If the electron could have any energy, hydrogen would give a continuous spectrum. The separate lines show that the energy of the electron is **quantized** 量子化的: it can only take fixed values.
- **The lines get closer together at higher frequency.** The levels themselves get closer together as n increases, so the lines **converge** 会聚. The bound-to-bound lines of that series approach its **convergence limit** 会聚极限. Beyond the limit there are no further bound-to-bound transitions in that same series; this is not a claim that no other series, or continuum radiation, can exist.

Which line appears depends on the level the electron falls to. Falls to $n = 1$ give the largest gaps, so those photons are ultraviolet. Falls to $n = 2$ include visible lines, such as the red 3→2 line at 656 nm, but higher members of that series extend into the near ultraviolet. Do not label the entire series visible. Falls to $n = 3$ give infrared.

> **Worked example.** The red line of hydrogen has $\lambda = 656$ nm. Find the energy gap it comes from.

1. Convert the wavelength: $\lambda = 656 \times 10^{-9}$ m.
2. Find the frequency: $f = \dfrac{c}{\lambda} = \dfrac{3.00 \times 10^{8}}{656 \times 10^{-9}} = 4.57 \times 10^{14}$ Hz.
3. Use the unrounded frequency: $E=hc/\lambda=3.0320122\ldots\times10^{-19}$ J, reported **3.03×10^{-19} J**.

This is the energy gap between $n = 3$ and $n = 2$ for **one** atom.

Energy levels, sublevels and orbitals

Main energy levels

The main energy levels are numbered by the **principal quantum number** 主量子数 $n = 1, 2, 3, \ldots$ Level n can hold at most $2n^2$ electrons. This is a capacity, not the filling sequence: 4s can be occupied before the 3d sublevel is filled.

n	**Maximum electrons** $2n^2$	**Sublevels**
1	2	1s
2	8	2s, 2p
3	18	3s, 3p, 3d
4	32	4s, 4p, 4d, 4f

Sublevels and orbitals

Each main level is split into **sublevels** 亚层 called s, p, d and f. Each sublevel is made of **atomic orbitals** 原子轨道. An orbital is a region around the nucleus where there is a high chance of finding an electron. One orbital holds at most two electrons.

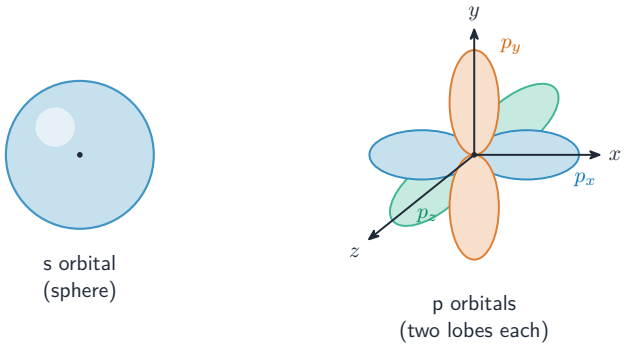
Sublevel	**Orbitals**	**Maximum electrons**
s	1	2
p	3	6
d	5	10
f	7	14

Check: level $n = 3$ has 3s + 3p + 3d = 2 + 6 + 10 = 18 electrons, which matches $2n^2 = 18$.

Shapes of s and p orbitals

You need to recognise two shapes:

- An **s orbital** is spherically symmetric around the nucleus. A drawn surface encloses a chosen probability region, not a hard boundary or an electron path. For the same atom, 2s extends farther on average than 1s.
- A **p orbital** has two lobes on opposite sides of the nucleus, like a dumbbell. The three p orbitals of one level point along the x, y and z axes, at right angles to each other. They are named p_x, p_y and p_z.



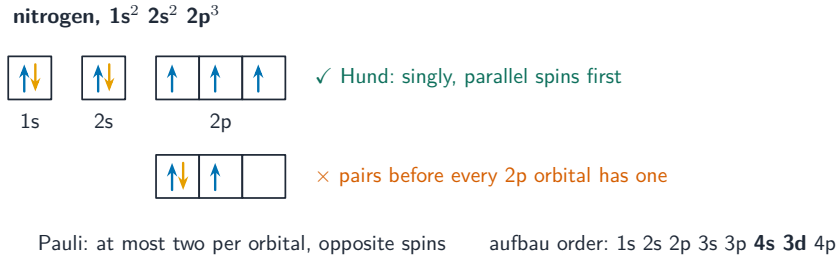
Schematic probability-region surfaces: spherical symmetry for s and two lobes for each p orientation. The colours distinguish orientations, not particle charges.

In an isolated atom without an external field, the three p orbitals of one sublevel have the same energy. Orbitals with equal energy are called **degenerate** 简并的.

Writing electron configurations

Three rules for filling orbitals

1. **Aufbau principle** 构造原理: electrons go into the lowest-energy orbital available first.
2. **Pauli exclusion principle** 泡利不相容原理: an orbital holds at most two electrons, and they must have **opposite spins** 相反的自旋.
3. **Hund's rule** 洪特规则: in a set of degenerate orbitals, electrons go in singly with parallel spins before any orbital gets a second electron. This is the lowest-energy arrangement for the stated degenerate sublevel; Pauli and Hund are different constraints.



Aufbau, Pauli and Hund in one orbital diagram

For atoms up to $Z = 36$, the order of filling is:

$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p$$

Notice that 4s fills **before** 3d. In a neutral atom up to calcium, 4s is lower in energy than 3d.

Full and condensed configurations

A **full electron configuration** 完整电子排布 lists every sublevel with its number of electrons as a superscript:

- sulfur, $Z = 16$: $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$
- iron, $Z = 26$: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$

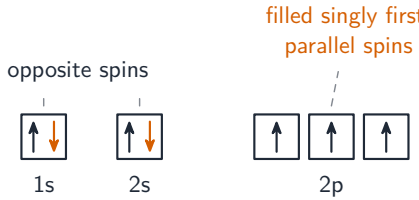
A **condensed configuration** 简化电子排布 replaces the inner electrons with the symbol of the noble gas before the element, in square brackets:

- sulfur: $[\mathrm{Ne}]\,3s^2\,3p^4$
- iron: $[\mathrm{Ar}]\,4s^2\,3d^6$

Always check that the superscripts add up to the number of electrons.

Orbital diagrams

An **orbital diagram** 轨道表示式 draws each orbital as a box and each electron as a half-arrow. Two arrows in one box point in opposite directions (Pauli). Within a sublevel, fill every box with one arrow, all pointing the same way, before you add a second arrow to any box (Hund).



Nitrogen, $1s^2\,2s^2\,2p^3$: paired spins in 1s and 2s; the three 2p electrons sit singly with parallel spins

Nitrogen therefore has **three unpaired electrons**. Oxygen, $2p^4$, has one pair and two unpaired electrons in its 2p sublevel.

> **Worked example.** Draw the orbital diagram of the 3d and 4s sublevels of iron.

Iron is $[\mathrm{Ar}]\,4s^2\,3d^6$. The 4s box holds two opposite arrows. Six electrons go into five 3d boxes: one up-arrow in each of the five boxes, then the sixth pairs up in the first box. Iron has **four** unpaired electrons.

Two exceptions: chromium and copper

Two atoms in the first row of the d-block do not follow the simple order:

- chromium, $Z = 24$: $[\mathrm{Ar}]\,4s^1\,3d^5$, not $4s^2\,3d^4$
- copper, $Z = 29$: $[\mathrm{Ar}]\,4s^1\,3d^{10}$, not $4s^2\,3d^9$

These observed ground-state arrangements have lower total energy than the naive Aufbau predictions for these atoms. The notation is not a claim that every atom first forms one configuration and then visibly promotes an electron. Learn Cr and Cu as the required exceptions; do not extend a "half-full is always best" slogan to every atom or ion.

Configurations of ions

- For a **negative ion** 阴离子, add electrons to the next available orbital. Oxide, O^{2-}: $1s^2\,2s^2\,2p^6$, the same as neon.
- For a **positive ion** 阳离子 of a main-group element, remove electrons from the outermost level. Na^+: $1s^2\,2s^2\,2p^6$.
- For a positive ion of a **transition element** 过渡元素, remove the **4s electrons first**, then 3d electrons. Once 3d is occupied, 4s is no longer the lower level.

Species	Configuration
Fe	$[\mathrm{Ar}]\,4s^2\,3d^6$
Fe^{2+}	$[\mathrm{Ar}]\,3d^6$
Fe^{3+}	$[\mathrm{Ar}]\,3d^5$
Cu^+	$[\mathrm{Ar}]\,3d^{10}$

A common error is to write Fe^{2+} as $[\mathrm{Ar}]\,4s^2\,3d^4$. Remember: **4s fills first and empties first.**

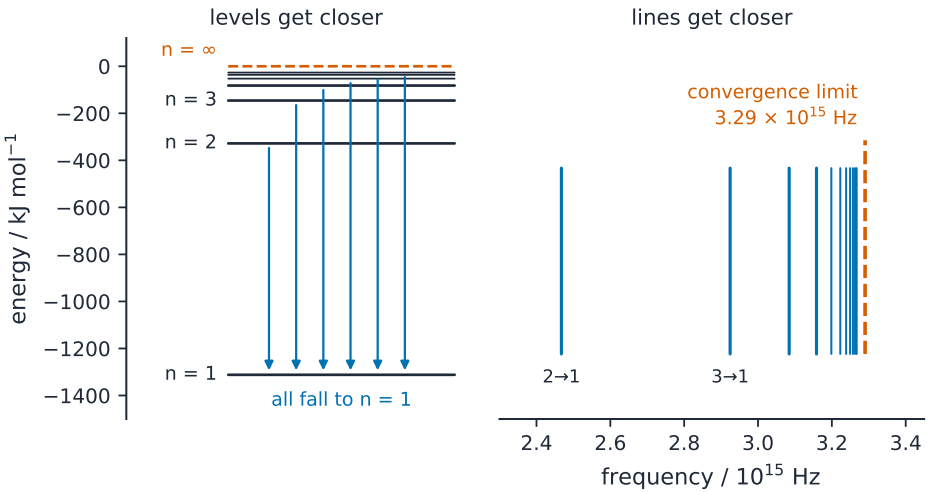
AHL: Ionization energy from the convergence limit

What the convergence limit means

The **first ionization energy** 第一电离能 is the minimum energy needed to remove one electron from each atom in one mole of gaseous atoms, in their ground state:

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

Look again at the lines that end on $n = 1$ in hydrogen. As the upper level gets higher, the lines crowd together. The limiting upper state is the ionization threshold, conventionally written $n = \infty$; this is a limiting energy, not an electron orbit at a literal infinite radius. For a series ending on ground-state $n = 1$, the limiting photon energy equals the energy needed to ionize ground-state hydrogen. A series ending on an excited level gives the ionization energy from that excited level instead, so its limit is not automatically the first ionization energy.



As the levels crowd together, the lines crowd together; the convergence limit gives the ionization energy

Calculating ionization energy from spectral data

The photon energy gives the energy for **one** atom. Multiply by the Avogadro constant to get the value for one mole, then convert to kJ:

$$\text{IE} = hf \times N_A$$

> **Worked example.** The lines in the ultraviolet spectrum of hydrogen converge at $\lambda = 91.2$ nm. Calculate the first ionization energy of hydrogen in kJ mol^{-1}.

1. Frequency: f=c/λ=$3.00\times10^{8}/(91.2\times10^{-9})$=**$3.2894737\ldots\times10^{15}$ Hz**.
2. One photon: E=hf=**$2.1809211\ldots\times10^{-18}$ J**, using unrounded f.
3. One mole: E×N_a/1000=**1312.914... kJ mol^{-1}**, reported **1.31×10^{3} kJ mol^{-1}** to three significant figures. The booklet value 1312 is consistent with this precision; do not round each intermediate step.

AHL: Ionization energies as evidence for sublevels

What decides the size of an ionization energy

An ionization energy measures how strongly the nucleus holds the electron being removed. Three factors decide it:

- **Nuclear charge** 核电荷: more protons pull harder, so the ionization energy is higher.
- **Distance from the nucleus**: an electron in a higher level is further away and held less strongly.
- **Shielding** 屏蔽: inner electrons repel the outer electron and cancel part of the nuclear pull.

Trends across a period and down a group

Across a period, the first ionization energy generally **increases**. The nuclear charge increases by one each time, but the new electron goes into the same main level, so shielding hardly changes. The outer electrons are held more tightly.

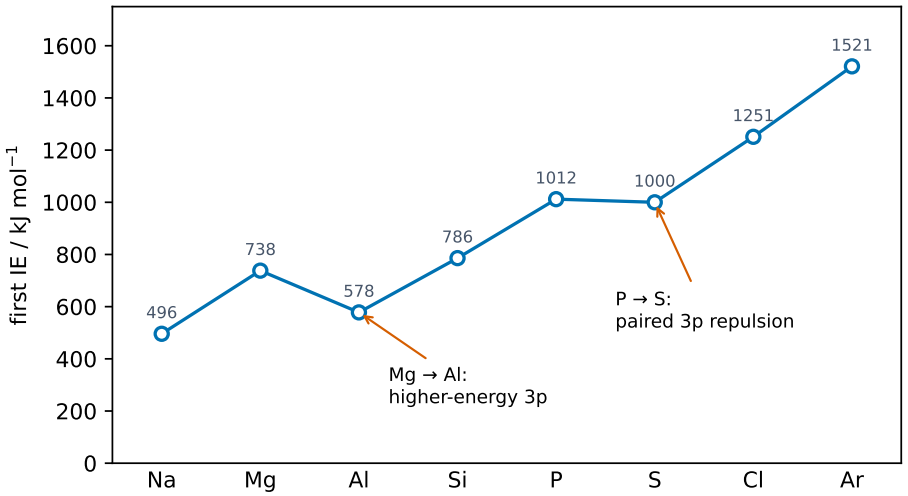
Down a group, the first ionization energy **decreases**. Each element has one more occupied level, so the outer electron is further from the nucleus and more shielded. This outweighs the larger nuclear charge.

The two dips across a period

The rise across Period 3 is not smooth. There are two small drops, and they are evidence that sublevels exist:

- **Mg → Al.** Magnesium is [Ne] $3s^2$. Aluminium is [Ne] $3s^2\,3p^1$, so its first electron is removed from a 3p orbital. The 3p sublevel is higher in energy than 3s, so less energy is needed.
- **P → S.** Phosphorus is [Ne] $3s^2\,3p^3$ with three unpaired 3p electrons. Sulfur, $3p^4$, has one 3p orbital with two electrons in it. These paired electrons repel each other, so one is easier to remove.

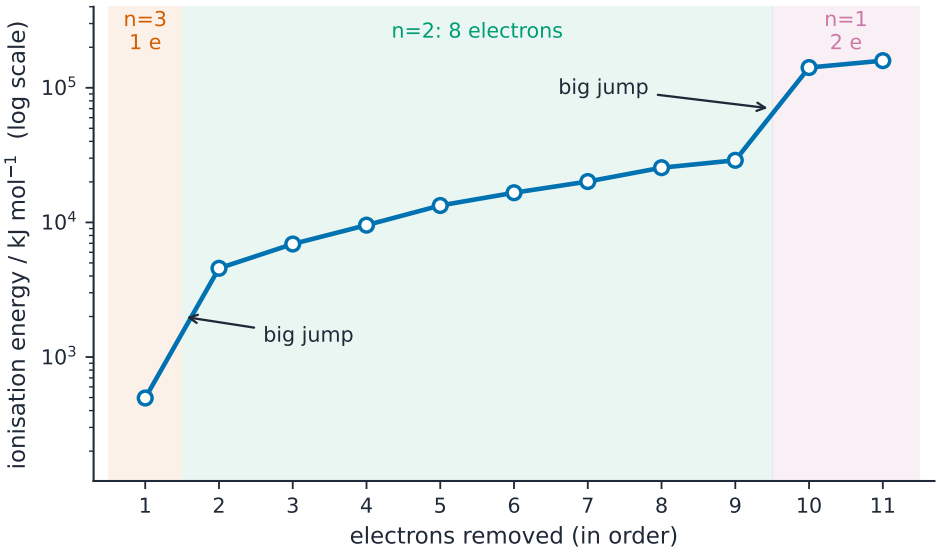
The same two dips appear in Period 2, at B and at O.



First ionization energy rises across Period 3 but drops at Al (3p above 3s) and at S (paired 3p electrons)

■ Successive ionization energies

The **second ionization energy** removes an electron from the +1 ion:

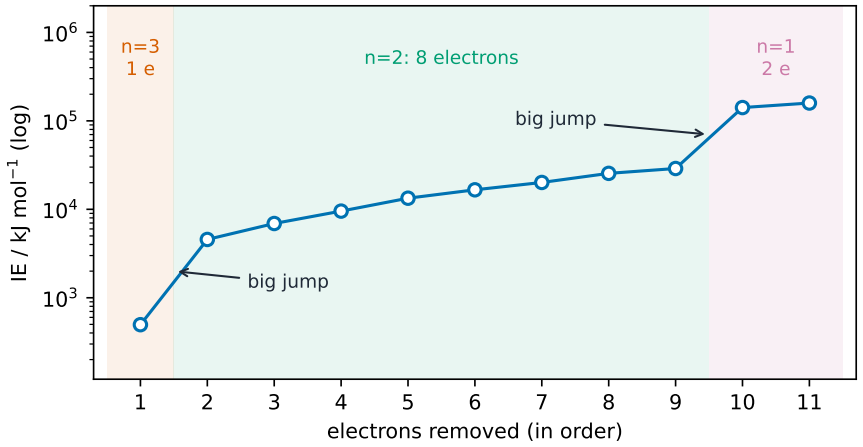


Successive ionisation energies reveal the shell structure through big jumps

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

Removing the electrons one at a time gives the **successive ionization energies** 逐级电离能. The successive values rise for the atoms considered here: removal from increasingly positive ions generally requires greater energy. Distinguish this sequence for one element from first ionization energies across different elements.

When you plot them, look for **big jumps**. A big jump means the next electron must come from a main level closer to the nucleus. For sodium, the pattern is 1 easy electron, a big jump, 8 more, another big jump, then the last 2. This matches the configuration 2, 8, 1.



Big jump: next electron from an inner shell

Successive ionization energies of sodium (log scale): the big jumps reveal the 2, 8, 1 arrangement

To find the group of a main-group element, count the electrons removed **before** the first big jump. That is the number of outer electrons: 1 suggests Group 1, 2 suggests Group 2, and 3–8 correspond to Groups 13–18 for the main-group cases considered. **Helium is an exception** to the two-electron group shortcut: its full $1s^2$ shell places it in Group 18. Do not use this simple rule to assign a d-block group from a short sequence.

> **Worked example.** The first five ionization energies of an element, in kJ mol^{-1}, are 578, 1817, 2745, 11 577 and 14 842. Identify its group.

The values rise steadily for the first three electrons. From the 3rd (2745) to the 4th (11 577) the value more than quadruples: that is the big jump. Three electrons came off before it, so the element has three outer electrons and is in **Group 13**. (This supplied rounded pattern is consistent with aluminium; the group inference follows the pattern, not memorization of the numbers.)

Smaller steps inside one main level also show sublevels. In aluminium, the first electron (from 3p) is easier to remove than the next two (from 3s).

Practice

Use $c=3.00\times10^8$ m s^{-1}, $h=6.63\times10^{-34}$ J s and $N_a=6.02\times10^{23}$ mol^{-1}. All newly constructed numerical cases use supplied illustrative inputs; keep intermediate precision.

1. A spectral line has wavelength 589 nm. Calculate its frequency and one-photon energy.

2. State the maximum electron capacity of n=4 and name its sublevels. Does this determine which sublevel fills next?
3. Write the full configuration of chlorine and condensed configuration of Cr^{3+}.
4. How many unpaired electrons does phosphorus have? Describe its 3s and 3p box diagram.
5. Explain why isolated excited hydrogen produces separate emission lines. Are all transitions ending on n=2 visible?
6. Compare photon energies for wavelengths 400 nm and 800 nm in vacuum. Find the energy ratio without calculating both energies.
7. Give the configurations and unpaired-electron counts of Fe^{2+} and Fe^{3+} in the isolated-ion model.
8. Give the configurations of Cu^{+} and Cu^{2+}. Identify the sublevel from which each electron was removed.
9. A proposed ground-state nitrogen 2p diagram has a pair in one box, a single electron in the second and the third empty. Does it satisfy Pauli? Does it satisfy Hund?
10. How many orbitals and electrons at full capacity are in n=3? Distinguish an orbital, a sublevel and a main level.
11. A p orbital is drawn with two lobes in different colours. Does that show two electrons of opposite electric charge? What does degeneracy mean for isolated atomic p orbitals?
12. **AHL.** A supplied ground-state convergence limit is at 241 nm. Calculate the first ionization energy in kJ mol^{-1}.
13. **AHL.** Explain why the first ionization energy of oxygen is lower than that of nitrogen.
14. **AHL.** A supplied hydrogen series ending on n=2 has limiting wavelength 364.8 nm. Calculate its limiting photon energy per mole. Is that the first ionization energy from n=1? Explain.

Worked answers.

1. $f=c/\lambda=3.00\times10^{8}/(589\times10^{-9})=5.0933786\ldots\times10^{14}$ Hz; $E=hc/\lambda=3.3769100\ldots\times10^{-19}$ J. Report **5.09×10^{14} Hz and 3.38×10^{-19} J**. Use the unrounded frequency for the second result.
2. $2n^2$=**32 electrons**; 4s,4p,4d,4f. Capacity does not set filling order; an orbital's energy and occupancy matter.
3. Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ (17 electrons). Cr is $[Ar]4s^1 3d^5$; remove 4s first, then two 3d electrons: **$Cr^{3+}=[Ar]3d^3$**, with 21 electrons.
4. **Three unpaired**. The 3s box contains two opposite arrows; each of the three 3p boxes contains one parallel arrow.
5. Only allowed discrete energy differences produce bound-to-bound photons with E=hf. Some n=2-series lines are visible, but higher members enter the near ultraviolet; a series label does not guarantee every wavelength is visible.
6. $E=hc/\lambda$, so $E_{400}/E_{800}=800/400=$**2**. The shorter-wavelength photon has twice the energy, not half.
7. $Fe^{2+}=[Ar]3d^6$, **four unpaired**; $Fe^{3+}=[Ar]3d^5$, **five unpaired**. Remove the neutral atom's 4s electrons first, then one 3d electron for the third positive charge. These are isolated-ion counts, not a universal prediction for every coordination complex.
8. Neutral $Cu=[Ar]4s^1 3d^{10}$. Removing 4s gives **$Cu^{+}=[Ar]3d^{10}$**; removing another electron from 3d gives **$Cu^{2+}=[Ar]3d^9$**. Electron totals are 28 and 27 respectively.
9. If the paired arrows have opposite spins, Pauli is satisfied. Hund is violated for the ground state: three degenerate p orbitals should first contain three singly occupied parallel arrows. A legal occupancy is not necessarily the ground state.
10. 3s,3p,3d contain **1+3+5=9 orbitals**, at most **18 electrons**. An orbital holds at most two electrons; several orbitals make a sublevel; the sublevels belong to a main level.
11. No: lobes describe one orbital's spatial form; colours can denote wavefunction phase in some diagrams or just identify orientations. They are not positive/negative electrons or a particle count. Degenerate orbitals have equal energy under the stated isolated-atom conditions.
12. **AHL.** $E=hc/\lambda=8.2531120\ldots\times10^{-19}$ J per atom. Multiply by N_a and divide by 1000: **496.8373... kJ mol^{-1}**, reported **497 kJ mol^{-1}**. The ground-state reference is essential.
13. **AHL.** Nitrogen has $2p^3$, with three singly occupied parallel orbitals. Oxygen has $2p^4$, including a pair; electron repulsion makes removal of one paired electron easier despite the greater nuclear charge.
14. **AHL.** $E=hcN_a/(\lambda\times1000)$=**328.2286... kJ mol^{-1}**, reported **328 kJ mol^{-1}**. This is ionization from excited n=2. First ionization starts at ground-state n=1 and requires a larger gap; do not call every series limit a first ionization energy.

Exam tips

- Explain lines through **allowed levels and emitted photons**. A series has a stated endpoint; not all n=2-series lines are visible.
- Check electron totals, Pauli, Hund and Cr/Cu exceptions; remove 4s before 3d in the ions taught here.
- **AHL:** first ionization needs the ground-state reference. Convert photon J to molar kJ with $N_a/1000$; use the group shortcut only for suitable main-group cases.

Counting particles by mass: the mole

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

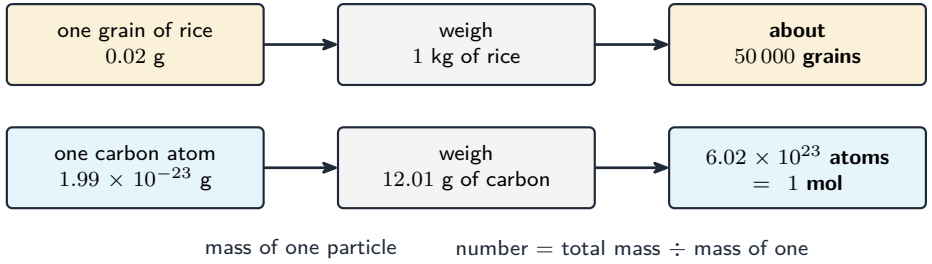
This handout teaches Structure 1.4, Counting particles by mass: the mole, for the course first assessed in 2025. All of it is SL and HL content. Numerical examples are constructed teaching cases; stated approximate isotope abundances are calculation inputs.

Prerequisites: atoms, isotopes and ions from Structure 1.2, chemical formulae, and standard form (6.02×10^{23}) on a calculator. Use the relative atomic masses from the data booklet.

The mole

How do you count grains of rice?

Nobody counts rice one grain at a time. A shop sells it by mass: if one grain has a mass of 0.02 g, then 1 kg holds about 50 000 grains. Chemists have the same problem with atoms, which are far too small and too many to count. They also count by weighing.



Number of particles = total mass ÷ mass of one particle: chemists count atoms the way a shop counts rice.

The Avogadro constant

The **mole** 摩尔 (symbol mol) is the unit of **amount of substance** 物质的量. One mole contains exactly **6.02214076×10^{23} specified elementary entities**, as defined in the SI. The **Avogadro constant** 阿伏伽德罗常数 is N_a=6.02214076×10^{23} mol^{-1} exactly. The course calculations below use the rounded value **6.02×10^{23} mol^{-1}**; that rounded value is not exact.

$$N = n \times N_A$$

N is the number of particles and n is the amount in moles.

- Always say which particles you mean: atoms, molecules, ions or **formula units** 化学式单位.
- One mole of H_2O molecules contains 2 mol of H atoms and 1 mol of O atoms.

Worked example: counting particles

How many molecules and how many atoms are in 0.500 mol of water?

- Molecules: $0.500 \times 6.02 \times 10^{23} = 3.01 \times 10^{23}$.
- Each H_2O molecule has 3 atoms, so atoms $= 3 \times 3.01 \times 10^{23} = 9.03 \times 10^{23}$.

Relative masses and molar mass

Relative atomic mass

The **relative atomic mass** 相对原子质量 A_r is the weighted mean mass of the atoms of an element, relative to one twelfth of the mass of a carbon-12 atom. It has no units.



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

A_r is a weighted mean of the isotope masses, so it is rarely a whole number

Natural chlorine is about 75% ^{35}Cl and 25% ^{37}Cl, so its A_r lies closer to 35 than to 37. The data booklet value is 35.45.

Relative formula mass

The **relative formula mass** 相对式量 M_r is the sum of the A_r values of all the atoms in the formula. "Relative molecular mass" is used for molecules.

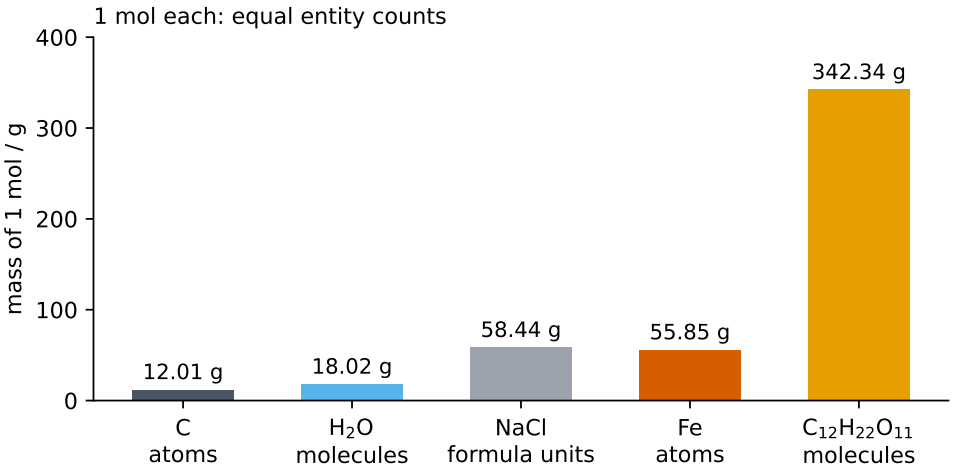
$$M_r(CaCO_3) = 40.08 + 12.01 + 3 \times 16.00 = 100.09$$

Molar mass

The **molar mass** 摩尔质量 M is the mass of one mole of a substance. At course precision its numerical value in g mol^{-1} matches M_r: $M(CaCO_3) = 100.09$ g mol^{-1}.



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



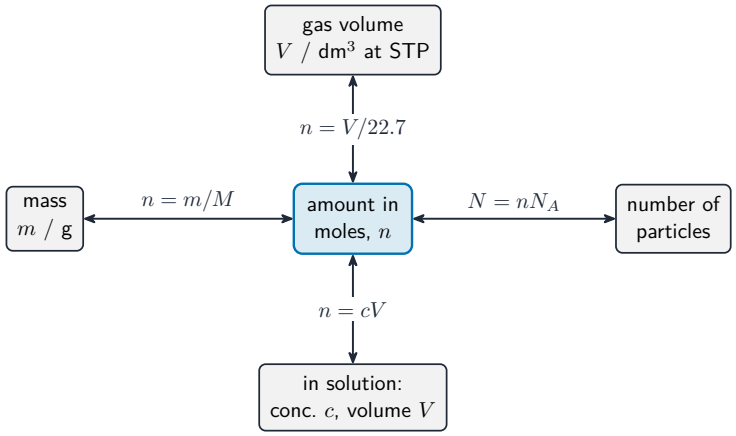
Equal amounts contain equal counts of the specified entities: atoms, molecules or formula units. Their masses differ; labels use course atomic-mass precision.

Moles, mass and the mole map

Mass to moles

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

m in g, M in g mol^{-1}, n in mol.



Every route between quantities passes through the amount in moles

Worked example: mass to particles

How many molecules are in 4.4 g of carbon dioxide?

- $M(CO_2) = 12.01 + 2 \times 16.00 = 44.01$ g mol^{-1}.
- n =4.4/44.01 =0.0999773… mol; retain this value for the next step.
- N =0.0999773…×6.02×10^{23} =6.018632…×10^{22} molecules, reported **6.0×10^{22}** to two significant figures.

Worked example: moles to mass

What is the mass of 0.250 mol of sodium chloride?

- $M(\mathrm{NaCl}) = 22.99 + 35.45 = 58.44$ g mol^{-1}.
- $m = n \times M = 0.250 \times 58.44 = 14.6$ g.

Percentage by mass

$$\%\ \text{of element} = \frac{(\text{number of atoms}) \times A_r}{M_r} \times 100$$

For ammonium nitrate, NH_4NO_3: $M_r = 80.06$, and it has 2 N atoms, so % N = $2 \times 14.01/80.06 \times 100 = 35.0\%$. Farmers compare fertilizers this way.

Empirical and molecular formulae

Two kinds of formula

- 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 is the actual number of atoms of each element in one molecule.

Compound	Molecular formula	Empirical formula
ethane	C_2H_6	CH_3
glucose	$C_6H_{12}O_6$	CH_2O
benzene	C_6H_6	CH
water	H_2O	H_2O

The molecular formula is always a whole-number multiple of the empirical formula.

Finding an empirical formula

1. Write the mass (or percentage) of each element.
2. Divide each by its A_r to get moles.
3. Divide every value by the smallest.
4. Inspect simple fractional ratios within the precision of the data: near 1.5 multiply **all** ratios by 2; near thirds use 3; near quarters use 4. Do not round 1.5 straight to 2 or force noisy values to a convenient formula without evaluating uncertainty.

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

empirical formula CH_2O; $M_r = 180$ gives $180/30 = 6$
molecular formula $C_6H_{12}O_6$

Illustrative 100 g basis with rounded masses C=12, H=1, O=16: divide mass by relative atomic mass, then normalize the amounts. Use the specified booklet values for other calculations.

Worked example: from masses to the molecular formula

A hydrocarbon contains 2.40 g of carbon and 0.60 g of hydrogen. Its M_r is 30.08.

- C: $2.40/12.01 = 0.200$ mol. H: $0.60/1.01 = 0.594$ mol.
- Divide by 0.200: C 1, H 2.97 ≈ 3. Empirical formula CH_3, with $M_r = 15.04$.
- $30.08/15.04 = 2$, so the molecular formula is C_2H_6.

Worked example: water of crystallization

In an invented measurement, 2.50 g of hydrated copper(II) sulfate, $CuSO_4 \cdot xH_2O$, leaves 1.60 g of anhydrous $CuSO_4$ after approved heating, cooling and weighing to constant mass. Assume only water was lost and the solid did not decompose. Colour alone does not establish complete dehydration.

- Water lost: $2.50 - 1.60 = 0.90$ g; $0.90/18.02 = 0.0499$ mol.
- $CuSO_4$: $1.60/159.62 = 0.0100$ mol.
- Use unrounded amounts: $(0.90/18.02)/(1.60/159.62)$ =**4.98259...**, consistent with x=5 at the supplied precision: **$CuSO_4 \cdot 5H_2O$**. Incomplete drying underestimates water loss; decomposition or spitting can make apparent water loss too large. Repeat safe heating/cooling/weighing and assess the assumptions.

Concentration of solutions

Molar concentration

A **solution** 溶液 is a **solute** 溶质 dissolved in a **solvent** 溶剂. The **concentration** 浓度 here is amount of the specified solute per unit **final solution volume**, not the volume of solvent added.



A real titration: solution from the burette is added to the flask, where the indicator has turned orange

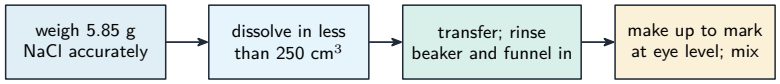
$$c = \frac{n}{V}$$

c in mol dm^{-3}, n in mol, V in dm^3. Remember 1 dm^3 = 1000 cm^3, so divide a volume in cm^3 by 1000.

Concentration can also be given in g dm^{-3}: multiply mol dm^{-3} by the molar mass.

Worked example: making a solution

5.85 g of NaCl is dissolved in water and made up to 250 cm^3.



$n = 5.85/58.44 = 0.100$ mol; $c = 0.100/0.250 = 0.400$ mol dm^{-3}
250 cm^3 of *solution*, not 250 cm^3 of water added

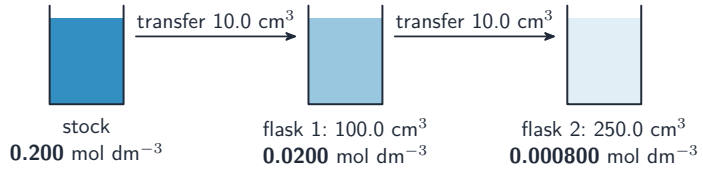
Making a standard solution: 0.100 mol in 0.250 dm^3

- $n = 5.85/58.44 = 0.100$ mol.
- $V = 250/1000 = 0.250$ dm^3.
- $c = 0.100/0.250 = 0.400$ mol dm^{-3}, which is $0.400 \times 58.44 = 23.4$ g dm^{-3}.

A **standard solution** 标准溶液 has an accurately known concentration. Use a suitable stable, sufficiently pure solute or account for its known purity. Weigh accurately, dissolve in less than the final volume and transfer quantitatively, rinsing the vessel and funnel into a volumetric flask. Allow the solution to reach the appropriate calibration temperature, set the meniscus at eye level to the mark, stopper and mix thoroughly. Adding 250 cm^3 water to a solute is not the same as making 250 cm^3 solution.

Dilution

For a simple dilution without reaction or solute loss, adding solvent conserves the amount of that solute:



$0.200 \times \frac{10.0}{100.0} \times \frac{10.0}{250.0} = 0.000800$ mol dm^{-3} (multiply the fractions)

A serial dilution multiplies the dilution fractions (invented stock)

$$c_1V_1 = c_2V_2$$

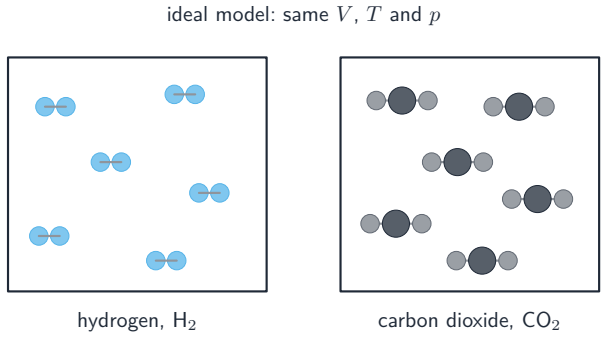
A supplied 25.0 cm^3 stock sample at 2.00 mol dm^{-3} made up to **500 cm^3 final volume** gives c_2=2.00×25.0/500=0.100 mol dm^{-3}. This is a calculation, not permission to dilute a reagent without an approved procedure. "Add 500 cm^3 solvent" does not specify the same final volume. For serial dilutions, conserve amount across each aliquot separately and multiply the dilution fractions.

Worked serial dilution. For an invented 0.200 mol dm^{-3} stock, transfer 10.0 cm^3 and make up to 100.0 cm^3: c=0.0200 mol dm^{-3}. Transfer 10.0 cm^3 of this diluted solution and make up to 250.0 cm^3. The final concentration is $0.200 \times (10.0/100.0) \times (10.0/250.0) =$ **0.000800 mol dm^{-3}**. Each transfer carries only the solute in its aliquot, not all solute in the preceding flask.

Avogadro's law

Equal volumes, equal numbers

Avogadro's law 阿伏伽德罗定律: equal volumes of ideal gases at the same temperature and pressure contain equal numbers of particles (molecules for the gases shown). Real gases approach this relationship under suitable conditions; atoms are the relevant entities for monatomic gases.



An invented ideal-particle sketch at common V,T,p: six molecules in each volume. Particle sizes are enlarged for visibility; the count is a model, not a measured sample.

In the ideal model, particle volume and intermolecular interactions are neglected, so common T,p gives volume proportional to amount, independent of identity. Volume also depends on T and p; amount alone does not determine it. High density or strong attractions can make the real-gas approximation inadequate.

At STP (273 K and 100 kPa) one mole of any ideal gas occupies 22.7 dm^3 (data booklet).

Volumes of reacting gases

For ideal gases compared at common temperature and pressure, the stoichiometric reacting-volume ratio equals the mole ratio for the **stated reaction extent**. Excess reactant, incomplete reaction, side reactions and phase changes must be handled separately.

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)}$$

For complete combustion, 20 $\mathrm{cm^3}$ methane requires 40 $\mathrm{cm^3}$ oxygen and forms 20 $\mathrm{cm^3}$ carbon dioxide when these dry gas volumes are compared at common T,p. After appropriate cooling, condensed liquid water is excluded from that dry gas comparison. Water vapour in a hot or wet collection cannot simply be assumed absent.

Practice

1. Calculate the number of atoms in 0.20 mol of ammonia, $\mathrm{NH_3}$.
2. Use illustrative boron abundances 20% $^{10}\mathrm{B}$ and 80% $^{11}\mathrm{B}$ with whole-number isotope-mass approximations. Calculate its A_r.
3. Calculate the molar mass of calcium hydroxide, $\mathrm{Ca(OH)_2}$.
4. Calculate the amount in moles in 8.0 g of methane, $\mathrm{CH_4}$.
5. Calculate the mass of 3.01×10^{23} molecules of oxygen, $\mathrm{O_2}$.
6. Calculate the percentage by mass of iron in iron(III) oxide, $\mathrm{Fe_2O_3}$.
7. A compound contains 85.6% carbon and 14.4% hydrogen by mass. Its M_r is 56.12. Find the empirical and molecular formulae.
8. 3.00 g of magnesium burns to give 4.97 g of oxide. Find the empirical formula of the oxide.
9. 4.80 g of hydrated magnesium sulfate, $\mathrm{MgSO_4 \cdot} x\mathrm{H_2O}$, loses 2.46 g of water on heating. Find x.
10. Calculate the concentration in mol $\mathrm{dm^{-3}}$ of 2.00 g of NaOH in 500 $\mathrm{cm^3}$ of solution.
11. What volume of 0.500 mol $\mathrm{dm^{-3}}$ HCl must be diluted to make 250 $\mathrm{cm^3}$ of 0.0200 mol $\mathrm{dm^{-3}}$ HCl?
12. 50 $\mathrm{cm^3}$ of propane burns: $\mathrm{C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)}$. Calculate the volume of oxygen used and of carbon dioxide made, at the same temperature and pressure.
13. A 10.0 $\mathrm{cm^3}$ stock aliquot at 0.500 mol $\mathrm{dm^{-3}}$ is made up to 250 $\mathrm{cm^3}$ solution. Find the final concentration. Explain why "add 250 $\mathrm{cm^3}$ water" is a different instruction.
14. Assuming complete dissociation, what amounts of calcium ions, chloride ions and total ions arise from 0.200 mol $\mathrm{CaCl_2}$? Distinguish formula units from constituent ions.

Worked answers.

1. Using rounded course N_a, molecules=$0.20\times6.02\times10^{23}$ =1.204×10^{23} before rounding. Four atoms per molecule give 4.816×10^{23}, reported $\mathbf{4.8\times10^{23}}$ **atoms** to two significant figures.
2. $(20 \times 10 + 80 \times 11)/100 = 10.8$.
3. $40.08 + 2 \times (16.00 + 1.01) = 74.10$ g $\mathrm{mol^{-1}}$.
4. $M = 16.05$ g $\mathrm{mol^{-1}}$; $n = 8.0/16.05 = 0.50$ mol.
5. $n = \dfrac{3.01 \times 10^{23}}{6.02 \times 10^{23}} = 0.500$ mol; $m = 0.500 \times 32.00 = 16.0$ g.
6. $M_r = 2 \times 55.85 + 3 \times 16.00 = 159.70$; % Fe $= 111.70/159.70 \times 100 = 69.9\%$.
7. C: 85.6/12.01 = 7.13; H: 14.4/1.01 = 14.3; ratio 1 : 2, so $\mathrm{CH_2}$ (M_r = 14.03). 56.12/14.03 = 4, so $\mathrm{C_4H_8}$.
8. O: 4.97 − 3.00 = 1.97 g. Mg: 3.00/24.31 = 0.123 mol; O: 1.97/16.00 = 0.123 mol. Ratio 1 : 1, so MgO.
9. $\mathrm{MgSO_4}$: 4.80 − 2.46 = 2.34 g, 2.34/120.38 = 0.0194 mol. Water: 2.46/18.02 = 0.137 mol. Use the unrounded ratio (2.46/18.02)/(2.34/120.38)=**7.02294…**, consistent with **x=7**. The inference assumes water-only mass loss and an unchanged anhydrous salt.
10. $n = 2.00/40.00 = 0.0500$ mol; $c = 0.0500/0.500 = 0.100$ mol $\mathrm{dm^{-3}}$.
11. $V_1 = 0.0200 \times 250/0.500 = 10.0$ $\mathrm{cm^3}$.
12. Oxygen $5 \times 50 = 250$ $\mathrm{cm^3}$; carbon dioxide $3 \times 50 = 150$ $\mathrm{cm^3}$.
13. Amount in the aliquot=0.500×0.0100=0.00500 mol. Final c=0.00500/0.250=**0.0200 mol $\mathrm{dm^{-3}}$**. The flask is made up to 250 $\mathrm{cm^3}$ solution, rather than adding that volume of water; liquid volumes need not be additive.
14. Each formula unit corresponds to one $\mathrm{Ca^{2+}}$ and two $\mathrm{Cl^-}$. The amounts are **0.200 mol $\mathrm{Ca^{2+}}$, 0.400 mol $\mathrm{Cl^-}$ and 0.600 mol total ions**, subject to the stated complete-dissociation assumption. A formula-unit count is not already the count of all ions.

Exam tips

- Name counted entities; use stated relative atomic masses and retain guard digits.
- Use final solution volume with compatible units. Scale all empirical ratios rather than rounding away simple fractions.
- Gas ratios require common temperature/pressure, gas phases and the stated reaction extent.

Ideal gases

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Structure 1.5, Ideal gases, for the course first assessed in 2025. All of it is SL and HL content.

Prerequisites: the amount of substance n in mol and molar mass from Structure 1.4, and rearranging an equation. You will use the gas constant $R = 8.31$ J K^{-1} mol^{-1} and the molar volume 22.7 dm^3 mol^{-1} from the data booklet.

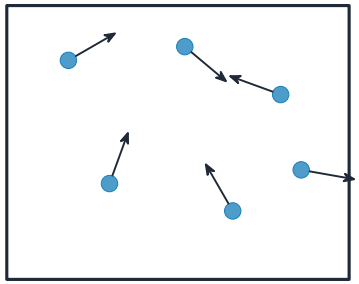
The ideal gas model

Why does a sealed can burst in a fire?

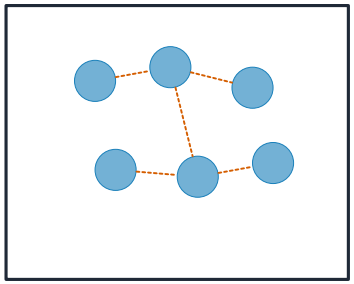
Heating a suitably confined gas can raise its pressure; whether a container fails also depends on its construction, contents and conditions. Pumping a tyre adds gas, while squeezing an air-filled syringe changes volume. These are different changes in the same model, not one rule that heating always determines pressure. They are explanatory examples, not practical instructions: never heat an improvised sealed container. Numerical cases below are invented unless explicitly identified otherwise.



Steam rising from boiling water: gases expand to fill space and obey the ideal gas law at high T and low P



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

Five assumptions

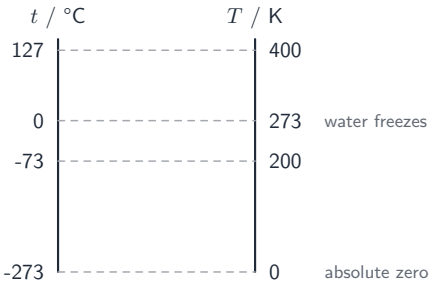
The **kinetic molecular theory** 分子动理论 pictures a gas as a huge number of tiny particles in fast, random motion. An **ideal gas** 理想气体 is one that obeys this model exactly:

1. The particles move randomly in straight lines until they collide.
2. The volume of the particles themselves is **negligible** compared with the volume of the container.
3. There are no **intermolecular forces** 分子间作用力 between the particles.
4. All collisions are **elastic** 弹性的: total kinetic energy is conserved in a collision, although individual particles can exchange energy.
5. The average kinetic energy of the particles is proportional to the kelvin temperature.

Pressure 压强 is the force per unit area that the particles exert when they hit the walls of the container. More hits per second, or harder hits, mean a higher pressure.

Temperature must be in kelvin

The **kelvin scale** 开尔文温标 starts at **absolute zero** 绝对零度, the lowest possible temperature, which is the zero of the thermodynamic scale. The classical ideal-gas model approaches zero mean translational kinetic energy there; it does not describe all motion in real quantum systems.



$T/\mathrm{K} = t/°\mathrm{C} + 273$

400 K is twice 200 K;
40 °C is not twice 20 °C

The kelvin scale starts at absolute zero

$$T/\mathrm{K} = t/°\mathrm{C} + 273.15$$

The offset is exactly 273.15. The whole-kelvin course estimates below use **273** consistently; use the precision specified in a question.

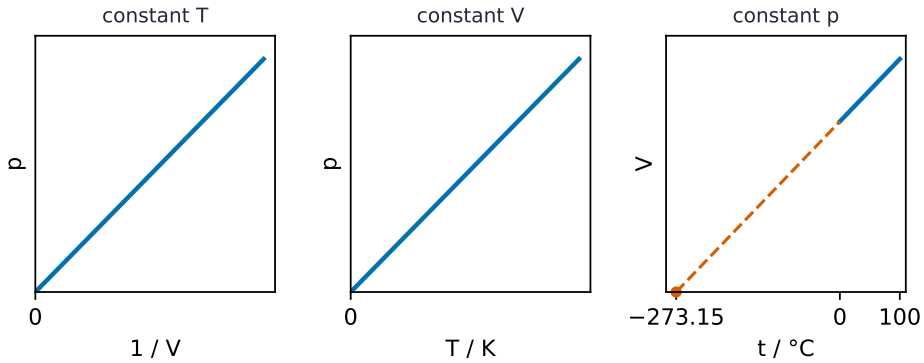
Kelvin temperature is proportional to the average kinetic energy of the particles. Celsius temperature is not: 40 °C is not twice as hot as 20 °C, but 400 K is twice 200 K and gives twice the ideal-gas mean translational kinetic energy. This does not mean every particle has the same energy or that total internal energy depends on temperature alone for every material. **Every gas calculation uses kelvin.**

How pressure, volume and temperature are linked

Three relationships for a fixed amount of gas

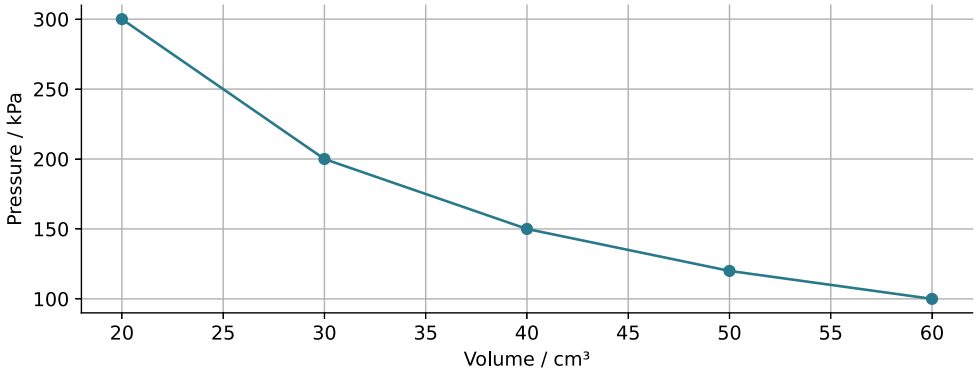
Change one quantity, hold one fixed, and watch the third. Each result has a particle explanation.

Held fixed	Relationship	Particle explanation
T	$p \propto \frac{1}{V}$, so pV is constant	smaller volume → particles hit the walls more often
V	$p \propto T$	hotter particles move faster, hit more often and harder
p	$V \propto T$	faster particles push the walls out until the pressure is back to its old value



Straight lines through the origin show proportionality; the volume line meets zero at $-273.15\ °C$*, absolute zero*

A plot of p against V can be tested using a suitable inverse model; a curve is not automatically poor evidence. Plotting p against 1/V can make the proposed proportionality easier to inspect. Check the intercept, residuals and uncertainties rather than accepting any roughly straight line. The Celsius-axis intercept is an **ideal-model extrapolation**: a real gas may condense before approaching it, so it is not a practical route to zero gas volume.



At constant temperature pV *stays constant:* $300 \times 20 = 100 \times 60 = 6000$

The combined gas law

The three relationships combine into one equation for a fixed amount of gas:



$$V_2 = \frac{p_1 V_1 T_2}{p_2 T_1}$$
$$= \frac{100\,000 \times 2.50 \times 10^{-4} \times 353}{150\,000 \times 293}$$
$$= 2.01 \times 10^{-4}\ \text{m}^3 = \mathbf{201\ cm^3}$$

The worked combined-gas-law example in SI units

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

For course calculations, convert pressure to **Pa**, volume to $\mathbf{m^3}$ and temperature to **K**. Compatible units on both sides can cancel algebraically, but this does not remove the syllabus requirement to use SI pressure/volume in ideal-gas calculations. The combined form also requires a fixed amount: a leak, reaction or gas added to the sample changes that assumption.

> **Worked example.** A gas occupies 250 cm^3 at 20 °C and 100 kPa. It is heated to 80 °C and the pressure rises to 150 kPa. Find the new volume.

1. Convert to kelvin: $T_1 = 293$ K, $T_2 = 353$ K.
2. Rearrange: $V_2 = \dfrac{p_1 V_1 T_2}{p_2 T_1}$.
3. Convert $p_1 = 100000$ Pa, $p_2 = 150000$ Pa and $V_1 = 2.50 \times 10^{-4}$ m^3. Substitute: $V_2 = (100000 \times 2.50 \times 10^{-4} \times 353)/(150000 \times 293) = \mathbf{2.0079636... \times 10^{-4}\ m^3}$, or $\mathbf{201\ cm^3}$ to three significant figures.
4. Check: T increases by a factor 353/293 = 1.20478…, while p increases by 1.50. The volume factor is **0.803185...**, so volume falls about **19.7 %**. Quantify the competing factors rather than saying they cancel.

Molar volume and the ideal gas equation

Equal volumes, equal numbers of particles

In an ideal gas the particles have negligible volume, so at specified pressure and temperature the ideal volume depends on **how many** particles there are, not their chemical identity. Volume also depends on pressure and temperature; amount alone does not determine it. **Avogadro's law** 阿伏伽德罗定律: equal volumes of all gases at the same temperature and pressure contain the same number of particles.

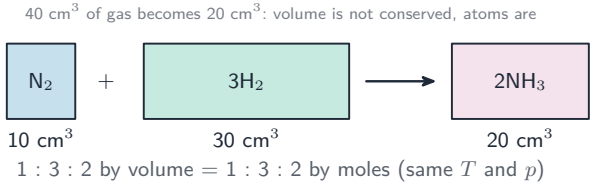
So one mole of any ideal gas has the same volume at a given temperature and pressure. This is the **molar volume** 摩尔体积. At standard temperature and pressure (STP: 273 K and 100 kPa):

$$V_m = 22.7\ \text{dm}^3\ \text{mol}^{-1}$$

$$n = \frac{V}{V_m}$$

For example, 0.500 mol of oxygen or of carbon dioxide at STP each occupy $0.500 \times 22.7 = 11.4$ dm^3.

Because volume is proportional to amount, the coefficients in a balanced equation for gases give their **volume ratio** too. In $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, 10 cm^3 of nitrogen reacts with 30 cm^3 of hydrogen to give 20 cm^3 of ammonia, all compared at the same temperature and pressure, assuming the stated reaction proceeds to the specified stoichiometric extent and the substances remain gases. Real ammonia equilibrium need not give complete conversion.



N_2 + $3H_2$ → $2NH_3$: at the same T and p, gas volumes follow the mole ratio

The ideal gas equation

Putting amount into the combined law gives the **ideal gas equation** 理想气体状态方程:

$$pV = nRT$$

R is the **gas constant** 气体常数, 8.31 $\text{J K}^{-1}\ \text{mol}^{-1}$. The units must fit R:

Quantity	SI unit	Convert from
p	Pa	1 kPa = 10^3 Pa
V	m^3	1 dm^3 = 10^{-3} m^3; 1 cm^3 = 10^{-6} m^3
T	K	add 273 to °C

The product kPa · dm^3 is dimensionally equal to a joule, but use the stated SI route **Pa with $\mathbf{m^3}$** for this course. Mixing kPa with m^3 while keeping the numerical R = 8.31 gives a factor-of-1000 error.

> **Worked example: finding a molar mass.** A 0.320 g sample of a gas occupies 180 cm^3 at 300 K and 100 kPa. Find its molar mass.

1. Convert: $p = 1.00 \times 10^5$ Pa, $V = 180 \times 10^{-6} = 1.80 \times 10^{-4}$ m^3.

2. Amount: $n = \dfrac{pV}{RT} = \dfrac{1.00 \times 10^5 \times 1.80 \times 10^{-4}}{8.31 \times 300} = 7.22 \times 10^{-3}$ mol.
3. Molar mass: $M = \dfrac{m}{n} = \dfrac{0.320}{7.22 \times 10^{-3}} = 44.3$ g mol^{-1}.
4. Interpret: this is close to 44.0 g mol^{-1}, so carbon dioxide or propane could be candidates. Molar mass alone does not identify a gas uniquely; uncertainty, composition and independent evidence matter. Using unrounded n gives M = **44.32 g mol^{-1}**, reported 44.3.

Real gases

When the model breaks down

A **real gas** 实际气体 behaves almost ideally at high temperature and low pressure. It deviates most at **low temperature and high pressure**, because two assumptions stop being true.

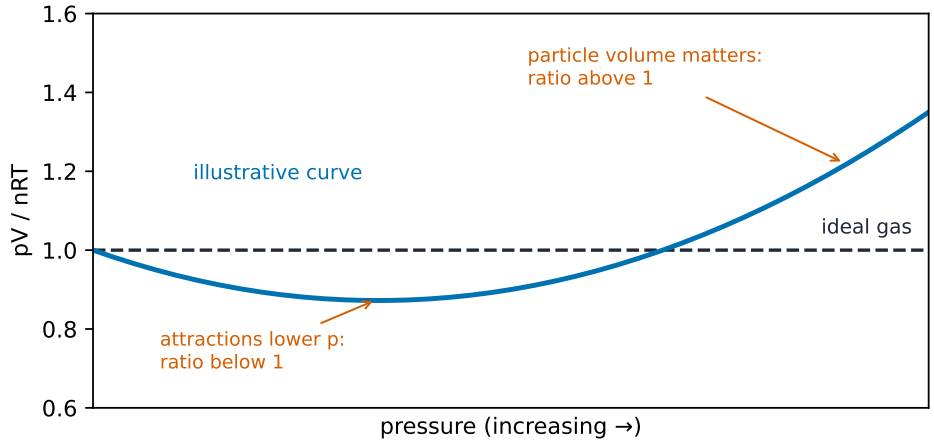


Liquid nitrogen boils at −196 °C: cooled enough, every real gas condenses, which an ideal gas never would

- **High pressure.** The particles are pushed close together, so their own volume is no longer negligible. Excluded-volume effects can push pV/(nRT) above 1 when they dominate. Attractions can oppose this; the net deviation depends on the gas, temperature and pressure, rather than every high-pressure state having one compulsory sign.
- **Low temperature.** Attractions become more important relative to thermal motion and can lower pressure relative to the ideal prediction for the same amount, volume and temperature. They act at other temperatures too; the relevant issue is their relative importance. Condensation can invalidate a single-gas-phase comparison.

Stronger attractions can increase deviations under suitable comparable conditions, but particle size, temperature, pressure and phase also matter. Do not rank every possible state of two gases from an attraction label alone.

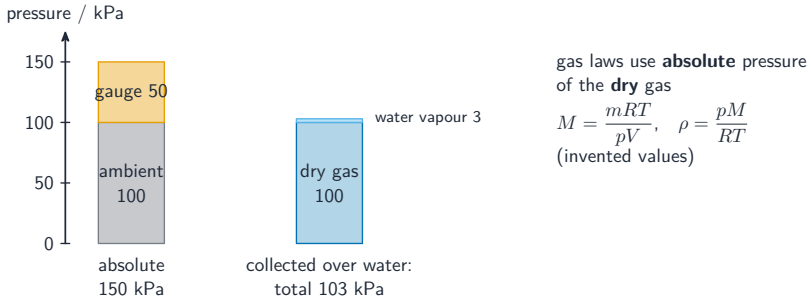
We can compare a real gas with the model by plotting $\dfrac{pV}{nRT}$ against pressure. For an ideal gas this ratio is exactly 1 at every pressure.



An illustrative curve, not measured data or a universal path for every gas. Below/above 1 are interpreted using the conditions and competing effects.

Absolute pressure, dry gas and density

Gas-law p is **absolute pressure**, referenced to vacuum. Gauge pressure is relative to ambient: p_absolute = p_gauge + p_ambient. Invented gauge 50 kPa at ambient 100 kPa means 150 kPa absolute. In a rigid fixed-amount ideal sample warming 300→360 K, pressure becomes 150 × 360/300 =180 kPa absolute, or 80 kPa gauge if ambient stays 100 kPa.



Use absolute pressure of the dry gas (invented values)

If gas is collected over water and the relevant pressure conditions are given, subtract the supplied water-vapour partial pressure to find dry-gas pressure. With total 103 kPa and water vapour 3 kPa, dry p =100 kPa; do not invent a water-vapour value or ignore a hydrostatic pressure difference. A mixture needs the appropriate component pressure/amount interpretation.

Combining n=m/M with pV=nRT gives **M=mRT/(pV)** and ρ**=pM/(RT)**. If density is kg/m^3, use M in kg/mol to obtain consistent SI mass units. A fitted slope of p against 1/V at fixed n,T is nRT, with units Pa $\cdot$ m^3 = J. It can estimate n if the model and calibration are justified.

■ Measuring gas behaviour in the lab

To test $p \propto T$, warm a sealed flask of air in a water bath connected to a pressure sensor. Let the gas reach the temperature of the bath before each reading, and keep within the temperature and pressure limits your teacher sets. **Never heat a sealed vessel that is not designed for it.**

Practice

1. Convert −23 °C and 127 °C to kelvin.
2. A gas at 300 K and 120 kPa in a rigid container is cooled to 250 K. Find the new pressure.
3. Calculate the volume of 0.0400 mol of a gas at STP, in cm^3.
4. Calculate the volume, in dm^3, of 0.500 mol of gas at 298 K and 101 kPa.
5. 1.00 g of a gas occupies 0.763 dm^3 at 273 K and 100 kPa. Find its molar mass and suggest the gas.
6. Explain, in terms of particles, why the pressure of a gas rises when it is heated at constant volume.
7. State two assumptions of the ideal gas model, and explain why each fails at high pressure or low temperature.
8. A gauge reads 50 kPa at ambient 100 kPa. In a rigid fixed-amount ideal sample, T changes 300→360 K. Find initial/final absolute pressure and final gauge pressure if ambient is unchanged.
9. A fixed ideal sample occupies 300 cm^3 at 300 K and 100 kPa, then reaches 360 K and 150 kPa. Find the new volume using SI intermediate units, and explain its direction of change.
10. A p-versus-1/V line at 300 K has slope 500 Pa $\cdot$ m^3. Using R=8.31, estimate n. Explain why an intercept or systematic residual pattern matters.
11. For supplied p=1.20×10^6 Pa, V=1.00×10^{-3} m^3, n=0.500 mol and T=300 K, find Z=pV/(nRT). What does its sign relative to 1 suggest, and what does it not identify by itself?
12. An invented gas density is 1.60 kg/m^3 at 300 K and 100000 Pa. Derive its molar mass in kg/mol and g/mol. Explain why that does not uniquely identify the gas.
13. A supplied equal-level water collection has total pressure 103 kPa, water-vapour partial pressure 3 kPa, volume 200 cm^3 and T=300 K. Find dry-gas amount. Name one measurement condition that must be checked.
14. A rigid sample changes from 200 kPa at 300 K to 204 kPa at 360 K. Assuming ideal behaviour and unchanged volume, find n_2/n_1. Does a higher final pressure alone prove the amount was unchanged?

Answers.

1. 250 K and 400 K.
2. $p_2 = 120 \times \dfrac{250}{300} = 100$ kPa.
3. $0.0400 \times 22.7 = 0.908$ dm^3 = 908 cm^3.
4. Convert p=101000 Pa. V=0.500 × 8.31 × 298/101000 = **0.0122593069... m^3 = 12.3 dm^3** to three significant figures.
5. $n = \dfrac{0.763}{22.7} = 0.0336$ mol; $M = \dfrac{1.00}{0.0336} = 29.8$ g mol^{-1}, close to 30: ethane, C_2H_6, or nitrogen monoxide, NO.
6. The particles gain kinetic energy and move faster. They hit the walls more often and with more force, so the force per unit area rises.
7. Particle volume is negligible: at high pressure the particles are close together and their own volume is a large share of the container. No intermolecular forces: at low temperature the particles move slowly and attractions pull them together, lowering the pressure.
8. Initially 50+100 = **150 kPa absolute**. Final absolute 150 × 360/300 = **180 kPa**. Final gauge 180−100 = **80 kPa**. A gauge value cannot be substituted as though it were absolute.
9. V_1=3.00×10^{-4} m^3; p_1=100000 Pa, p_2=150000 Pa. $V_2=p_1V_1T_2/(p_2T_1)$=**2.40×10^{-4} m^3 =240 cm^3**. Temperature factor 1.20 is outweighed by pressure factor 1.50, giving volume factor 0.80.
10. n=slope/(RT)=500/(8.31×300)=**0.2005616... mol**, about 0.201 mol. A nonzero intercept or residual pattern can indicate offset, changed conditions or model inadequacy; straightness alone does not prove the assumptions.
11. pV=1200 J; nRT=1246.5 J; **Z=0.9626955...**, about 0.963. Below 1 is consistent with attractions being important; it does not identify the gas or eliminate measurement uncertainty.
12. From M=ρRT/p, M=1.60×8.31×300/100000=**0.039888 kg/mol =39.888 g/mol**, reported 0.0399 kg/mol or 39.9 g/mol. Identity needs independent chemical evidence.
13. Dry p=(103−3)×1000 =100000 Pa; V=2.00×10^{-4} m^3. n=pV/(RT)=**0.00802246... mol**, about 0.00802 mol. For example, check that liquid levels are equal and temperature is measured.

14. At fixed V, $n_2/n_1=(p_2/p_1)(T_1/T_2)=(204/200)(300/360)=\mathbf{0.85}$. The model implies 15% less gas despite a 2% pressure rise. A leak is possible, but pressure alone does not establish its cause.

Exam tips

- Use **kelvin**, **absolute Pa** and $\mathbf{m^3}$ with R=8.31; convert requested output units afterwards.
- Check fixed amount, wet/dry gas, physical states and stated molar-volume conditions before choosing a relation.
- Explain competing attraction/particle-volume effects. An extrapolation, schematic or single molar mass does not uniquely identify a gas or mechanism.

The ionic model

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

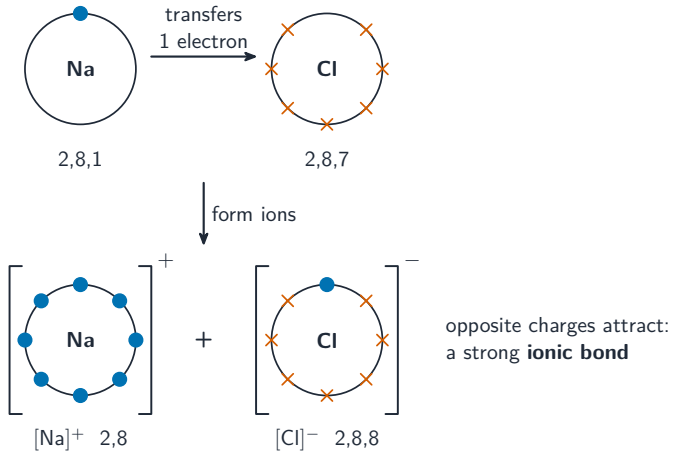
This handout teaches Structure 2.1, The ionic model, for the course first assessed in 2025. All of it is SL and HL content.

Prerequisites: electron configurations and the periodic table groups from Structure 1.3. Use supplied lattice enthalpies for comparisons; this unit does not require a Born–Haber calculation. Lattice enthalpy here always uses the dissociation convention.

Ions and their charges

Why does salt conduct only when it melts?

Push two electrodes into solid table salt and no current flows. Molten salt conducts because its ions can move. Dissolving salt adds water, which surrounds and separates the ions; a sufficiently concentrated aqueous solution also conducts. The charge carriers in either case are mobile ions. The **ionic model** 离子模型 explains this with one idea: salt is made of charged particles that are locked in place in the solid and free to move in the liquid.



Sodium gives its outer electron to chlorine; both reach full outer shells and the opposite charges attract (the blue electron came from sodium)

How ions form

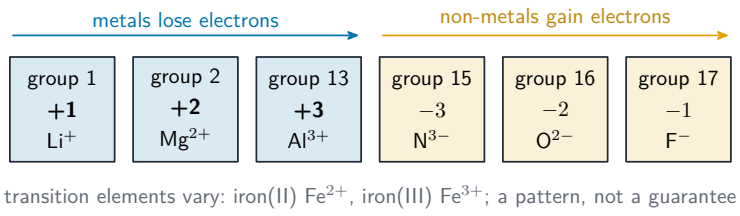
An **ion** 离子 is an atom or group of atoms with an electric charge. A monatomic ion forms by losing or gaining electrons; the proton number stays unchanged. Many simple main-group ions have a noble-gas electron configuration. This is a useful pattern, not a claim that every ion has an octet or that removing electrons from an isolated atom releases energy. Whether a compound forms depends on the overall energetic balance.

- Metal atoms **lose** electrons and form positive ions, called **cations** 阳离子. Sodium, [Ne] $3s^1$, loses one electron to form Na^+, [Ne].
- Non-metal atoms **gain** electrons and form negative ions, called **anions** 阴离子. Chlorine, [Ne] $3s^2\,3p^5$, gains one electron to form Cl^-, [Ar].

In an ionic compound the electrons lost by the metal are the electrons gained by the non-metal, so the total charge is zero.

Predicting the charge from the group

For common simple ions, group position and electron configuration help predict these charges. The table is a working pattern, not a guarantee that every element in a group forms a stable monatomic ion of that charge in every environment:



transition elements vary: iron(II) Fe^{2+}, iron(III) Fe^{3+}; a pattern, not a guarantee

Typical simple-ion charges by group: a pattern, not a guarantee

Group	1	2	13	15	16	17
Electrons lost or gained	lose 1	lose 2	lose 3	gain 3	gain 2	gain 1
Ion charge	+1	+2	+3	−3	−2	−1
Example	Li^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	F^-

Transition elements 过渡元素 can form ions with different charges, so the name gives the charge as a Roman numeral: iron(II) is Fe^{2+} and iron(III) is Fe^{3+}; copper(I) is Cu^+ and copper(II) is Cu^{2+}.

Polyatomic ions

A **polyatomic ion** 多原子离子 is a group of covalently bonded atoms that carries an overall charge. Learn these:

Ion	Formula	Ion	Formula
ammonium	NH_4^+	carbonate	CO_3^{2-}
hydroxide	OH^-	hydrogencarbonate	HCO_3^-
nitrate	NO_3^-	sulfate	SO_4^{2-}
		phosphate	PO_4^{3-}

Ionic bonding, formulas and names

The ionic bond

An **ionic bond** 离子键 is the **electrostatic attraction** 静电吸引 between oppositely charged ions. The attraction acts in every direction, so each ion attracts oppositely charged ions around it, not just one partner. Like charges also repel; the lattice arrangement reflects the balance of attractions and repulsions. Electron transfer accounts for ion formation, whereas electrostatic attraction is the bond itself.

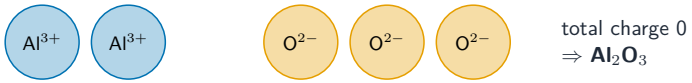


Sodium chloride crystals: ionic solids form a lattice of oppositely charged ions

Ionic bonding happens between elements with a large difference in **electronegativity** 电负性: typically a metal on the left of the periodic table and a non-metal on the right. The larger the difference, the more ionic the bond. (Structure 2.4 shows bonding as a scale, not three separate boxes.)

Writing the formula

The formula shows the simplest ratio of ions that makes the total charge zero.



$2 \times (+3) = +6$ $3 \times (-2) = -6$

total charge 0
⇒ **Al_2O_3**

smallest whole-number ratio that makes the charges sum to zero

Balance the charges to find the formula: Al_2O_3

1. Write the two ions with their charges.
2. Find the smallest numbers of each that make the charges add up to zero.
3. Write the ratio as subscripts. Put a polyatomic ion in brackets if you need more than one.

Ions	Balance	Formula	Name
Na^+, Cl^-	$1 \times (+1) + 1 \times (-1) = 0$	NaCl	sodium chloride
Mg^{2+}, Cl^-	$1 \times (+2) + 2 \times (-1) = 0$	$MgCl_2$	magnesium chloride
Al^{3+}, O^{2-}	$2 \times (+3) + 3 \times (-2) = 0$	Al_2O_3	aluminium oxide
Ca^{2+}, NO_3^-	$1 \times (+2) + 2 \times (-1) = 0$	$Ca(NO_3)_2$	calcium nitrate
NH_4^+, SO_4^{2-}	$2 \times (+1) + 1 \times (-2) = 0$	$(NH_4)_2SO_4$	ammonium sulfate

Naming ionic compounds

Name the cation first, then the anion. A simple anion ends in **-ide**: chloride, oxide, nitride, sulfide. A polyatomic ion keeps its own name: sulfate, nitrate. Give a transition-metal charge as a Roman numeral: $FeCl_3$ is iron(III) chloride.

Ionic lattices and lattice enthalpy

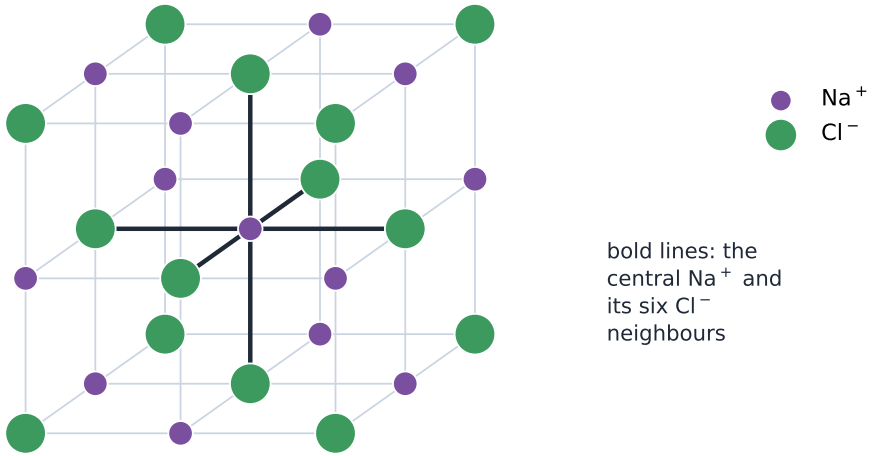
A giant three-dimensional lattice

Ionic compounds do not form molecules. The ions pack into a regular, repeating three-dimensional arrangement called a **lattice** 晶格. The formula NaCl gives only the **ratio** of ions, 1 : 1, not a molecule.

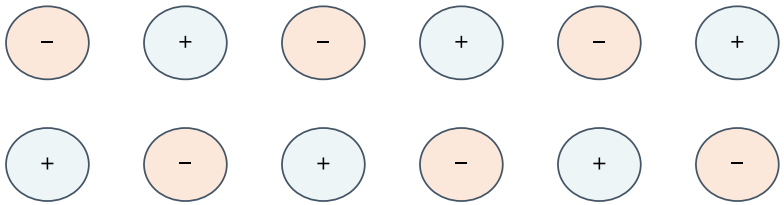


A halite crystal: sodium chloride's cubic shape is the ionic lattice inside it, made big enough to see

In sodium chloride each Na^+ ion is surrounded by six Cl^- ions, and each Cl^- ion by six Na^+ ions.



In NaCl every ion has six nearest neighbours of the opposite charge



Alternating charges in an ionic lattice

A two-dimensional slice of an extended three-dimensional lattice; the drawing does not show every neighbour

Lattice enthalpy measures the strength of the bonding

The **lattice enthalpy** 晶格焓 is the enthalpy change when one mole of a solid ionic compound is separated into its gaseous ions:

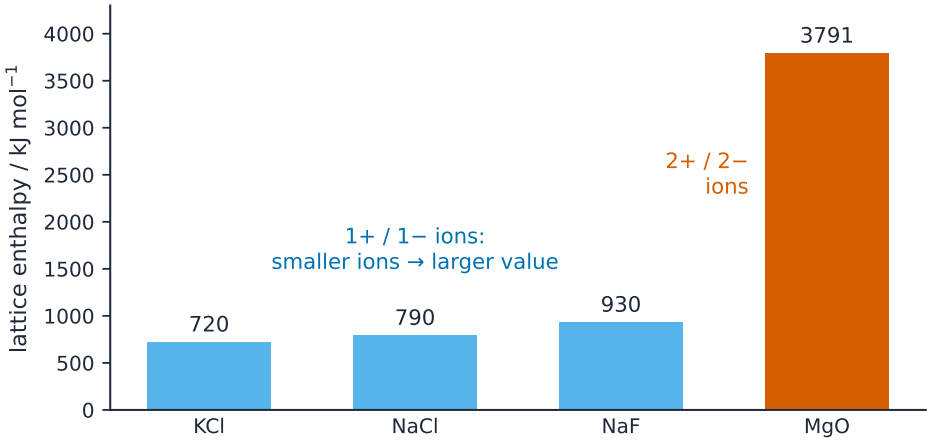
$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \qquad \Delta H_{\mathrm{lattice}} = +790 \text{ kJ mol}^{-1}$$

With this **dissociation convention**, lattice enthalpy is positive (endothermic). The reverse lattice-formation process has the opposite, negative sign. Always state the process before interpreting a sign. Lattice dissociation enthalpy compares separation into gaseous ions, not the enthalpy of melting or dissolving.

Two factors decide its size, because the attraction between two ions is stronger when the charges are larger and the ions are closer together:

- **Ionic charge:** larger charges attract more strongly, so the lattice enthalpy is larger.
- **Ionic radius:** smaller ions sit closer together, so the lattice enthalpy is larger.

Compound	Ions	Lattice enthalpy / kJ mol^{-1}	Reason
KCl	K^+, Cl^-	720	K^+ is larger than Na^+
NaCl	Na^+, Cl^-	790	reference
NaF	Na^+, F^-	930	F^- is smaller than Cl^-
MgO	Mg^{2+}, O^{2-}	3791	both charges are doubled



Supplied rounded comparison values, not measurements made here: MgO has much greater lattice dissociation enthalpy than these singly charged salts

Worked example. Explain why magnesium oxide melts at 2852 °C but sodium chloride melts at 801 °C.

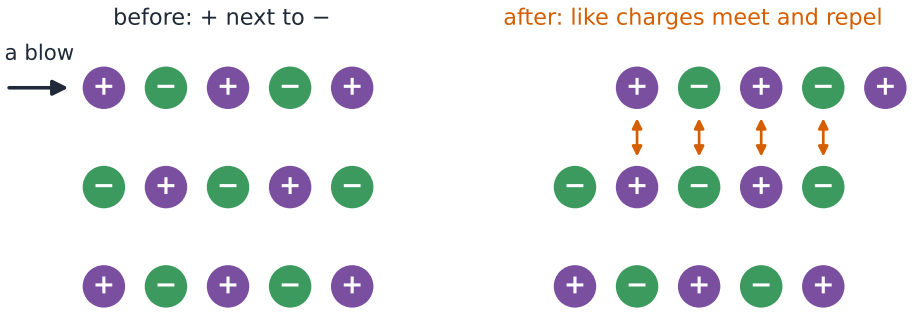
Both are giant ionic lattices, so melting means overcoming electrostatic attractions between ions. Mg^{2+} and O^{2-} carry twice the charges of Na^+ and Cl^-, and they are also smaller. So the attraction between the ions is much stronger, the lattice enthalpy is much larger (3791 against 790 kJ mol^{-1}), and generally more energy is needed to disrupt the ordered lattice. The molten liquid still contains nearby interacting ions: melting does not separate them into gaseous ions. Lattice enthalpy supports a qualitative comparison, not an exact proportional formula for melting temperature.

Properties of ionic compounds

Explaining properties from the structure

To explain any property, name the **structure**, the **particles**, the **forces** between them, and whether there are **mobile charged particles**.

Property	Typical behaviour	Explanation
melting and boiling point	high; low **volatility** 挥发性	many strong electrostatic attractions in a giant lattice must be overcome
electrical conductivity	none as a solid; conducts when molten or in solution	ions are fixed in the solid; they can move and carry charge when molten or dissolved
solubility	often soluble in water, insoluble in non-polar solvents such as hexane	water can stabilize separated ions by ion–dipole interactions; dissolution depends on the overall free-energy balance, so many ionic solids are sparingly soluble
brittleness	shatters when hit	a blow shifts a layer so that like charges line up and repel



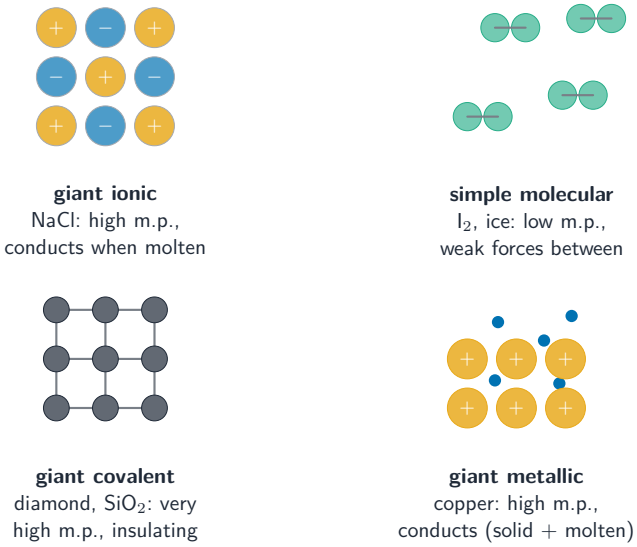
Shift one layer by one ion and like charges meet: the lattice splits apart

Not every ionic solid dissolves readily: silver chloride and calcium carbonate are examples of low-solubility salts. Solubility is not decided by lattice enthalpy alone; interactions with the solvent and entropy also matter. A sparingly soluble solid may still produce a small concentration of dissolved ions. Sugar dissolves but remains mainly neutral molecules, so solubility alone does not establish an ionic structure.

Note that an ionic compound conducts by **moving ions** through its bulk, not by moving electrons. Electrolysis of a molten salt shows this: the ions move to the electrodes and are discharged there.

Use a pattern of evidence

One property alone rarely proves a structure. A giant covalent solid such as silicon dioxide also has a very high melting point, and some simple molecular substances dissolve in water. Look for the full pattern: high melting point, **and** no conduction as a solid, **and** conduction when molten.



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

> **Worked example.** Substance X melts at 801 °C, does not conduct as a solid, conducts when molten, and dissolves in water. Substance Y melts at 60 °C and does not conduct as a solid or as a liquid. Which is ionic?

X fits every part of the ionic pattern: a high melting point from strong attractions in a lattice, and conduction only when the ions are free to move. Y does not: its low melting point and lack of conduction suggest a simple molecular substance with weak forces between neutral molecules.

Practice

1. Give the charge on the ion formed by: (a) potassium, (b) sulfur, (c) aluminium, (d) nitrogen.
2. Write the formulas of: (a) calcium fluoride, (b) sodium oxide, (c) aluminium sulfate, (d) iron(III) hydroxide, (e) ammonium carbonate.
3. Name: (a) K_2S, (b) Mg_3N_2, (c) $CuSO_4$ (copper is +2), (d) $NaHCO_3$.

4. Write the equation for the lattice enthalpy of calcium oxide, including state symbols.
5. Put these in order of increasing lattice enthalpy and explain: NaCl, CaO, KBr.
6. Explain why sodium chloride conducts electricity when dissolved in water but not when solid.
7. Explain why an ionic crystal shatters when hit with a hammer.
8. For Na, Mg and Cl, state the electron count and configuration of the common monatomic ion. Explain whether the proton count changes.
9. A student writes Mg_2O_2 and calls it a magnesium oxide molecule. Correct both statements and distinguish ion ratio from coordination number.
10. Deduce the iron charge and name in $Fe_2(SO_4)_3$. How many sulfate ions and oxygen atoms occur per formula unit?
11. In an invented comparison, salts A and B have singly charged ions and the same lattice type; their nearest unlike-ion distances are 240 and 300 pm. Use a simple pair-attraction model to compare force magnitudes. Does this determine their exact melting points?
12. Explain why an insoluble ionic solid does not contradict the ionic model and why a sugar solution is not evidence for mobile ions merely because the sugar dissolved.
13. An invented conductivity investigation finds: P does not conduct solid but does when molten; Q conducts in both states; R dissolves but its solution conducts very poorly. Suggest a structural model for each and one limitation of the evidence. State a safe way to improve the aqueous comparison.
14. A supplied lattice-formation enthalpy for an invented MX salt is $-810\ \text{kJ mol}^{-1}$. Write the dissociation equation, state its enthalpy, and explain why this number is neither its melting enthalpy nor its enthalpy of solution.

Worked answers.

1. (a) +1, (b) −2, (c) +3, (d) −3.
2. (a) CaF_2, (b) Na_2O, (c) $Al_2(SO_4)_3$, (d) $Fe(OH)_3$, (e) $(NH_4)_2CO_3$.
3. (a) potassium sulfide, (b) magnesium nitride, (c) copper(II) sulfate, (d) sodium hydrogencarbonate.
4. $CaO(s) \rightarrow Ca^{2+}(g) + O^{2-}(g)$
5. KBr < NaCl < CaO. KBr has the largest ions with single charges, so the weakest attraction. CaO has 2+ and 2− ions, so by far the strongest attraction.
6. In the solid the ions are held in fixed positions in the lattice. In solution the ions are free to move, so they can carry charge through the liquid.
7. The blow shifts one layer of ions by one position. Ions of the same charge then line up next to each other, they repel, and the crystal splits along that plane.
8. Na^+ has 10 electrons, $1s^2 2s^2 2p^6$, with 11 protons. Mg^{2+} also has 10 electrons and that configuration, with 12 protons. Cl^- has 18 electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, with 17 protons. Electron loss or gain changes charge; it does not change the element's proton number.
9. Mg^{2+} and O^{2-} balance in a 1:1 ratio, so the empirical formula is MgO. It describes an extended ionic lattice, not discrete molecules. A coordination number counts nearest neighbours around an ion; it need not equal a formula subscript.
10. Three sulfate ions contribute −6 total charge, so two iron ions supply +6 and each is Fe^{3+}. The name is iron(III) sulfate. One formula unit contains three sulfate ions, hence 12 oxygen atoms; there are five constituent ions under complete dissociation, not 17 ions counting every oxygen separately.
11. With equal charge products, the pair-force magnitude is proportional to $1/r^2$. Therefore $F_A/F_B = (300/240)^2 = 1.5625$, approximately 1.56. A has the stronger pair attraction in this simplified model. Pair potential-energy magnitude instead scales as $1/r$. Neither ratio is an exact melting-point ratio: a real lattice has many interactions and melting involves both energy and entropy.
12. Ionic bonding describes the solid's particles and interactions; it does not guarantee that water stabilizes the dissolved state sufficiently for high solubility. Sugar dissolves as neutral molecules. Compare charge carriers and the complete property pattern, not just disappearance of solid.
13. P is consistent with an ionic lattice; mobile ions become available on melting. Q is consistent with metallic bonding and mobile electrons in both states. R is consistent with a molecular nonelectrolyte, but low concentration or limited dissolution could also give a small signal. These are models supported by limited observations, not unique identifications. For approved safe aqueous samples, use the same temperature, concentrations, electrode spacing and instrument settings, a deionized-water blank, and rinse electrodes between samples. Do not melt unknown materials or put mains electricity into solutions.
14. $MX(s) \rightarrow M^+(g) + X^-(g)$, $\Delta H = +810\ \text{kJ mol}^{-1}$. Reversing the formation equation reverses the sign. Melting ends with a liquid containing interacting ions; dissolution ends with solvated ions and includes solvent interactions. Neither has gaseous separated ions as its final state.

Exam tips

- Define an ionic bond as "electrostatic attraction between **oppositely charged ions**". "Transfer of electrons" describes how ions form, not the bond.
- An ionic formula is a **ratio**: never call NaCl a molecule.
- Ionic compounds conduct by **mobile ions**, never by "free electrons".
- For lattice enthalpy, compare **charge** first, then **radius**, and say that both change the electrostatic attraction.
- Write lattice enthalpy as the solid going to **gaseous** ions, with a positive value.

- Put brackets around a polyatomic ion when you need two or more of it: $Ca(OH)_2$, not $CaOH_2$.

The covalent model

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

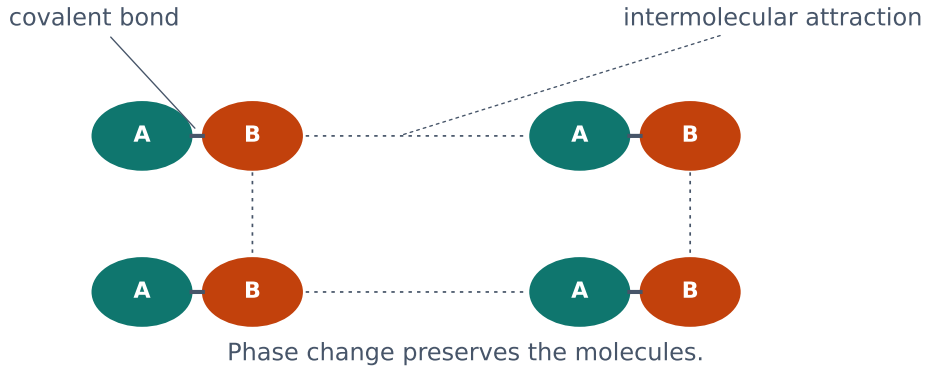
This handout teaches Structure 2.2, The covalent model, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: electron configurations and valence electrons from Structure 1.3, and the ionic model from Structure 2.1. You will use electronegativity values from the data booklet.

The covalent bond

Why does iodine melt so easily?

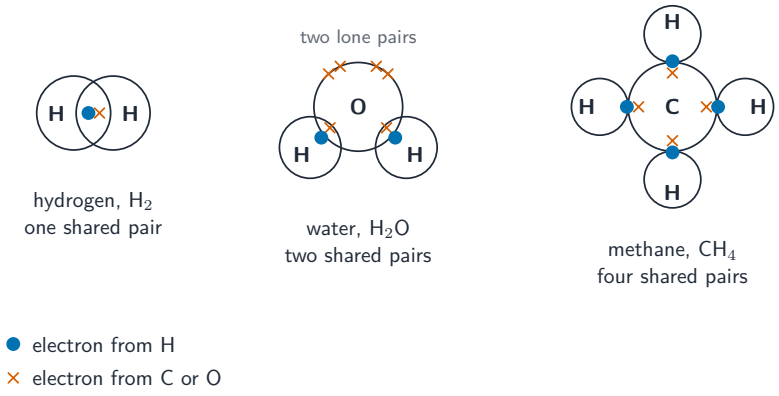
Iodine is made of I_2 molecules. The bond that holds the two iodine atoms together is strong: the supplied gas-phase I–I bond enthalpy is about 151 kJ mol^{-1}. Yet solid iodine melts at only 114 °C and turns to a purple vapour with gentle heating. Under ordinary melting or gentle sublimation conditions the particles remain mainly I_2: intermolecular attractions are overcome while the intramolecular I–I bonds remain intact. This unit explains the difference between the strong **covalent bonds** 共价键 inside a molecule and the weak **intermolecular forces** 分子间作用力 between molecules.



Bonds inside molecules are strong; forces between them are weak, so melting leaves the molecules intact

What a covalent bond is

A covalent bond is the electrostatic attraction between a **shared pair** 共用电子对 of electrons and the positively charged nuclei of the two bonded atoms. The covalent model describes shared electron density between atoms and is especially useful for non-metal compounds. Sharing need not be equal: electronegativity differences can polarize a covalent bond. Bonding is a continuum, so this is not an absolute classification by element names.

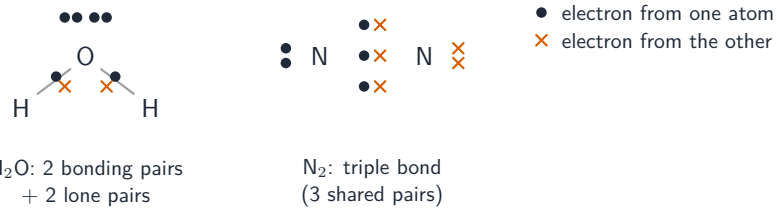


In a covalent bond, atoms share pairs of electrons so each reaches a full outer shell

- Most atoms in covalent molecules end with eight electrons in their outer shell. This is the **octet rule** 八隅体规则. Hydrogen is the exception: it is full with two.
- Some small atoms have fewer than eight. In BF_3 boron has only six outer electrons, and in $BeCl_2$ beryllium has only four. These are **incomplete octets** 不完全八隅体.
- Pairs of outer electrons that are not shared are **lone pairs** 孤对电子. They matter for shape and for hydrogen bonding.

Lewis formulas

A **Lewis formula** 路易斯结构式 shows every valence electron: shared pairs as lines (or dot-cross pairs) and lone pairs as pairs of dots. To draw one:



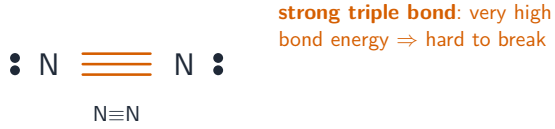
Dot-and-cross diagrams show the bonding pairs and lone pairs in a molecule

1. Add up the valence electrons of all the atoms. Add one for each negative charge and subtract one for each positive charge.
2. Put the least electronegative atom in the centre (never H) and join each outer atom with a single bond.
3. Complete the octets of the outer atoms with lone pairs, then put any electrons left on the central atom.
4. If appropriate for the species, use outer-atom lone pairs to form multiple bonds and complete the central octet. Check total electron count and allowed exceptions: do not force extra bonds into an incomplete-octet BF_3 or $BeCl_2$ model merely to make eight.

For CO_2: $4 + 2(6) = 16$ valence electrons. Two C–O single bonds and full octets on both O use all 16, but C has only four. Moving one lone pair from each O gives O = C = O, with two lone pairs on each O and eight electrons round C.

Single, double and triple bonds

Two atoms can share one, two or three pairs. More shared pairs pull the nuclei closer together and hold them more strongly.



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

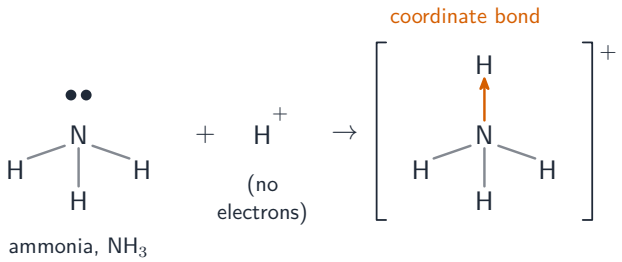
Nitrogen is unreactive for two reasons: a very strong triple bond, and a symmetrical, non-polar molecule

Bond	Shared pairs	Length / pm	Bond enthalpy / kJ mol^{-1}
C–C	1	154	346
C=C	2	134	614
C≡C	3	120	839

For these carbon–carbon comparisons, the triple bond is the **shortest** and **strongest**. This is a comparison of bond order between the same elements, not a ranking of every triple bond above every single bond. Note that a double bond is not twice as strong as a single bond.

Coordination bonds

In a **coordination bond** 配位键 (a dative covalent bond) both shared electrons come from the same atom. The donor origin is electron bookkeeping; it is still a covalent bond after formation. Equivalent bonds in a symmetric species need not retain different physical properties because their drawn electron origins differ.



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

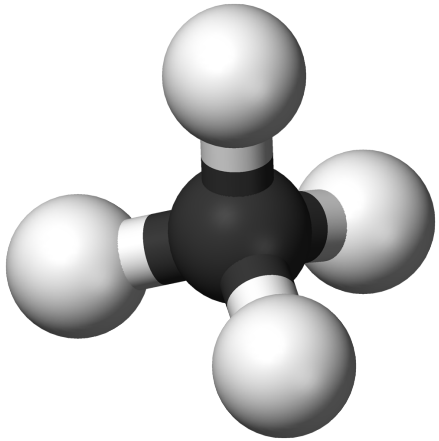
- $NH_3 + H^+ \rightarrow NH_4^+$: the lone pair on N bonds to the H^+ ion. All four N–H bonds in NH_4^+ are the same.
- $H_2O + H^+ \rightarrow H_3O^+$, a useful hydrated-proton representation for aqueous acid solutions; actual proton hydration involves surrounding water molecules.
- Carbon monoxide, C ≡ O: two of the three shared pairs come from both atoms, but one comes from oxygen alone.

Draw a coordination bond as an arrow from the donor atom to the acceptor atom.

Shapes of molecules: VSEPR

Electron domains repel

The **valence shell electron pair repulsion** 价层电子对互斥 (VSEPR) model predicts shape from one idea: groups of electrons round the central atom repel and spread as far apart as possible. Each group is an **electron domain** 电子域: a single bond, a double bond, a triple bond or a lone pair each counts as **one** domain.

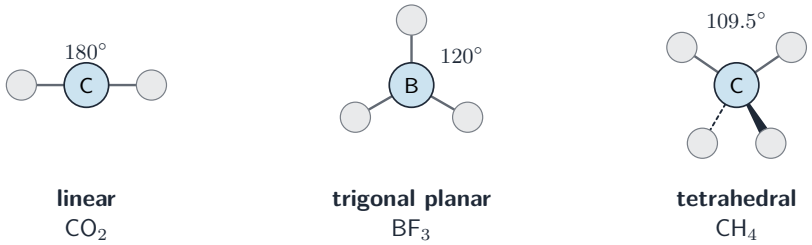


A molecular model shows the three-dimensional shape of a covalent molecule.

1. Draw the Lewis formula.
2. Count the electron domains round the central atom: this gives the **electron domain geometry**.
3. Count how many domains are bonds: the positions of the atoms give the **molecular geometry** 分子几何构型 (the shape).

Lone-pair electron density is typically more concentrated around the central atom, so lone pairs exert greater repulsion than bonding domains in the simple model. Multiple bonds can also repel more strongly than single-bond domains. There is no fixed angle subtraction per lone pair: exact angles depend on the atoms and bonding. The familiar 107° and 104.5° values below belong to NH_3 and H_2O, not every pyramidal or bent molecule. NIST phosphine data give about 93.3° for PH_3.

Domains	Lone pairs	Shape	Angle	Example
2	0	linear	180°	CO_2, $BeCl_2$
3	0	trigonal planar	120°	BF_3, CO_3^{2-}
3	1	bent (V-shaped)	below 120°	SO_2, O_3
4	0	tetrahedral	109.5°	CH_4, NH_4^+
4	1	trigonal pyramidal	107°	NH_3
4	2	bent (V-shaped)	104.5°	H_2O



linear CO_2 | **trigonal planar** BF_3 | **tetrahedral** CH_4

pyramidal NH_3 | **bent** H_2O

Common examples with up to four electron domains. Wedges point towards you and dashed bonds away; labelled angles are specific to these examples.

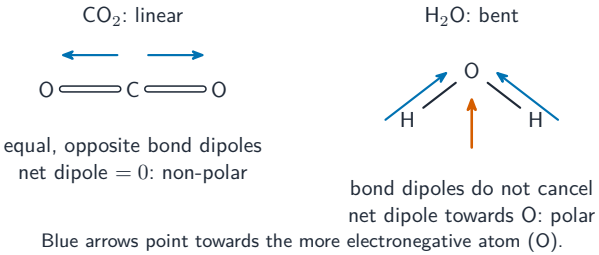
■ Worked example: the shape of NH_3

- Valence electrons: $5 + 3(1) = 8$, so four pairs round N.
- Three are N–H bonds and one is a lone pair: four domains, so the electron domain geometry is tetrahedral.
- Only three positions hold atoms, so the shape is **trigonal pyramidal**.
- The lone pair repels more strongly than the bonds, so the angle closes from 109.5° to 107°.

Bond polarity and molecular polarity

■ Polar bonds

Electronegativity 电负性 is the ability of an atom to attract a shared pair of electrons. When the two bonded atoms have different electronegativities, the shared pair sits closer to the more electronegative atom. That atom gains a small negative charge, $\delta-$, and the other a small positive charge, $\delta+$. The bond is a **polar bond** 极性键 and has a **bond dipole**.



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

Atom	H	C	N	O	F	Cl
Electronegativity	2.2	2.6	3.0	3.4	4.0	3.2

The larger the electronegativity difference, the more polar the bond. O–H (difference 1.2) is much more polar than C–H (difference 0.4). A large difference tends to increase ionic character, but no universal numerical cutoff proves a bonding category. Use the bonding continuum and structural evidence.

■ Polar molecules

A molecule is **polar** 极性的 when its bond dipoles do not cancel, so it has a net **dipole moment** 偶极矩. Whether they cancel depends on the shape.

- CO_2 has two polar C=O bonds, but the molecule is linear: the two dipoles point in opposite directions and cancel. CO_2 is **non-polar**.
- H_2O has two polar O–H bonds, but the molecule is bent: the dipoles add up towards the oxygen. Water is **polar**.
- CH_4 and CCl_4 are symmetrical tetrahedra, so they are non-polar. In CH_3Cl one bond is different, the dipoles no longer cancel, and the molecule is polar.

For a symmetric arrangement of equivalent bond dipoles, the vectors cancel. Apply that vector test to the actual geometry: lone pairs do not automatically imply polarity, and an apparently irregular drawing does not establish a net dipole.

Giant covalent structures

■ Networks instead of molecules

In a **covalent network structure** 共价网状结构 (giant covalent structure) every atom is joined to its neighbours by covalent bonds in a continuous lattice. There are no separate molecules, so melting means breaking strong covalent bonds. These extended networks generally have high melting or decomposition temperatures and low volatility. They are usually insoluble in ordinary solvents without reaction; a chemical reaction with a solvent is not simple physical dissolution.



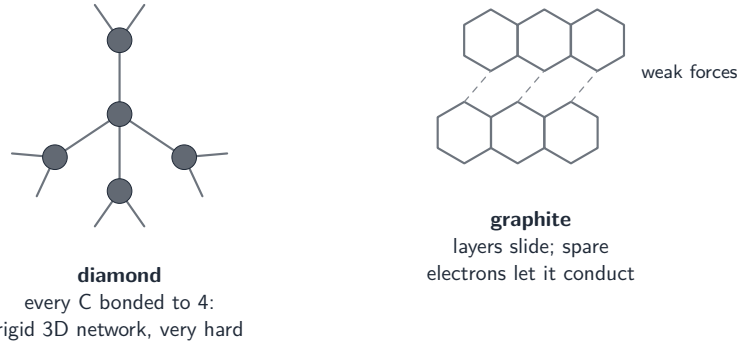
Natural graphite: those weak forces between the layers are why the specimen flakes, and why it marks paper



Quartz is a giant covalent structure of silicon and oxygen.

Carbon has several **allotropes** 同素异形体: different structural forms of the same element in the same state.

Allotrope	Bonding of each C	Structure	Key properties
diamond	4 C, tetrahedral	3D network	hardest natural substance; does not conduct
graphite	3 C, trigonal planar	flat hexagonal layers, weak forces between them	soft, slippery; conducts along the layers
graphene	3 C, trigonal planar	a single layer of graphite	very strong and light; conducts very well
fullerene C_{60}	3 C	hollow ball of 60 atoms	a molecular solid with weaker inter-cage forces than network bonds; relatively soft; poor conductor



Diamond is a rigid 3D network. In graphite one electron per carbon is free to move along each layer.

In graphite, graphene and C_{60} each carbon uses three electrons in bonds. The fourth is **delocalized** 离域的: spread over many atoms rather than held between two. Mobile delocalized electrons explain why graphite and graphene conduct.

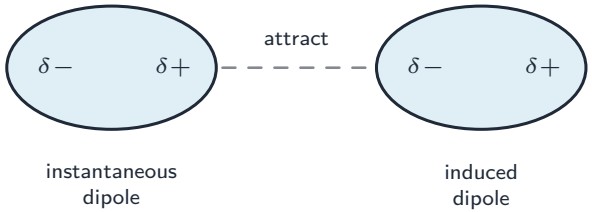
Silicon and silicon dioxide

- **Silicon** has the same tetrahedral network as diamond, but the Si–Si bond is longer and weaker, so silicon melts lower (1414 °C) and is a semiconductor.
- **Silicon dioxide** 二氧化硅, SiO_2 (quartz, sand), is a network in which each Si bonds to four O atoms and each O bonds to two Si atoms. The ratio 1 : 2 gives the formula. Compare it with CO_2: carbon dioxide is a small molecule and a gas at room temperature, while silicon dioxide melts above 1600 °C.

Intermolecular forces

Four kinds of attraction between molecules

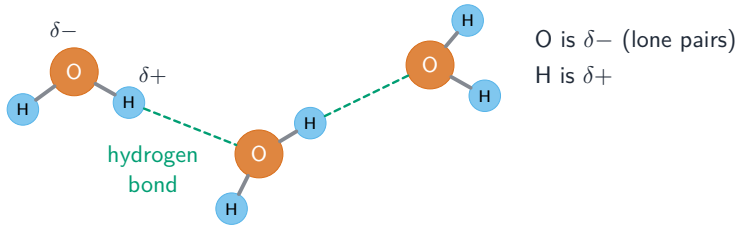
Intermolecular forces act between molecules in simple molecular substances. The following types should be recognized. For comparable molar mass, dispersion < dipole–dipole < hydrogen bonding is a useful general trend, not a universal numerical ranking of every pair of molecules:



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

1. **London forces** 伦敦色散力 (dispersion forces) act between all molecules. Electrons move, so at any instant one side of a molecule may have more electrons than the other: an **instantaneous dipole**. It induces a dipole in the next molecule, and the two attract. London forces grow with the number of electrons (larger molar mass) and with greater surface contact between molecules.
2. **Dipole–induced dipole forces** act between a polar molecule and a non-polar one: the permanent dipole distorts the electrons of its neighbour.
3. **Dipole–dipole forces** 取向力 act between polar molecules: the $\delta+$ end of one attracts the $\delta-$ end of the next, in addition to London forces.
4. **Hydrogen bonding** 氢键 is often the strongest of these interactions in comparisons of similar-sized molecules. It forms when H is bonded to N, O or F, and interacts attractively with a suitable lone pair on a nearby electronegative atom. Intermolecular examples commonly involve N, O or F; intramolecular hydrogen bonds can also occur when geometry permits.

These three forces together, London, dipole–induced dipole and dipole–dipole, are called **van der Waals forces** 范德华力.

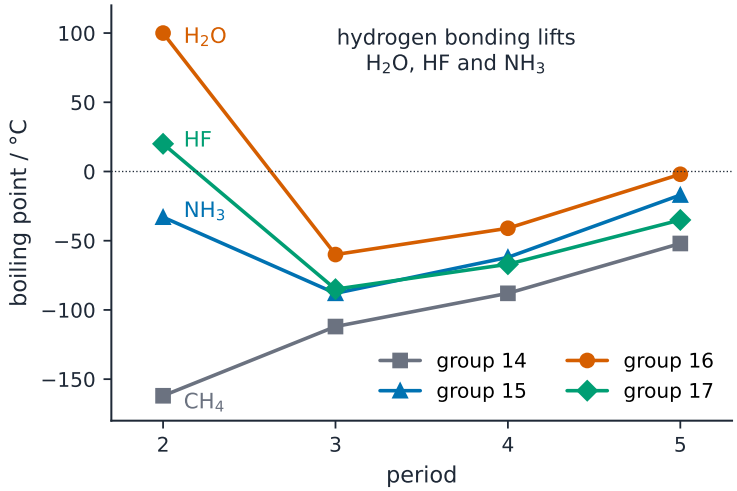


Each water molecule can form up to four hydrogen bonds: two through its H atoms and two through its lone pairs

An N–H, O–H or F–H bond is strongly polarized, giving H a partial positive charge. Its small size permits a close, directional interaction with a suitable acceptor; a hydrogen-bonded H is not a free or bare proton.

Evidence from boiling points

Down each group the hydrides boil higher, because the molecules have more electrons and stronger London forces. Three hydrides break the pattern.



Hydrogen bonding lifts H_2O, HF and NH_3 far above the trend. CH_4 has no hydrogen bonding and follows it.

At approximately atmospheric pressure water boils at 100°C. Its unusually high value relative to the heavier group-16 hydrides supports an important role for hydrogen

bonding; extrapolating a trend does not measure a unique boiling point for a hypothetical water with that interaction removed.

Properties of covalent substances

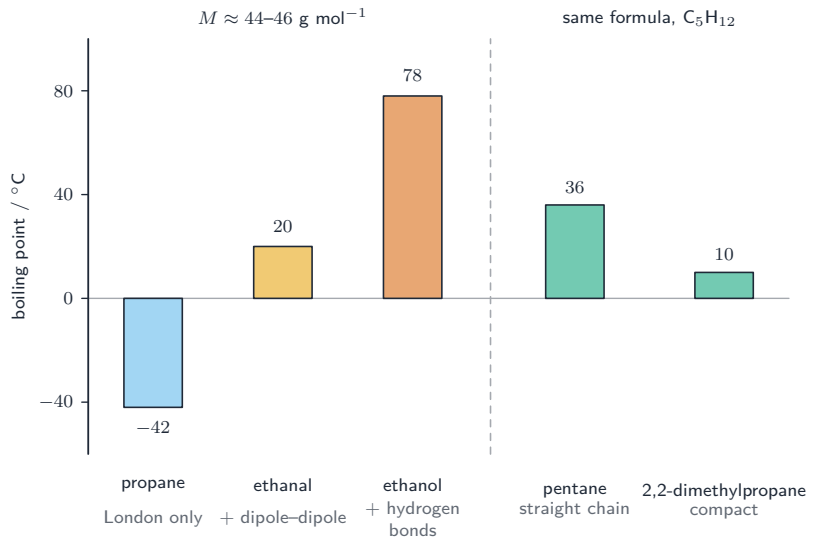
Explaining a property

To explain a physical property, name the structure, the particles, the forces that must be overcome and any mobile charged particles.

Property	Simple molecular	Covalent network
melting and boiling point	low: only weak intermolecular forces are overcome	very high: strong covalent bonds must break
volatility 挥发性	often high	very low
conductivity	usually very low in a pure molecular liquid: few mobile charge carriers; dissolved molecules can react to form ions	varies: diamond/silica have few mobile carriers; graphite/graphene conduct; silicon is a semiconductor
solubility	depends on polarity	insoluble

Comparing boiling points: a method

1. Check the structure and physical conditions. Extended covalent networks generally require much more energy to disrupt than similar small-molecule solids; some decompose or sublime rather than boil.
2. For molecular substances, list all interactions and compare the overall pattern; similar mass helps make an interaction-type comparison meaningful.
3. If the strongest force is the same kind, compare London forces through the number of electrons and the shape.



Similar molar mass, different forces: each extra kind of attraction raises the boiling point. Branching lowers it.

Example: propane, C_3H_8 ($M = 44$), boils at −42 °C; ethanal, CH_3CHO ($M = 44$), at 20 °C; ethanol, C_2H_5OH ($M = 46$), at 78 °C. Similar masses mean similar London forces. Ethanal adds dipole–dipole forces; ethanol adds hydrogen bonding through its O–H group.

Shape matters too: pentane (a straight chain) boils at 36 °C but its branched isomer 2,2-dimethylpropane at 10 °C, because the compact molecules touch over a smaller surface.

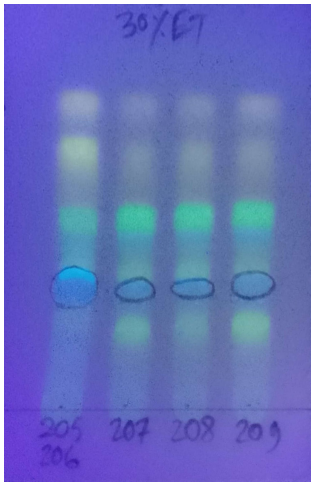
Solubility: like dissolves like

Solubility reflects the overall free-energy change, including attractions disrupted and formed and entropy. “Like dissolves like” is a useful qualitative guide, not a sufficient numerical condition or a universal rule for polar substances.

- Some polar and hydrogen-bonding substances dissolve well in water: ethanol and glucose form hydrogen bonds with water molecules.
- Non-polar substances such as iodine or hexane dissolve in non-polar solvents but hardly in water: they cannot replace the hydrogen bonds between water molecules.
- In a series such as methanol, ethanol, propanol, butanol, solubility in water falls as the non-polar hydrocarbon chain grows longer.

Chromatography

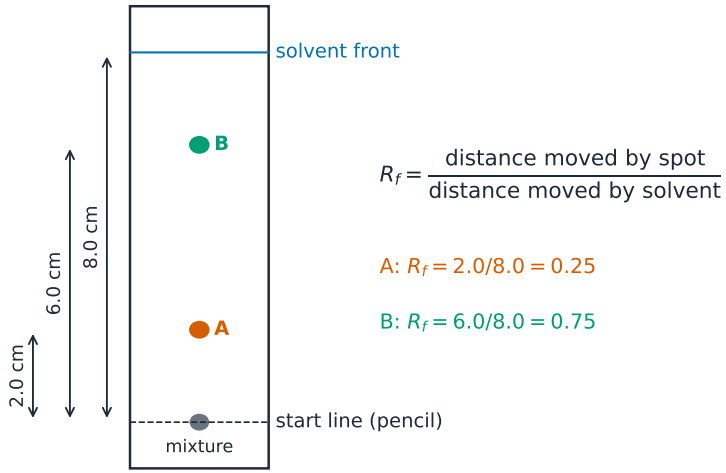
Chromatography 色谱法 separates the components of a mixture by how strongly each one is attracted to two phases:



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

- the **stationary phase** 固定相, which does not move: water held in the fibres of the paper, or a thin layer of silica on a plate in thin-layer chromatography (TLC);
- the **mobile phase** 流动相, the solvent that moves through it.

A component that is more attracted to the mobile phase moves further. A component that is more attracted to the stationary phase stays near the start. Intermolecular attractions, solvent composition and the nature of each phase influence the result: on polar silica with a non-polar solvent, polar components move least.



Invented illustrative chromatogram: measure from the start line to each spot's centre; the ratios are 2.0/8.0 and 6.0/8.0.

The **retardation factor** 比移值, R_f, is

$$R_f = \frac{\text{distance moved by the component}}{\text{distance moved by the solvent front}}$$

R_f always lies between 0 and 1 and has no units. Under controlled conditions (stationary phase, solvent composition, temperature and sample loading), comparable R_f values support identification against reference samples run alongside. Different substances can share a value, so a match alone is not proof of identity or purity. Draw the start line in pencil, because ink would itself separate, and keep it above the level of the solvent. Colourless spots may be located by an approved method under the laboratory protocol; direct exposure to UV and casual handling of locating reagents are inappropriate. Specific locating agents are not required syllabus knowledge.

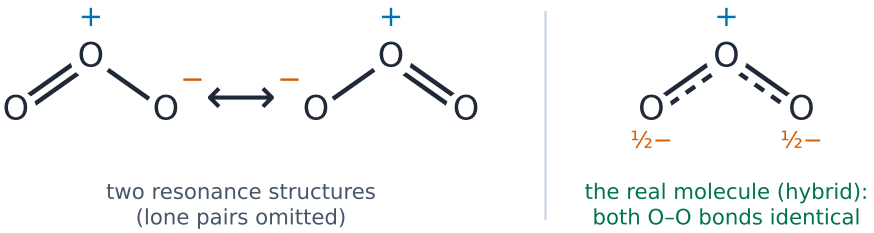
AHL: Coordination in transition-metal complexes

A ligand donates an electron pair to a central metal ion to form a coordination bond. For example, in $[Co(NH_3)_6]^{3+}$ six ammonia ligands donate one nitrogen lone pair each; draw donor arrows from N towards Co. Neutral NH_3 contributes no net ionic charge, so cobalt is +3 and the overall complex charge is +3. Six donor atoms give coordination number six and an octahedral arrangement in this example. The N–H bonds within each ligand remain ordinary covalent bonds. Do not confuse the number of ligands, their charge, coordination number and oxidation state; a ligand with two donor atoms can contribute two coordination bonds.

AHL: Resonance and delocalization

When one Lewis formula is not enough

Ozone, O_3, can be drawn as O = O − O or as O − O = O. One drawing predicts one short and one long bond. Experiments show both O–O bonds are the **same** length, 128 pm, between an O–O single bond (148 pm) and an O=O double bond (121 pm).



Ozone has two resonance structures; the real molecule is their hybrid

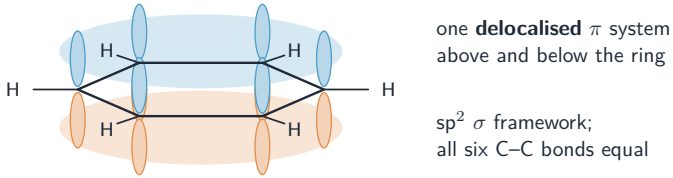
The real molecule is a single structure in between the two drawings. The drawings are **resonance structures** 共振结构, joined by a double-headed arrow. The electrons of the extra bond are **delocalized** over all three atoms.

- The carbonate ion, CO_3^{2-}, has three resonance structures. All three C–O bonds are equal, each with a **bond order** 键级 of 4/3 ≈ 1.33 (four shared pairs across three bonds).
- Other examples: NO_3^-, NO_2^-, SO_2 and the carboxylate ion, $RCOO^-$.

Delocalization spreads electrons over more atoms, and this lowers the energy: delocalized structures are more stable than any single resonance structure suggests.

Benzene

Benzene 苯, C_6H_6, is a flat ring of six carbon atoms. A structure with alternating single and double bonds (the Kekulé structure) does not match the evidence:



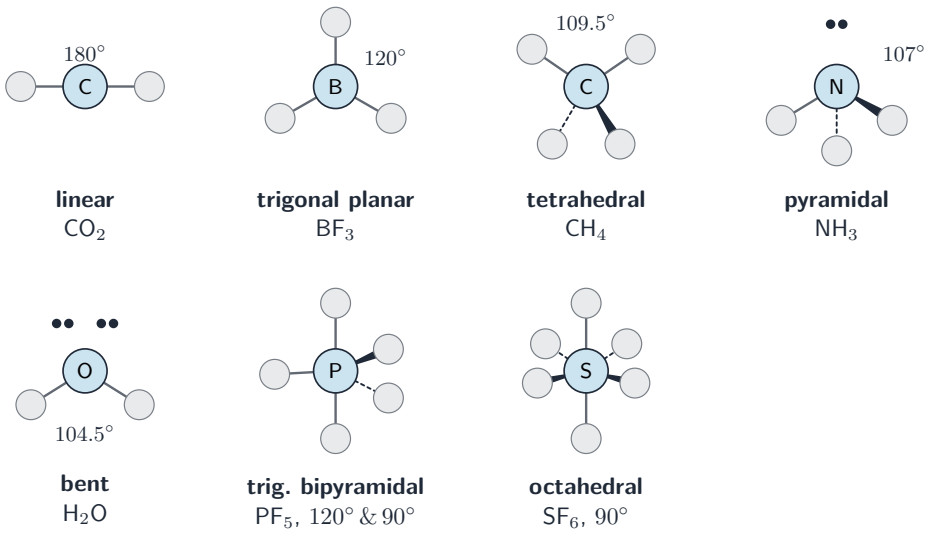
Benzene's bonding: an sp^2 σ framework makes the flat hexagon, while the p orbitals overlap into one delocalised π system above and below the ring

Evidence	Alternating C–C and C=C predicts	Benzene shows
bond lengths	three at 154 pm and three at 134 pm	six equal bonds of 140 pm
enthalpy of hydrogenation	three times cyclohexene: $3(-120) = -360$ kJ mol^{-1}	−208 kJ mol^{-1}, a 152 kJ mol^{-1} difference from this supplied localized comparison
reactions	addition, like alkenes (decolourizes bromine water)	substitution; keeps the ring
isomers of $C_6H_4Br_2$	two different 1,2-isomers	only one 1,2-isomer

Each carbon uses three electrons in sigma bonds (two C–C, one C–H). The six remaining p electrons form one delocalized ring of electron density above and below the plane. That is why benzene is drawn as a hexagon with a circle inside.

AHL: Expanded octets and formal charge

Five and six electron domains



The final two examples illustrate the additional five- and six-domain geometries.

Lewis formulas for some period-3 and heavier main-group species place more than eight electrons around the central atom, called an **expanded octet** 扩展八隅体. This is a Lewis-model description, not evidence that low-energy d orbitals expand the shell. Modern bonding analyses do not support the old d-orbital hybridization explanation; only sp, sp^2 and sp^3 hybridization are required here. VSEPR still works:

count domains, then lone pairs.

Domains	Lone pairs	Shape	Angles	Example
5	0	trigonal bipyramidal	90°, 120°, axial 180°	PCl_5
5	1	see-saw	below 90° and 120°; distorted axial pair below 180°	SF_4
5	2	T-shaped	near 90° and 180°, distorted	ClF_3
5	3	linear	180°	XeF_2, I_3^-
6	0	octahedral	90°, 180°	SF_6
6	1	square pyramidal	near 90°, distorted	BrF_5
6	2	square planar	90°, 180°	XeF_4

In the usual five-domain examples here, lone pairs prefer the **equatorial** positions (round the middle), where they have more room. With six, two lone pairs sit opposite each other.

Worked example, XeF_4: Xe has 8 valence electrons; four go into Xe–F bonds and four remain as two lone pairs. Six domains give an octahedral electron domain geometry; the lone pairs sit opposite, so the four F atoms form a **square planar** shape. The molecule is non-polar, because the four Xe–F dipoles cancel.

Formal charge

When you can draw more than one Lewis formula, **formal charge** 形式电荷 (FC) helps you choose. For each atom:

✓ O=C=O
FC: 0 0 0
preferred

O≡C−O
FC: +1 0 −1
charges further from zero

FC $= V - \frac{1}{2}B - L$
sum of FC = charge on species;
prefer FCs closest to zero

Formal charges choose between Lewis formulas for CO_2

$$\text{FC} = V - \tfrac{1}{2}B - L$$

where V is the number of valence electrons in the free atom, B the number of bonding (shared) electrons round it, and L the number of non-bonding (lone-pair) electrons. The formal charges add up to the charge on the species.

The preferred structure has formal charges **closest to zero**; if a negative formal charge is needed, it should sit on the most electronegative atom.

Worked example, CO_2:

- O = C = O: each O has $6 - \frac{1}{2}(4) - 4 = 0$; C has $4 - \frac{1}{2}(8) - 0 = 0$. All zero.
- O ≡ C − O: the triple-bonded O has $6 - 3 - 2 = +1$; C has 0; the single-bonded O has $6 - 1 - 6 = -1$.

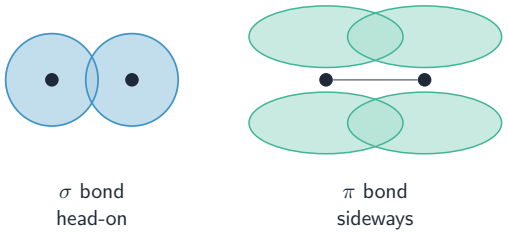
The first structure has all formal charges zero, so it is preferred, which matches the two equal C=O bonds found by experiment.

AHL: Sigma and pi bonds and hybridization

Two ways for orbitals to overlap

A covalent bond forms where atomic orbitals overlap.

- A **sigma bond** 西格玛键 (σ) forms by head-on overlap along the line between the nuclei. Every single bond is a sigma bond.
- A **pi bond** 派键 (π) forms by sideways overlap of parallel p orbitals, above and below that line. It is weaker than a sigma bond, because the overlap is smaller.



Sigma overlap lies on the axis between the nuclei; pi overlap lies above and below it

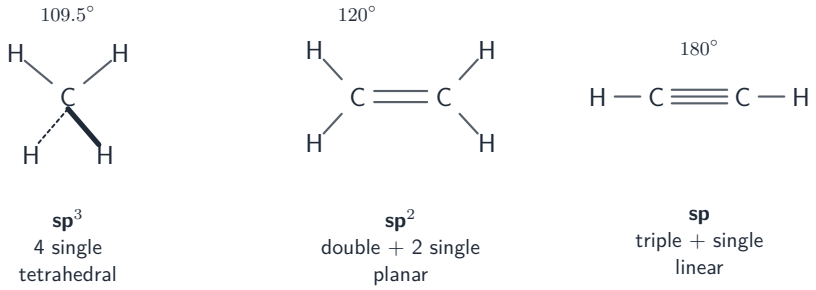
A double bond is one σ and one π; a triple bond is one σ and two π. This is why C=C (614) is less than twice C–C (346): the second bond is a weaker pi bond. Rotation about a double bond would break the pi overlap, so it does not happen at room temperature.

Ethene, $CH_2 = CH_2$, has five sigma bonds (four C–H, one C–C) and one pi bond.

Hybridization

Carbon's ground state, $2s^2\,2p^2$, has only two unpaired electrons, yet carbon forms four equal bonds in methane. **Hybridization** 杂化 explains this: atomic orbitals on one atom mix to form the same number of new, equal **hybrid orbitals** 杂化轨道 that point in the directions VSEPR predicts.

Hybridization	Orbitals mixed	Domains	Geometry	Example
sp^3	one s, three p	4	tetrahedral, 109.5°	CH_4; also N in NH_3, O in H_2O
sp^2	one s, two p	3	trigonal planar, 120°	each C in C_2H_4; C in benzene
sp	one s, one p	2	linear, 180°	each C in C_2H_2; C in CO_2



The number of electron domains tells you the hybridization

Hybrid orbitals form sigma bonds or hold lone pairs. The p orbitals left unhybridized form the pi bonds: one in sp^2 carbon, two in sp carbon. For the localized main-group examples represented by this model, infer the conventional hybridization from electron domains: 4 is sp^3, 3 is sp^2, 2 is sp.

Practice

1. Draw the Lewis formula of: (a) N_2, (b) HCN, (c) NH_4^+, showing the coordination bond.
2. State and explain which is shorter and stronger: the C–O bond in methanol or the C=O bond in methanal.
3. Predict the shape and bond angle of: (a) PH_3, (b) BCl_3, (c) H_2S, (d) CS_2.
4. Explain why CCl_4 is non-polar but $CHCl_3$ is polar.
5. Explain why diamond is hard and does not conduct electricity, but graphite is soft and conducts.
6. Put these in order of increasing boiling point and explain: CH_3OCH_3, C_2H_5OH, C_3H_8 (all have $M \approx 44$–46).
7. Explain why ethanol mixes with water but hexane does not.
8. In a chromatogram the solvent front is 9.0 cm from the start line. Spot X has moved 3.6 cm. Calculate its R_f.
9. A student predicts every AX_3E molecule has angle 107°. Explain why this goes beyond VSEPR and how a multiple bond can affect neighbouring angles.
10. An invented TLC sample and reference both have $R_f = 0.40$ on one plate. Does this prove identity or purity? State two conditions to control.
11. Compare water, ammonia and methoxymethane as hydrogen-bond donors and acceptors. Can methoxymethane interact with water by hydrogen bonding?
12. **AHL.** Draw two resonance structures of the nitrate ion and state the bond order of each N–O bond. Also calculate the formal charges on all atoms in one nitrate Lewis structure.
13. **AHL.** Predict the shape and bond angles of: (a) SF_4, (b) SF_6, (c) ICl_4^-.
14. **AHL.** For propene, $CH_2 = CH - CH_3$, count the sigma and pi bonds and state the hybridization of each carbon.

Worked answers.

1. (a) N ≡ N with one lone pair on each N. (b) H − C ≡ N with one lone pair on N. (c) N in the centre with four N–H bonds; one is drawn as an arrow from N to H; overall charge +1, shown with square brackets.
2. The C=O bond in methanal: two shared pairs pull the nuclei closer together and attract them more strongly than one.
3. (a) trigonal pyramidal, less than 109.5° (four domains, one lone pair). VSEPR predicts the pyramidal arrangement, not a universal 107°: the measured H–P–H angle in PH_3 is about 93.3°. (b) trigonal planar, 120°. (c) bent, less than 109.5° (two lone pairs). (d) linear, 180°.
4. Both are tetrahedral. In CCl_4 the four equal C–Cl dipoles cancel by symmetry. In $CHCl_3$ the C–H bond has a much smaller dipole, so the dipoles do not cancel and there is a net dipole moment.
5. In diamond every C forms four strong covalent bonds in a rigid 3D network, and all outer electrons are in bonds, so there are no mobile charged particles. In graphite each C bonds to three others in layers held by weak London forces, so layers slide; the fourth electron of each C is delocalized and moves along the layers.
6. C_3H_8 (−42 °C) < CH_3OCH_3 (−24 °C) < C_2H_5OH (78 °C). Similar masses give similar London forces. Methoxymethane is polar and adds dipole–dipole forces. Ethanol has an O–H group and forms hydrogen bonds, the strongest intermolecular force.
7. Ethanol forms hydrogen bonds with water molecules through its O–H group, so the new attractions replace the ones broken. Hexane is non-polar: water–hexane interactions include dispersion and dipole-induced dipole attraction, but mixing is not sufficiently favourable to overcome the overall free-energy cost under ordinary conditions.
8. $R_f = 3.6/9.0 = 0.40$.

9. VSEPR supports a trigonal-pyramidal shape for the four-domain AX_3E model, but not a fixed measured angle. NH_3 and PH_3 need not share an angle. A multiple-bond domain typically occupies more angular space than a single-bond domain and can compress neighbouring single-bond angles.
10. No. Distinct compounds can have the same ratio; unresolved components can overlap in one spot. Run authentic references alongside and seek a second solvent system or another analytical method. Control stationary phase, solvent composition and temperature; avoid overloaded spots. A ratio is condition-dependent and dimensionless.
11. Water has O–H donor groups and oxygen lone-pair acceptors; ammonia has N–H donors and a nitrogen lone-pair acceptor. Methoxymethane has an oxygen acceptor but lacks an N–H/O–H/F–H donor, so it does not self-hydrogen-bond in the usual course model. It can accept a hydrogen bond from water's O–H group.
12. **AHL.** N in the centre, one N=O and two N–O bonds (N carries +1, each single-bonded O −1, and the double-bonded O zero; total −1); the double bond can sit on any of the three O atoms. Bond order $4/3 \approx 1.33$ for every N–O bond. The central N formal charge is $5 - 0 - 4 = +1$; double-bonded O is $6 - 4 - 2 = 0$ and each single-bonded O is $6 - 6 - 1 = -1$. These sum to −1.
13. **AHL.** (a) see-saw (five domains, one equatorial lone pair), axial–equatorial below 90°, equatorial–equatorial below 120°, opposite axial below 180°. (b) octahedral, 90° and 180°. (c) square planar (six domains, two opposite lone pairs), 90° and 180°.
14. **AHL.** Eight sigma bonds (six C–H, two C–C) and one pi bond. The two carbons of the C=C are sp^2; the CH_3 carbon is sp^3.

Exam tips

- Define a covalent bond as the attraction between a **shared pair** of electrons and the **nuclei** of the bonded atoms.
- In VSEPR count **domains**, not bonds: a double bond is one domain. Then name the shape from the atoms only.
- Where lone pairs are present, explain how their greater repulsion affects bond angles; do not infer a lone pair from an angle alone.
- For molecular polarity, combine the actual bond dipoles with the geometry and state whether their vector sum cancels.
- Melting a simple molecular substance overcomes **intermolecular forces**; never write that it breaks covalent bonds.
- Hydrogen bonding needs H bonded **directly** to N, O or F; pure CH_3F has no N–H, O–H or F–H donor for the usual self-hydrogen-bonding comparison.
- For R_f, measure to the **centre** of the spot and from the start line, not from the bottom of the paper.

- **AHL.** Resonance structures are not switching between forms: there is one real structure with delocalized electrons.
- **AHL.** In five-domain shapes, lone pairs go in the **equatorial** positions.

The metallic model

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Structure 2.3, The metallic model, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: electron configurations and ionization energy from Structure 1.3, and the ionic and covalent models from Structures 2.1 and 2.2. You will compare melting points from the data booklet.

The metallic bond

Why can a copper wire bend and conduct?

A copper wire carries current when it is cold and when it is red hot. You can bend it, hammer it flat or pull it into a thinner wire, and it does not shatter. A typical ionic crystal does neither as a solid: it has no freely mobile ions and often fractures under a blow. Molten salts and aqueous solutions containing mobile ions can conduct. The **metallic model** 金属模型 explains both properties of metals with one picture.

Cations in a sea of electrons

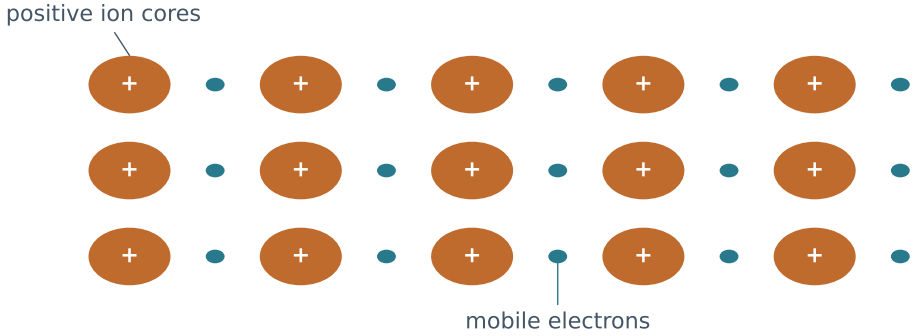
In the simple metallic model, outer electrons are shared throughout an extended solid rather than confined to individual atoms. Describe its positive ion cores and mobile electron density; do not imagine a collection of isolated aqueous ions. In a solid metal:



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

- positive ion cores, described as **cations** 阳离子 in the model, are packed in a **lattice** 晶格;
- the lost electrons are not attached to any one ion. They are **delocalized electrons** 离域电子, free to move through the whole structure, often called a "sea" of electrons.

The **metallic bond** 金属键 is the electrostatic attraction between a lattice of cations and the delocalized electrons.



Schematic monovalent-metal model: 15 positive cores and 15 delocalized electrons give zero net charge. Cores vibrate about lattice positions in the solid; the drawing is not to scale.

Three points a complete model explanation needs:

- There are **no anions** in a metal. The negative charge is carried by electrons.
- The attraction acts in every direction: the bonding is **non-directional** 无方向性的.
- Each ion is attracted to many electrons, and each electron to many ions, so there are no separate bonds between pairs of atoms.

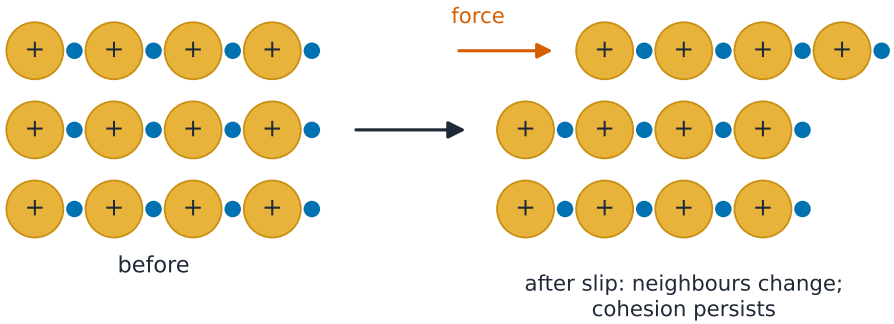
Properties of metals

Explaining each property

To explain any property, name the structure, the particles, the force and the mobile charge carriers.

Property	Explanation
electrical conductivity 导电性 in solid and liquid	delocalized electrons acquire a net drift under an applied potential difference; a molten metal also retains mobile electrons
thermal conductivity 导热性	delocalized electrons (and vibrating ions) pass kinetic energy quickly through the metal
malleability 延展性 and **ductility** 延性	slip can rearrange the positive cores while delocalized electron density maintains cohesion; defects, temperature and microstructure affect how readily this happens
high melting and boiling points (most metals)	strong attraction between many cations and the electron sea in a giant lattice
shiny (lustre)	delocalized electrons absorb and re-emit light

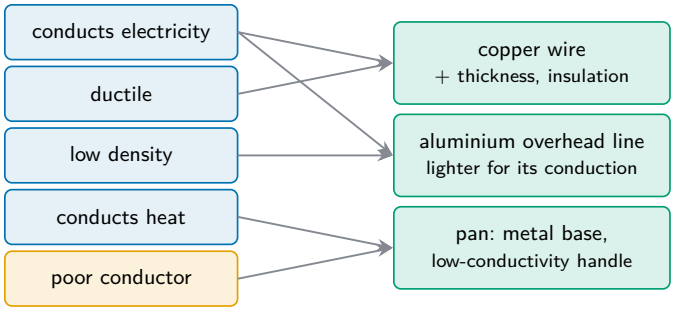
Malleable means it can be hammered into shape; ductile means it can be drawn into a wire.



Schematic slip: non-directional metallic attraction can maintain cohesion as cores change neighbours. Real deformation involves defects and does not leave every local interaction identical.

From a property to a useful design

Copper combines electronic conduction with ductility, so it can be drawn into wire. A wire also needs suitable thickness, insulation and mechanical strength; conductivity alone does not establish a safe cable design. Aluminium is useful for lightweight conductors because its low density can compensate for a lower conductivity than copper in a suitable design.



high melting point alone does not prove conduction or hardness

Designs combine properties

A metal cooking-pan base transfers energy quickly, while a low-conductivity handle limits transfer to a hand. Strong cohesion and the processing of a metal help it retain shape in use. These are separate properties: high melting point does not by itself prove high thermal conductivity or hardness.

Metals compared with ionic compounds

	Metal	Ionic compound
particles	cations and delocalized electrons	cations and anions
conducts when solid	yes, by electrons	no: ions are fixed
conducts when molten	yes, by electrons	yes, by ions
effect of a blow	layers slide, metal bends	like charges meet, crystal shatters

Notice the different charge carriers: always say **electrons** for a metal and **ions** for a molten ionic compound.

Strength of the metallic bond

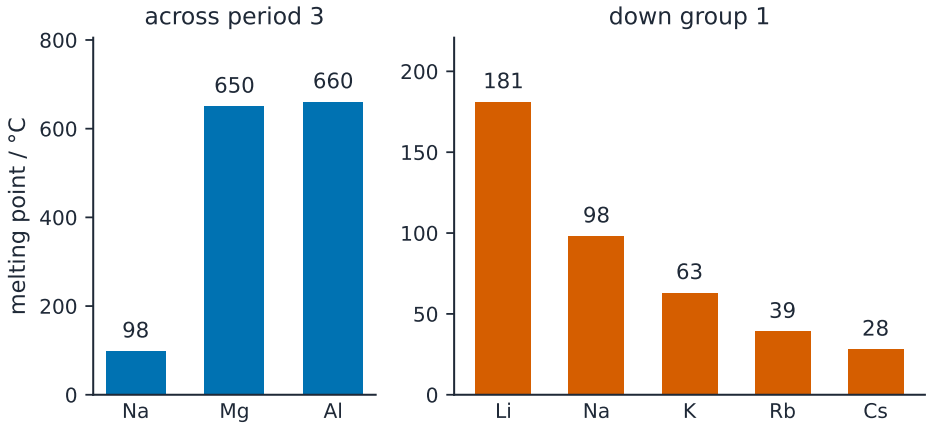
What makes the bond stronger

The metallic bond is stronger when the attraction between the cations and the electron sea is stronger. For simple comparisons of s- and p-block metals, two useful factors are:

1. **Charge of the cation and number of delocalized electrons.** A larger charge gives more delocalized electrons per ion and a stronger attraction.

2. **Radius of the cation.** A smaller ion lets the electrons come closer to the nucleus, so the attraction is stronger.

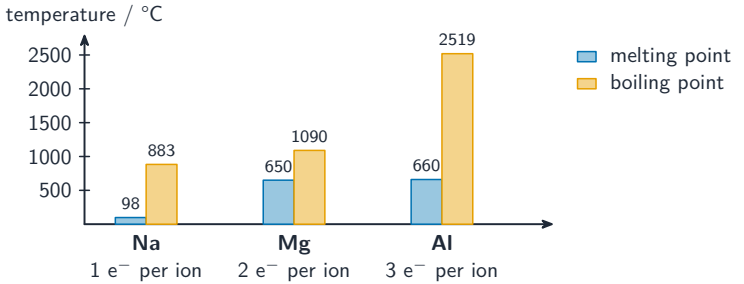
Stronger overall cohesion generally supports a higher melting or boiling temperature in a comparable series. The simple charge/radius model is qualitative: packing, electronic structure and the entropy change also matter, so it does not give an exact melting-point formula.



Supplied rounded melting points. The panels use different vertical scales: compare the labelled values, not bar heights across panels. Charge/electron density and size help explain these selected trends.

Across period 3: Na, Mg, Al

- Na^+ gives one delocalized electron per ion, Mg^{2+} two and Al^{3+} three.
- The simple model also compares smaller, more highly charged cores across Na, Mg and Al. Tabulated ionic radii for ions in compounds depend on coordination; they are not direct measurements of isolated Na^+, Mg^{2+} and Al^{3+} spheres inside these elemental metals.
- Both changes strengthen the attraction, so the melting point rises from 98 °C to 650 °C and 660 °C.



More delocalized electrons per ion: higher melting and boiling points

At approximately atmospheric pressure, supplied rounded boiling points show a stronger increase in this selected set: Na 883 °C, Mg 1090 °C, Al 2519 °C. Melting destroys long-range order while retaining strong interactions in a conducting liquid. Boiling separates the metal into vapour particles, predominantly neutral atoms for the simple model; it does not by itself produce a gas of bare cations and free electrons. Vaporization and ionization are different processes.

Down group 1: Li to Cs

Every group 1 metal gives one delocalized electron per ion. Down the group the cations get larger, so the delocalized electrons are further from each nucleus and the attraction is weaker. The melting point falls from 181 °C (Li) to 28 °C (Cs): this value is near a warm-room temperature. This observation is not an instruction to handle reactive caesium; use supplied data rather than a skin-contact demonstration.

Evidence and limits of a comparison

For a fair electrical comparison use approved solid samples with the same length and cross-sectional area, at controlled temperature and with clean contacts. At the same applied voltage, a larger current means lower resistance, but a thicker sample or a better contact can also increase current. Use a low-voltage instrument and avoid heating unknown metals or reactive group-1 samples. A simple bonding model identifies the charge carriers; it does not predict the exact resistance of a real wire.

sample A	1.5 V → 0.30 A ⇒ $R = 1.5/0.30 = 5.0\ \Omega$
sample B	1.5 V → 0.15 A ⇒ $R = 1.5/0.15 = 10\ \Omega$

A has half B's resistance here; that does not prove twice the delocalized electrons (invented data)

control: same length and cross-section, temperature, clean contacts, low voltage

A controlled resistance comparison (invented data)

Worked data example (invented). Equal-sized samples A and B at the same temperature give currents 0.30 A and 0.15 A at 1.5 V. Their resistances are $R_A = 1.5/0.30 = 5.0\ \Omega$ and $R_B = 1.5/0.15 = 10\ \Omega$. A has half B's resistance in this controlled comparison. It does not follow that A has exactly twice as many delocalized electrons: carrier mobility and scattering can differ.

Worked example

Explain why magnesium has a higher melting point than sodium.

- **Structure:** both are giant metallic lattices; melting disrupts the ordered solid while metallic interactions persist in the liquid.
- **Ions:** Mg^{2+} has a higher charge than Na^+ and is smaller.
- **Electrons:** magnesium has two delocalized electrons per atom, sodium only one.
- **Conclusion:** the attraction between cations and delocalized electrons is stronger in magnesium, so more energy is needed to melt it.

AHL: Transition elements

Delocalized d electrons

The **transition elements** 过渡元素 include elements whose atoms or cations have an incomplete d subshell; the first transition series involves 3d states. The 4s and 3d sublevels are very close in energy, so both the 4s and some of the 3d electrons can become delocalized. Participation of d electrons can increase cohesion compared with a simple outer-s-electron-only model. Avoid assigning an arbitrary aqueous ionic charge to a pure transition metal or assuming every d electron makes an identical contribution.



Transition metals form coloured compounds: each of these solutions contains a different transition-metal ion

Metal	Block	Delocalized electrons per atom (approx.)	Melting point / °C
potassium	s	1	63
calcium	s	2	842
iron	d	more than 2 (4s and 3d)	1538
chromium	d	more than 2 (4s and 3d)	1907

So transition metals have:

- generally **high melting points** and high boiling points compared with many s-block metals, with important variations across the series;
- high **density** 密度, because the ions are small and heavy and pack closely;
- high **electrical conductivity**, because mobile electronic states carry charge; the magnitude also depends on scattering, not just an electron count;
- great strength and hardness, which is why iron, titanium and their alloys are used for structures.

In zinc the filled 3d states contribute less to metallic cohesion in this simple comparison: it melts at only 420 °C, much lower than its neighbours.

Practice

1. Define the metallic bond.
2. Explain why solid copper conducts electricity but solid copper(II) chloride does not.
3. Explain why a metal bends when hammered, but a crystal of sodium chloride shatters.
4. Explain why aluminium has a higher boiling point than sodium.
5. Explain why the melting point of the group 1 metals decreases from lithium to caesium.
6. Predict, with a reason, which has the higher melting point: potassium or calcium.
7. Explain why molten magnesium can still conduct even though its crystal lattice has lost long-range order. Does melting remove all metallic interactions?
8. Choose one useful metal property for each: (a) a drawn copper wire, (b) a pan base, (c) a shaped metal sheet. Explain with the model and give one additional practical constraint.
9. In the invented equal-size comparison above, A carries 0.30 A and B 0.15 A at 1.5 V. Calculate both resistances and their ratio. Why is the current ratio not a direct count of conduction electrons?
10. A student says boiling aluminium produces $Al^{3+}(g)$ and three electrons per atom. Correct the physical interpretation and distinguish vaporization from ionization.

11. The Na/Mg/Al chart uses a 0–800°C scale while a separate Li–Cs chart uses 0–200°C. May bar heights across the panels be compared directly? Explain why Mg and Al's similar melting points do not prove identical bonding.
12. **AHL.** Explain why iron has a much higher melting point than calcium.
13. **AHL.** Explain why an increasing count of d electrons does not establish a monotonic melting-point or conductivity trend across every transition metal.
14. **AHL.** In an invented comparison, wires X and Y have the same conduction-electron density. X has the larger measured conductivity. Does this contradict mobile-electron conduction? Explain without inventing different ionic charges.

Worked answers.

1. The electrostatic attraction between a lattice of positive ions (cations) and delocalized electrons.
2. Copper contains delocalized electrons that can move through the lattice and carry charge. In solid copper(II) chloride the ions are held in fixed positions and there are no mobile electrons, so no charge can move.
3. In a metal the bonding is non-directional: layers of cations slide and the delocalized electrons move with them, so the attraction holds the new arrangement. In NaCl a shift brings ions of the same charge next to each other, they repel and the crystal splits.
4. Al^{3+} has a higher charge and a smaller radius than Na^+, and aluminium has three delocalized electrons per atom against one. The attraction between cations and delocalized electrons is stronger, so generally more energy is needed to separate neutral vapour particles from the condensed metal. Do not describe boiling as producing gaseous Al^{3+} or Na^+ ions.
5. Each ion gives one delocalized electron, but the ions get larger down the group. The delocalized electrons are further from the nucleus, the attraction is weaker, and less energy is needed to melt the metal.
6. Calcium: Ca^{2+} has a higher charge and is smaller than K^+, and gives two delocalized electrons per atom, so its metallic bond is stronger (842 °C against 63 °C).
7. The liquid still has delocalized mobile electrons, which acquire net drift under an applied potential difference. Melting changes long-range positional order; it does not eliminate metallic cohesion or require electrons to become localized on fixed atoms.
8. (a) Ductility allows wire drawing and delocalized electrons carry current; choose thickness, insulation and strength for the use. (b) Mobile electrons and lattice vibrations transfer energy through the pan base; also consider chemical stability and a suitable handle. (c) Malleability permits shaping while attraction maintains cohesion; thickness and microstructure affect fracture or springback. A single property is not a complete design specification.
9. $R_A = 1.5/0.30 = 5.0\ \Omega$; $R_B = 1.5/0.15 = 10\ \Omega$; $R_A/R_B = 0.50$. Carrier mobility/scattering, contact resistance and sample geometry can affect current. Only a controlled comparison supports a material-resistance inference; it still does not identify an exact carrier-number ratio.
10. Ordinary vaporization forms metal vapour, predominantly neutral atoms in the simple model. Producing gaseous Al^{3+} additionally requires successive ionizations and a separate energy input. Strong metallic bonding does not imply permanent isolated +3 ions remain after boiling.
11. No: different vertical scales give different temperatures per drawn millimetre. Read the labelled temperatures or replot on a common scale. The charge/electron-density model predicts a qualitative tendency; crystal structure, electronic contributions and entropy of melting also matter. Melting temperature is not a unique measurement of bond strength.
12. **AHL.** Iron is a transition element. Its 4s and 3d electrons are close in energy, so 3d electrons are delocalized as well as 4s ones. Participation of d electrons helps strengthen metallic cohesion compared with calcium's simpler outer-s model. This is not a claim that iron metal consists of freely separated Fe^{3+} ions.
13. **AHL.** d states participate in bonding, but filling, orbital overlap and crystal structure vary across the series. Melting also depends on the change in entropy; conductivity depends on mobile states and scattering. The simple model supports the generally strong cohesion of many transition metals, not a one-electron-per-degree or universal monotonic rule.
14. **AHL.** No. Mobile electrons remain the charge carriers, but their mobility and scattering can differ between materials and conditions. Equal carrier density does not force equal conductivity. Ionic charges assigned to separate aqueous compounds cannot simply be transferred to a pure metal to explain the result.

Exam tips

- Define the metallic bond as an attraction between **cations** and **delocalized electrons**; never mention anions or "molecules".
- Metals conduct by **delocalized electrons** in both solid and liquid states; molten ionic compounds conduct by **ions**.
- For malleability, say that layers **slide** and the **non-directional** bonding is kept.
- Compare metallic bond strength with **charge** (number of delocalized electrons) and **ionic radius**, and link it to the energy needed.
- **AHL.** For transition metals, say that **d electrons** are delocalized too.

Structure 2.4 · From models to materials

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

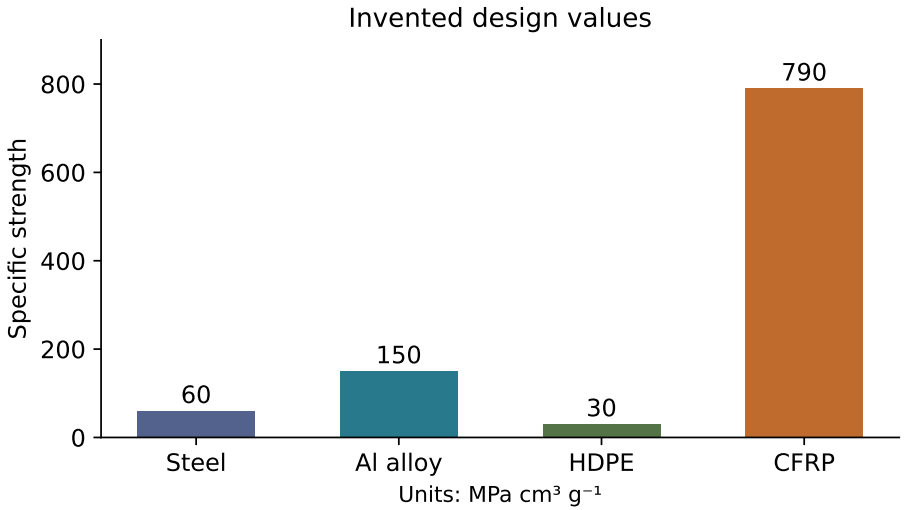
This handout teaches Structure 2.4, From models to materials, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: the ionic, covalent and metallic models from Structures 2.1 to 2.3, and electronegativity values from the data booklet. You will draw structural formulas of simple organic molecules.

Bonding is a continuum

Why is a bicycle frame made of carbon fibre?

A racing bicycle frame must be strong, stiff and light. Steel is strong but heavy. Aluminium alloy is lighter. Carbon-fibre reinforced polymer combines stiff, strong graphitic carbon fibres with a polymer matrix that transfers load and protects the fibres. It can provide high strength per unit mass in specified loading directions. Choosing a **material** 材料 means comparing bonding, structure, processing, direction of loading and practical constraints, rather than naming one universally best substance.



Invented design data, not material specifications: strength/density pairs are steel 480 MPa/8.0 g cm^{-3}, aluminium alloy 405/2.7, HDPE 28.5/0.95 and CFRP 1264/1.6. The ratios are 60, 150, 30 and 790 MPa cm^3 g^{-1}. Grade, fibre direction, stiffness, toughness, cost and damage tolerance also matter.

Three models, one continuum

Ionic, covalent and metallic bonding are models: ideal cases. Real substances often sit between them.

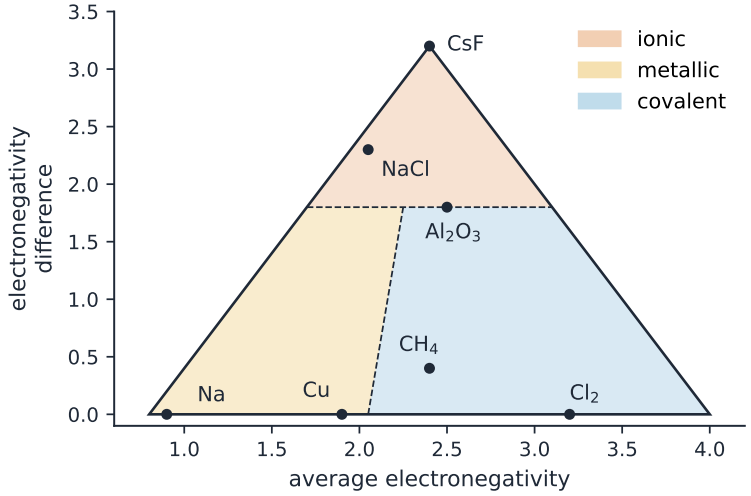
- **Ionic** character tends to increase with a large electronegativity difference; the ionic bond itself is attraction between oppositely charged ions, not the electron-transfer event.
- **Covalent** character describes shared electron density and is often associated with two relatively electronegative elements.
- **Metallic** character involves delocalized electron density among positive cores and is associated with relatively electropositive elements.

Most bonds have some character of more than one type. In aluminium oxide the bonding is mainly ionic, but the small, highly charged Al^{3+} ion pulls the electrons of the oxide ion towards it, giving the bond some covalent character.

The bonding triangle

The **bonding triangle** 键型三角形 (the van Arkel–Ketelaar triangle in the data booklet) places a binary substance by two numbers:

- the **average electronegativity** of the two elements on the x-axis;
- the **electronegativity difference** on the y-axis.



Illustrative approximate regions using consistently rounded electronegativities; the elemental points are model references. Use the supplied booklet diagram for a specified binary compound, without treating a drawn boundary as a universal cutoff.

Worked example: placing a compound

Use the triangle to predict the bonding in magnesium oxide. Electronegativities: Mg 1.3, O 3.4.

- Average: $(1.3 + 3.4)/2 = 2.35$.
- Difference: $3.4 - 1.3 = 2.1$.
- The point (2.35, 2.1) is in the ionic region, so MgO is predicted to be mainly ionic: generally high melting point and ionic conduction when molten; a solution would conduct if enough ions dissolved. This prediction does not guarantee high water solubility.

For silicon dioxide (Si 1.9, O 3.4): average 2.65, difference 1.5. The point lies in the covalent region, which fits its giant covalent structure.

From position to properties

Region	Typical properties
ionic (top)	high melting point, brittle, conducts only when molten or dissolved, solubility varies
covalent (bottom right)	molecular: often low melting/poor conduction; network: high disruption energy, with conductivity exceptions such as graphite and silicon
metallic (bottom left)	conducts when solid, malleable, shiny, most melt high

The triangle predicts bonding; it does not decide between a molecular and a network covalent structure. Use other evidence, such as the melting point, for that.

Composites combine structures at a larger scale

Composites retain distinct components and transfer load across interfaces. In CFRP, graphitic fibres mainly carry tension along their length; a polymer matrix transfers load and protects fibres. Layer direction changes laminate behaviour; specific strength does not fix stiffness, toughness or damage tolerance.

In reinforced concrete, the cement-based matrix and aggregate support compression, while steel carries tension and limits cracking. Interface bonding transfers forces. The combination has ionic/covalent components and metallic steel, rather than one new bond type.

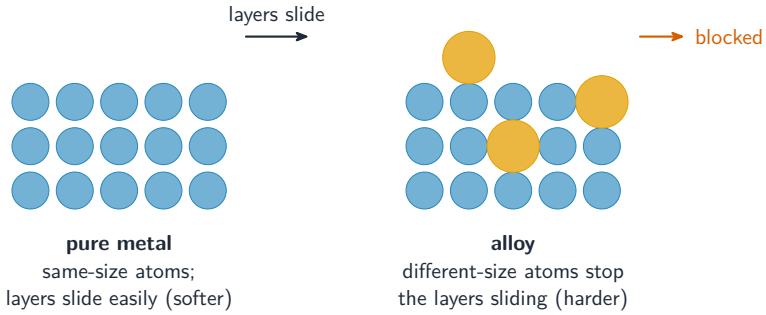
Alloys

Metals mixed with other elements

An **alloy** 合金 is a mixture of a metal with other metals, or with a non-metal such as carbon. Many alloys are made by combining molten components and cooling, but other processing routes also exist. They still have metallic bonding: cations of different elements in a sea of delocalized electrons.

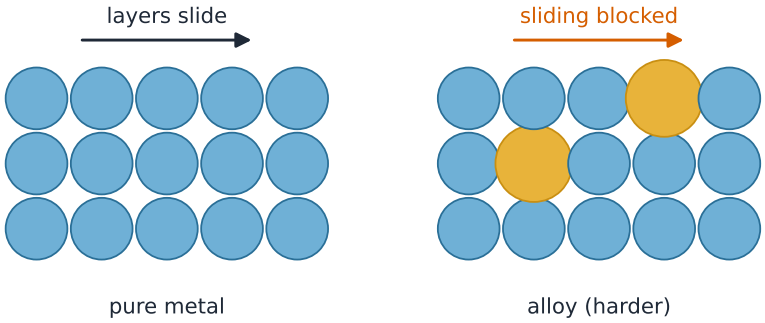


Aircraft bodies are built from aluminium alloys: still light, but much stronger than the pure metal



Different-sized atoms in an alloy stop the layers sliding, so it is harder

Pure metals are often too soft. In a pure metal all the cations are the same size, so the layers slide easily. In an alloy, atoms of a different size distort the regular layers. Slip can become more difficult, making many alloys **harder** or stronger than the corresponding pure metal. Properties depend on composition, phases and heat treatment; alloying does not guarantee an improvement in every property.



Substitutional-alloy cartoon: differently sized atoms can hinder slip. Carbon in steel can occupy interstitial sites, and steel properties also depend on phases and processing; this is not a literal oversized-carbon drawing.

Alloy	Composition	Improved property	Use
steel	iron with up to about 2% carbon	harder and stronger than iron	buildings, bridges
stainless steel	iron with sufficient chromium; many grades also contain nickel	resists corrosion	cutlery, medical tools
brass	copper and zinc	harder than copper, resists corrosion	taps, musical instruments
bronze	copper and tin	harder, resists corrosion	statues, bearings
duralumin	aluminium with copper and magnesium	stronger, still light	aircraft bodies

Alloys can also change other properties: some melt at lower temperatures than any of their parts (solder), and some resist corrosion because the added element forms a protective oxide layer (chromium in stainless steel).

Polymers

Long chains from small units

A **polymer** 聚合物 consists of macromolecules with many repeating structural units. They may form linear or branched chains, or cross-linked networks. The small molecules that join are **monomers** 单体, and the part of the chain that repeats is the **repeating unit** 重复单元.

Polymers can be natural, such as starch, cellulose, proteins and DNA, or synthetic, such as poly(ethene) and nylon. Most plastics are synthetic polymers.

Properties of plastics

The properties of a plastic come from its long chains:



Most plastics are non-biodegradable, so waste plastic collects on beaches and in the oceans for hundreds of years

- For uncross-linked chains, intermolecular interactions, chain entanglement and crystallinity affect properties. Increasing chain length can change strength and softening behaviour, but there is no universal linear relation between chain length and melting temperature.
- Relatively little-branched HDPE chains can pack more regularly and have greater crystallinity; more-branched LDPE chains pack less regularly, so LDPE is softer and more flexible.
- Many common plastics have low density and useful chemical resistance and are electrical insulators. Additives, structure, processing and specialized conducting polymers prevent these from being universal properties of every plastic.

Many common plastics are not readily **biodegradable** 可生物降解的 in ordinary disposal environments. Persistence depends on polymer, additives, thickness and con-

ditions; fragmentation is not the same as complete biodegradation. Combustion of carbon-containing plastics can release CO_2; PVC can also release corrosive hydrogen chloride. A resin identification code helps identify a polymer family but does not guarantee local collection or successful recycling.

Thermoplastic and thermoset behaviour

A thermoplastic can soften on heating enough for chains to move and can often be reshaped. A thermoset contains a covalently cross-linked network: it does not simply melt into freely sliding separate chains and commonly degrades on sufficiently strong heating. Distinguish reversible softening from chemical decomposition. Neither behaviour by itself guarantees easy or environmentally favourable recycling.

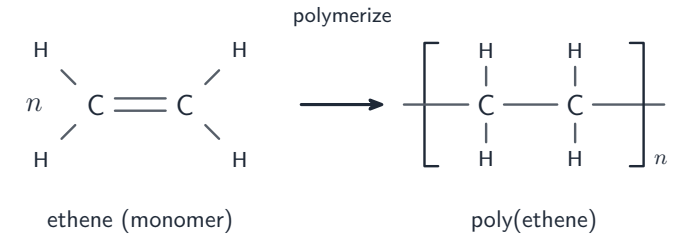
Addition polymers

Joining alkenes

In **addition polymerization** 加成聚合 monomers with a C=C double bond join together. The pi bond in each double bond breaks, and the electrons form new single bonds to the neighbouring monomers. No other product forms: every atom of the monomers ends up in the polymer.



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



The double bond opens; the repeating unit has the same atoms as the monomer, joined by single bonds

To draw the repeating unit from a monomer:

1. Draw the two carbons of the C=C with a **single** bond between them.
2. Keep every group that was attached to those carbons in the same place.
3. Add a continuation bond on each side, through square brackets, and write n after the bracket.

Monomer	Formula	Polymer	Repeating unit
ethene	$CH_2=CH_2$	poly(ethene)	$-CH_2-CH_2-$
propene	$CH_2=CHCH_3$	poly(propene)	$-CH_2-CH(CH_3)-$
chloroethene	$CH_2=CHCl$	poly(chloroethene), PVC	$-CH_2-CHCl-$
tetrafluoroethene	$CF_2=CF_2$	PTFE (Teflon)	$-CF_2-CF_2-$

To go backwards from a polymer to its monomer, find the two-carbon repeating unit and put a double bond between those two carbons.

Note that the side group (such as CH_3 or Cl) hangs **off** the main chain; it is never part of the chain itself.

AHL: Condensation polymers

Joining two functional groups

In **condensation polymerization** 缩合聚合 each new bond forms between two functional groups, and a small molecule, usually water or hydrogen chloride, is released. For the simple linear examples here, monomers have two reactive functional groups so a chain can grow in both directions. A hydroxycarboxylic acid can supply both required kinds of group in one molecule; monomers with more reactive sites can produce branching or cross-linking.



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)

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)

Every new ester or amide link releases one small molecule

- **Polyesters** 聚酯 form from a dicarboxylic acid and a diol. Each link is an **ester link**, −COO−. Example: PET, from benzene-1,4-dicarboxylic acid and ethane-1,2-diol, used for drinks bottles and polyester fibres.
- **Polyamides** 聚酰胺 form from a dicarboxylic acid (or a diacyl chloride) and a diamine. Each link is an **amide link**, −CONH−. Examples: nylon-6,6 from hexanedioic acid and hexane-1,6-diamine; Kevlar, whose flat chains form many hydrogen bonds, which makes it strong enough for body armour.
- With a diacyl chloride, $\mathrm{Cl-C(=O)-R-C(=O)-Cl}$, the small molecule released is HCl instead of water.

Draw and reverse a condensation repeating unit

For a diol HO–R–OH and a dicarboxylic acid HOOC–R′–COOH, a polyester repeating unit can be written $[-\mathrm{O-R-O-C(=O)-R'-C(=O)}-]_n$. Track each carbonyl carbon and oxygen; put continuation bonds through the brackets. For a diamine H_2N–R–NH_2, replace the two diol oxygen positions by NH to obtain a polyamide unit. To infer monomers, cut each ester or amide linkage and restore the relevant acid/alcohol/amine end groups for the stated synthesis route.

A single hydroxyacid HO–R–COOH can form a polyester with repeating unit $[-\mathrm{O-R-C(=O)}-]_n$. For a finite, unbranched chain formed without cyclization, joining m separate monomer molecules into one connected chain creates $m-1$ inter-monomer links. Thus ten diol molecules plus ten diacid molecules can give one chain with 19 links and 19 water molecules lost in this ideal acid/alcohol condensation. Do not automatically use "one water per repeating unit": a repeat unit and a newly formed linkage are different counts, and finite end groups matter.

Biological condensation polymers

The following are formal condensation/hydrolysis relationships between structures, rather than complete cellular synthesis mechanisms:

proteins	**polysaccharides**	**nucleic acids**
amino acids	glucose residues	nucleotides
↓	↓	↓
amide (peptide) links	glycosidic links	phosphodiester links

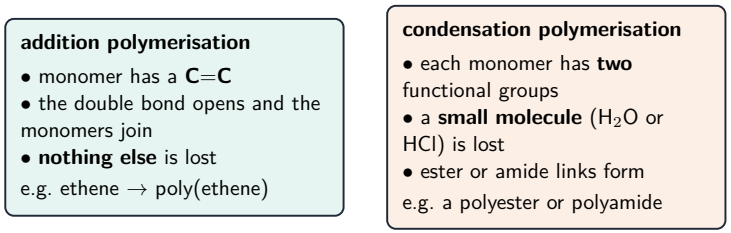
formal relationship: monomers − H_2O → polymer; hydrolysis adds water back
cells actually use activated precursors (e.g. nucleotide triphosphates)

Three biological condensation polymers and their links

- **Proteins** are polyamides of amino-acid residues linked through amide (peptide) bonds, corresponding to formal loss of water between amino acid groups. Cellular synthesis uses activated precursors.
- **Polysaccharides**, such as starch and cellulose, contain glucose residues joined through glycosidic links; the structural relationship corresponds to formal loss of water. Cellular synthesis uses activated sugar precursors.
- **Nucleic acids** (DNA and RNA) contain nucleotide units linked through phosphodiester bonds and are often represented by a formal condensation relationship. Actual cellular chain extension uses activated nucleotide triphosphates and releases pyrophosphate; "loss of water" is not the literal product of that enzymatic synthesis step (primary study of DNA polymerase chemistry).

■ Addition against condensation

	Alkene addition examples	Polyester/polyamide examples
monomer	contains C=C	bifunctional monomer(s) for linear chains
other product	none	a small molecule (H_2O or HCl)
main chain	C–C bonds only	contains ester or amide links
breaking down	very slow; not hydrolysed	ester/amide links may be hydrolysed under suitable conditions; this does not establish rapid biodegradation



The two kinds of polymerisation: addition opens a C=C and loses nothing; condensation joins two-group monomers and loses a small molecule

Hydrolysis cleaves susceptible links using water; partial cleavage gives shorter chains or fragments, while sufficiently complete cleavage under suitable conditions can yield the corresponding monomer-derived species. This is how the body digests proteins and starch, and how some polyesters can be chemically recycled.

Practice

1. Electronegativities: Na 0.9, Cl 3.2, C 2.6, H 2.2, Cu 1.9, Zn 1.6. (a) Plot NaCl and (b) CH_4 using both triangle coordinates. (c) Explain why a brass sample's metallic bonding does not make "CuZn" a fixed molecular formula for every brass composition.
2. Explain why aluminium oxide is described as ionic with some covalent character.
3. Explain why steel is harder than pure iron.
4. Draw the repeating unit of poly(propene), and the monomer of a polymer with repeating unit $-CH_2-CH(CN)-$.
5. State two properties that make poly(ethene) useful for packaging and one environmental problem it causes.
6. Explain why HDPE is stronger and denser than LDPE.
7. For the invented CFRP data, strength is 1264 MPa and density 1.6 g cm^{-3}. Calculate specific strength and explain why this is not proof of the best bicycle frame in every loading direction.
8. Explain how steel reinforcement and a concrete matrix can supply complementary mechanical properties. Is this one new chemical bond type?
9. Compare the response to heating of an uncross-linked thermoplastic and a heavily cross-linked thermoset. Distinguish softening, melting and decomposition.
10. Draw an addition repeating unit from $CH_2{=}CCl_2$, keeping every substituent and showing continuation bonds. Is any small molecule lost in the ideal propagation model?
11. A package has a resin identification code and breaks into smaller fragments outdoors. Does either observation prove complete biodegradation or local recyclability? Explain.
12. **AHL.** Name the two monomers needed to make nylon-6,6, state the link formed and name the other product.
13. **AHL.** Give two differences between alkene addition polymerization and the linear polyester/polyamide condensation examples.
14. **AHL.** Ten diol and ten dicarboxylic-acid molecules form one finite unbranched polyester chain without cyclization. How many links and water molecules are formed? Explain why hydrolysability alone does not prove rapid environmental biodegradation.

Worked answers.

1. (a) average 2.05, difference 2.3: ionic. (b) average 2.4, difference 0.4: covalent. (c) Brass is a Cu–Zn alloy with variable composition and metallic bonding, not a collection of CuZn molecules. The two elemental electronegativities alone do not specify its composition or phase structure.
2. The electronegativity difference (Al 1.6, O 3.4: difference 1.8) is on the boundary of the ionic region. The small Al^{3+} ion with a high charge distorts the electron cloud of O^{2-}, pulling electron density between the ions, so the bond has some covalent character.
3. Small carbon atoms can occupy interstitial positions in iron-based structures and affect slip; phase composition and heat treatment also matter. Steel is not simply a row of oversized carbon atoms replacing iron. These mechanisms can increase hardness or strength, with trade-offs in ductility depending on the steel.
4. Poly(propene): $-CH_2-CH(CH_3)-$ in square brackets with continuation bonds and n. The monomer is $CH_2=CHCN$ (propenenitrile).
5. Any two of: light, cheap, flexible, waterproof, unreactive, easy to shape. Problem: many grades resist biodegradation under ordinary disposal conditions and can per-

sist or fragment; burning carbon-containing plastic can release CO_2. No universal lifetime follows from the polymer name alone.

6. HDPE typically has less branching than LDPE, so chains can pack more regularly and crystallinity is greater. There is more contact between chains, so the London forces are stronger and more mass fits in the same volume.
7. Specific strength = $1264/1.6 = 790\ \mathrm{MPa\,cm^3\,g^{-1}}$. These are invented example values. Fibre orientation, grade, stiffness, toughness, damage tolerance, joints and manufacturing also affect frame performance. A high strength/density ratio does not establish all those properties.
8. The concrete matrix supports compression; steel reinforcement helps carry tension and limit crack opening, with load transferred at the interface. The composite combines existing structures and interactions on a larger scale, rather than creating one universal new bond type.
9. A thermoplastic can soften as segmental/chain motion becomes easier, and crystalline regions may melt. A heavily cross-linked thermoset retains a connected covalent network rather than becoming a liquid of separate chains; sufficient heating can decompose it. Reversible softening is not the same process as breaking the polymer chemically.
10. The repeat is $[-CH_2-CCl_2-]_n$, with the left and right continuation bonds passing through brackets. Both Cl substituents stay on the second backbone carbon. The ideal alkene addition model loses no small molecule; initiator/end-group details are separate from the repeat-unit drawing.
11. No. A code identifies a resin family but does not promise a local collection/reprocessing route. Smaller fragments may still be polymer; complete biodegradation requires suitable biological conversion under specified conditions. Polymer chemistry, additives and the actual disposal environment matter.
12. **AHL.** Hexanedioic acid and hexane-1,6-diamine. An amide link, −CONH−, forms and water is released.
13. **AHL.** Any two: alkene addition uses C=C monomers and retains all repeat atoms without a small product; these linear condensations use bifunctional monomers and release H_2O or HCl; their backbones contain hydrolysable ester or amide links, whereas the alkene-addition examples have C–C backbones.
14. **AHL.** 20 molecules − 1 = 19 joins: hence 19 ester links and 19 H_2O for the stated finite, non-cyclic acid/alcohol route. Hydrolysis may need suitable pH, temperature or catalysts; biological access and morphology also affect degradation, so hydrolysable does not imply rapidly biodegradable.

Exam tips

- Plot both electronegativity coordinates; boundaries are approximate.
- Explain alloy slip using the actual structure. Retain substituents and bracket-crossing continuation bonds in addition repeats.
- **AHL.** Identify condensation links/products and count finite-chain joins before water molecules.

Structure 3.1 · The periodic table: classification of elements

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

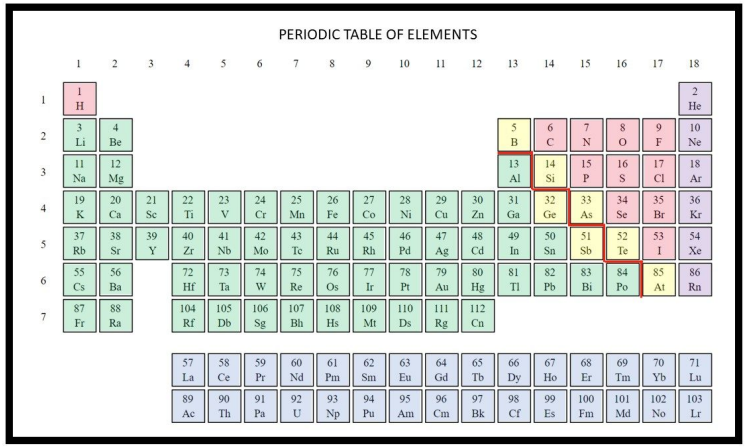
This handout teaches Structure 3.1, The periodic table: classification of elements, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: electron configurations and ionization energy from Structure 1.3, and ionic and covalent bonding from Structures 2.1 and 2.2. You will use the periodic table, ionic radii and electronegativity values from the data booklet.

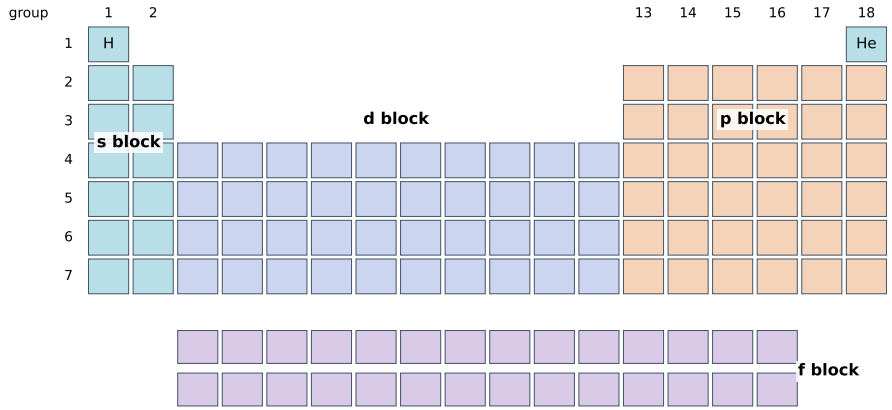
Organizing the periodic table

One table, many predictions

In 1869 Dmitri Mendeleev arranged the known elements in order of atomic mass and left gaps where the pattern said an element should be. He predicted the properties of "eka-silicon", and germanium, found in 1886, matched them closely. The **periodic table** 元素周期表 works because the properties of elements repeat in a regular way: **periodicity** 周期性.



A display periodic table with a sample of each element: patterns repeat across each period

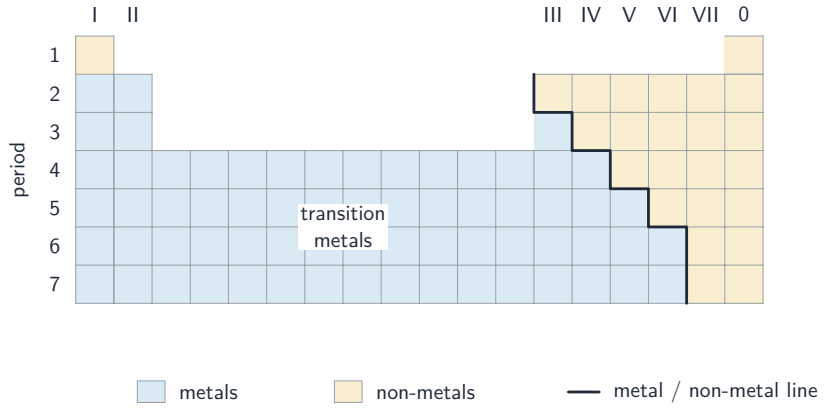


He: group 18, configuration $1s^2$; detached f rows are schematic

Helium has an s configuration but noble-gas placement. Detached f rows are schematic; no unique group-3 boundary is implied.

Periods, groups and blocks

The modern table orders the elements by atomic number Z.



Groups are the columns and periods are the rows; metals lie to the left of the staircase, non-metals to the right

- A **period** 周期 is a horizontal row. The period number is the number of the outer energy level: sodium, $[Ne]\,3s^1$, is in period 3.
- A **group** 族 is a vertical column, numbered 1 to 18. Main-group elements in a group usually have related outer configurations and chemical properties. For groups 1 and 2 the usual outer-electron count equals the group number; for groups

13 to 18 it is the group number minus 10, except helium, which has two. Hydrogen is not an alkali metal, and d-block chemistry cannot be predicted by a main-group outer-electron rule alone.

- A **block** 区 is named after the characteristic sublevel being filled: s (groups 1 and 2, plus helium by configuration), p (groups 13 to 18 except helium), d (the central ten columns) and f (the detached inner-transition rows). The printed position of helium does not change its $1s^2$ configuration.

Worked example: chlorine is $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$. The outer level is $n = 3$, so period 3; the last electron enters a p sublevel, so p block; seven outer electrons, so group 17.

Recovering configurations from position

Up to krypton, use the preceding noble-gas core and fill the intervening sublevels. Bromine is period 4, group 17: $[\mathrm{Ar}]\,3d^{10}\,4s^2\,4p^5$, with $18 + 10 + 2 + 5 = 35$ electrons. The 3d sublevel fills before 4p. For the first d row, the starting pattern is $[\mathrm{Ar}]\,3d^n\,4s^2$, with Cr ($3d^5 4s^1$) and Cu ($3d^{10} 4s^1$) exceptions. Period 4 includes filling 3d; the sublevel's first number alone does not specify the period.

Metals, metalloids and non-metals

Metals are on the left and in the middle of the table; non-metals are on the right. A diagonal band of **metalloids** 准金属 (B, Si, Ge, As, Sb, Te) separates them. Metalloids have some properties of both: silicon looks shiny but is brittle, and it is a semiconductor.

Some groups have names: group 1 the **alkali metals** 碱金属, group 2 the alkaline earth metals, group 17 the **halogens** 卤素 and group 18 the noble gases.

Periodic trends

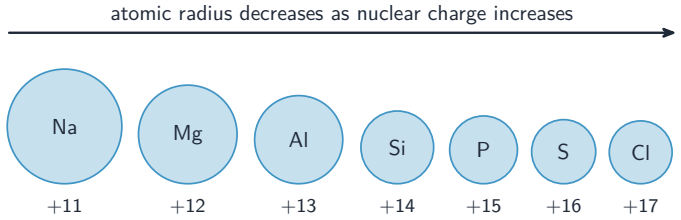
Attraction, shielding and distance

Explain broad trends using attraction, shielding and distance; use configurations for local exceptions:

- **nuclear charge** 核电荷: more protons pull the electrons more strongly;
- **shielding** 屏蔽: inner electrons repel the outer electrons and reduce the pull they feel.

Across a main-group period, nuclear charge rises while electrons enter the same main level: similar inner shielding gives stronger attraction overall. Down a main group, outer electrons occupy a higher principal level; greater distance and shielding usually outweigh the larger nuclear charge. These are broad patterns, not exact effective-charge calculations.

Atomic radius



Circles scale the example radii. Compare like measurement conventions: electron clouds have no hard boundary.

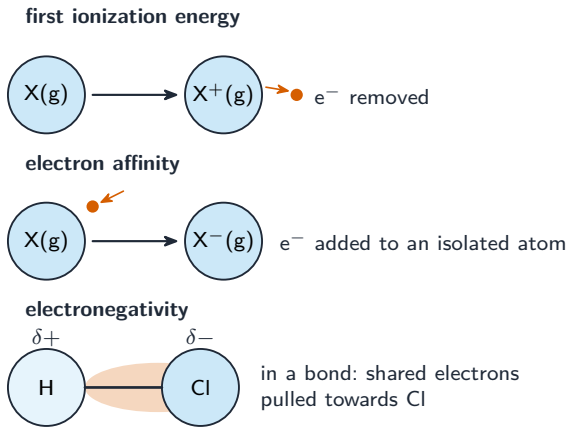
- **Across a period** the atomic radius decreases: Na 186 pm to Cl 102 pm.
- **Down a group** the atomic radius increases: one extra occupied energy level each time.

Ionic radius

- A **cation** is smaller than its atom: electron loss reduces repulsion and may remove an outer level, as in $\mathrm{Na} \to \mathrm{Na}^+$ (186 → 102 pm). Not every cation loses a complete shell.
- An **anion** is larger: added electrons increase repulsion at the same nuclear charge. $\mathrm{Cl} \to \mathrm{Cl}^-$ gives 102 → 181 pm in these example conventions.
- For ions with the **same electron configuration** (isoelectronic ions), the radius falls as the nuclear charge rises: $\mathrm{N}^{3-} > \mathrm{O}^{2-} > \mathrm{F}^- > \mathrm{Na}^+ > \mathrm{Mg}^{2+} > \mathrm{Al}^{3+}$, all with the configuration of neon.

Ionization energy, electron affinity and electronegativity

Property	Meaning	Broad pattern
first ionization energy	molar removal energy: isolated ground-state $\mathrm{X(g)} \to \mathrm{X}^+\mathrm{(g)} + \mathrm{e}^-$	across: generally rises down: generally falls
electron affinity 电子亲和能	molar electron-gain enthalpy: $\mathrm{X(g)} + \mathrm{e}^- \to \mathrm{X}^-\mathrm{(g)}$ (sign used here)	towards halogens: often more exothermic many exceptions
electronegativity	relative attraction of a bonded atom for shared electron density	across: generally rises down: generally falls



Two processes on isolated gaseous atoms, and one property of an atom in a bond: keep the definitions apart.

The first process removes an electron; the second adds one to an isolated atom; the third describes an atom in a bond. Do not replace one definition with another. Fluorine is the most electronegative element on the usual Pauling scale; noble gases often have no value on a supplied school table.

Check affinity signs: **positive energy released** is the reverse of the electron-gain enthalpy convention used here, where exothermic gain is negative. Chlorine releases about 349 kJ/mol, fluorine about 328: fluorine's compact 2p region increases incoming-electron repulsion. Thus group-17 affinity is not steadily more exothermic from iodine to fluorine. Filled or half-filled sublevels also interrupt across-period patterns. Isolated-atom gain energies alone do not determine halogen-molecule reactions in solution. (RSC chlorine data)

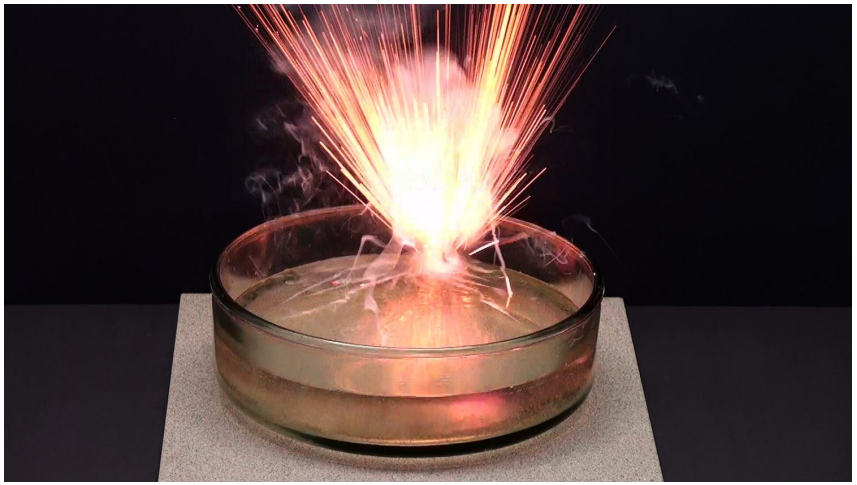
■ Metallic and non-metallic character

In the usual simple-ion reactions, metals undergo oxidation by **losing** electrons. Metallic character therefore increases as ionization energy decreases: **down** a group and **to the left** across a period. Non-metallic character increases up and to the right. This explains the broad group-1 and group-17 patterns. Do not extrapolate one perfectly monotonic numerical trend to francium or infer every reaction rate from ionization energy alone: bonding, phases, products and conditions also matter.

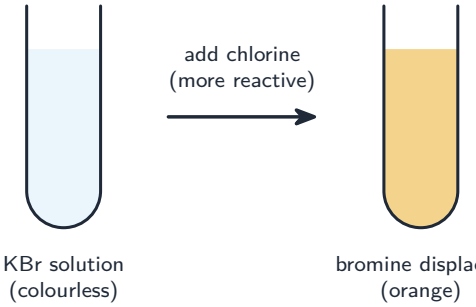
Group 1 and group 17

■ The alkali metals

Group 1 metals are soft, have low melting points and react quickly with water to give a hydroxide and hydrogen:



Potassium reacts violently with water, giving off hydrogen that burns with a lilac flame – reactivity increases down Group I



Chlorine is more reactive, so it displaces bromine from the solution; the released bromine turns the colourless solution orange

$$2\mathrm{Na(s)} + 2\mathrm{H_2O(l)} \rightarrow 2\mathrm{NaOH(aq)} + \mathrm{H_2(g)}$$

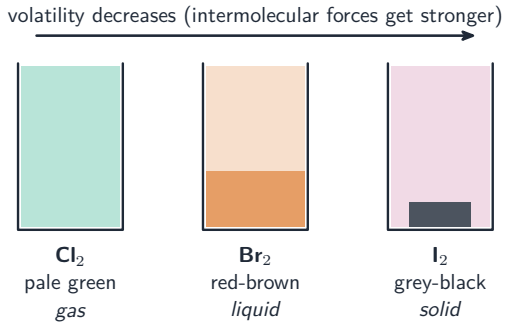
Reactivity **increases** down the group. The outer electron is further from the nucleus and more shielded, so it is lost more easily. In a small-scale teacher demonstration, lithium commonly fizzes and potassium can melt and ignite with a lilac flame; the observed vigour also depends on sample size, surface and conditions. Use observations as evidence for the broad trend, rather than treating ignition as guaranteed.

The halogens

Halogens exist as diatomic molecules: F_2 and Cl_2 are gases, Br_2 a liquid and I_2 a solid at room temperature (London forces increase down the group). In halide-forming redox reactions, a halogen molecule is reduced: $X_2 + 2e^- \rightarrow 2X^-$. Oxidizing ability generally decreases down group 17. Increasing distance and shielding help explain the broad pattern, but the overall reaction also involves breaking X–X and solvation; it is not identical to the isolated atom's electron affinity. Fluorine reacts with water, so ordinary aqueous halide-displacement comparisons use chlorine, bromine and iodine.



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



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

A more reactive halogen **displaces** a less reactive one from a solution of its halide ions:

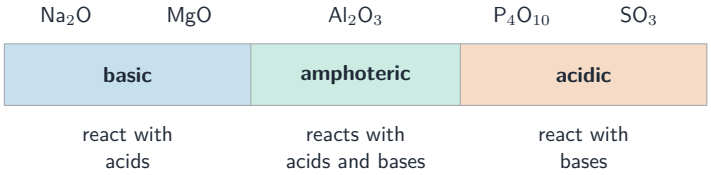
$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

The solution turns orange-yellow as bromine forms. Bromine cannot displace chloride ions, because chlorine is more reactive.

Oxides of the elements

From basic to acidic

Many common metal oxides are mostly ionic and **basic** 碱性的: they neutralize acids, and those that react appreciably with water can give alkaline solutions. Many non-metal oxides are covalent and **acidic** 酸性的, reacting with bases. These are patterns with exceptions: CO is a neutral oxide, and acidic SiO_2 does not form an acidic solution merely by being placed in water.



SiO_2: acidic, but unreactive with water

Oxide character describes reactions. Actual pH also depends on solubility, amount, water volume and conditions.

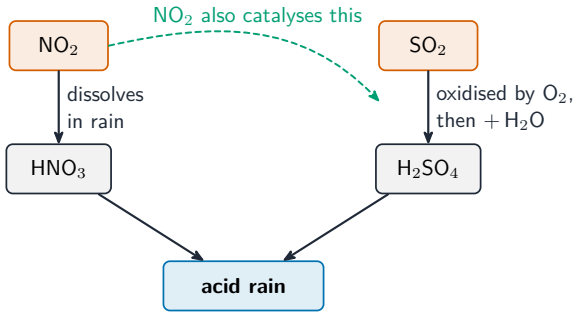
Oxide	Bonding	Reaction with water	Character
Na_2O	ionic	$Na_2O + H_2O \rightarrow 2NaOH$	basic
MgO	ionic	$MgO + H_2O \rightarrow Mg(OH)_2$ (sparingly soluble)	basic
Al_2O_3	ionic with covalent character	no appreciable reaction	**amphoteric** 两性的
SiO_2	giant covalent	no appreciable reaction	acidic: reacts with hot NaOH
P_4O_{10}	molecular covalent	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$	acidic
SO_3	covalent	$SO_3 + H_2O \rightarrow H_2SO_4$	acidic

An amphoteric oxide reacts with both acids and bases:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \qquad Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

Acid deposition and ocean acidification

Non-metal oxides in the air make rain more acidic. Burning fuels that contain sulfur forms SO_2, and the high temperature in engines forms nitrogen oxides. Atmospheric oxidation and reactions in water droplets can form sulfuric and nitric acids. For example, these overall equations summarize oxidation and hydration; they are not elementary one-step mechanisms:



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

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad 4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

This **acid deposition** 酸沉降 damages limestone buildings, forests and lakes. Carbon dioxide dissolving in the oceans forms carbonic acid, $CO_2 + H_2O \rightleftharpoons H_2CO_3$, which lowers the pH of seawater: **ocean acidification** 海洋酸化. A useful aqueous model is $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$. Added H^+ shifts carbonate towards hydrogencarbonate, reducing carbonate availability for many calcifying organisms. Acidification means a decrease in pH: seawater can become less alkaline while remaining above pH 7. CO is not an acid-forming substitute for CO_2.

For required group-1 and group-2 oxide equations, compare $K_2O + H_2O \rightarrow 2KOH$ and $CaO + H_2O \rightarrow Ca(OH)_2$. Both give basic hydroxides under appropriate conditions, but MgO reacts less readily and $Mg(OH)_2$ is only sparingly soluble. Sulfur dioxide in water forms an acidic equilibrium mixture, often represented as $SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$; do not label that alone the formation of sulfuric acid.

Oxidation states

Rules for assigning oxidation states

An **oxidation state** 氧化态 is the charge an atom would have if all its bonds were ionic. It is written with the sign first: +2, −1.

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 ($Mn = +7$)

1. An uncombined element is 0: Fe, O_2, Cl_2.
2. A simple ion has its charge: Na^+ is +1, O^{2-} is −2.
3. In a compound, oxygen is usually −2 (except in peroxides, −1, and with fluorine), hydrogen is usually +1 (except in metal hydrides, −1), and fluorine in its compounds is −1 (elemental F_2 is 0).
4. The oxidation states add up to zero in a neutral compound, and to the total charge in a polyatomic ion. Assigning equal shared electrons between identical atoms gives no electron transfer for an uncombined element, so its oxidation state is 0.

Worked example: the oxidation state of Mn in MnO_4^-. Four oxygens give $4(-2) = -8$. The total must be −1, so $\text{Mn} + (-8) = -1$, and Mn is +7.

For NaH, Na is +1 and H is −1. In H_2O_2, hydrogen is +1 and oxygen is −1; in OF_2, fluorine is −1 and oxygen is +2. The sum rule still holds. If a formula contains inequivalent atoms of one element, solving for one symbol can give only an average: thiosulfate has average sulfur +2, not two necessarily equivalent S atoms.

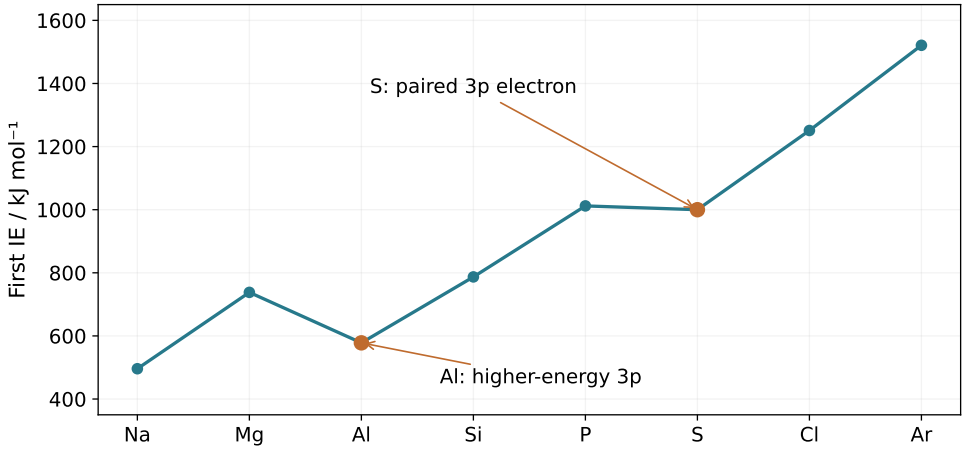
Naming with Roman numerals

When an element can have more than one oxidation state, the name shows it in Roman numerals: iron(II) chloride is $FeCl_2$, iron(III) chloride is $FeCl_3$. Oxyanions are named the same way: SO_4^{2-} is sulfate(VI) and SO_3^{2-} is sulfate(IV), commonly called sulfite; NO_3^- is nitrate(V).

AHL: Ionization-energy discontinuities

An across-period increase is a broad pattern, not a smooth staircase. For period 3, Mg has $3s^2$ and Al has $3s^2 3p^1$. Removing Al's higher-energy, more shielded 3p electron requires less energy than removing Mg's 3s electron, despite Al's greater nuclear charge. Similarly, B is below Be in period 2.

Phosphorus is $3p^3$ with one electron in each p orbital; sulfur is $3p^4$, with a paired electron in one orbital. Repulsion within that pair makes removal easier, giving a small decrease from P to S (and N to O). Explain the energy of the electron removed; merely saying "a half-filled sublevel is specially stable" does not explain the evidence.



Rounded reference values in kJ/mol, not invented observations. The two dips support sublevels and electron pairing; the broad increase reflects increasing attraction.

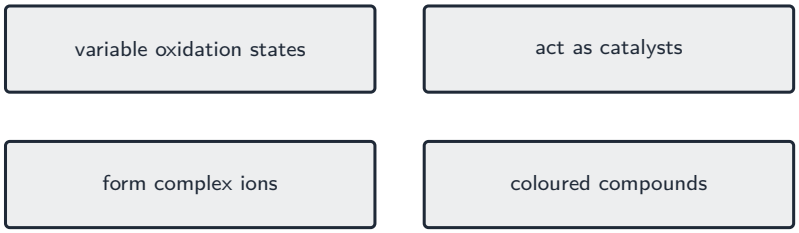
AHL: Transition elements

What makes an element a transition element

A **transition element** 过渡元素 has an incomplete d sublevel in its atom or can form a cation with an incomplete d sublevel. This broad definition includes scandium because the atom is [Ar] $3d^1 4s^2$. However, its usual Sc^{3+} ion is d^0 and lacks many characteristic coloured, variable-state behaviours. Some school conventions therefore discuss Ti–Cu as the characteristic first-row transition set. State the criterion when discussing Sc rather than claiming that an incomplete atomic d sublevel and exclusion of Sc follow from the same definition. Zinc's atom and usual Zn^{2+} ion both have d^{10}, so zinc is a d-block element without the characteristic transition classification. (IUPAC definition)



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

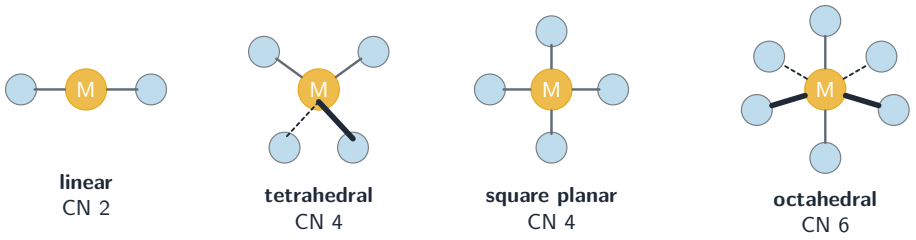


The four key properties of the transition elements

When a transition element forms an ion, it loses its **4s electrons first**: Fe is [Ar] $3d^6 4s^2$ and Fe^{2+} is [Ar] $3d^6$.

Characteristic properties

Characteristic properties include the following; not every element, ion and compound displays every one. Strong metallic cohesion commonly gives high melting points, with variation across the d block rather than one monotonic main-group trend.



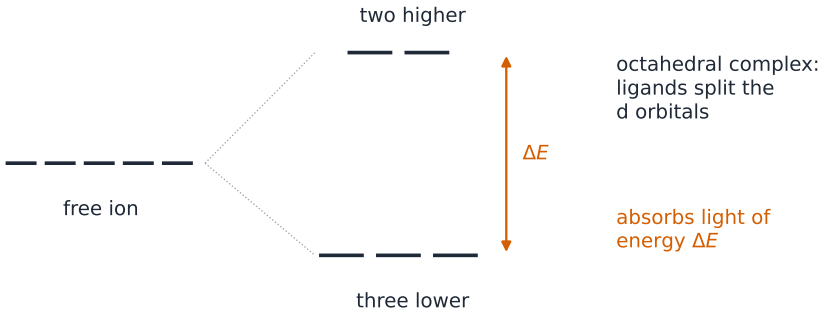
Complex shapes follow the coordination number: 2 is linear, 4 is tetrahedral or square planar, 6 is octahedral

1. **Variable oxidation states.** The 4s and 3d sublevels are close in energy, so successive removals of the available outer s and d electrons need not cross the abrupt core-shell gap seen after a main-group valence shell is exhausted. Different oxidation states can be stabilized by different ligands and products; close sublevel energies do not mean all successive ionization energies are equal or that Mn(VII) must be a bare aqueous Mn^{7+} ion. Manganese shows every state from +2 to +7, as in Mn^{2+}, MnO_2 and MnO_4^-.
2. **Complex ions.** A central metal ion bonds to **ligands** 配体: molecules or ions with a lone pair that form coordination bonds to the metal, such as H_2O, NH_3, Cl^- and CN^-. The number of donor atoms directly attached to the metal is the **coordination number** 配位数; a ligand can donate through more than one atom, so ligand count alone is not always sufficient. Example: $[Cu(H_2O)_6]^{2+}$ is octahedral, with coordination number 6.
3. **Coloured compounds**, explained below.
4. **Catalytic activity.** Reversible oxidation-state changes can support catalytic cycles in solution; adsorption and suitable reaction pathways explain many solid-surface examples. A catalyst supplies a lower-activation-energy pathway without changing the equilibrium constant: iron in the Haber process, V_2O_5 in the Contact process, nickel in the hydrogenation of alkenes, and MnO_2 in the decomposition of hydrogen peroxide.

The charge on a complex ion is the oxidation state of the metal plus the charges of the ligands. In $[CuCl_4]^{2-}$, four Cl^- give -4, so copper is +2.

Why transition metal complexes are coloured

In the simple isolated-ion orbital model, the five d orbitals are degenerate; a ligand field removes that degeneracy. In a complex, the lone pairs of the ligands repel the d electrons. In an octahedral complex, two of the d orbitals point straight at the ligands and are raised in energy; the other three are lowered. The d orbitals **split** into two sets separated by an energy gap ΔE.



An electron absorbs light of energy ΔE to move to a higher d orbital

An electron in a lower d orbital absorbs a photon of visible light with energy equal to ΔE and moves to a higher d orbital. The light that is **not** absorbed passes through, so we see the **complementary colour** 互补色. $[Cu(H_2O)_6]^{2+}$ absorbs orange-red light and looks blue.

The size of ΔE, and so the colour, depends on:

- the **metal** and its **oxidation state**: Fe^{2+} solutions are pale green, Fe^{3+} yellow-brown;
- the **ligand**: adding ammonia to blue $[Cu(H_2O)_6]^{2+}$ gives deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$, because NH_3 splits the d orbitals more strongly;
- the **coordination number** and shape of the complex.

A d^0 or d^{10} centre cannot undergo this d–d promotion: many simple Sc^{3+} and Zn^{2+} complexes are colourless. This does not prove every d^0/d^{10} compound is colourless; ligand or charge-transfer absorption can also cause colour. Likewise, observed Fe^{3+} solution colour depends on ligands, hydrolysis and conditions.

Reading a colour wheel and calculating frequency

Use the supplied wheel to connect observed and absorbed colours, and read the appropriate wavelength range rather than assuming identical values for every "blue" complex. For an **invented spectrum** of a blue complex with an orange-red absorption maximum at 620 nm, convert 620 nm $= 6.20 \times 10^{-7}$ m. Then $f = c/\lambda = (3.00 \times 10^8)/(6.20 \times 10^{-7}) = 4.84 \times 10^{14}$ Hz. The absorbed photon has $\Delta E = hf = 3.21 \times 10^{-19}$ J. These are absorbed-light quantities; they are not the frequency of a single blue photon emitted by the solution. A broad transmitted spectrum can produce a perceived colour without a single observed wavelength.

■ Magnetic properties

Electrons spin, and an unpaired electron behaves like a tiny magnet.

- A substance with **unpaired** electrons is **paramagnetic** 顺磁性的: it is attracted into a magnetic field. For otherwise comparable cases, more unpaired electrons generally give a greater paramagnetic contribution. A high-spin Fe^{3+} d^5 complex has five unpaired electrons; a sufficiently strong ligand field can change the pairing, so d^5 alone does not specify the unpaired count in every complex.
- A substance with **all electrons paired** is **diamagnetic** 抗磁性的: it is weakly repelled by a magnetic field. Zn^{2+}, $3d^{10}$, is diamagnetic.

Iron, cobalt and nickel are also **ferromagnetic**: the unpaired electrons of neighbouring atoms line up, so the metals can become permanent magnets.

Practice

1. Without a periodic table, state the period, group and block of the atom with configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$.
2. Explain why the atomic radius generally decreases from sodium to chlorine.
3. Order these ions by increasing radius and explain: Mg^{2+}, Na^+, F^-, O^{2-}.
4. Explain why potassium generally reacts more vigorously with water than sodium under comparable conditions.
5. Write an ionic equation for chlorine added to aqueous iodide; state an observation and whether iodine displaces chloride under the same conditions.
6. Write equations for Na_2O and SO_3 with water. Can their formulas alone specify pH 14 and 0 respectively?
7. Deduce oxidation states: (a) Cr in $Cr_2O_7{}^{2-}$, (b) average S in $Na_2S_2O_3$, (c) N in $NH_4{}^+$. Explain the word "average" in (b).
8. Give Br's configuration and electron count from its period-4/group-17 position. Explain He's group-18 placement despite $1s^2$.
9. Write CaO/CO_2 water equations. Explain acidification above pH 7 and acidic SiO_2's lack of reaction with water.
10. Deduce H in NaH, O in H_2O_2 and O in OF_2, showing the sum rule.
11. For F −328 and Cl −349 kJ/mol electron-gain enthalpies, compare exothermicity, explain the exception and convert to positive-release values.
12. **AHL.** Explain both period-3 IE dips, Mg→Al and P→S. Explain the Sc classification issue and why Zn is excluded by the incomplete-d definition.
13. **AHL.** For $[Fe(CN)_6]^{3-}$, find the metal oxidation state, coordination number and d-electron count. Can the d count alone guarantee five unpaired electrons? Compare isolated Mn^{2+}, and identify one catalytic example and its function.
14. **AHL.** An invented spectrum of a blue complex absorbs most strongly at 620 nm. Explain the d–d model, calculate absorbed frequency and photon energy using $c = 3.00 \times 10^8$ m s^{-1} and $h = 6.63 \times 10^{-34}$ J s, and explain why d^0 does not guarantee absence of all colour.

Worked answers.

1. Period 3 (outer n = 3), group 16 (six outer electrons), p block: sulfur.
2. Nuclear charge rises from +11 to +17 while electrons enter the same main level. Similar inner shielding gives stronger attraction and contraction; shielding is not exactly constant.
3. $Mg^{2+} < Na^+ < F^- < O^{2-}$. Each has ten electrons; nuclear charges 12, 11, 9 and 8 give greater attraction and contraction at the higher charge.
4. Potassium's outer electron occupies a higher, more shielded level, farther from the nucleus. Easier removal explains the broad trend despite the greater nuclear charge; conditions affect observations.
5. $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$: a brown iodine-containing solution forms. Iodine does not ordinarily oxidize chloride in the reverse aqueous displacement; chlorine is the stronger oxidizing agent here.
6. $Na_2O + H_2O \rightarrow 2NaOH$ gives an alkaline solution; $SO_3 + H_2O \rightarrow H_2SO_4$ gives an acidic solution. Exact pH requires concentration and conditions, not an oxide formula alone.
7. (a) $2Cr - 14 = -2$, so Cr +6. (b) $2 + 2S - 6 = 0$ gives average S +2, without proving identical local sulfur states. (c) $N + 4 = +1$ gives N −3.
8. Br is [Ar] $3d^{10}4s^24p^5$: $18 + 10 + 2 + 5 = 35$ electrons. He's filled $1s^2$ level supports noble-gas group-18 placement, with two outer electrons.
9. $CaO + H_2O \rightarrow Ca(OH)_2$; $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3{}^-$. Falling alkaline pH is acidification. SiO_2 reacts with bases, not appreciably with water.
10. NaH: $+1 + H = 0$ gives H −1. H_2O_2: $2(+1) + 2O = 0$ gives O −1. OF_2: $O + 2(-1) = 0$ gives O +2. Elemental F_2 remains 0.
11. Cl releases $349 - 328 = 21$ kJ/mol more; compact F 2p increases incoming-electron repulsion. Positive-release values are F +328 and Cl +349 kJ/mol.
12. **AHL.** Al loses a higher-energy 3p electron rather than Mg's 3s electron; paired-electron repulsion makes one S 3p electron easier to remove than P's singly occupied set. Sc's atom is d^1, satisfying the broad atom-or-cation definition, but usual Sc^{3+} is d^0 and lacks many characteristic properties. Zn atom and usual Zn^{2+} are d^{10}, with no incomplete d sublevel.
13. **AHL.** Six CN^- donors contribute −6, so Fe is +3, coordination number 6, d^5 after loss of two 4s electrons and one 3d electron. Ligand-field pairing matters: this strong-field complex does not justify assuming five unpaired electrons. Isolated Mn^{2+} is [Ar] $3d^5$ with five singly occupied orbitals. Fe catalyses Haber ammonia synthesis by providing a lower-activation-energy surface pathway; a catalyst does not change the equilibrium constant.

14. **AHL.** Ligands split the d orbitals; a suitable electron absorbs light matching the energy gap. Orange-red absorption gives complementary blue transmitted light. $f = (3.00 \times 10^{8})/(620 \times 10^{-9}) = 4.84 \times 10^{14}$ Hz; $E = hf = 3.21 \times 10^{-19}$ J. These refer to absorbed light, not blue emission. A d^0 centre lacks this d–d process, but charge-transfer or ligand absorption may still produce colour.

Exam tips

- Use configuration, nuclear charge, shielding and distance; compare like radius conventions.
- Balance equations and oxidation-state sums; check exceptions. Oxide character does not set pH.
- **AHL.** Explain IE dips, remove 4s before 3d, and state Sc/pairing criteria. Convert wavelength units and distinguish absorbed from observed colour.

Functional groups: classification of organic compounds

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Structure 3.2, Functional groups: classification of organic compounds, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: covalent bonding and molecular shapes from Structure 2.2, intermolecular forces and hydrogen bonding, and the mole and empirical formulae from Structure 1.4.

Representing organic molecules

Same formula, different substances

Ethanol and methoxymethane both have the formula C_2H_6O. Ethanol is the liquid in alcoholic drinks and boils at 78 °C; methoxymethane is a gas used in aerosol sprays and boils at −24 °C. The atoms are the same, but they are joined in a different order. In organic chemistry the formula alone is not enough: you need to show the structure.

Types of formula

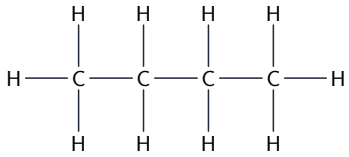
molecular

C_4H_{10}

condensed

$CH_3CH_2CH_2CH_3$

full structural



skeletal



A molecular formula gives atom counts; connectivity needs a structural formula. A skeletal drawing keeps bond connectivity while omitting carbon labels and carbon-bound hydrogens.

Formula	What it shows	Butan-1-ol
molecular	the number of atoms of each element	$C_4H_{10}O$
empirical	the simplest whole-number ratio	$C_4H_{10}O$
condensed structural	the atoms on each carbon, in order	$CH_3CH_2CH_2CH_2OH$
full structural	every atom and every bond	all 15 atoms and 14 bonds drawn
skeletal	carbon chain as a zigzag; C and H on carbon left out	4 carbons at two corners and two ends, with OH at one end

In a **skeletal formula** 骨架式 each corner and each line end is a carbon atom, and each carbon has enough hydrogen atoms to make four bonds. Atoms other than carbon, and hydrogens attached to them such as O–H, are shown explicitly. Carbon-bound H atoms are normally omitted.

A full displayed formula is still a two-dimensional representation: it need not show the true three-dimensional bond angles. Build a simple carbon model with four tetrahedral bond directions, approximately 109.5° for an isolated sp^3 centre. Around a C=C, each carbon is approximately trigonal planar; a C≡C region is linear. In wedge-dash notation, a solid tapered wedge comes towards the viewer, a dashed wedge goes away and ordinary lines lie approximately in the paper's plane. Model kits or a labelled drawing can reveal connections hidden by a flat formula; model colours and stick lengths are conventions, not literal atom surfaces.

A benzene ring, C_6H_6, is drawn as a hexagon with a circle inside, which shows the delocalized electrons. A benzene ring attached to a chain is a **phenyl** 苯基 group, C_6H_5–.

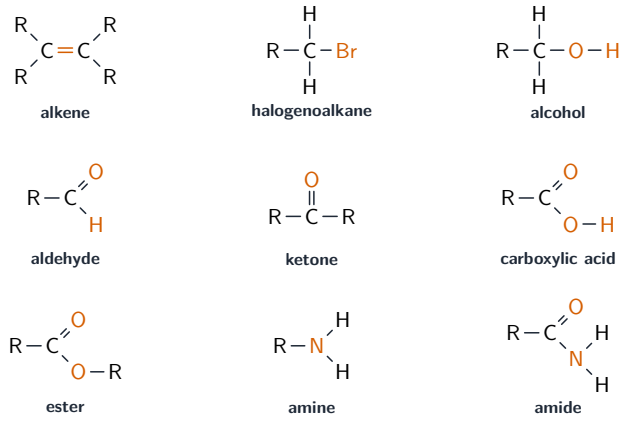
Functional groups and homologous series

Functional groups

A **functional group** 官能团 is the atom or group of atoms that gives a compound its typical reactions. Compounds with the same functional group react in similar ways.



Crude oil is a mixture of hydrocarbons, mostly members of the alkane homologous series



The coloured atoms define each class; R stands for the rest of the molecule.

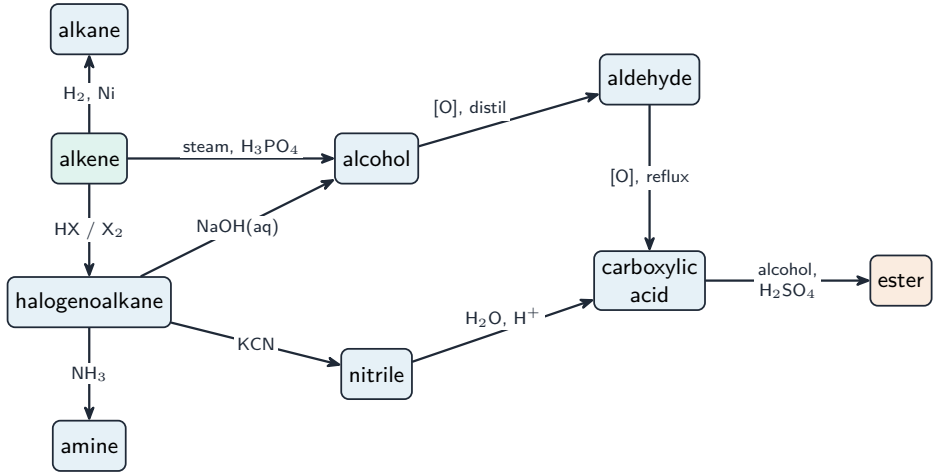
Class	Functional group	Suffix or prefix	Example
alkane	C–C/C–H single bonds	-ane	propane, $CH_3CH_2CH_3$
alkene	C=C	-ene	propene, $CH_2{=}CHCH_3$

Class	Functional group	Suffix or prefix	Example
alkyne	C≡C	-yne	ethyne, HC≡CH
halogenoalkane	–X (F, Cl, Br, I)	fluoro-, chloro-, bromo-, iodo-	bromoethane, CH_3CH_2Br
alcohol	–OH (hydroxyl)	-ol	ethanol, CH_3CH_2OH
aldehyde	–CHO (carbonyl at the chain end)	-al	ethanal, CH_3CHO
ketone	C=O inside the chain (carbonyl)	-one	propanone, CH_3COCH_3
carboxylic acid	–COOH (carboxyl)	-oic acid	ethanoic acid, CH_3COOH
ether	C–O–C (ether)	alkoxy-	methoxymethane, CH_3OCH_3
ester	–COO– (ester)	-yl -oate	methyl ethanoate, CH_3COOCH_3
amine	N bonded to carbon; $–NH_2$ is a primary example	-amine	ethylamine, $CH_3CH_2NH_2$
amide	carbonyl bonded to N; $–CONH_2$ is a primary example	-amide	ethanamide, CH_3CONH_2
nitrile	–C≡N	-nitrile	ethanenitrile, CH_3CN

A **saturated** carbon framework has no C=C or C≡C bonds; an **unsaturated** framework has a carbon–carbon multiple bond. Do not call a carbonyl compound an alkene merely because it contains a double bond: the atoms of the functional group matter. Alkoxy is R–O– as a group attached through oxygen; phenyl is the $C_6H_5–$ ring group. An amide's nitrogen is attached directly to a carbonyl carbon; an ordinary amine lacks that defining connection.

■ Recognize reactions by the bonds that change

Trace the structural formula before and after reaction; the reagent and conditions belong on the reaction arrow.



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

- **Addition:** $CH_2{=}CH_2 + H_2 \xrightarrow{\text{Ni, heat}} CH_3CH_3$. The C=C becomes C–C and two C–H bonds form; both carbons remain.
- **Substitution:** $CH_3CH_2Br + OH^- \xrightarrow{\text{aqueous, heat}} CH_3CH_2OH + Br^-$. A C–Br bond is replaced by C–O; the two-carbon skeleton stays intact. Ethanolic hydroxide favours elimination instead, so the solvent matters.
- **Oxidation:** $CH_3CH_2OH + [O] \xrightarrow{\text{acidified dichromate, distil}} CH_3CHO + H_2O$. Here [O] represents oxidizing oxygen, not a free oxygen atom in the mechanism. The alcohol carbon loses a C–H bond and gains a second bond to O. Distilling the aldehyde limits further oxidation; reflux with excess oxidant gives ethanoic acid.
- **Addition polymerization:** $n CH_2{=}CH_2 \rightarrow [-CH_2-CH_2-]_n$ under suitable initiator/catalyst conditions. Each C=C opens and new C–C links join monomers; no small molecule is lost in this repeating-unit model.

AHL synthesis route. Ethene → ethanol → ethanoic acid retains two carbons at every stage. Hydrate ethene with steam using a phosphoric-acid catalyst at elevated temperature and pressure; then oxidize ethanol under reflux with excess acidified dichromate. The second step is $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$. Write each reagent and condition above its own arrow; a hydrogenation catalyst would instead turn ethene into ethane.

Homologous series

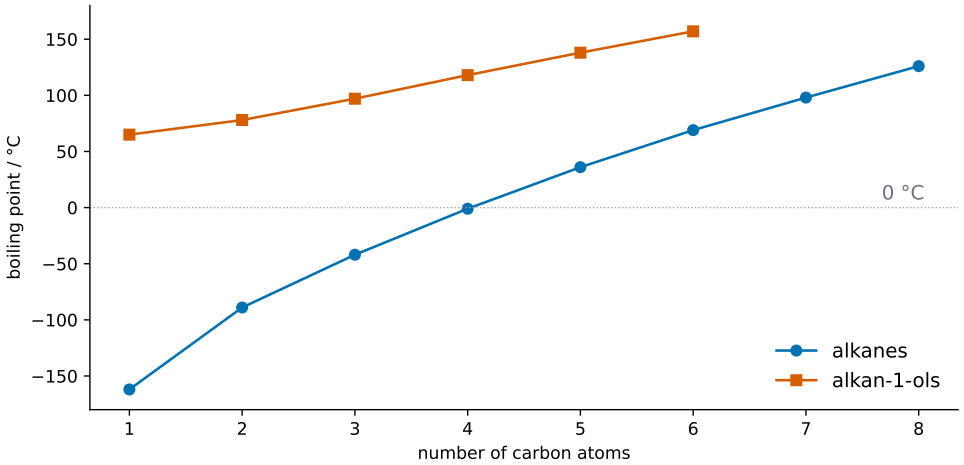
A **homologous series** 同系列 is a family of compounds with the same functional group and the same general formula.

- Each member differs from the next by CH_2.
- They have similar chemical properties.
- Physical properties, such as boiling point, change gradually along the series.

Series	General formula
alkanes	C_nH_{2n+2}
alkenes	C_nH_{2n}
alcohols	$C_nH_{2n+1}OH$
carboxylic acids	$C_nH_{2n}O_2$

Here n counts **all** carbon atoms. These formulas describe the stated simple acyclic series: alkenes have one C=C, alcohols one OH and no other functional group, and carboxylic acids one COOH. A ring or an extra multiple bond changes the general formula.

Trends in boiling point



Rounded normal boiling points for the named unbranched series, at comparable pressure. Greater dispersion raises the general trend; alcohol hydrogen bonding adds an important interaction.

- Each extra CH_2 adds electrons and surface area, so London forces between molecules get stronger and the boiling point rises.
- More compact branching commonly lowers boiling points among comparable alkane isomers by reducing effective intermolecular contact. This is a trend, not a universal ranking of every functionalized molecule.
- Alcohols and carboxylic acids boil much higher than alkanes of similar mass because their molecules form hydrogen bonds.

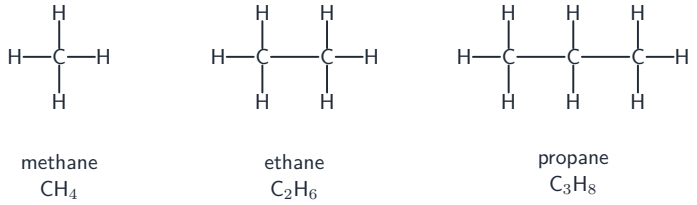
Melting points require packing as well as attraction

Increasing chain length often raises melting temperatures over a sufficiently broad range, but successive values can alternate or show irregularities because symmetry and crystal packing matter. Branching can reduce surface contact yet improve packing for a sufficiently symmetrical isomer. Do not copy a boiling-point trend mechanically into an exact melting-point order. Use supplied measurements and explain both intermolecular attractions and the solid arrangement.

Naming organic compounds

The IUPAC rules

IUPAC rules build systematic names using a parent, substituents and a suffix. Preferred names follow a defined convention, but accepted alternatives can exist; a molecular formula alone need not identify one compound.



The alkanes are a homologous series: each member has one more CH_2 unit (general formula C_nH_{2n+2})

Carbons	1	2	3	4	5	6
Stem	meth-	eth-	prop-	but-	pent-	hex-

1. Find the longest carbon chain that contains the functional group. Its length gives the stem.
2. Add the suffix of the main functional group (-ene, -ol, -al, -one, -oic acid).
3. Number the chain from the end that gives the functional group the lowest number. Put the number before the suffix: but-1-ene, propan-2-ol.
4. Name side chains (methyl-, ethyl-) and halogens (chloro-, bromo-) as prefixes with their position numbers, in alphabetical order.
5. Use di-, tri- for repeated groups: 2,2-dimethylpropane.

Worked examples

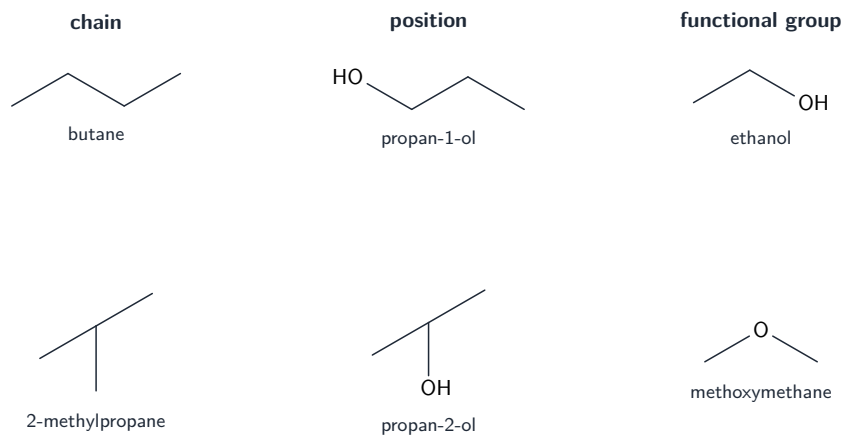
- $CH_3CH(OH)CH_3$: 3 carbons, –OH on carbon 2 → **propan-2-ol**.
- $CH_3CH_2CH(CH_3)CH_3$: longest chain 4 carbons, methyl on carbon 2 → **2-methylbutane** (not 3-methylbutane).
- $CH_2{=}CHCH_2CH_3$: 4 carbons, C=C starting at carbon 1 → **but-1-ene**.
- $CH_3CHBrCH_3$: **2-bromopropane**.
- CH_3CH_2COOH: 3 carbons including the COOH carbon → **propanoic acid**.

In these simple open-chain mono-aldehyde and mono-carboxylic-acid examples, the terminal characteristic carbon is carbon 1 and its locant is normally omitted.

Structural isomers

Same molecular formula, different structure

Structural isomers 结构异构体 have the same molecular formula but a different structural formula: the atoms are joined in a different order.



Structural isomers differ in their chain, in the position of a group, or in the functional group itself

Type	What changes	Example, C_n...
chain	the carbon skeleton is branched differently	butane and 2-methylpropane, C_4H_{10}
position	the functional group sits on a different carbon	propan-1-ol and propan-2-ol, C_3H_8O
functional group	the atoms form a different functional group	ethanol and methoxymethane, C_2H_6O

Alcohols are classified by the carbon that holds the –OH: **primary** 伯 (that carbon has one other carbon attached), **secondary** 仲 (two) or **tertiary** 叔 (three). Propan-1-ol is primary; propan-2-ol is secondary; 2-methylpropan-2-ol is tertiary. Halogenoalkanes use the number of carbon neighbours of the carbon bonded to the halogen. Methanol and methyl halides have no carbon neighbour and need separate treatment rather than forcing the usual alkyl examples onto them.

For **amines**, count carbon-containing groups directly bonded to **nitrogen**, not neighbours of a carbon next to N: CH_3NH_2 is primary, $(CH_3)_2NH$ secondary and $(CH_3)_3N$ tertiary. The last has no N–H bond but still has a lone pair. This is a different counting centre from alcohol or halogenoalkane classification. A compound can also contain more than one functional group; identify every connection before choosing a class.

AHL: Identifying compounds

Organic MS, IR and proton-NMR interpretation belong to the additional Higher-Level scope in the 2025 course. Use the supplied data booklet.



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

Index of hydrogen deficiency

As supporting structure analysis, the **index of hydrogen deficiency** 缺氢指数 (IHD) counts how many rings and π bonds a molecule has. Each ring or double bond counts 1; a triple bond counts 2. For a compound $C_cH_hN_nO_oX_x$ (X = halogen):

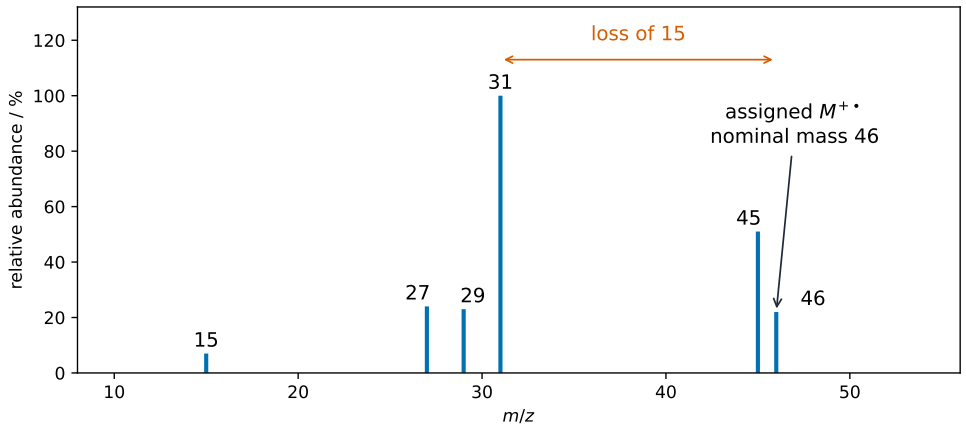
$$\text{IHD} = \frac{2c + 2 + n - h - x}{2}$$

This formula assumes the usual neutral closed-shell valences for these elements; it is

not a universal rule for arbitrary ions or unusual valences. Oxygen does not affect the IHD. For C_3H_6O: $(6 + 2 - 6)/2 = 1$, so one C=C, one C=O or one ring. Benzene, C_6H_6: $(12 + 2 - 6)/2 = 4$ (one ring and three double bonds).

Mass spectrometry

In an electron-impact **mass spectrometer** 质谱仪, molecules can form radical cations and fragment. Ionization method and conditions affect the spectrum. The spectrum shows each ion's mass-to-charge ratio, m/z.



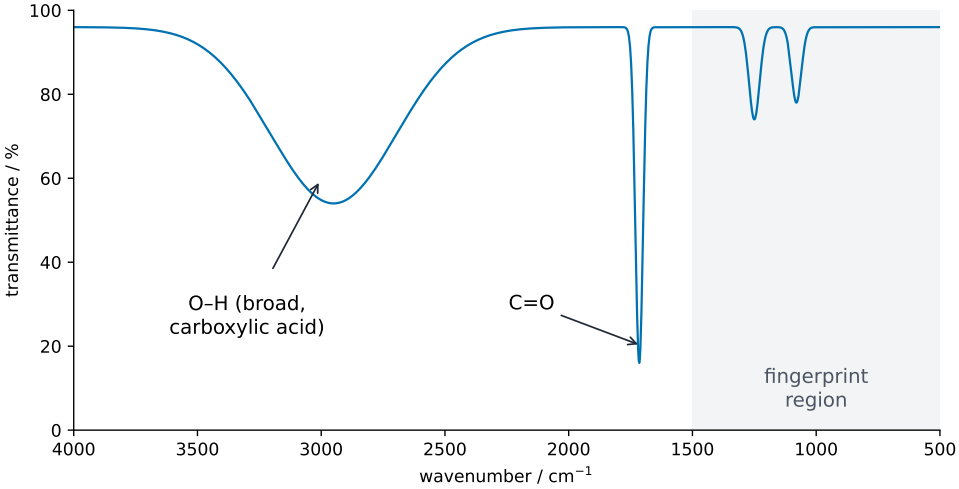
Illustrative EI pattern; isotope peaks omitted

Illustrative rounded ethanol EI pattern, not a newly measured spectrum. An assigned singly charged molecular ion helps establish molecular mass; fragment differences support proposed losses.

- An assigned singly charged **molecular ion** 分子离子 at nominal m/z 46 is consistent with ethanol's nominal molecular mass. It can be weak or absent; isotope peaks such as M+1 and M+2 can lie above it, so "highest peak position" is not a universal identification rule. The tallest peak is the base peak, not necessarily the molecular ion.
- Compare assigned parent and fragment masses to propose a neutral loss, retaining charge on the detected fragment. A difference of 15 can support loss of a methyl radical; nominal masses alone need not distinguish different formulas or prove a unique pathway. Use the supplied fragment table and the molecular composition.
- For ethanol, 31 is CH_2OH^+: the molecule lost CH_3 $(46 - 15)$.

Infrared spectroscopy

Bonds absorb infrared radiation at frequencies that make them vibrate. Each type of bond absorbs in its own range, so an IR spectrum shows which **bonds**, and so which functional groups, are present. The x-axis is the **wavenumber** 波数 in cm^{-1}; absorptions appear as dips in transmittance.



A deliberately schematic transmittance spectrum. A very broad acid O–H band together with C=O supports a carboxylic-acid assignment; combine evidence rather than treating one dip as unique proof.

Bond	**Approximate wavenumber / cm^{-1}**	**Look**
O–H in alcohols	3200–3600	broad
O–H in carboxylic acids	roughly 2500–3300; use the supplied table	very broad
N–H	3300–3500	medium
many sp^3/sp^2 C–H	about 2850–3100	common; terminal alkyne C–H is nearer 3300
C=O	broadly 1650–1850, depending on the group	strong, sharp
C=C	1620–1680	medium
C–O	1050–1410	strong

These are approximate orientation ranges, not an exhaustive transcription of the IB booklet; use the table supplied in the question. Carbonyl position changes with the

functional group and environment. (Instrument reference)

Below about 1500 cm^{-1} lies the **fingerprint region** 指纹区: a complex pattern useful for comparison with reference spectra under comparable conditions. A partial match, an overlapping mixture or limited resolution is not absolute proof of purity or identity.

An IR-active vibration changes the molecule's dipole moment. CO_2 has IR-active bending and asymmetric-stretching modes despite having no permanent dipole; N_2 and O_2 do not absorb ordinary IR through their fundamental homonuclear stretching vibrations. Greenhouse-gas absorption depends on active vibrational modes, wavelength and abundance, not simply on the presence of any bond.

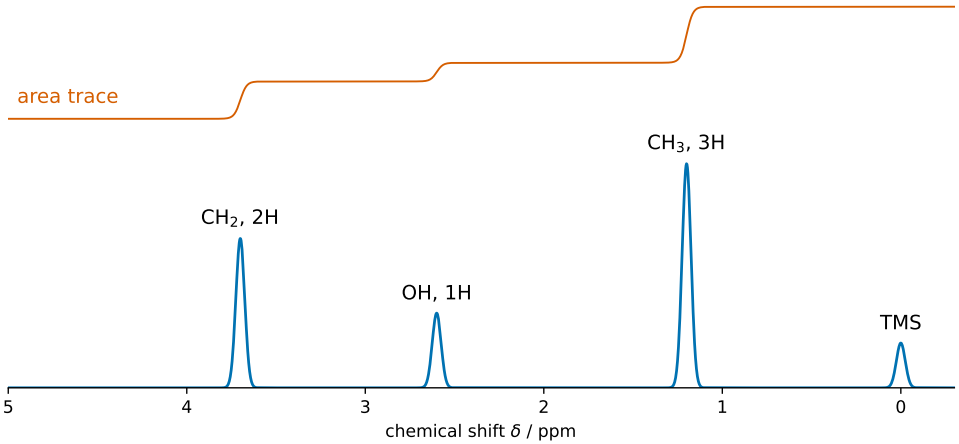
AHL: ^{1}H NMR spectroscopy

What the spectrum shows

In ^{1}H **nuclear magnetic resonance** 核磁共振 (NMR) spectroscopy, hydrogen nuclei in a strong magnetic field absorb radio waves. Hydrogen atoms in different surroundings absorb at slightly different frequencies.



An NMR spectrometer: the large cylinder holds a superconducting magnet that makes the very strong magnetic field the technique needs



Schematic low-resolution signals for ethanol under stated example conditions. Integration compares total areas, not individual line heights; the exchangeable OH shift can vary with solvent, concentration and temperature.

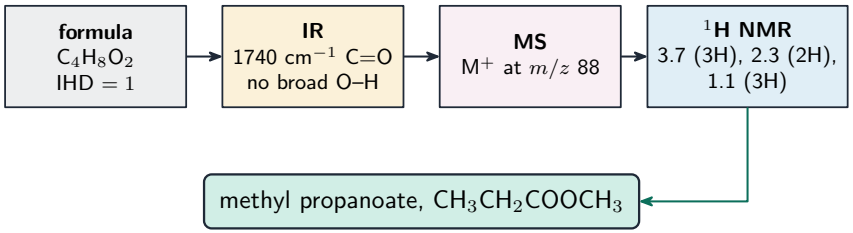
- **Number of signals** corresponds to distinguishable proton environments under the measurement conditions. Ethanol has three in this simple achiral-solution example; a signal can split into several lines at high resolution. Do not count those lines as additional environments.
- **Chemical shift** 化学位移, δ in ppm, tells you what each hydrogen is near. Electronegative atoms nearby move the peak to a higher shift.
- **Integration** 积分: the area under each peak is proportional to the number of hydrogen atoms in that environment: 2 : 1 : 3 for ethanol.
- **TMS**, tetramethylsilane, $Si(CH_3)_4$, is the reference at $\delta = 0$. It gives one strong peak away from most others, and it is inert.

Hydrogen type	Illustrative δ / ppm range
R–CH_3	0.9–1.0
CH next to C=O (–CH_2–CO–)	2.2–2.7
CH next to O (–O–CH_2–)	3.3–3.7
CH next to the O of an ester (–COO–CH_2–)	3.7–4.8
R–OH	1.0–6.0
on a benzene ring	6.9–9.0
–CHO	9.4–10.0
–COOH	9.0–13.0

These selected shift ranges are guides, not fixed constants for every molecule. Solvent, substitution and hydrogen bonding affect them; use the supplied data for an assessment. (NMR reference and solvent examples)

Worked example: using several techniques

For this invented combined-data exercise, a compound has molecular formula $C_4H_8O_2$.



each technique narrows the options (invented data)

Combining formula, IR, MS and NMR evidence (invented data)

- IHD = $(8+2-8)/2 = 1$: one C=O, C=C or ring before the other evidence is used.
- IR: strong peak at 1740 cm^{-1} (C=O), no broad band at 2500–3600 cm^{-1}, so no O–H: not an acid. An ester is likely.
- MS: an assigned singly charged molecular ion at m/z 88, matching the nominal mass 4(12) + 8(1) + 2(16) = 88. The NMR integrations sum to eight H, not six.
- ^{1}H NMR: three peaks at 3.7 (3H), 2.3 (2H) and 1.1 (3H). The 3.7 peak is CH_3 next to O; the 2.3 peak is CH_2 next to C=O.

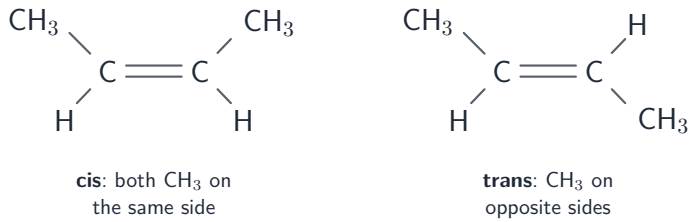
The compound is methyl propanoate, $CH_3CH_2COOCH_3$.

AHL: Stereoisomers

What stereoisomers are

Stereoisomers 立体异构体 have the same structural formula (the same atoms joined in the same order) but a different arrangement of the atoms in space.

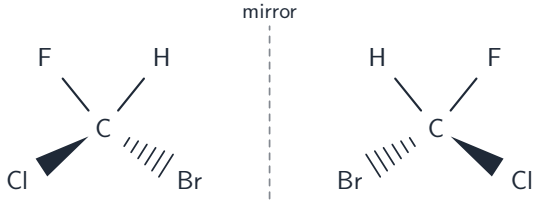
Cis–trans isomers



Ordinary rotation does not freely interconvert these forms while the π bond remains intact; suitable reactions or photochemical excitation can enable isomerization.

- A C=C double bond cannot rotate, because rotation would break the π bond.
- Different groups on each C=C carbon permit geometric stereoisomerism. **Cis–trans isomers** 顺反异构体 use an identical reference group on the two carbons to define same or opposite sides, as in but-2-ene; four different substituents need a different naming convention, outside this assessment requirement.
- **Cis**: the same groups on the same side. **Trans**: on opposite sides.
- Small rings constrain interchange of substituent faces: cis groups lie on the same ring face, trans on opposite faces. Examples include 1,2-dichlorocyclopropane and 1,2-dimethylcyclobutane. Cyclobutane can pucker without thereby converting cis to trans.
- Cis and trans isomers often have different physical properties. Cis-but-2-ene boils at 4 °C and trans-but-2-ene at 1 °C.

Optical isomers



A carbon with four different groups has two mirror-image forms

- A **chiral** 手性 carbon atom (a stereocentre) has four different atoms or groups attached.
- A molecule with one chiral carbon exists as two **enantiomers** 对映异构体: mirror images that cannot be superimposed, like a left and a right hand.

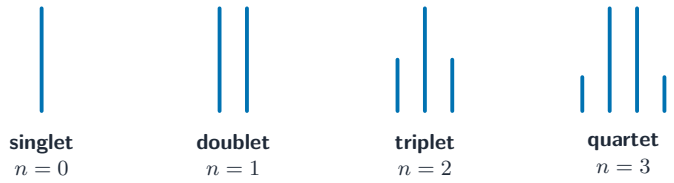
- Enantiomers have the same ordinary properties in achiral environments, apart from equal and opposite optical rotation under identical measurement conditions. They can interact differently with chiral reagents or biological environments.
- Enantiomers rotate **plane-polarized light** 平面偏振光 by the same angle in opposite directions. A polarimeter measures this rotation.
- A **racemic mixture** 外消旋混合物 has equal amounts of the two enantiomers. Their rotations cancel under the same conditions. Optical inactivity alone does not prove an absence of chiral molecules: a racemate is a counterexample.

Example: butan-2-ol, $CH_3CH(OH)CH_2CH_3$. Carbon 2 carries H, OH, CH_3 and C_2H_5, four different groups, so it is chiral. Many drugs are chiral, and the two enantiomers can act very differently in the body.

AHL: Splitting in ^{1}H NMR

The n + 1 rule

In a high-resolution spectrum each peak can be split into several lines. In the simple first-order examples, splitting comes from spin–spin coupling to appropriate nearby nuclei, commonly hydrogens on an adjacent carbon. It is not an unrestricted count of every hydrogen anywhere in the molecule.



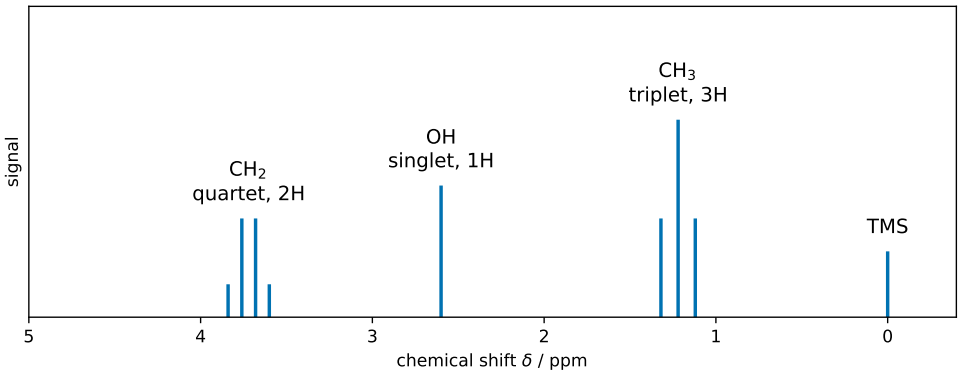
n equivalent neighbours split a peak into $n + 1$ lines

A first-order signal coupled to one set of n equivalent neighbouring protons gives n + 1 lines. More complex coupling lies beyond this simple pattern.

Neighbouring H	Lines	Name	Line heights
0	1	singlet	1
1	2	doublet	1 : 1
2	3	triplet	1 : 2 : 1
3	4	quartet	1 : 3 : 3 : 1

- Equivalent protons do not split one another in the simple first-order examples here; a signal can still be split by a different coupled set.
- With rapid proton exchange, O–H commonly appears as a broad unsplit signal. Slower exchange under suitable dry conditions can reveal coupling, so the singlet is not an unconditional property of every alcohol spectrum.

Reading a high-resolution spectrum



n+1 rule · integration 3 : 2 : 1 · TMS = 0 ppm

CH_3 next to CH_2 gives a triplet; CH_2 next to CH_3 gives a quartet

In ethanol, CH_3 has 2 neighbouring H (on CH_2), so it is a triplet; CH_2 has 3 neighbouring H (on CH_3), so it is a quartet. A 3H triplet paired with a 2H quartet at compatible shifts supports an ethyl group, CH_3CH_2–; multiplicity alone is not proof of the whole molecule.

In methyl propanoate from the worked example, the 3.7 peak (O–CH_3) is a singlet, because its carbon is joined to O, which carries no H; the CH_2 is a quartet and the CH_3 at 1.1 is a triplet.

Practice

1. Draw pentan-2-ol as a skeletal and a condensed structural formula. State how many carbons are at corners and ends.
2. Name (a) $CH_3CH_2CH_2CHO$, (b) $CH_3COCH_2CH_3$, (c) $(CH_3)_3CBr$; draw 2-methylbutane.
3. Give the general formula for simple acyclic monoalkenes and an example with five carbons. Would the formula alone distinguish it from a cycloalkane?
4. Explain why butan-1-ol (117 °C) boils higher than pentane (36 °C) at comparable pressure despite similar relative molecular masses.
5. Draw and classify all alcohol constitutional isomers of $C_4H_{10}O$.
6. Classify CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$. Explain how this differs from classifying 2-bromopropane.
7. Identify the characteristic groups in CH_3COOH, CH_3COOCH_3, CH_3CONH_2 and CH_3OCH_3. Explain why C=O alone does not make a compound an alkene.

8. Explain why increasing chain length often raises boiling point, while successive melting points can be less smooth. Must every branched isomer have a lower melting point?
9. Butan-1-ol has $C_4H_{10}O$. Give its empirical formula, atom count and bond count in a full single-bond structural drawing. Explain one limitation of a flat drawing compared with a 3D model.
10. Explain what a homologous series shares and how adjacent members differ. Give formulas of methanoic and ethanoic acids using a general formula in which n counts all carbon atoms.
11. Draw an alcohol and an ether with formula C_2H_6O. Explain why molecular formula alone cannot determine connectivity or hydrogen bonding between their pure molecules.
12. **AHL.** For invented $C_4H_8O_2$ data, an assigned singly charged molecular ion is at 88, IR has C=O at 1740 cm^{-1} and no broad O–H, and low-resolution NMR signals are 3.7 (3H), 2.3 (2H), 1.1 (3H). Calculate IHD and mass, identify a consistent structure and state a limit of each individual technique. Explain IR-active CO_2 despite its lack of permanent dipole.
13. **AHL.** Predict the simple splitting/integration of CH_3CH_2Cl. Explain TMS's reference signal, rapid-exchange OH behaviour and why a quartet is not four environments. For ethanol EI, assign a plausible 31 fragment from 46 and the neutral loss.
14. **AHL.** Explain cis/trans in but-2-ene but not but-1-ene, and in a disubstituted small ring. Identify the stereocentre of 2-chlorobutane; explain tapered wedges, enantiomer rotation and a racemic mixture.

Worked answers.

1. $CH_3CH(OH)CH_2CH_2CH_3$; a five-carbon open zigzag has three internal corners and two ends. Place OH on carbon 2 and retain its H explicitly in the OH label.
2. (a) Butanal; (b) butan-2-one; (c) 2-bromo-2-methylpropane. 2-Methylbutane is $CH_3CH(CH_3)CH_2CH_3$, with a four-carbon parent chain and a methyl substituent at carbon 2.
3. C_nH_{2n}, e.g. pent-1-ene C_5H_{10}. A simple cycloalkane can share that formula; connectivity is still needed.
4. Both have dispersion attractions; the alcohol additionally forms intermolecular hydrogen bonds. Stronger overall attractions require more energy for vaporization. Similar mass is a useful comparison, not proof that all dispersion contributions are identical.
5. Butan-1-ol $CH_3CH_2CH_2CH_2OH$, primary; butan-2-ol $CH_3CH(OH)CH_2CH_3$, secondary; 2-methylpropan-1-ol $(CH_3)_2CHCH_2OH$, primary; 2-methylpropan-2-ol $(CH_3)_3COH$, tertiary. These are four alcohol constitutional isomers, not the complete set including ethers or separate enantiomers.
6. Respectively primary, secondary and tertiary: nitrogen has one, two or three carbon groups attached. For 2-bromopropane, count the two carbon neighbours of the carbon bonded to Br: secondary halogenoalkane.
7. Carboxyl; ester; amido; alkoxy/ether linkage. An alkene needs a carbon–carbon double bond, not a carbon–oxygen double bond. The full group's connections distinguish an acid, ester and amide.
8. Larger comparable chains have greater polarizability and usually stronger dispersion. Melting also depends on crystal packing and symmetry, so branching does not impose one universal lower-melting order.
9. $C_4H_{10}O$ has no common divisor, so its empirical formula is unchanged. There are $4 + 10 + 1 = 15$ atoms and 14 single bonds in the connected acyclic structure. A flat drawing can show connectivity without the actual tetrahedral angles; a 3D model can show those directions.
10. The same characteristic group and a common general formula, with adjacent members typically differing by CH_2. For simple monocarboxylic acids $C_nH_{2n}O_2$ gives CH_2O_2 (HCOOH) and $C_2H_4O_2$ (CH_3COOH). Here n includes the carboxyl carbon.
11. Ethanol CH_3CH_2OH and methoxymethane CH_3OCH_3. Only ethanol has O–H donors for hydrogen bonding between its pure molecules; an ether can accept hydrogen bonds from water without donating one itself. The shared molecular formula does not specify these connections.
12. **AHL.** IHD $= (8 + 2 - 8)/2 = 1$; nominal mass $= 4(12) + 8(1) + 2(16) = 88$. Methyl propanoate, $CH_3CH_2COOCH_3$, fits all the data: OCH_3 3H, CH_2CO 2H, terminal CH_3 3H. The integrations total eight H. A molecular-ion mass alone does not identify connectivity; IR groups do not prove a unique molecule; NMR assignments need formula and other evidence. CO_2's asymmetric stretch and bending change dipole moment and can absorb IR.
13. **AHL.** CH_3 is a triplet (2 adjacent H), CH_2 a quartet (3 adjacent H), total areas 3:2 under simple first-order conditions. TMS has twelve equivalent H and defines 0 ppm. Rapid exchange commonly suppresses OH coupling; slower exchange can change this. A quartet is four lines within one signal. Ethanol can give CH_2OH^+ at nominal 31 with loss of a CH_3 radical: $46 - 15 = 31$.
14. **AHL.** Each but-2-ene C=C carbon has H and CH_3, allowing the identical methyl groups on the same or opposite sides; but-1-ene has two H on one carbon. Small-ring substituents can occupy the same or opposite faces. C2 of 2-chlorobutane has H, Cl, CH_3 and C_2H_5. Solid tapered wedges point towards the viewer, dashed wedges away. A pure enantiomer pair rotates polarized light equally and oppositely under identical conditions; a 1:1 racemate cancels the rotations without removing the chiral molecules.

Exam tips

- Count corners **and ends**, complete carbon valences, and retain heteroatoms and their attached H.
- Give the parent chain and locants; for amines classify at nitrogen, for alcohols/halides at the attached carbon.
- **AHL.** Separate signals, split lines and integrated areas. Check formula, mass and H count together; label invented data and qualify a structural deduction.
- **AHL.** Use an identical reference group for cis/trans and tapered wedges for tetrahedral stereochemistry. Optical inactivity can result from a racemate.

Measuring enthalpy change

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 1.1, Measuring enthalpy changes, for the course first assessed in 2025. This unit has the same content at SL and HL; there are no additional higher-level understandings here.

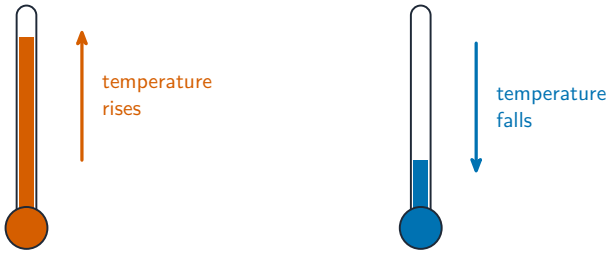
Prerequisites: balancing equations, $n = m/M$, $n = cV$, limiting reactants and the particle model. All experimental data and questions are original, invented teaching examples.

Energy transfer: choose the system

A reacting mixture warms an insulated cup. Has energy been created? No: energy has been transferred from chemical stores into thermal motion. Total energy is conserved.



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



exothermic

heat given out, so the surroundings get hotter ($\Delta H < 0$)

endothermic

heat taken in, so the surroundings get colder ($\Delta H > 0$)

An exothermic reaction warms the surroundings; an endothermic one cools them

The **system** is the part studied; everything else is the **surroundings**. Here the chemical reaction is the system; the solution and cup are the thermal surroundings. The solution contains the reacting particles while also absorbing heat from their reaction.

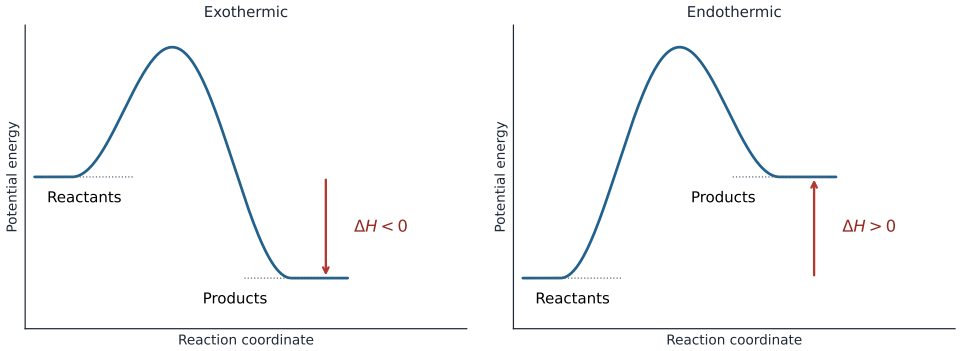
Heat is energy transferred because of a temperature difference, measured in joules. **Temperature** relates to average particle kinetic energy, not an amount of energy. Two water samples at the same temperature can require different heat transfers for the same rise because their masses differ.

An **exothermic** 放热的 reaction transfers energy from the system to the surroundings: the solution normally warms and the reaction has a negative **enthalpy change** 焓变. An **endothermic** 吸热的 reaction takes energy from its surroundings: the solution normally cools and the reaction has a positive enthalpy change. A cooling solution has lost thermal energy even though the reaction has gained energy.

At constant pressure, with only pressure–volume work, the heat transferred to the reacting system equals its enthalpy change. We measure an enthalpy *difference*, not the absolute enthalpy of a substance.

Reaction profiles and relative stability

An energy profile plots **potential energy** against **reaction coordinate**: progress along a pathway, not time. Label both axes and the reactant and product levels; connect the levels through a peak.



The sign of the enthalpy change comes from the product level minus the reactant level, not from the height of the peak.

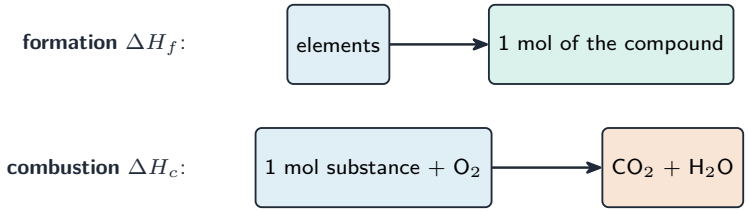
- Exothermic: products have lower potential energy and are more stable in this energetic sense than reactants; $\Delta H < 0$.
- Endothermic: products have higher potential energy and are less stable in this energetic sense; $\Delta H > 0$.
- The peak represents a barrier. Its height above the reactants relates to **activation energy** 活化能; it does not equal the enthalpy change. An exothermic fuel may still need ignition.

Bond breaking requires energy; bond formation releases energy. The net balance determines the sign. Do not say that burning releases energy because bonds are broken. Quantitative bond-energy calculations belong to the next unit. Nor does a negative enthalpy change, by itself, tell us how fast a reaction occurs or fully determine whether it is thermodynamically favourable.

Worked comparison. On an arbitrary common energy scale, reactants are at 80 kJ, products at 30 kJ and the peak at 140 kJ for one stated reaction amount. The endpoint change is $\Delta H = 30 - 80 = -50$ kJ: exothermic. The forward barrier is $140 - 80 = 60$ kJ. Reversing the reaction gives $+50$ kJ, not -60 kJ.

Standard enthalpy changes

A **standard enthalpy change** refers to a specified reaction at constant pressure with substances in their standard states. Standard pressure is 100 kPa (1 bar). A temperature must also be stated; tables commonly use 298 K. Standard does not mean 0 °C, and 298 K is not part of the definition of standard pressure.



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

Specify physical states; for a solution, the school-level standard concentration is 1 $\mathrm{mol\,dm^{-3}}$. Include state symbols in thermochemical equations: producing water vapour rather than liquid water changes the enthalpy change.

A quoted molar reaction enthalpy is tied to the equation as written. Double every coefficient and the heat change for that reaction amount doubles; reverse the equation and its sign reverses. Always explain the basis of "per mole": per mole of fuel burned, salt dissolved, water formed, or reaction as written. A cup experiment at other conditions yields an experimental estimate; do not attach a standard symbol merely because a thermometer was used.

Calorimetry: from temperature to energy

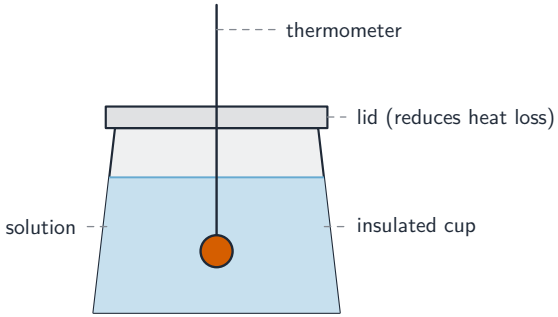
Calorimetry measures heat transfer through a temperature change. For a substance whose specific heat capacity is approximately constant over the range,



A coffee-cup calorimeter: an insulated cup, lid and thermometer measure the temperature change of a reaction in solution

$$q = mc\Delta T, \qquad \Delta T = T_{\text{final}} - T_{\text{initial}}.$$

Here m is the mass being heated or cooled, c its specific heat capacity and q the heat it gains. Specific heat capacity is the energy needed to raise the temperature of unit mass by 1 K. With m in grams and $c = 4.18\ \mathrm{J\,g^{-1}\,K^{-1}}$, q is in joules. A temperature *difference* of 1 °C equals 1 K: no 273 conversion is needed for a difference.



Measure the mass and temperature change of the material that absorbs the heat; reduce exchange with the room.

For dilute aqueous mixtures we often approximate density as $1.00\ \mathrm{g\,cm^{-3}}$ and specific heat capacity as that of water. Use the **total** solution mass, not just the acid volume or the mass of solid added. If dissolving a solid and the stated model includes it, add its mass to the water mass. These are assumptions to justify, not universal properties of all solutions.

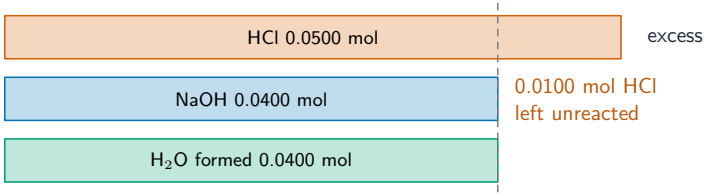
If heat exchange with the room and the cup's heat capacity are neglected,

$$q_{\text{reaction}} = -q_{\text{solution}}, \qquad \Delta H_{\text{r}} = -\frac{q_{\text{solution}}}{1000\, n_{\text{reaction}}}.$$

Convert J to kJ before division. The smallest reactant amount/coefficient ratio gives n_{reaction}; for 1:1 equations, use the **limiting reactant** 限量反应物 amount.

■ Worked example: neutralization with unequal amounts

Mix 25.0 $\mathrm{cm^3}$ of 2.00 $\mathrm{mol\,dm^{-3}}$ HCl with 40.0 $\mathrm{cm^3}$ of 1.00 $\mathrm{mol\,dm^{-3}}$ NaOH. Both start at 21.0 °C and the mixture reaches 28.0 °C. Use the water approximations above and neglect the cup.



$\Delta H_r = -q/(1000 \times \mathbf{0.0400}) \approx -48$ kJ mol^{-1}; dividing by 0.0500 counts acid that never reacted

Divide by the amount that reacted

The equation is $\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$.

$$n_{\mathrm{HCl}} = cV = 2.00 \times 0.0250 = 0.0500 \text{ mol}.$$

$$n_{\mathrm{NaOH}} = cV = 1.00 \times 0.0400 = 0.0400 \text{ mol}.$$

NaOH limits this 1:1 reaction; 0.0400 mol of water forms. The heated solution mass is $(25.0 + 40.0) \times 1.00 = 65.0$ g, and $\Delta T = 7.0$ K.

$$q_{\mathrm{solution}} = mc\Delta T = 65.0 \times 4.18 \times 7.0 = 1901.9 \text{ J}.$$

$$\Delta H_{\mathrm{r}} = -\frac{q_{\mathrm{solution}}}{1000n} = -\frac{1901.9}{1000 \times 0.0400} \approx -48 \text{ kJ mol}^{-1}.$$

The solution gains heat; the reaction loses heat. Dividing by 0.0500 mol would include unreacted acid. The result is an experimental estimate, not evidence that heat loss was absent.

■ Worked example: an endothermic dissolution

Dissolve 4.00 g of a salt of molar mass 80.0 g mol^{-1} in 100.0 g water. The temperature falls from 22.0 to 18.5 °C. Include the salt in the solution mass and assume $c = 4.18$ J g^{-1} K^{-1}.

$$n = \frac{m_{\mathrm{salt}}}{M} = \frac{4.00}{80.0} = 0.0500 \text{ mol}.$$

$$q_{\mathrm{solution}} = mc\Delta T = 104.0 \times 4.18 \times (-3.5) = -1521.52 \text{ J}.$$

$$\Delta H_{\mathrm{solution}} = -\frac{q_{\mathrm{solution}}}{1000n} = -\frac{-1521.52}{1000 \times 0.0500} \approx +30 \text{ kJ mol}^{-1}.$$

Keep the negative temperature change through the calculation. The solution loses heat while the dissolving process gains it.

■ If the cup absorbs appreciable heat

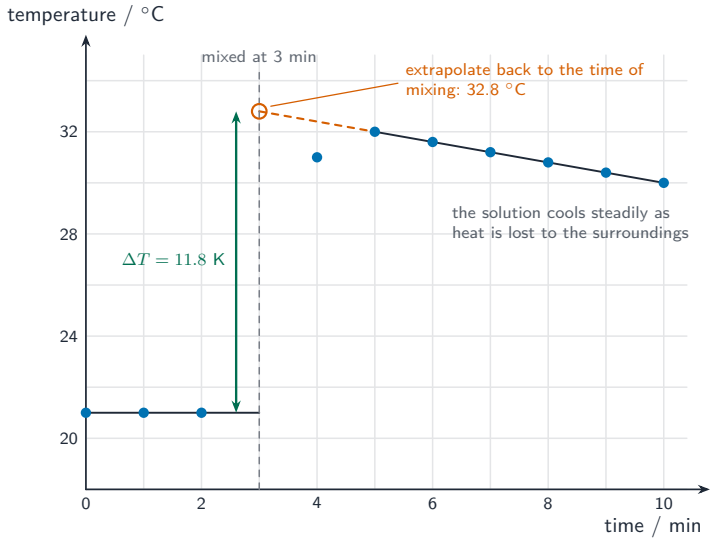
A calibrated calorimeter heat capacity C_{cal} is in J K^{-1}, so it needs no mass factor. When cup and solution undergo the same temperature change,

$$q_{\mathrm{surroundings}} = (mc + C_{\mathrm{cal}})\Delta T.$$

For 100.0 g solution, $c = 4.18$ J g^{-1} K^{-1}, $C_{\mathrm{cal}} = 32.0$ J K^{-1} and a 5.00 K rise, $q_{\mathrm{surroundings}} = (418 + 32.0) \times 5.00 = 2250$ J. If 0.0500 mol reacts, $\Delta H = -45.0$ kJ mol^{-1}. Ignoring the cup gives -41.8 kJ mol^{-1}, a smaller magnitude.

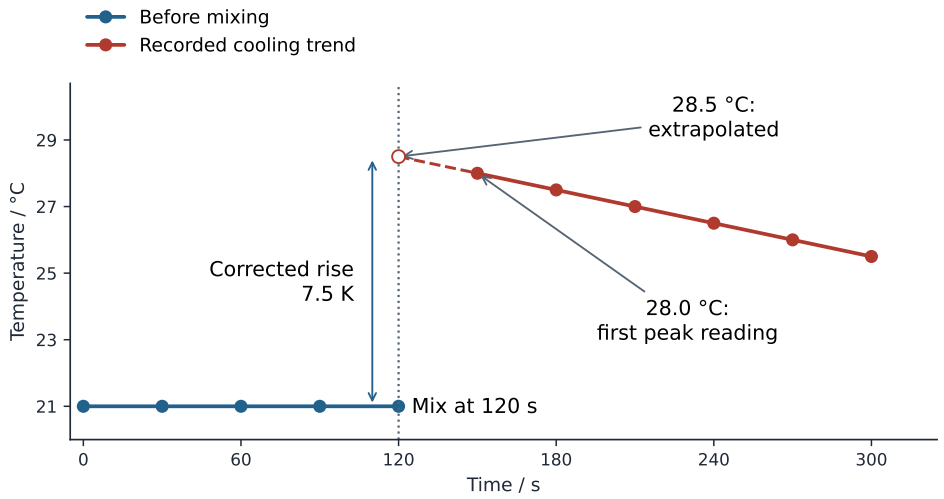
Designing and interpreting an experiment

Use approved apparatus, eye protection and teacher-specified reagents and quantities. An insulated cup and lid reduce heat exchange; a stirrer makes temperature more uniform. Immerse the thermometer bulb without touching the cup. Bring solutions to the same initial temperature, or account for their different starting temperatures; averaging them without regard to their masses and heat capacities is not generally valid.



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

Record temperature regularly before mixing, note the mixing time, then record through the rise or fall and subsequent return towards room temperature. A single observed maximum may miss heat already lost while mixing and reading.



Extrapolate suitable pre- and post-reaction trends to the same mixing time; do not read the extrapolated value at a later time.

In this simplified invented example, mixing is at 120 s, the baseline is 21.0 °C, and the later cooling trend extrapolates to 28.5 °C at mixing. The corrected rise is $28.5 - 21.0 = 7.5$ K rather than the observed $28.0 - 21.0 = 7.0$ K. If all else is unchanged, the corrected heat and enthalpy magnitude are $7.5/7.0 \approx 1.07$ times larger. The cooling trend must represent heat exchange during the short reaction. Slow reaction, evaporation or changing conditions can invalidate that assumption.

For combustion, heat water above a spirit burner and weigh the capped burner before and after. The fuel amount comes from mass *lost* divided by molar mass; the heated mass in $mc\Delta T$ is the water. Keep the burner–container distance consistent and reduce draughts without restricting oxygen. A flame shield must not turn the apparatus into a sealed vessel. Extinguish before weighing; never refill a hot burner.

Heat escaping to the air, heat absorbed by apparatus and incomplete combustion commonly make a measured combustion enthalpy less negative than the complete-combustion value. Soot suggests incomplete combustion. Fuel evaporation increases apparent fuel use without supplying the measured heat and also reduces the calculated magnitude. Repetition reduces random uncertainty, not systematic heat-loss bias.

Distinguish **uncertainty** 不确定度 from percentage disagreement with a reference. If each temperature reading has a stated maximum uncertainty of ±0.1 °C, conservative addition gives ±0.2 K in the difference. A 2.0 K rise has 10% temperature-difference uncertainty; a 10.0 K rise has 2%. Do not increase quantities beyond safe limits merely to improve this percentage.

Practice

Use $c = 4.18\ \mathrm{J\,g^{-1}\,K^{-1}}$ unless stated otherwise. Neglect apparatus heat capacity except in question 8. All data are invented.

1. Explain the difference between heat and temperature. Compare the heat needed to warm 50 g and 100 g of water by the same 4 K.
2. A reaction cools its solution. State the signs of q_{solution} and $\Delta H_{\mathrm{reaction}}$, and identify the direction of energy transfer.
3. An energy profile has reactants at 40 kJ, products at 90 kJ and a peak at 130 kJ for a stated reaction amount. Find the forward enthalpy change, forward barrier and reverse enthalpy change. State which endpoint is lower in energy.
4. A student calls any reaction measured at 25 °C “standard” and omits state symbols. Explain two problems with this claim.
5. A 75.0 g solution warms from 20.0 to 24.0 °C. Calculate the heat it gains and the molar reaction enthalpy if 0.0250 mol reacts.
6. Mix 30.0 $\mathrm{cm^3}$ of 1.00 mol $\mathrm{dm^{-3}}$ HCl with 20.0 $\mathrm{cm^3}$ of 1.00 mol $\mathrm{dm^{-3}}$ NaOH. Both start at 20.0 °C; the final temperature is 25.0 °C. Use density 1.00 g $\mathrm{cm^{-3}}$. Determine the limiting reactant and enthalpy change per mole of water formed.
7. A 2.00 g salt, molar mass 100 g $\mathrm{mol^{-1}}$, dissolves in 50.0 g water. Temperature falls by 2.0 K. Include the salt in the heated/cooled mass. Calculate the molar enthalpy of solution.
8. A 100.0 g solution and calorimeter of heat capacity 40.0 J $\mathrm{K^{-1}}$ warm by 4.00 K when 0.0400 mol reacts. Calculate the enthalpy change including the calorimeter. Explain the effect of ignoring it.
9. An alcohol of molar mass 46.0 g $\mathrm{mol^{-1}}$ loses 0.460 g from a burner while 200.0 g water warms by 12.0 K. Calculate the experimental molar combustion enthalpy. Explain why using 0.460 g in $mc\Delta T$ is wrong.
10. A reaction starts at 20.0 °C. The observed peak is 26.0 °C; extrapolation to mixing gives 26.8 °C. Find both temperature rises and the factor by which the calculated enthalpy magnitude changes.
11. Give two separate reasons why a spirit-burner result may be less negative than a complete-combustion reference, and one appropriate improvement for each. Would repeating the unmodified experiment remove these biases?
12. Two temperature readings each have a maximum uncertainty of ±0.1 °C. Find the conservative percentage uncertainty in a 3.0 K rise. Distinguish this from percentage disagreement when an experimental enthalpy is −42.0 kJ $\mathrm{mol^{-1}}$ and the stated reference is −50.0 kJ $\mathrm{mol^{-1}}$.
13. In the equation $\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)}$, the stated enthalpy change is −286 kJ per mole of reaction. Find the heat transferred by the reaction when 0.250 mol water forms, then state the enthalpy changes for the doubled equation and the reversed original equation.

Worked answers

1. Heat is energy transferred because of a temperature difference; temperature relates to average particle kinetic energy. $q = mc\Delta T$: the 50 g sample needs $50 \times 4.18 \times 4 = 836$ J and the 100 g sample needs 1672 J. Doubling the mass doubles the required heat, although both temperature rises are equal.
2. $q_{\text{solution}} < 0$, so $q_{\text{reaction}} > 0$ and $\Delta H_{\text{reaction}} > 0$: endothermic. Energy transfers from the thermal surroundings to the reacting system.
3. $\Delta H = H_{\text{products}} - H_{\text{reactants}} = 90 - 40 = +50$ kJ; forward barrier $= 130 - 40 = 90$ kJ. The reverse enthalpy change is -50 kJ. Reactants are lower in potential energy; the forward reaction is endothermic.
4. Temperature alone does not establish standard states: pressure, solution concentration where applicable and physical states matter. State symbols distinguish different initial and final states, whose enthalpies differ. The temperature must be specified too.
5. $q = mc\Delta T = 75.0 \times 4.18 \times 4.0 = 1254$ J. $\Delta H = -q/(1000n) = -1254/(1000 \times 0.0250) \approx -50$ kJ mol^{-1}; the reaction supplies the heat gained by solution.
6. $n = cV$: HCl is $1.00 \times 0.0300 = 0.0300$ mol; NaOH is $1.00 \times 0.0200 = 0.0200$ mol. NaOH limits the 1:1 reaction, giving 0.0200 mol water. Total mass is 50.0 g. $q = mc\Delta T = 50.0 \times 4.18 \times 5.0 = 1045$ J. $\Delta H = -q/(1000n) = -1045/20.0 \approx -52$ kJ mol^{-1}.
7. $n = m/M = 2.00/100 = 0.0200$ mol. $q = mc\Delta T = 52.0 \times 4.18 \times (-2.0) = -434.72$ J. $\Delta H = -q/(1000n) = +434.72/20.0 \approx +22$ kJ mol^{-1}. The dissolution absorbs energy.
8. $q = (mc + C_{\text{cal}})\Delta T = (100.0 \times 4.18 + 40.0) \times 4.00 = 1832$ J. $\Delta H = -q/(1000n) = -1832/40.0 = -45.8$ kJ mol^{-1}. Ignoring the calorimeter gives -41.8 kJ mol^{-1}, underestimating the magnitude because it omits energy gained by the cup.
9. $q = mc\Delta T = 200.0 \times 4.18 \times 12.0 = 10032$ J. $n = m_{\text{fuel}}/M = 0.460/46.0 = 0.0100$ mol. $\Delta H = -q/(1000n) = -10032/10.0 \approx -1.00 \times 10^3$ kJ mol^{-1}. The water is the material whose temperature rise is measured; fuel mass instead determines how many moles burned.
10. $\Delta T_{\text{observed}} = 26.0 - 20.0 = 6.0$ K; $\Delta T_{\text{corrected}} = 26.8 - 20.0 = 6.8$ K. The magnitude increases by a factor $6.8/6.0 \approx 1.13$ (about 13%); the exothermic sign stays negative.
11. Heat escapes to the room: insulation or a suitable draught shield reduces that transfer. Incomplete combustion produces less heat than complete combustion: ensure an adequate oxygen supply and inspect for soot. Repetition alone does not eliminate either systematic bias; a shield that restricts oxygen could worsen combustion.
12. Conservative uncertainty in the difference is $0.1 + 0.1 = 0.2$ K, so percentage uncertainty is $(0.2/3.0) \times 100 \approx 6.7\%$. Percentage disagreement is $|-42.0 - (-50.0)|/50.0 \times 100 = 16\%$. The first quantifies measurement uncertainty; the second compares a result with a specified reference and may reflect systematic effects.
13. $q_{\text{reaction}} = n\Delta H = 0.250 \times (-286) = -71.5$ kJ: 71.5 kJ transfers to the surroundings. For $2H_2 + O_2 \rightarrow 2H_2O(l)$, the enthalpy change is -572 kJ per mole of the doubled reaction. Reversing the original equation gives $+286$ kJ per mole of that reversed reaction.

Exam tips

- Balance the equation and find the limiting amount; use all the solution mass in $mc\Delta T$. Name the system before assigning a sign: warming solution means a negative reaction enthalpy in this model.
- Show the J-to-kJ conversion, retain guard digits and state the mole basis. A standard symbol needs standard conditions and states; a negative sign does not prove a fast reaction.
- Label profile axes and draw ΔH between endpoints. Explain an experimental error through its cause, direction of bias and a specific improvement; "human error" is insufficient.

Reference: IB Chemistry guide, Reactivity 1.1.

Reactivity 1.2 · Energy cycles in reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 1.2, Energy cycles in reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: enthalpy change, exothermic and endothermic reactions, and calorimetry from Reactivity 1.1; covalent bonds from Structure 2.2. You will use bond enthalpies and enthalpy data from the data booklet.

Bond enthalpy

Where does the energy of a reaction come from?

Burning one mole of methane in a gas cooker releases about 800 kJ. No atoms are created or destroyed, so the energy must come from the bonds: forming the product bonds releases more energy in total than breaking the reactant bonds requires. Individual bond strengths alone are not enough: count how many bonds of each type occur. This unit shows how to calculate enthalpy changes from bond data and from **energy cycles** 能量循环 when they cannot be measured directly.

Breaking and making bonds

- Breaking a bond **needs** energy: bond breaking is **endothermic**.
- Making a bond **releases** energy: bond making is **exothermic**.

The **bond enthalpy** 键焓 is the energy needed to break one mole of a covalent bond, with the substances in the **gaseous** state. It is always positive. For example, $H_2(g) \rightarrow 2H(g)$, $\Delta H = +436$ kJ mol^{-1}.

The value for a bond such as C–H differs a little from one molecule to another, so the data booklet gives an **average bond enthalpy** 平均键焓: the mean over many compounds.

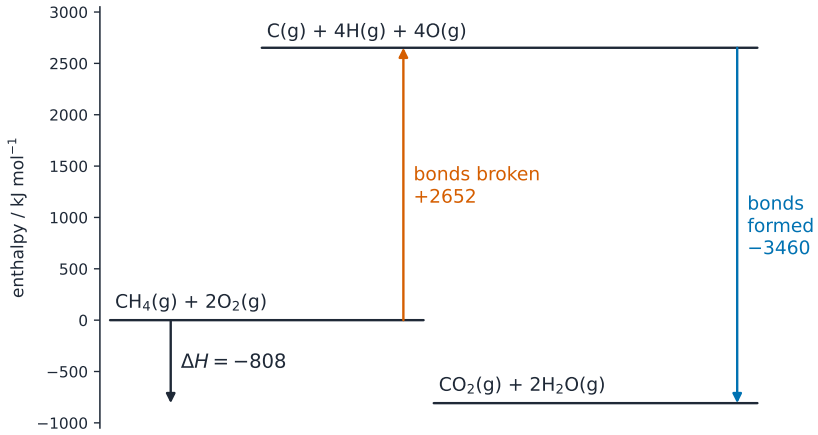
Calculating ΔH from bond enthalpies

$$\Delta H = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

Worked example: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

Bonds broken	Energy / kJ	Bonds formed	Energy / kJ
4 C–H: 4×414	1656	2 C=O: 2×804	1608
2 O=O: 2×498	996	4 O–H: 4×463	1852
total	2652	total	3460

$\Delta H = 2652 - 3460 = -808$ kJ mol^{-1}. More energy is released by forming bonds than is needed to break them, so the reaction is exothermic.



Every bond is broken to gaseous atoms, then the new bonds form; ΔH is the difference

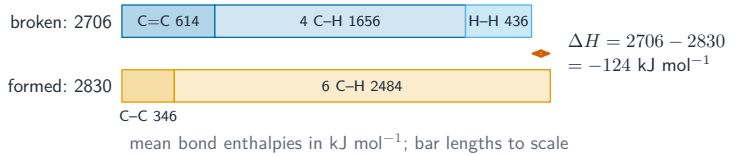
Why the answer is only approximate

The measured value for this reaction is -802 kJ mol^{-1} (with water as a gas). The bond enthalpy answer differs because:

- **average** bond enthalpies are used, not the values for these exact molecules;
- bond enthalpies apply only to **gases**. If a substance is a liquid or solid, the energy to change its state is missing. With liquid water as a product the true value is -890 kJ mol^{-1}.

Count a complete inventory before cancelling

For ethene hydrogenation, draw $CH_2{=}CH_2 + H{-}H \rightarrow CH_3{-}CH_3$. A complete inventory breaks one C=C, four C–H and one H–H, then forms one C–C and six C–H. Using 614, 414, 436 and 346 kJ per mole respectively gives $(614 + 4\times414 + 436) - (346 + 6\times414) = -124$ kJ mol^{-1}. Cancelling four identical average C–H contributions gives the same shortcut. This bookkeeping route through isolated atoms does not assert that a real reaction simultaneously breaks every bond, or that an average C–H value is identical in every molecule.



A complete bond inventory for ethene hydrogenation: -124 kJ mol^{-1}

A stronger comparable bond generally has a larger dissociation enthalpy and a shorter length, but bond type and environment matter. Neither bond polarity alone nor a bond count without bond energies determines the overall heat change. A negative reaction enthalpy also does not imply a fast reaction: activation barriers concern the pathway, not just its endpoints.

Put a phase correction on the correct side

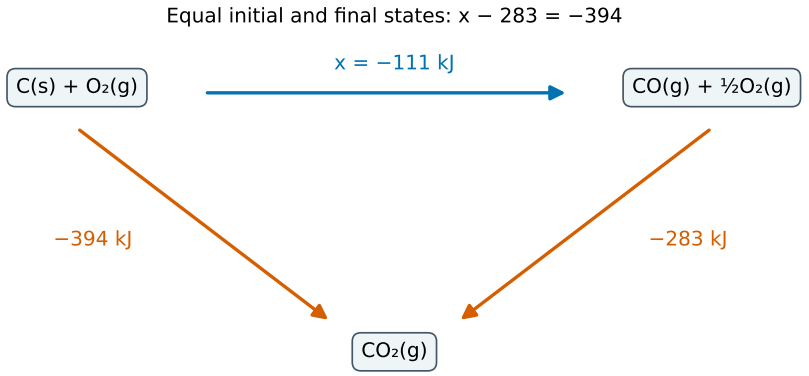
Suppose supplied rounded data give a gas-phase reaction change of -808 kJ per mole of methane and water condensation releases 44 kJ per mole. Two moles of product water condense, so the estimate for liquid products is $-808 + 2(-44) = -896$ kJ mol^{-1}. This remains an estimate from the supplied bond data, rather than the measured -890 value. Condensation releases energy; vaporizing a liquid reactant would require energy before its gaseous bonds could be broken. Write the extra state-change equation instead of guessing its sign.

Hess's law

Same start, same end

Hess's law 盖斯定律: the enthalpy change of a reaction is the same whatever route is taken, as long as the initial and final conditions are the same. Enthalpy is a **state function**: it depends only on where you start and where you finish, like the difference in height between the bottom and the top of a mountain, whichever path you climb.

This lets you calculate enthalpy changes that cannot be measured directly. Build an **energy cycle** with the target reaction on one route and reactions with known ΔH on the other.



Both routes start with $C(s) + O_2(g)$ and finish with $CO_2(g)$: $x - 283 = -394$, so $x = -111$ kJ for the equation shown.

Working with equations

You can also combine equations directly, like algebra:

(1)	$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -394$	multiply an equation ⇒ multiply ΔH
(2)	$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	-283	
	↓		reverse (2): flip the sign
(2′)	$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	$+283$	
	$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	-111 **kJ mol^{-1}**	add; CO_2 cancels

Reverse, multiply, add, cancel

- If you **reverse** an equation, change the sign of ΔH.
- If you **multiply** an equation by a number, multiply ΔH by the same number.
- Add the equations and their ΔH values; species that appear on both sides cancel.

Worked example: find ΔH for $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$, which is difficult to isolate by direct combustion calorimetry because oxidation can also produce CO_2.

- (1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -394$ kJ mol^{-1}
- (2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -283$ kJ mol^{-1}

Keep (1) and reverse (2): $CO_2 \rightarrow CO + \frac{1}{2}O_2$, $\Delta H = +283$. Adding them, CO_2 cancels and $\frac{1}{2}O_2$ is left on the left:

$$\Delta H = -394 + 283 = -111 \text{ kJ mol}^{-1}$$

Worked example: three equations

Find ΔH for $2C(s) + H_2(g) \rightarrow C_2H_2(g)$, given:

- (1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -394$
- (2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H = -286$
- (3) $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$, $\Delta H = -1301$

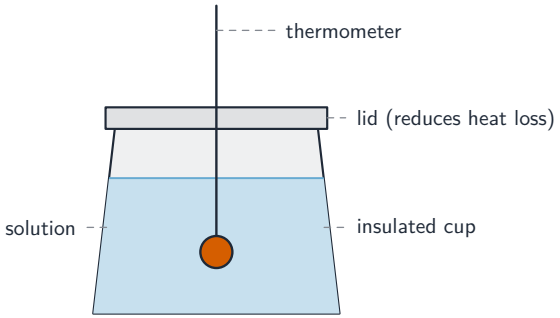
Take $2 \times$ (1) (two C on the left), $1 \times$ (2), and reverse (3) (C_2H_2 on the right):

$$\Delta H = 2(-394) + (-286) + 1301 = +227 \text{ kJ mol}^{-1}$$

Check that the oxygen, CO_2 and water cancel: $\frac{5}{2}O_2$ on each side, $2CO_2$ on each side, one H_2O on each side.

Link a measured heat change to a cycle

A cycle can use an enthalpy change obtained by calorimetry. Use an insulated cup and lid, stir, start the solutions at the same temperature and record a temperature–time series. Extrapolate appropriate pre- and post-reaction trends to the mixing time to estimate the corrected temperature rise; a single observed maximum can miss cooling during measurement.



Calorimetry: measure the temperature change of a known mass of solution

In an invented neutralization experiment, 0.0500 mol of water forms in HCl(aq) + NaOH(aq) − The total solution mass is 100.0 g, its specific heat capacity is 4.18 $\mathrm{J\,g^{-1}\,K^{-1}}$ and its corrected temperature rise is 5.00 K. Neglect the cup's heat capacity and any remaining heat exchange:

$$q_{\text{solution}} = mc\Delta T = 100.0 \times 4.18 \times 5.00 = 2090 \text{ J}.$$

$$\Delta H_{\text{r}} = -\frac{q_{\text{solution}}}{1000n} = -\frac{2090}{1000 \times 0.0500} = -41.8 \text{ kJ mol}^{-1}.$$

The warming solution gains heat, so the reaction transfers energy to the surroundings and has a negative enthalpy change. This is an experimental estimate, not automatically a standard value. A Hess sum using this measured arrow must retain its states, conditions and reaction amount; reversing or scaling the equation also reverses or scales its enthalpy.

■ Match states, coefficients and reaction amount

A valid cycle returns to precisely the same substances, amounts, states, temperature and pressure. Water vapour cannot cancel against liquid water without including condensation or vaporization. Likewise, carbon graphite and diamond are different initial states. A cycle diagram is a map of alternative processes, not a time trace or a mechanism.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad \Delta H = -572$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad -286$ kJ $\quad \div 2$

$4H_2O(l) \rightarrow 4H_2(g) + 2O_2(g)$ $\quad +1144$ kJ $\quad$ reverse, $\times 2$

0.250 mol water formed: $0.250 \times (-286) = -71.5$ kJ $\quad$ states must match: $H_2O(l) \neq H_2O(g)$

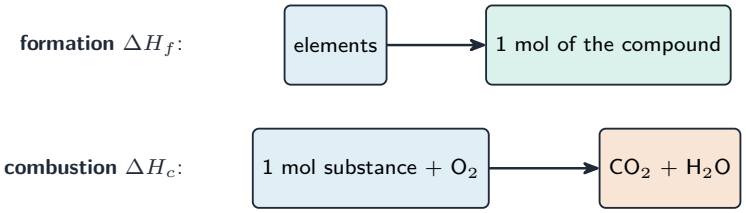
ΔH scales and changes sign with the equation as written

For $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$, supplied $\Delta H = -572$ kJ applies to the equation as written. Halving it gives −286 kJ for one mole of water; reversing and doubling the original gives +1144 kJ for decomposing four moles of water. If 0.250 mol of water forms, the corresponding heat change is $0.250(-286) = -71.5$ kJ. A molar value and the heat of a particular sample are different quantities.

AHL: Formation and combustion cycles

■ Standard enthalpy changes

Standard conditions are 100 kPa and a stated temperature, usually 298 K, written with the symbol ⊖.



Formation makes a compound from its elements; combustion burns it in oxygen

- The **standard enthalpy change of formation** 标准生成焓, $\Delta H_f^{\ominus}$, is the enthalpy change when one mole of a substance forms from its elements in their standard states. For an element in its standard state, $\Delta H_f^{\ominus} = 0$.
- The **standard enthalpy change of combustion** 标准燃烧焓, $\Delta H_c^{\ominus}$, is the enthalpy change when one mole of a substance burns completely in oxygen under standard conditions.

Standard state means the specified reference state at standard pressure and the stated temperature; it is not the same as standard temperature and pressure used for a gas-volume calculation. Graphite is carbon's reference form at 298 K. Diamond has a

nonzero formation enthalpy relative to graphite even though both contain only carbon. Zero formation enthalpy is a reference convention, not a claim that an element contains no energy. A compound can have a positive or negative formation enthalpy.

A formation equation must produce exactly one mole of the named substance: $2C(s,\text{ graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$. Fractions are necessary when they enforce this basis. A combustion equation instead consumes one mole of the named fuel and specifies complete-combustion products and their states.

■ Using formation data

When $\Delta H_f^\ominus$ values are known for every substance, use the products-minus-reactants rule, which comes from a cycle through the elements:

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

Worked example: the combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$. Data: $\Delta H_f^\ominus$ ethanol -278, CO_2 -394, $H_2O(l)$ -286 kJ mol^{-1}; O_2 is an element, so 0.

$$\Delta H_c^\ominus = [2(-394) + 3(-286)] - [(-278) + 0] = -1646 + 278 = -1368 \text{ kJ mol}^{-1}$$

■ Using combustion data

When combustion values are known, the arrows of the cycle point **down** to the combustion products, and the rule turns round:

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

Worked example: the formation of methane, $C(s) + 2H_2(g) \rightarrow CH_4(g)$. Data: $\Delta H_c^\ominus$ carbon -394, hydrogen -286, methane -890 kJ mol^{-1}.

$$\Delta H_f^\ominus = [(-394) + 2(-286)] - (-890) = -966 + 890 = -76 \text{ kJ mol}^{-1}$$

The two routes must contain the same total oxygen and finish with the same amounts of carbon dioxide and liquid water.

AHL: Born–Haber cycles

■ Lattice enthalpy from a cycle

Lattice enthalpy cannot be measured directly, because you cannot separate a crystal into gaseous ions in one step. A **Born–Haber cycle** 玻恩-哈伯循环 is an energy cycle for forming an ionic compound from its elements, through gaseous atoms and gaseous ions. Combine independently determined atomic, ionic and formation data to calculate lattice enthalpy. Values may themselves require indirect measurements or models; a cycle does not make every individual step directly measurable.

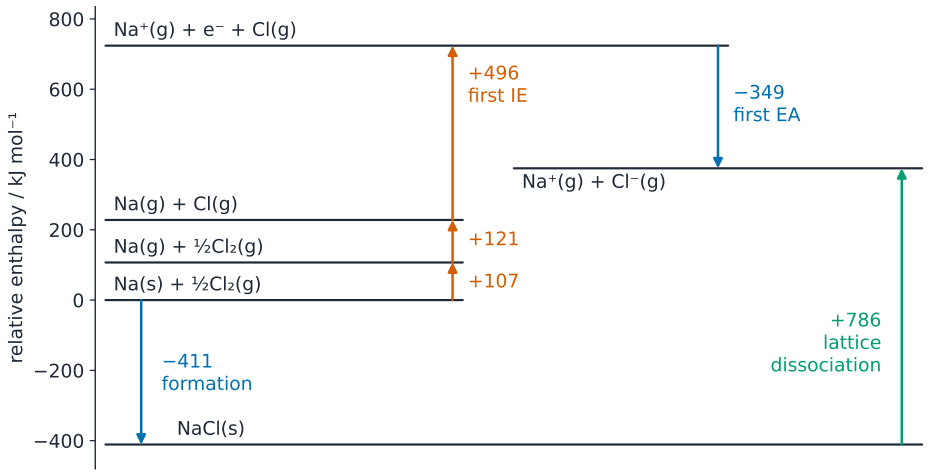


Sodium chloride crystals: a Born–Haber cycle finds the lattice enthalpy that holds this giant ionic lattice together

The steps for sodium chloride:

Step	Process	ΔH / kJ mol^{-1}
atomization of Na	$Na(s) \rightarrow Na(g)$	+107
atomization of Cl	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	+121
first IE of Na	$Na(g) \rightarrow Na^+(g) + e^-$	+496
first electron gain of Cl	$Cl(g) + e^- \rightarrow Cl^-(g)$	−349
formation of NaCl	$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$	−411
lattice dissociation	$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$	unknown

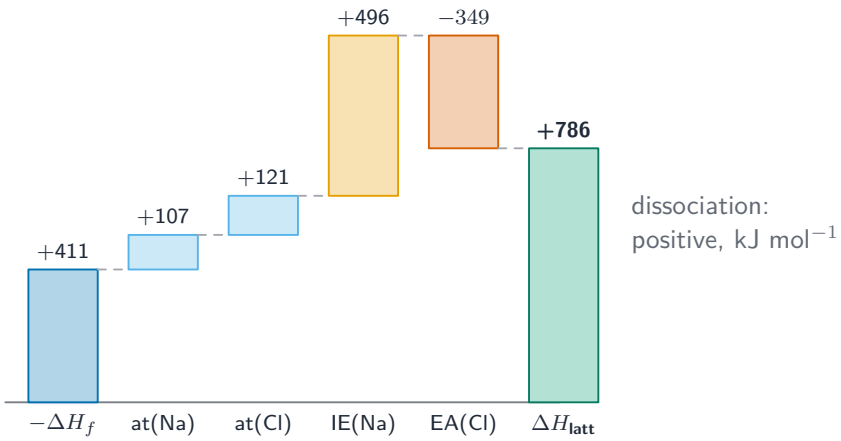
The **enthalpy of atomization** 原子化焓 is the enthalpy change to form one mole of gaseous atoms from the element in its standard state. For chlorine it is half the Cl–Cl bond enthalpy, because one mole of Cl atoms comes from half a mole of Cl_2.



Two routes from NaCl(s) to the gaseous ions have the same total enthalpy change

Calculating the lattice enthalpy

Going round the cycle, the route from NaCl(s) to the gaseous ions directly must equal the route back through the elements:



The cycle as a running total

$$\Delta H_{\text{latt}} = -\Delta H_f^{\ominus} + \Delta H_{\text{at}}(\text{Na}) + \Delta H_{\text{at}}(\text{Cl}) + \text{IE}(\text{Na}) + \text{EA}(\text{Cl})$$

$$\Delta H_{\text{latt}} = 411 + 107 + 121 + 496 - 349 = +786 \text{ kJ mol}^{-1}$$

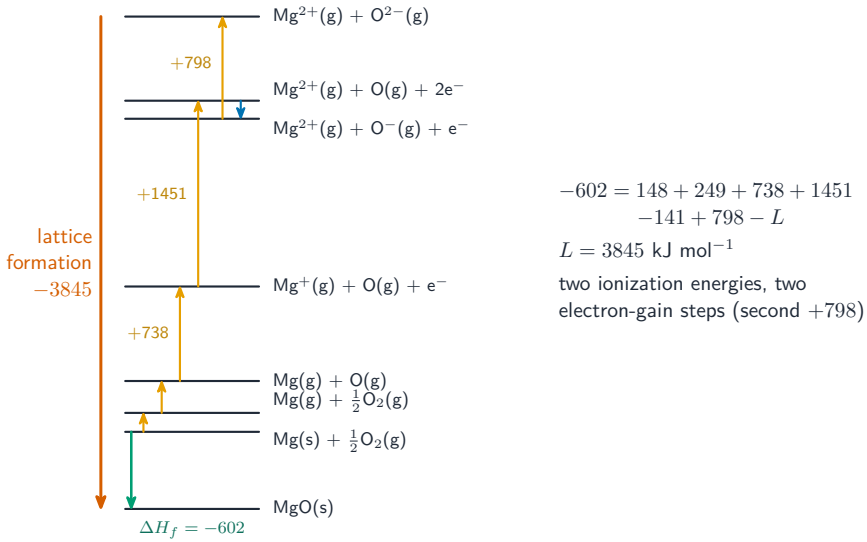
A different reference table may give a nearby value. Use one internally consistent set of supplied data; do not force the result to match a separate rounded table.

Electron affinity here means the signed enthalpy for electron gain: $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$ is -349 kJ per mole with the supplied data. A table that instead reports the positive energy released uses a different sign convention. Read the defining equation. The IB lattice convention here is **dissociation**, positive for separating the stable solid; the reverse lattice-formation arrow has the same magnitude and opposite sign.

For a group 2 compound such as MgO, the cycle includes the first **and** second ionization energies of magnesium, and the first **and** second electron affinities of oxygen. The second electron affinity is positive: adding an electron to O^- means pushing it against the negative charge already there.

Worked divalent example: magnesium oxide

Use the following supplied rounded teaching data, all in kJ per mole of the defined process: Mg atomization +148; O_2 bond dissociation +498; Mg first IE +738 and second IE +1451; O first electron-gain enthalpy −141 and second +798; MgO formation −602. These numbers define this calculation rather than claiming exact agreement with a reference table.



The MgO cycle with supplied teaching data: $L = 3845$ kJ mol^{-1}

One mole of MgO needs one mole of Mg atoms and one mole of O atoms, so oxygen atomization is half a mole of O_2 dissociation: +249. The two successive magnesium ionizations cost $738 + 1451 = 2189$; the two oxygen electron-gain steps total $-141 + 798 = +657$. Electron counts balance: two electrons lost by Mg are gained by O.

If L is the positive lattice-dissociation enthalpy, formation along the atomic route gives $-602 = 148+249+738+1451-141+798-L$. Thus $L = 3243+602 = 3845$ kJ mol^{-1}. Do not halve either Mg ionization energy, omit the positive second affinity or treat -141 as the entire conversion $O \rightarrow O^{2-}$. The larger lattice magnitude for small, doubly charged ions is consistent with stronger electrostatic attraction, but the cycle is needed for a quantitative result.

Interpret supplied cycles by labelling species, arrows and their signs. The current syllabus asks for interpreting and determining values from cycles, rather than constructing a complete Born–Haber cycle from memory. Charge and atom conservation are still essential checks.

Practice

1. Explain, in terms of bonds, why the combustion of methane is exothermic.
2. Use bond enthalpies (H–H 436, Cl–Cl 242, H–Cl 431 kJ mol^{-1}) to calculate ΔH for $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$.
3. Use bond enthalpies (C=C 614, H–H 436, C–C 346, C–H 414 kJ mol^{-1}) to calculate ΔH for $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.
4. Give two reasons why an enthalpy change calculated from average bond enthalpies differs from the measured value.
5. State Hess's law.
6. Given $S(s) + O_2(g) \rightarrow SO_2(g)$, $\Delta H = -297$, and $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, $\Delta H = -198$ kJ mol^{-1}, calculate ΔH for $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$.
7. A supplied enthalpy change for $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is -572 kJ. Find the change for decomposition of four moles of water and the heat released when 0.250 mol of water forms.
8. Explain why $H_2O(l)$ on one side of a Hess sum cannot simply cancel against $H_2O(g)$ on the other. If a gas-product estimate is -808 kJ per mole of methane and condensation is -44 kJ per mole of water, find the liquid-product estimate.
9. For $CH_3Cl(g) + H_2(g) \rightarrow CH_4(g) + HCl(g)$, supplied average C–H, H–H and H–Cl values are 414, 436 and 431 kJ per mole. An illustrative gas-phase reaction enthalpy is -70 kJ per mole. Estimate the C–Cl bond enthalpy within this model.
10. Supplied teaching data give A$\rightarrow$B $+35$ kJ and A$\rightarrow$C -80 kJ for the same amount and conditions. Find B$\rightarrow$C and C$\rightarrow$B; explain why a catalyst cannot change either endpoint difference.
11. A learner calls a reaction exothermic because it breaks many weak bonds and says its average-bond answer proves the mechanism. Explain both errors. Draw the full bond inventory for ethene hydrogenation before using the shortcut.
12. **AHL.** Use $\Delta H_f^\ominus$ values (NH_3 -46, NO $+90$, $H_2O(g)$ -242 kJ mol^{-1}) to calculate $\Delta H^\ominus$ for $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$.
13. **AHL.** Use $\Delta H_c^\ominus$ values (C -394, H_2 -286, C_2H_6 -1560 kJ mol^{-1}) to calculate $\Delta H_f^\ominus$ of ethane. Also explain why graphite, but not diamond, has zero standard formation enthalpy at 298 K.
14. **AHL.** Write oxygen first electron-gain and MgO lattice-dissociation equations. For KCl use atomizations K $+89$ and Cl $+121$, IE $+419$, electron gain -349 and formation -437 kJ/mol; find positive lattice enthalpy. For MgO use the data above; explain ½O_2 and both electron-transfer steps.

Answers.

1. Breaking 4 C–H and 2 O=O absorbs 2652 kJ; forming 2 C=O and 4 O–H releases 3460 kJ. Net release: 808 kJ per mole methane.
2. Broken: $436 + 242 = 678$. Formed: $2 \times 431 = 862$. $\Delta H = 678 - 862 = -184$ kJ mol^{-1}.
3. Cancel four matching average C–H terms: $614 + 436 - 346 - 2(414) = -124$ kJ mol^{-1}. The full inventory is explained above.
4. The supplied values average different molecular environments; gases-only bond data also omit any required state-change steps.
5. The enthalpy change of a reaction is independent of the route taken, provided the initial and final conditions are the same.
6. Keep the first equation and halve the second: $\Delta H = -297 + \frac{1}{2}(-198) = -297 - 99 = -396$ kJ mol^{-1}.
7. Reverse and double the original: decomposition of four moles gives $+1144$ kJ. Formation of 0.250 mol gives $0.250(-572/2) = -71.5$ kJ, so 71.5 kJ is released.
8. Different phases have different enthalpies. Add the state-change equation; two product water molecules per methane give $-808 + 2(-44) = -896$ kJ mol^{-1}. This is still the stated average-bond estimate.
9. Three matching C–H contributions cancel. With $x = D(C - Cl)$, $-70 = x + 436 - 414 - 431 = x - 409$, giving $x = 339$ kJ mol^{-1}. The number is an illustrative estimate, not an exact bond measurement.
10. Reverse A$\rightarrow$B then add A$\rightarrow$C: B$\rightarrow$C gives $-35 - 80 = -115$ kJ; the reverse gives $+115$ kJ. A catalyst supplies another pathway but does not change these specified endpoints.
11. Bond breaking absorbs energy; compare total absorbed with total released. Break C=C, 4 C–H and H–H; form C–C and 6 C–H. Cancelling four average C–H terms gives -124 kJ/mol. This route is bookkeeping, not proof of a mechanism.
12. **AHL.** $[4(+90)+6(-242)] - [4(-46)+0] = (360-1452) - (-184) = -1092+184 = -908$ kJ mol^{-1}.
13. **AHL.** $2C + 3H_2 \rightarrow C_2H_6$: $\Delta H_f^\ominus = [2(-394) + 3(-286)] - (-1560) = -1646 + 1560 = -86$ kJ mol^{-1}. Graphite is the chosen elemental reference form at 298 K; diamond has a different enthalpy relative to that reference.

14. **AHL.** $O(g) + e^- \rightarrow O^-(g)$; $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$. KCl: 437+89+121+419−349 = +717 kJ/mol. MgO: 602+148+249+738+1451−141+798 = +3845 kJ/mol. One O atom requires ½O_2; Mg loses two electrons and O gains two.

Exam tips

- Write **broken minus formed**, count every bond and use gaseous states. Cancel matching average terms only after checking the full inventory.
- Reverse an equation: reverse its sign. Multiply coefficients: multiply its enthalpy. Match phases and state the mole basis.
- **AHL.** Formation data: products minus reactants; combustion data: reactants minus products. Include coefficients and reference states.
- **AHL.** Read the defining arrow: lattice dissociation is positive here. Divalent cycles need both ionizations and both electron gains.

Energy from fuels

International Baccalaureate · IB Diploma · Chemistry · HL

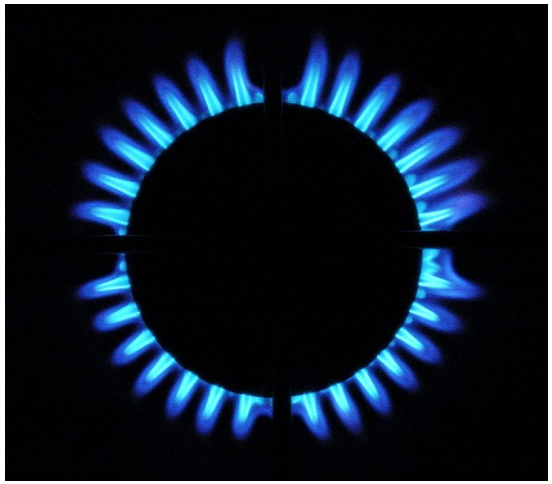
Scope and prerequisites

This handout teaches Reactivity 1.3, Energy from fuels, for the course first assessed in 2025. The understandings in this unit are shared by SL and HL. It also develops the life-cycle comparisons and functional-unit reasoning in the course objectives.

Prerequisites: balancing equations, mole calculations, enthalpy changes and oxidation–reduction. Numerical scenarios are original and invented unless a reference value is explicitly identified. They are not official examination questions.

Combustion: where the energy comes from

A **fuel** stores chemical energy that can be transferred in a useful process. During **combustion**, a substance reacts with oxygen. Many metals, non-metals and organic substances burn when sufficiently heated. Examples include



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

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s),$$

$$C(s) + O_2(g) \rightarrow CO_2(g),$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l).$$

These reactions release energy overall because forming the product bonds releases more energy than breaking the reactant bonds requires. The energy is not released simply

by “breaking the fuel’s bonds”. An ignition source overcomes an activation barrier; a fuel that releases much energy can still be relatively unreactive during safe storage.

Complete combustion of a hydrocarbon or an alcohol produces carbon dioxide and water. Balance carbon first, hydrogen second and oxygen last. An alcohol already contains oxygen, so include that oxygen when calculating the external oxygen supply.

■ Worked example: ethanol

Ethanol is C_2H_5OH, with two carbon atoms, six hydrogen atoms and one oxygen atom per molecule. Two carbon atoms give $2CO_2$; six hydrogen atoms give $3H_2O$. The products contain seven oxygen atoms. One comes from ethanol, leaving six to be supplied by three oxygen molecules:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l).$$

Water may leave a hot flame as vapour. If using a tabulated combustion enthalpy, match its specified water state; a value for liquid water includes the additional energy released on condensation. Do not compare fuel values defined with different product states without accounting for that difference.

Limited oxygen and incomplete combustion

Incomplete combustion occurs when carbon is not fully oxidized to carbon dioxide. Carbon monoxide and/or solid carbon can form, usually alongside some carbon dioxide and water. The following equations are idealized limiting cases, not a claim that a real flame produces only one carbon-containing product:

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

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

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

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g),$$

$$CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(g).$$

Carbon monoxide is colourless and odourless and is toxic because it binds strongly to haemoglobin, impairing oxygen transport. Soot consists of carbon-rich particles; inhaled particles damage health. A yellow, sooty flame can indicate incomplete combustion, but the absence of visible soot does not prove the absence of carbon monoxide.

Hydrocarbons with higher carbon-to-hydrogen ratios, such as longer-chain alkanes, tend to soot more under comparable burning conditions. Oxygen delivery, vaporization and mixing also affect the outcome.

More chemical energy remains in CO or carbon than in fully oxidized products, so incomplete combustion releases less heat per mole of original fuel than complete combustion to the same final water state. It wastes fuel as well as increasing health risks. Provide a suitable oxygen supply and ventilation; never use an unvented flame in an enclosed room. This is a reason to improve apparatus, not an instruction to experiment with unsafe oxygen restrictions.

■ Worked example: balancing an incomplete reaction

For ethanol producing only CO and water as the carbon/hydrogen products, begin with $C_2H_5OH \rightarrow 2CO + 3H_2O$. Products contain five oxygen atoms; ethanol supplies one, so two O_2 molecules supply the remaining four:

$$C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(g).$$

Check every atom after balancing. A smaller oxygen coefficient than in the complete-combustion equation is consistent with incomplete oxidation.

Compare fuels on the same basis

A more negative molar enthalpy does not automatically identify the most useful fuel. A large molecule can release more energy per mole simply because it contains more atoms. **Specific energy** compares energy per unit mass; **energy density** compares energy per unit volume. Storage volume, safety, cost, availability, transport and conversion efficiency also matter.

Use positive magnitudes when comparing energy released. For molar mass M and molar combustion enthalpy ΔH_c,

$$\text{specific energy} = \frac{|\Delta H_c|}{M}.$$

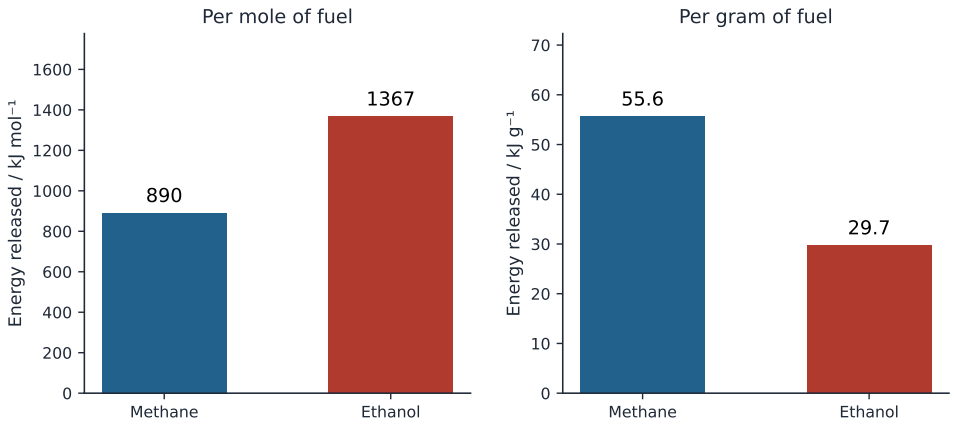
If ΔH_c is in $\mathrm{kJ\,mol^{-1}}$ and M in $\mathrm{g\,mol^{-1}}$, the result is in $\mathrm{kJ\,g^{-1}}$, numerically equal to $\mathrm{MJ\,kg^{-1}}$.

■ Worked comparison: methane and ethanol

Use rounded comparison values of $-890\ \mathrm{kJ\,mol^{-1}}$ for methane and $-1367\ \mathrm{kJ\,mol^{-1}}$ for liquid ethanol, both for complete combustion to liquid water. Use $M = 16.0$ and $46.0\ \mathrm{g\,mol^{-1}}$, respectively.

$$E_{\text{methane}} = \frac{890}{16.0} = 55.6\ \mathrm{kJ\,g^{-1}},$$

$$E_{\text{ethanol}} = \frac{1367}{46.0} = 29.7\ \mathrm{kJ\,g^{-1}}.$$

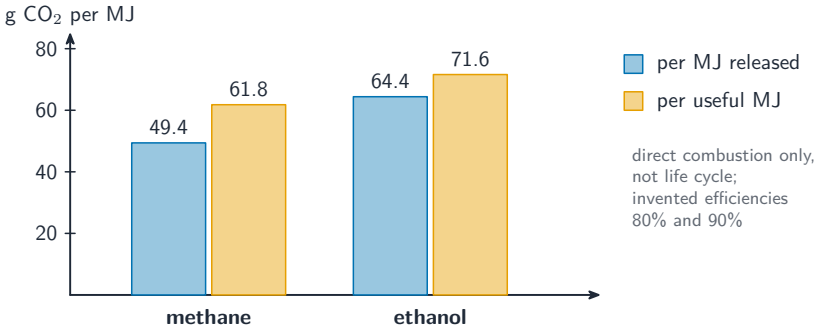


The denominator changes the question being answered; use a common basis before comparing fuels.

Ethanol releases more per mole, but methane more per gram. Methane is a gas under ordinary conditions, requiring a storage strategy such as compression; ethanol is a liquid. The mass comparison alone does not settle a vehicle-storage decision.

■ Carbon dioxide per unit energy

From the balanced equations, one mole methane makes one mole CO_2, while one mole ethanol makes two. With $M_{CO_2} = 44.0\ \mathrm{g\,mol^{-1}}$,



Direct CO_2 per MJ released and per useful MJ (invented efficiencies)

$$I_{\text{methane}} = \frac{44.0}{0.890} = 49.4\ \mathrm{g\ CO_2\,MJ^{-1}},$$

$$I_{\text{ethanol}} = \frac{88.0}{1.367} = 64.4\ \mathrm{g\ CO_2\,MJ^{-1}}.$$

These are **direct combustion** emissions per energy released, not full life-cycle emissions. The carbon source in ethanol and energy used during production have not yet been counted.

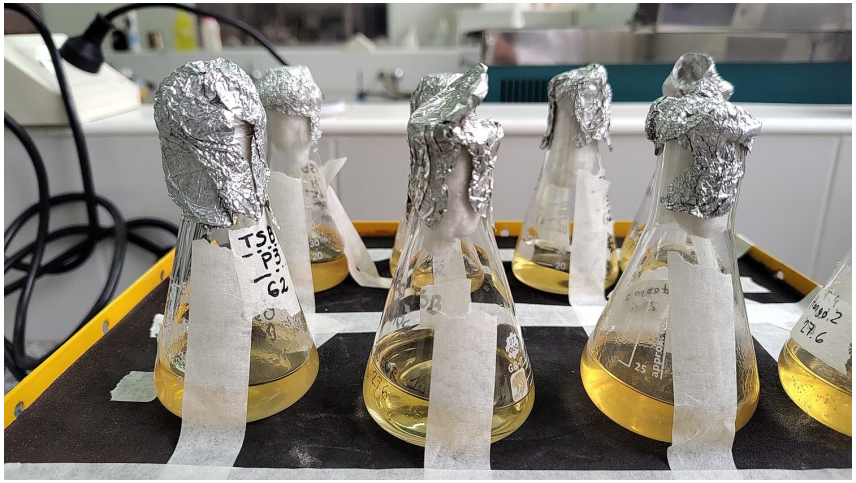
A **functional unit** 功能单位 specifies a common service, such as 1 MJ of useful heat, rather than one mole or one tank. If a heater transfers only a fraction η of the fuel energy usefully,

$$\text{direct } CO_2 \text{ per useful MJ} = \frac{\text{direct } CO_2 \text{ per released MJ}}{\eta}.$$

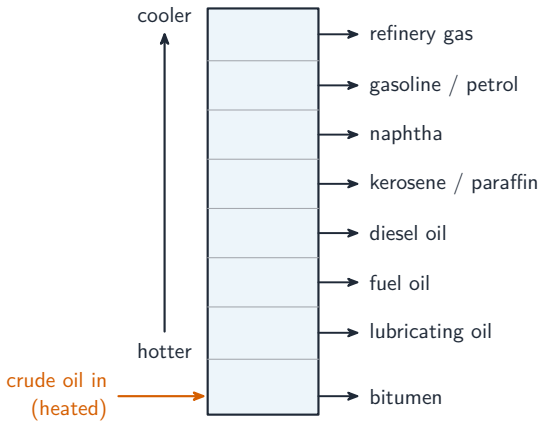
For invented efficiencies of 80% for methane and 90% for ethanol, the respective intensities become $(44.0/0.890)/0.80 \approx 61.8$ and $(88.0/1.367)/0.90 \approx 71.5$ g per useful MJ. Retain unrounded combustion intensities until the final rounding; rounding ethanol to 64.4 first would instead give 71.6. Write percentages as fractions. Comparing released energy on one side with useful energy on the other is unfair.

Fossil fuels and biofuels

Fossil fuels are formed from ancient biological material over geological timescales and are non-renewable on human timescales. Coal is a carbon-rich solid with impurities; crude oil is a mixture refined into useful fractions; natural gas is methane-rich, with composition varying by source.



Fermenting sugar makes bioethanol, a renewable fuel: its carbon came from the air only a season ago



up the column: smaller molecules, lower boiling points, more volatile, runnier (less viscous)

Fractions separate by boiling point: small molecules leave the cool top, thick bitumen stays at the hot bottom

- Coal can be stored as a solid but produces substantial direct CO_2 per released energy; impurities and ash create additional pollution concerns.
- Oil-derived liquid fuels are convenient for transport and energy storage, but combustion emits CO_2 and spills can damage ecosystems.
- Natural gas generally emits less direct CO_2 per released energy than coal, but extraction and transport can leak methane, itself a greenhouse gas. Lower combustion emissions do not remove the need for life-cycle assessment.

CO_2 absorbs and emits infrared radiation at particular wavelengths. Increasing its atmospheric concentration initially reduces net energy escaping to space; warming changes the energy balance towards a new equilibrium. This enhanced greenhouse effect is distinct from ozone depletion. Direct CO_2 accounting therefore addresses a climate impact, while CO and soot introduce additional health and pollution effects.

A **renewable** source is replenished on a timescale relevant to its use; a finite source is not made renewable merely by using it more slowly. Solar energy captured by plants can become a **biofuel**. Photosynthesis fixes atmospheric carbon into biological material:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2.$$

Light supplies energy; photosynthesis is not an energy source independent of sunlight. Fermentation can convert glucose into ethanol and carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

Biomass can regrow, but this does not guarantee that a biofuel is carbon neutral. Growing, harvesting, fertilizer production, processing and transport consume energy and may emit greenhouse gases. Land-use change can release stored carbon or displace food production; regrowth and land availability matter. Waste-derived fuels may have different impacts from crops grown specifically for fuel. Carbon taken up during growth must be counted consistently with carbon released later, without counting the same uptake twice.

Life-cycle assessment and a defensible decision

A **life-cycle assessment** 生命周期评价 follows impacts from raw materials and production through transport, use and end-of-life processes. Specify the boundary and functional unit before comparing options. Carbon dioxide alone does not describe water demand, land use, toxicity, local air pollution or waste.

■ Worked comparison: useful heat with upstream emissions

In an invented comparison per 1 MJ of useful heat, fuel A has 62 g direct CO_2 and 14 g CO_2-equivalent upstream emissions. Fuel B has 72 g direct CO_2; its stated accounting credits 60 g of uptake during feedstock growth, and assigns 25 g CO_2-equivalent upstream emissions.

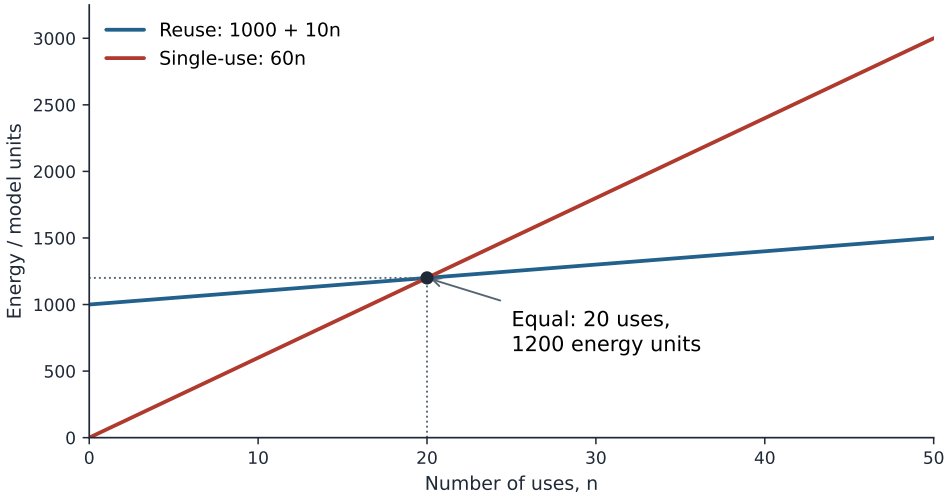
$$I_A = 62 + 14 = 76 \text{ g } CO_2\text{-equivalent},$$

$$I_B = 72 - 60 + 25 = 37 \text{ g } CO_2\text{-equivalent}.$$

B has lower net greenhouse-gas emissions under these assumptions, despite higher direct CO_2. This is a conditional result: the uptake credit, land-use boundary and upstream data must be justified. CO_2-equivalent is an accounting measure combining greenhouse gases on a stated basis; it is not a claim that the exhaust contains that mass of CO_2 alone.

The same logic applies beyond fuels. In a simplified invented reusable-container model, manufacturing costs 1000 energy units and cleaning costs 10 per use, whereas a disposable costs 60 per use. With the same delivered service,

$$E_{\text{reuse}} = 1000 + 10n, \qquad E_{\text{single}} = 60n.$$

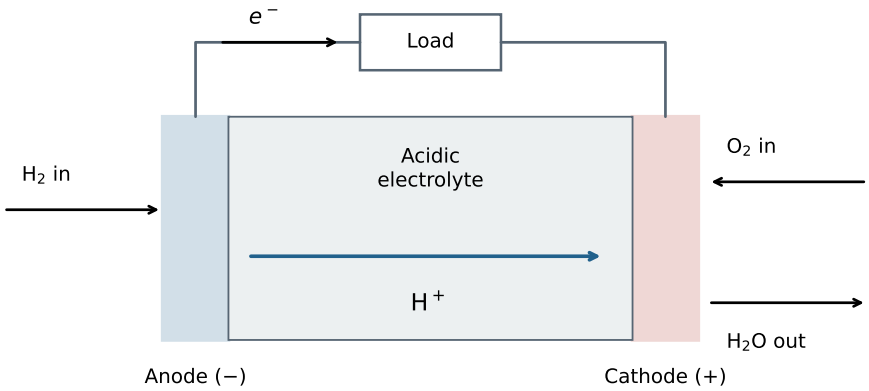


Equal at 20 uses; the reusable option uses less energy after that point.

Equality occurs at $n = 1000/(60 - 10) = 20$ uses. The reusable option uses less energy only **after** 20 uses. Cleaning assumptions, transport and disposal can change the crossover; energy break-even does not establish break-even for water or emissions. "Recyclable" describes a possibility, not proof of collection and recycling. State which impacts and priorities support the final judgement.

Fuel cells: chemical energy directly to electricity

A **fuel cell** separates fuel oxidation from oxygen reduction at electrodes. Electrons travel through an external circuit and can do electrical work; ions carry charge through an electrolyte. The electrolyte must not provide an electron short circuit. Fuel and oxidant are supplied continuously, unlike the finite stored reactants of a primary cell. A fuel cell is not simply a battery that must be recharged after consuming its original reactants.



Oxidation supplies electrons; reduction consumes them.

Oxidation at the anode supplies electrons to the external circuit; oxygen is reduced at the cathode.

Hydrogen in acidic conditions

At the anode, hydrogen is oxidized:

$$H_2 \rightarrow 2H^+ + 2e^-.$$

At the cathode, oxygen is reduced:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O.$$

Add and cancel electrons and hydrogen ions to obtain $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Check both atoms and charge in each half-equation. In this operating cell the anode is negative and the cathode positive; the definitions oxidation/anode and reduction/cathode remain valid in other electrochemical cells too.

In alkaline conditions, balance using hydroxide ions. At the anode:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-.$$

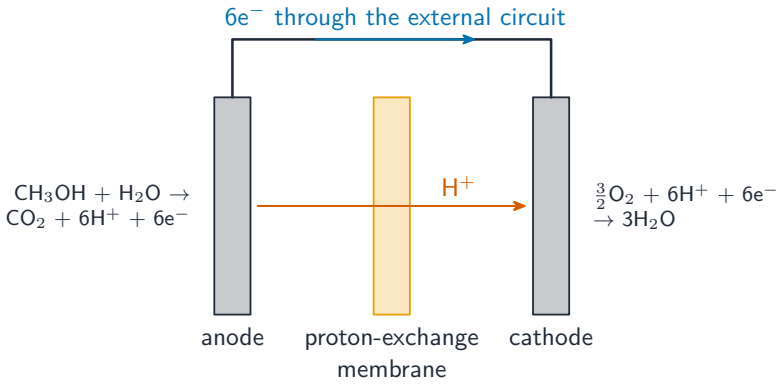
At the cathode:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-.$$

The overall reaction is unchanged. Keep both half-equations in the same medium.

Methanol as a fuel

For a direct methanol cell in acidic conditions, anode oxidation is



overall: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$ (CO_2 is still produced)

A direct methanol fuel cell still produces CO_2

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-.$$

Multiply the acidic oxygen-reduction equation by three:

$$\tfrac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O.$$

After cancelling species, the overall reaction is $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$. Methanol is a convenient liquid to store, but it is toxic and its use produces CO_2. It is incorrect to say all fuel cells emit only water.

Hydrogen cells have no direct CO_2 from the hydrogen–oxygen reaction. However, hydrogen is an **energy carrier**: producing, compressing, transporting and storing it require resources and energy. Emissions depend on the production pathway and energy supply. Fuel cells can avoid an intermediate combustion heat engine, but still have losses; neither direct conversion nor a water-only cell product proves 100% efficiency or zero life-cycle impact.

Practice

Use the rounded fuel data above where needed. All additional scenarios are invented.

1. Balance complete combustion equations for propane, C_3H_8, and methanol, CH_3OH. Include water as a liquid.
2. Balance separate idealized equations for propane forming (a) only CO and water vapour and (b) only carbon and water vapour as products. Why can a real flame differ from both equations?
3. Explain why an exothermic fuel can need ignition. Identify the error in "energy is released when fuel bonds break".
4. Compare methane and ethanol on energy released per mole and per gram, using the given data. Why do the rankings differ?
5. Calculate direct CO_2 produced when methane releases 4.45 MJ and when ethanol releases 4.101 MJ. Then express each as g per released MJ.
6. A methane heater has efficiency 70%. Calculate direct CO_2 per useful MJ and the mass of methane required to deliver 7.00 MJ useful heat.
7. Explain one advantage and one limitation each of coal, oil-derived fuels and natural gas. Distinguish a combustion-emissions comparison from a life-cycle comparison.
8. Write the photosynthesis and ethanol-fermentation equations. Explain two reasons why crop-derived ethanol need not be carbon neutral.
9. A reusable product needs 900 energy units to manufacture and 6 per use; a disposable needs 36 per use. Find the equality point and the first whole number of uses for which reuse consumes less energy. State two model limitations.
10. For the life-cycle example, suppose B's upstream emissions rise to 70 g CO_2-equivalent and its uptake credit falls to 50 g, all per useful MJ. Recalculate B's total and compare with A. What does this show about the decision?
11. Write and add acidic hydrogen-cell half-equations. Identify the electron direction, the oxidation electrode and the species carrying charge through the electrolyte.
12. Derive the acidic methanol-cell overall equation from its two half-equations. Explain why "fuel cells have no carbon emissions" is too broad.
13. A cell receives 100 kJ chemical energy and supplies 58 kJ electricity and 30 kJ useful heat. Find electrical efficiency and total useful-energy efficiency. Explain why neither value alone establishes the lower-impact fuel supply.

Worked answers

1. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O(l)$; $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O(l)$. Carbon and hydrogen balance first; then count oxygen already present in methanol.
2. (a) $2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O(g)$. (b) $C_3H_8 + 2O_2 \rightarrow 3C + 4H_2O(g)$. Real flames can produce mixtures of CO_2, CO, soot and unburned fuel because mixing and oxygen availability vary.
3. Ignition supplies the activation energy needed to begin a pathway. Bond breaking absorbs energy; product bond formation releases energy. A negative net enthalpy does not imply a negligible barrier.
4. Per mole: ethanol 1367 > methane 890 kJ mol^{-1}. Per gram: $E = |\Delta H_c|/M$ gives methane $890/16.0 = 55.6$ and ethanol $1367/46.0 = 29.7$ kJ g^{-1}. The molar masses differ; neither ranking alone describes storage or life-cycle impact.

5. Methane: $n = 4450/890 = 5.00$ mol, giving $m_{CO_2} = 5.00 \times 44.0 = 220$ g; $220/4.45 = 49.4$ g MJ^{-1}. Ethanol: $n = 4101/1367 = 3.00$ mol, giving $m_{CO_2} = 2 \times 3.00 \times 44.0 = 264$ g; $264/4.101 = 64.4$ g MJ^{-1}.
6. Intensity $= 49.4/0.70 \approx 70.6$ g per useful MJ. Released energy $= E_{\text{useful}}/\eta = 7.00/0.70 = 10.0$ MJ. $n = 10000/890 = 11.24$ mol and $m = nM = 11.24 \times 16.0 \approx 180$ g methane. Guard digits avoid premature rounding.
7. Coal: solid storage is straightforward, but combustion and impurities create CO_2/pollution concerns. Oil fuels: convenient liquid transport, but CO_2 and spills matter. Gas: lower direct CO_2 per released energy than coal in a suitable comparison, but methane leakage and storage/infrastructure matter. Life-cycle assessment also counts production, transport and other upstream/downstream impacts.
8. $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ using light; $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. Fossil energy in production and transport can emit CO_2; fertilizer use and land-use change can add greenhouse-gas emissions. Biomass uptake must be assessed over the stated boundary and timescale.
9. $900 + 6n = 36n$, so $n = 900/30 = 30$. Totals are equal at 30 uses; reuse uses less from 31 whole uses onwards. Cleaning and transport assumptions may change the result; energy equality does not establish equality in water use or waste impacts.
10. $I_B = 72 - 50 + 70 = 92$ g CO_2-equivalent per useful MJ, exceeding A's 76. The ranking reverses when the assumptions change. State the boundary, uncertain inputs and priorities rather than declaring one fuel universally preferable.
11. Anode: $H_2 \rightarrow 2H^+ + 2e^-$. Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$. Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Electrons travel from the oxidation anode through the load to the reduction cathode; hydrogen ions carry charge through the acidic electrolyte in this model.
12. Add $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ to $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$. Cancel electrons, hydrogen ions and one water: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$. Methanol cells directly produce CO_2; even hydrogen cells can have upstream emissions.
13. Electrical efficiency $= 58/100 \times 100 = 58\%$. Total useful efficiency $= (58+30)/100 \times 100 = 88\%$; the remaining 12 kJ is not useful output in this boundary. A full comparison also needs fuel production emissions, storage/transport and a common service; useful heat is only credited if there is an actual use for it.

Exam tips

- Balance all atoms, including oxygen already in alcohols, and check charge in half-equations. Use one electrolyte medium consistently.
- Compare the same functional unit. Distinguish direct emissions from life-cycle impacts, and renewable supply from a justified carbon-neutral claim.
- Support a conditional judgement with data, boundaries and uncertain assumptions. Hydrogen cells have no direct CO_2, but fuel production can emit it; methanol cells directly produce CO_2.

References: IB guide, R1.3; NIST ethanol data; DOE fuel cells.

Entropy and spontaneity

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

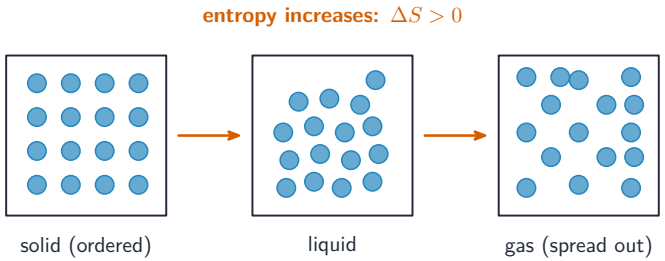
This handout teaches Reactivity 1.4, Entropy and spontaneity, for the course first assessed in 2025. The whole unit is additional higher level (AHL); there is no SL counterpart. Prerequisites: enthalpy changes, balanced equations, equilibrium and logarithms. Numerical model reactions are original teaching examples, not experimental measurements or official examination questions.

AHL: Entropy and accessible arrangements

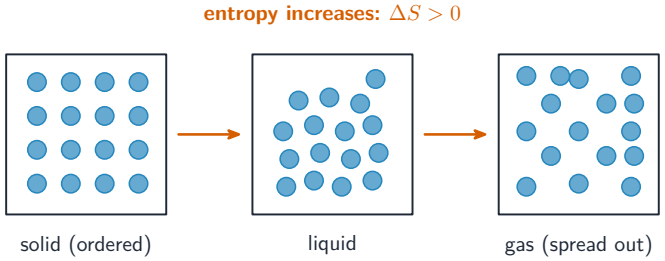
An endothermic change can occur without continuous external driving: enthalpy alone cannot predict the favoured direction. The second ingredient is **entropy** 熵, a state property related to the ways matter and energy can be distributed among accessible microscopic arrangements. "Disorder" is a rough analogy, not a sufficient explanation. A state with more accessible arrangements has higher entropy.



An instant cold pack feels cold because its salt dissolves endothermically (a positive ΔH_{sol}), driven by the rise in entropy



Entropy rises from solid to liquid to gas



Entropy rises from solid to liquid to gas as the particles spread into more arrangements, so ΔS is positive

Imagine four labelled, independently moving model particles, each able to occupy the left or right half of a box. There is one arrangement with all four on the left but six distinct arrangements with two on each side. A spread-out distribution is more probable because more microscopic arrangements produce it, not because particles actively seek disorder. These counts illustrate the idea; they are not a quantitative entropy calculation for a real gas.

For the same substance under comparable conditions, the gas generally has higher entropy than the liquid, and the liquid higher than the solid: particles and energy have more accessible arrangements. Melting, vaporization and expansion of a gas normally increase entropy; freezing, condensation and compression at constant temperature normally decrease it.

In a reaction, an increase in the total amount of gas often suggests a positive system entropy change. For $N_2O_4(g) \rightarrow 2NO_2(g)$, one mole of gas becomes two, suggesting an increase. This is a useful qualitative guide, not a replacement for entropy data when gas amounts are unchanged or different substances must be compared.

A standard molar entropy S° is an entropy per mole under specified standard conditions, usually tabulated in $\mathrm{J\,K^{-1}\,mol^{-1}}$. Unlike standard enthalpies of formation, the standard molar entropies of elements at room temperature are **not zero**. The

third-law reference is a perfect crystal at 0 K, with zero entropy in that ideal limit.

AHL: Calculating a reaction entropy change

Use coefficients from the balanced equation:

$$\Delta S^\circ = \sum \nu S^\circ_{\text{products}} - \sum \nu S^\circ_{\text{reactants}}.$$

Multiply each molar entropy by its stoichiometric coefficient before subtracting. Reversing the reaction reverses the sign; doubling the equation doubles its reaction entropy change.

Worked example: a model dissociation

For the invented model reaction $\mathrm{AB(g)} \rightarrow \mathrm{A(g)} + \mathrm{B(g)}$, assign $S^\circ_{\mathrm{AB}} = 220$, $S^\circ_{\mathrm{A}} = 150$ and $S^\circ_{\mathrm{B}} = 160\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

$$\Delta S^\circ = (150 + 160) - 220 = +90\ \mathrm{J\,K^{-1}\,mol^{-1}}.$$

The positive sign agrees with the increase in gas amount. It describes the reacting **system**, not system plus surroundings. A negative system entropy change is possible when the surroundings gain sufficient entropy.

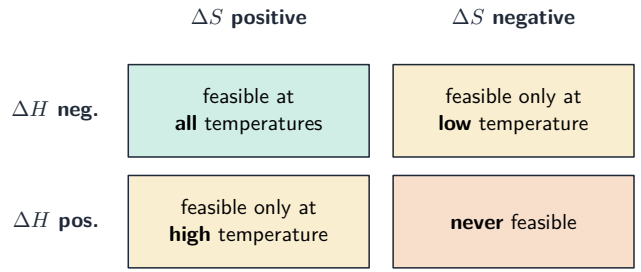
For rounded example data $S^\circ_{\mathrm{N_2}} = 192$, $S^\circ_{\mathrm{H_2}} = 131$ and $S^\circ_{\mathrm{NH_3}} = 193$ in the same units, the equation $\mathrm{N_2(g)} + 3\mathrm{H_2(g)} \rightarrow 2\mathrm{NH_3(g)}$ gives

$$\Delta S^\circ = 2(193) - [192 + 3(131)] = -199\ \mathrm{J\,K^{-1}\,mol^{-1}}.$$

The negative sign is consistent with four moles of gas becoming two. The value refers to the equation as written, forming two moles of ammonia; it is not automatically the change per mole of ammonia.

AHL: Gibbs energy and spontaneity

Gibbs energy 吉布斯能 combines the system's enthalpy and entropy changes. At constant temperature and pressure,



Whether a reaction is feasible ($\Delta G \leq 0$) depends on the signs of ΔH and ΔS, and sometimes on temperature

$$\Delta G = \Delta H - T\Delta S.$$

Here T is absolute temperature in kelvin. Use one energy unit throughout: either all J or all kJ. If ΔH is in $\mathrm{kJ\,mol^{-1}}$ and ΔS in $\mathrm{J\,K^{-1}\,mol^{-1}}$, divide the entropy value by 1000 before substitution.

- $\Delta G < 0$: the forward change is thermodynamically spontaneous for the **current composition and conditions**.
- $\Delta G > 0$: the reverse change is favoured; the forward direction would require coupling or external driving.
- $\Delta G = 0$: there is no net thermodynamic driving force; a reacting mixture is at equilibrium.

Spontaneous does not mean instantaneous, complete, explosive or requiring no initial activation. An activation barrier can make a favourable change extremely slow. A catalyst changes the pathway and rates, not the initial/final thermodynamic states: it does not change ΔG° or the equilibrium constant at a fixed temperature.

The criterion includes the surroundings indirectly. At constant pressure, an exothermic system transfers heat to its surroundings, increasing their entropy. For a closed system at constant temperature and pressure, with only pressure–volume work and heat exchange with surroundings at temperature T, $\Delta S_{\text{total}} = -\Delta G/T$. This explains why the system's entropy may decrease while the total entropy increases under these assumptions.

■ Worked example: an endothermic change

Assign $\Delta H^\circ = +20.0\ \text{kJ mol}^{-1}$, $\Delta S^\circ = +100\ \text{J K}^{-1}\,\text{mol}^{-1}$ and $T = 300$ K to an invented reaction.

$$\Delta S^\circ = \frac{100}{1000} = 0.100\ \text{kJ K}^{-1}\,\text{mol}^{-1}.$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 20.0 - 300(0.100) = -10.0\ \text{kJ mol}^{-1}.$$

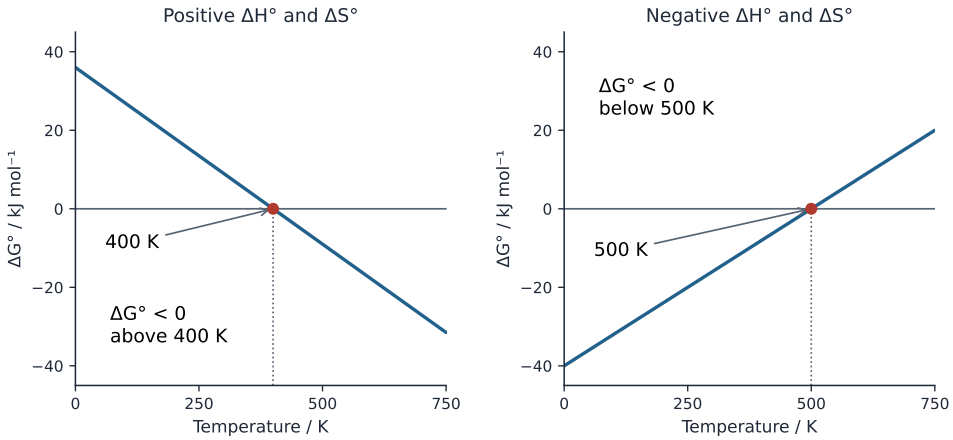
The positive entropy contribution outweighs the positive enthalpy term. The negative **standard** Gibbs energy change favours products in the equilibrium sense, but the actual direction at an arbitrary composition also depends on the reaction quotient, developed below.

AHL: Temperature thresholds

If ΔH° and ΔS° are approximately constant over a temperature range, a plot of ΔG° against T is a straight line. Its intercept is ΔH° and gradient is $-\Delta S^\circ$. Set $\Delta G^\circ = 0$ to find a crossing:

$$T_{\text{cross}} = \frac{\Delta H^\circ}{\Delta S^\circ}.$$

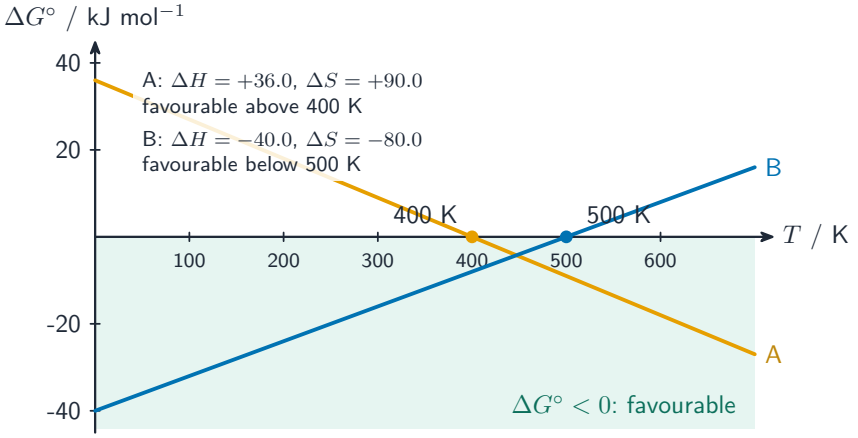
Convert units first. A crossing is a boundary, not an interval of negative Gibbs energy. Test a temperature on either side, or reason from the gradient, before writing an inequality.



Temperature trends assume constant enthalpy and entropy and unchanged phases over the range shown.

■ Worked comparison: opposite slopes

For model A, $\Delta H^\circ = +36.0\ \text{kJ mol}^{-1}$ and $\Delta S^\circ = +90.0\ \text{J K}^{-1}\,\text{mol}^{-1}$:



Two models with opposite slopes: favourable above 400 K, or below 500 K

$$T_{\text{cross}} = 36.0/0.0900 = 400\ \text{K}.$$

At 300 K, $\Delta G^\circ = 36.0 - 300(0.0900) = +9.0\ \text{kJ mol}^{-1}$; at 500 K it is $-9.0\ \text{kJ mol}^{-1}$. Thus $\Delta G^\circ < 0$ above 400 K in this model.

For model B, $\Delta H^\circ = -40.0\ \text{kJ mol}^{-1}$ and $\Delta S^\circ = -80.0\ \text{J K}^{-1}\,\text{mol}^{-1}$:

$$\Delta G^\circ = -40.0 + 0.0800T, \qquad T_{\text{cross}} = 500\ \text{K}.$$

At 300 K the value is -16.0 kJ mol^{-1}; at 600 K it is $+8.0$ kJ mol^{-1}. The negative-entropy model instead has $\Delta G^\circ < 0$ **below** 500 K.

Sign of ΔH°	**Sign of ΔS°**	**When $\Delta G^\circ < 0$**
−	+	all positive temperatures in the model
+	−	no positive temperature in the model
+	+	above the positive crossing
−	−	below the positive crossing

These predictions are conditional. Enthalpy and entropy vary with temperature; phase changes can invalidate a straight-line extrapolation. A mathematically calculated

threshold outside the stated range of stable phases is not proof of a real operating condition.

AHL: Composition, reaction quotient and equilibrium

Standard and actual Gibbs energy changes answer different questions. For the current mixture,

$$\Delta G = \Delta G^\circ + RT \ln Q.$$

Q is the reaction quotient, built from the current composition with stoichiometric powers. Rigorous thermodynamic Q uses dimensionless activities; school ideal-mixture calculations use concentrations or pressures relative to their standard values. Pure solids and pure liquids have activity approximately one and do not appear as variable concentration factors. Do not take a logarithm of a quantity carrying units.

For an ideal model $\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)}$, Q is the ratio of the activities of B to A. As B accumulates relative to A, Q rises and the forward driving force becomes less negative. Equilibrium means $Q = K$ and $\Delta G = 0$, giving

$$\Delta G^\circ = -RT \ln K.$$

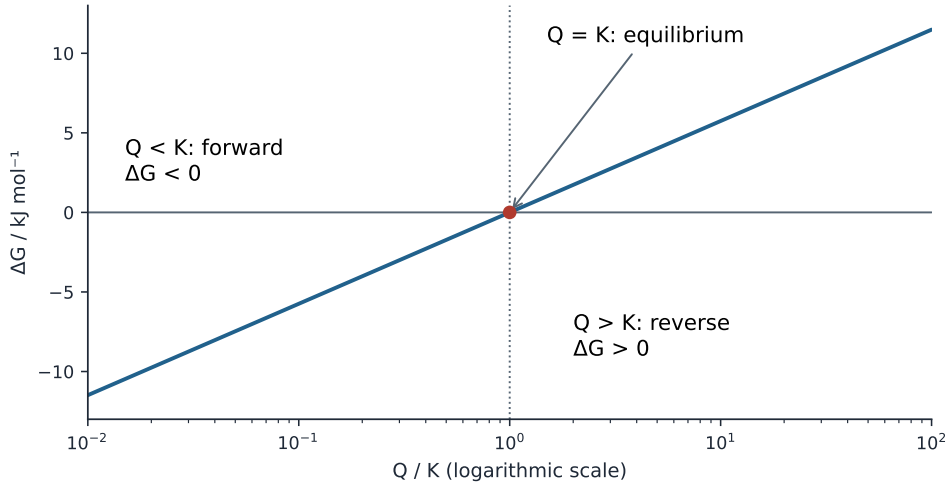
Use $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$ with ΔG° in $\mathrm{J\ mol^{-1}}$, or $R = 0.008314$ with $\mathrm{kJ\ mol^{-1}}$. The logarithm is natural, not base ten.

- $K > 1$ means $\ln K > 0$ and $\Delta G^\circ < 0$.
- $K < 1$ means $\Delta G^\circ > 0$; reactants are favoured in the equilibrium ratio, not the exclusive species present.
- $K = 1$ means $\Delta G^\circ = 0$. It does not imply equal concentrations of every species for every possible equation.

Combining the equations gives a particularly useful direction test:

$$\Delta G = RT \ln\left(\frac{Q}{K}\right).$$

If $Q < K$, the forward change is favoured; if $Q > K$, the reverse change is favoured. At equilibrium, $\Delta G = 0$ even when ΔG° is nonzero.



The standard value can stay unchanged while composition changes the actual driving force.

Worked example: an unfavourable standard value, but forward change

For an invented reaction at 300 K, let $\Delta G^\circ = +6.00\ \mathrm{kJ\,mol^{-1}}$ and $Q = 0.0100$.

$$\Delta G = 6.00 + 0.008314(300)\ln(0.0100) = -5.49\ \mathrm{kJ\,mol^{-1}}.$$

The forward change is favoured at this composition even though the standard value is positive. Separately, $K = \exp[-6000/(8.314 \times 300)] \approx 0.0902$, so $Q < K$, confirming the direction independently. Do not replace the actual ΔG with the standard value.

Practice

All model data are invented unless identified as rounded example data. Use $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

1. Explain entropy using accessible arrangements, and explain why "particles want to become disordered" is inadequate. Compare liquid and gas of the same substance under suitable comparable conditions.
2. Predict the sign of the system entropy change for water freezing, isothermal compression of a gas, and $2\mathrm{N_2O_5(g)} \rightarrow 4\mathrm{NO_2(g)} + \mathrm{O_2(g)}$. State the reasoning and one limitation of gas-amount counting.
3. Use the rounded ammonia data above to calculate ΔS° for the balanced synthesis equation. Give the value for the reversed equation and for forming one mole of ammonia.

4. A student sets the standard molar entropy of nitrogen at 298 K to zero because it is an element. Correct the error and identify the relevant zero-entropy reference.
5. Calculate ΔG° at 300 K for $\Delta H^\circ = +20.0$ kJ mol^{-1} and $\Delta S^\circ = +100$ J K^{-1} mol^{-1}. Explain why an endothermic standard change can have a negative standard Gibbs energy change.
6. For $\Delta H^\circ = +40.0$ kJ mol^{-1} and $\Delta S^\circ = +80.0$ J K^{-1} mol^{-1}, find ΔG° at 400 K. Find the crossing temperature and the interval with $\Delta G^\circ < 0$ under the constant-value approximation.
7. State the sign combinations giving $\Delta G^\circ < 0$ at all positive temperatures and at no positive temperature in the simple model. Explain each from $\Delta H^\circ - T\Delta S^\circ$.
8. For $\Delta H^\circ = -40.0$ kJ mol^{-1} and $\Delta S^\circ = -80.0$ J K^{-1} mol^{-1}, determine the interval with $\Delta G^\circ < 0$. Check it using 300 K and 600 K.
9. A model has $\Delta H^\circ = +18.0$ kJ mol^{-1} and $\Delta G^\circ = -6.00$ kJ mol^{-1} at 300 K. Calculate ΔS° in J K^{-1} mol^{-1}.
10. An equilibrium has $K = 1000$ at 298 K. Calculate ΔG° and explain what its sign says about K, without claiming the reaction goes to completion.
11. At 300 K, $\Delta G^\circ = +6.00$ kJ mol^{-1} and $Q = 0.0100$. Calculate the actual ΔG. Calculate K as a separate check of the predicted direction.
12. A model reaction has $K = 10.0$ at 300 K. Use $\Delta G = RT\ln(Q/K)$ to find ΔG for $Q = 0.100$, 10.0 and 100. Identify the direction favoured in each case.
13. Explain why a catalyst does not change K at fixed temperature, why a spontaneous reaction can be slow, and why a temperature crossing calculated from constant thermodynamic values may fail outside the stated range.

■ Worked answers

1. Entropy relates to the number of accessible ways matter/energy can be distributed, a state property rather than an intention of particles. A gas generally has more accessible arrangements than the same substance as a liquid; qualitative "disorder" alone does not explain the microscopic counting.
2. Freezing: negative, fewer accessible arrangements in the solid. Isothermal gas compression: negative, less available spatial distribution. Decomposition: positive is expected as 2 mol gas becomes 5 mol. Gas amount is a guide; compare entropy data when changes of substance or similar gas amounts make the prediction uncertain.
3. $\Delta S^\circ = 2(193) - [192 + 3(131)] = -199$ J K^{-1} mol^{-1} per equation as written. Reverse: +199 J K^{-1} mol^{-1}. For $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$, halve the value: -99.5 J K^{-1} mol^{-1}.
4. The zero convention for elemental standard enthalpy of formation is not an entropy convention. Nitrogen gas at 298 K has nonzero molar entropy. The ideal third-law reference is a perfect crystal at 0 K.
5. Convert $\Delta S^\circ = 0.100$ kJ K^{-1} mol^{-1}. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 20.0 - 300(0.100) = -10.0$ kJ mol^{-1}. The positive entropy term outweighs the endothermic enthalpy term; the actual direction also depends on composition.
6. $\Delta G^\circ = 40.0 - 400(0.0800) = +8.00$ kJ mol^{-1}. $T_{\text{cross}} = 40.0/0.0800 = 500$ K. Because the gradient is negative, $\Delta G^\circ < 0$ for $T > 500$ K; equality at 500 K is not a negative value.
7. Negative enthalpy and positive entropy: both terms make ΔG° negative at every positive T. Positive enthalpy and negative entropy: subtracting $T\Delta S^\circ$ adds a positive term, so no positive T makes it negative in this model.
8. $\Delta G^\circ = -40.0 + 0.0800T$; it is negative below 500 K. At 300 K it is -16.0 kJ mol^{-1}; at 600 K it is +8.0 kJ mol^{-1}. The direction of the inequality differs from question 6 because ΔS° is negative.
9. $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = [18.0 - (-6.00)]/300 = 0.0800$ kJ K^{-1} mol^{-1} = 80.0 J K^{-1} mol^{-1}.
10. $\Delta G^\circ = -RT\ln K = -8.314(298)\ln(1000) = -17114$ J mol^{-1}, or -17.1 kJ mol^{-1}. The negative standard value corresponds to $K > 1$; finite K does not mean all reactants disappear.
11. $\Delta G = \Delta G^\circ + RT\ln Q = 6.00 + 0.008314(300)\ln(0.0100) = -5.49$ kJ mol^{-1}: forward change is favoured. $K = \exp[-6000/(8.314 \times 300)] \approx 0.0902$; $0.0100 < K$ independently gives the same direction.
12. At $Q = 0.100$, $\Delta G = 0.008314(300)\ln(0.0100) = -11.5$ kJ mol^{-1}: forward. At $Q = 10.0$, $\Delta G = RT\ln 1 = 0$: equilibrium. At $Q = 100$, $\Delta G = 0.008314(300)\ln 10 = +5.74$ kJ mol^{-1}: reverse.
13. A catalyst lowers a kinetic barrier but does not change the Gibbs-energy difference of the states, so ΔG° and K are unchanged at fixed T. A high barrier can make a favourable process slow. Thermodynamic values change with temperature and phases can change, invalidating a constant-value extrapolation.

Exam tips

- Write T in kelvin. Convert J to kJ before combining entropy with a kJ enthalpy; keep R consistent too.
- Use products minus reactants, including all coefficients, for entropy changes. Elements at 298 K do not have zero standard molar entropy.
- A crossing needs an inequality and stated assumptions. For negative entropy, increasing temperature makes ΔG° more positive.
- Distinguish ΔG from ΔG°: equilibrium requires the first to be zero, not generally the second. Use natural logarithms and dimensionless Q and K.
- State spontaneity separately from rate and completion. A catalyst changes neither K nor the thermodynamic direction at a specified composition.

Reference: IB Chemistry guide, Reactivity 1.4.

How much? The amount of chemical change

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 2.1, How much? The amount of chemical change, for the course first assessed in 2025. All of it is SL and HL content.

Prerequisites: the mole, molar mass and concentration from Structure 1.4, and the molar volume of a gas from Structure 1.5. Use the relative atomic masses from the data booklet.

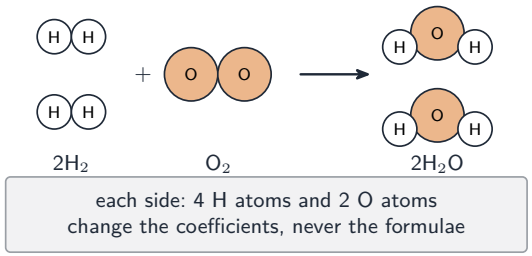
Balanced equations

A recipe for a reaction

A cake recipe says 2 eggs for every 250 g of flour. With 6 eggs you need 750 g of flour, and if you have only 500 g of flour, the flour runs out first. A balanced equation is a recipe for a reaction, but it counts particles, not eggs.

Conservation of mass

In a chemical reaction atoms are rearranged, never made or destroyed. This is the **conservation of mass** 质量守恒: in a closed system, the total mass after an ordinary chemical reaction equals the total mass before it. Gas escaping from an open flask can reduce the measured mass of the flask and its contents; it has not destroyed atoms. So a balanced equation has the same number of atoms of each element on both sides.



A balanced equation rearranges atoms: four H and two O on each side

Balancing an equation

Change only the numbers in front of the formulae, the **coefficients** 系数. Never change a formula itself.

Propane burns in oxygen:

- Unbalanced: $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$.
- Balance C: 3 C on the left, so $3CO_2$.
- Balance H: 8 H on the left, so $4H_2O$.
- Balance O last: $3 \times 2 + 4 \times 1 = 10$ O atoms on the right, so $5O_2$.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

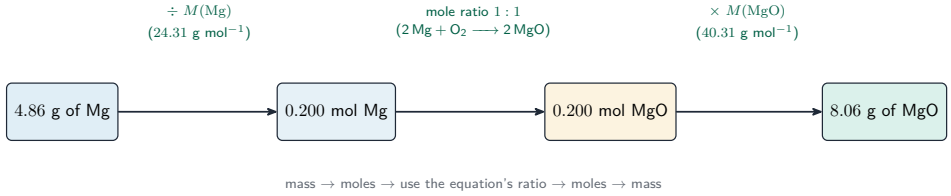
State symbols: (s) solid, (l) liquid, (g) gas, (aq) dissolved in water.

What the coefficients mean

The coefficients give the **mole ratio** 摩尔比 of the reaction. For propane: 1 mol of C_3H_8 reacts with 5 mol of O_2 to give 3 mol of CO_2 and 4 mol of H_2O. The study of these amounts is **stoichiometry** 化学计量.

Reacting masses

Three steps



Mass → amount → balanced ratio → amount → mass. Molar masses carry g/mol units; retain intermediate precision.

1. Convert the mass you know to moles: $n = m/M$.
2. Use the mole ratio from the balanced equation.
3. Convert the moles you want back to a mass: $m = n \times M$.

■ Worked example: lime from limestone

What mass of calcium oxide forms when 50.0 g of calcium carbonate is heated?

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

- $n(\mathrm{CaCO_3}) = 50.0/100.09 = 0.500$ mol.
- Ratio 1 : 1, so $n(\mathrm{CaO}) = 0.500$ mol.
- $m(\mathrm{CaO}) = 0.500 \times 56.08 = 28.0$ g.

■ Worked example: iron from iron ore

What mass of iron forms from 16.0 g of iron(III) oxide?

$$\mathrm{Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)}$$

- $n(\mathrm{Fe_2O_3}) = 16.0/159.70 = 0.100$ mol.
- Ratio $\mathrm{Fe_2O_3}$: Fe = 1 : 2, so $n(\mathrm{Fe}) = 0.200$ mol.
- $m(\mathrm{Fe}) = 0.200 \times 55.85 = 11.2$ g.

■ Charges and units are conserved too

An ionic equation must balance charge as well as atoms: $\mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)}$ has zero net charge on each side. Coefficients are dimensionless ratios of numbers of entities or amounts; they are not mass ratios. A subscript belongs to the identity of the compound, so changing $\mathrm{H_2O}$ to $\mathrm{H_2O_2}$ describes another substance rather than balancing water formation.

Keep intermediate precision. The calcium-carbonate example uses $(50.0/100.09) \times 56.08 = 28.0148\ldots$ g, reported as 28.0 g. The displayed 0.500 mol is rounded for reading, not a replacement for the unrounded value in the calculator. If the starting solid is impure, first determine the mass of the reacting component. A theoretical calculation also assumes the named reaction occurs completely without competing products.

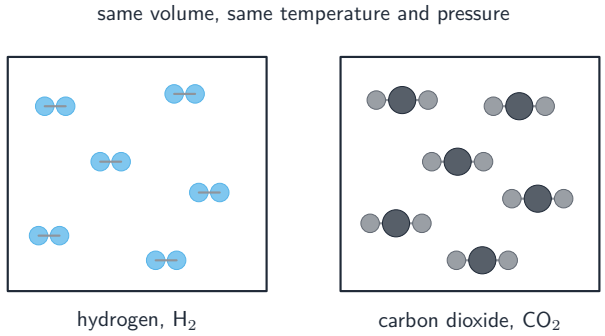
Reacting gas volumes

■ Using the molar volume

At STP (273.15 K, 100 kPa) one mole of any ideal gas occupies 22.7 $\mathrm{dm^3}$. This is the **molar volume** 摩尔体积 (data booklet).



A deployed curtain airbag: a fast reaction makes a calculated volume of nitrogen gas to fill it in milliseconds



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

$$n = \frac{V}{22.7} \quad (V \text{ in } \mathrm{dm^3} \text{ at STP})$$

Worked example: gas from a reaction

What volume of carbon dioxide, at STP, forms when 2.50 g of calcium carbonate reacts with excess hydrochloric acid?

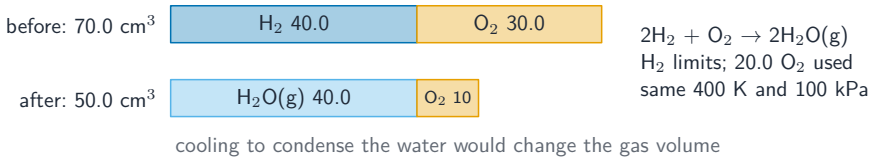
$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

- $n(CaCO_3) = 2.50/100.09 = 0.0250$ mol.
- Ratio 1 : 1, so $n(CO_2) = 0.0250$ mol.
- $V = 0.0250 \times 22.7 = 0.567$ dm^3 $= 567$ cm^3.

For two gases at the same temperature and pressure you do not need the molar volume: the volume ratio is the mole ratio (Avogadro's law, Structure 1.4).

Compare gas volumes only under matching conditions

For an original idealized case, mix 40.0 cm^3 H_2 with 30.0 cm^3 O_2 and allow complete reaction at a common 400 K and 100 kPa. The equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ uses 20.0 cm^3 oxygen for the 40.0 cm^3 hydrogen. Thus hydrogen limits; 10.0 cm^3 oxygen remains and 40.0 cm^3 steam forms. If the final gases are compared at the original temperature and pressure, their total volume is 50.0 cm^3, assuming water remains gaseous and ideal behaviour.

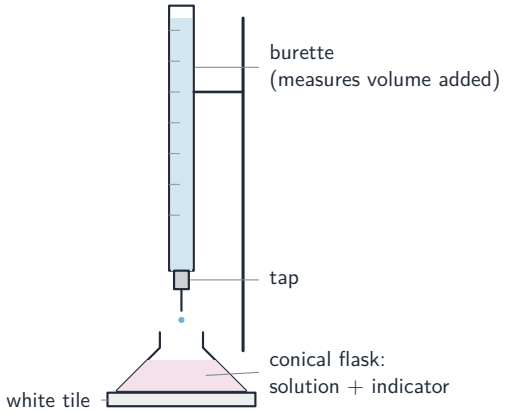


Gas volumes before and after: hydrogen limits

Cooling and condensing the water changes the gas count, and changing temperature changes the volume even for the remaining oxygen. For non-STP data use $pV = nRT$ with matching pressure, volume and R units. A gas collected over water may contain water vapour; use the dry-gas partial pressure when it is supplied, rather than assigning the entire pressure to the reaction gas. Specify whether a quoted volume is wet, dry or an ideal prediction.

Titrations

What a titration does



The titre is the final burette reading minus the initial reading

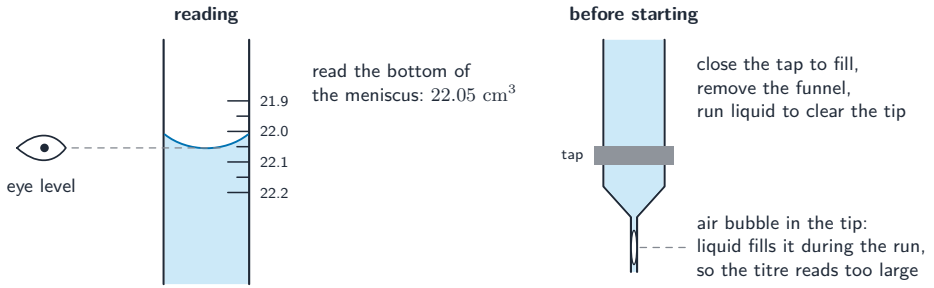
A **titration** 滴定 finds the concentration of a solution by reacting it with a **standard solution** 标准溶液 of known concentration.

- A calibrated **pipette** 移液管 delivers a specified volume with a finite uncertainty, often 25.00 cm^3, of one solution into a conical flask.
- Add a few drops of **indicator** 指示剂.
- Add the other solution from a **burette** 滴定管 until the indicator just changes colour: the **end point** 终点.
- The volume added from the burette is the **titre** 滴定体积.

The **end point** is an observed indicator change; the equivalence point is the stoichiometric condition where the added amount matches the equation ratio. Choose an indicator whose transition occurs near that condition. A repeatable colour change is not by itself proof that the concentration is accurate: an unsuitable indicator or miscalibrated apparatus can produce concordant but biased results.

Good technique

Wear appropriate eye protection throughout the titration.



Read the meniscus bottom at eye level, and clear the tip of air before the first reading

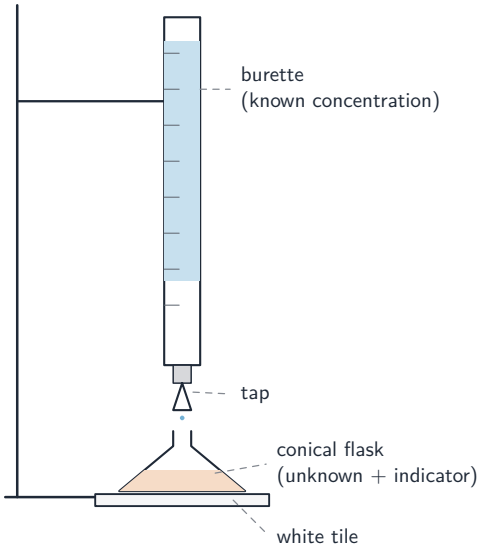
- Rinse the burette with the solution it will hold, and the pipette with the solution it will deliver. Rinse the flask with distilled water only; extra water does not change the amount in it.
- Stand the flask on a white tile so the colour change is easy to see.
- Do a rough titration first. Then add the solution drop by drop near the end point, swirling the flask.
- For a clear aqueous solution in a suitable burette, read the bottom of the meniscus at eye level. A common 0.1 cm^3 scale is estimated to 0.05 cm^3; use the instrument scale and stated uncertainty rather than assuming every burette has this resolution.
- Repeat until titres are **concordant** 一致的 under the stated method. Here use a school criterion of a range no greater than 0.10 cm^3; this is a specified protocol, not a universal definition for every instrument. Average the accepted careful runs, not the rough trial.

Close the tap while filling, remove the filling funnel before reading, and check that the burette tip is full with no air bubble. A bubble that fills during delivery makes part of the apparent titre fill the tip instead of reaching the flask. For a known titrant used to infer analyte amount, this can overestimate that amount. Read a delivered volume as final minus initial; a burette need not start at zero.

If each reading has a stated maximum uncertainty of 0.05 cm^3, the maximum uncertainty in their difference is 0.10 cm^3. For a 21.50 cm^3 titre this contributes $0.10/21.50 \times 100 \approx 0.47\%$. This maximum estimate is not the same as a statistical uncertainty from repeated trials, and neither automatically accounts for a biased endpoint. Use the specified method when combining uncertainties.

■ Worked example: a titration calculation

25.00 cm^3 of sodium hydroxide solution is titrated with 0.100 mol dm^{-3} sulfuric acid.



Titration apparatus: a burette delivers a known solution into a conical flask

Titration	rough	1	2	3
Final reading / cm^3	22.10	43.65	21.45	42.95
Initial reading / cm^3	0.00	22.10	0.00	21.45
Titre / cm^3	22.10	21.55	21.45	21.50

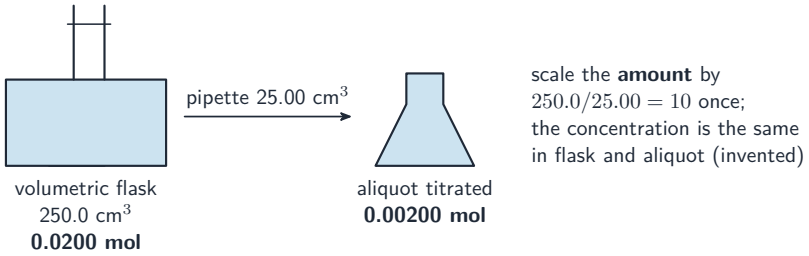
The concordant titres are 21.55, 21.45 and 21.50 cm^3; the mean is 21.50 cm^3. The rough titre is left out.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

- $n(H_2SO_4) = 0.100 \times 21.50/1000 = 2.150 \times 10^{-3}$ mol.
- Ratio 1 : 2, so $n(NaOH) = 4.300 \times 10^{-3}$ mol.
- $c(NaOH) = 4.300 \times 10^{-3}/0.02500 = 0.172$ mol dm^{-3}.

■ Aliquots and the original sample

A titration measures the amount in the aliquot transferred by the pipette. Suppose an original invented sample is dissolved and made up to 250.0 cm^3; a 25.00 cm^3 aliquot requires 0.00200 mol titrant in a 1:1 reaction. The aliquot contains 0.00200 mol analyte, so the full prepared solution contains ten times that amount, 0.0200 mol. The flask volume divided by aliquot volume supplies the factor; do not multiply the final concentration by ten a second time when it already refers to the diluted solution.

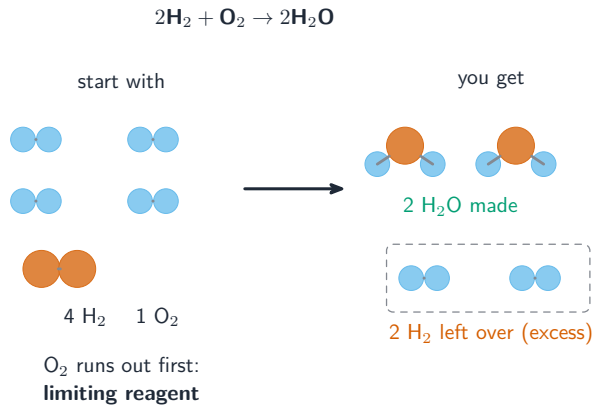


Scale the aliquot amount to the whole flask once (invented)

A calculated concentration can require a correction for an earlier dilution. For a tenfold dilution, the original stock concentration is ten times the concentration in the diluted solution. Keep amount scaling and concentration scaling distinct, and label every vessel and volume in the calculation.

Limiting reactant and yield

The limiting reactant



The reactant that runs out first decides how much product forms

The **limiting reactant** 限量反应物 is used up first and stops the reaction. The other reactant is **in excess** 过量: some of it is left over.

To find the limiting reactant, work out the amount of each reactant in moles and **divide by its coefficient** in the equation. The smaller result is the limiting reactant.

Worked example: aluminium and chlorine

5.40 g of aluminium is heated with 14.2 g of chlorine.

$$2\mathrm{Al(s)} + 3\mathrm{Cl_2(g)} \rightarrow 2\mathrm{AlCl_3(s)}$$

- $n(\mathrm{Al}) = 5.40/26.98 = 0.200$ mol; $0.200/2 = 0.100$.
- $n(\mathrm{Cl_2}) = 14.2/70.90 = 0.200$ mol; $0.200/3 = 0.0667$.
- 0.0667 is smaller, so chlorine is the limiting reactant and aluminium is in excess.
- Retain the unrounded chlorine amount: $n(\mathrm{AlCl_3}) = (14.2/70.90) \times 2/3 = 0.133521\ldots$ mol. Then $m = (14.2/70.90) \times (2/3) \times 133.33 = 17.8$ g to three significant figures.

Equal amounts in moles do not mean neither is limiting. Always use the coefficients.

Percentage yield

The **theoretical yield** 理论产量 is the mass of product calculated from the limiting reactant. The mass you actually collect is the actual yield.

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

If 14.2 g of $\mathrm{AlCl_3}$ is collected in the example above: $14.2/17.8 \times 100 = 79.8\%$.

A pure, dry product often gives less than 100% of the theoretical yield because:

- the reaction may be reversible and reach equilibrium;
- side reactions make other products;
- product is lost when it is filtered, transferred or purified.

Check excess amount and apparent yields above 100 percent

In the aluminium example, use unrounded amounts: chlorine consumes $2/3 \times (14.2/70.90) = 0.133521\ldots$ mol Al. Initially $5.40/26.98 = 0.200148\ldots$ mol Al was present, leaving about 0.0666 mol, or 1.80 g. The excess is the initial amount minus the amount consumed in the balanced ratio, not the difference between the two starting masses.

A measured "yield" above 100% can indicate retained solvent, an incompletely dried solid, impurities or a mistaken limiting-reactant calculation. It does not show that atoms have been created. Compare the actual mass of the desired pure product against a theoretical mass for that same product and reaction; mixtures and wet solids do not satisfy that comparison.

Worked solution precipitation case

The following data are invented for practice. Mix 25.0 cm^3 of 0.120 mol/dm^3 $CaCl_2$ with 40.0 cm^3 of 0.0500 mol/dm^3 Na_2CO_3. Assume quantitative precipitation, additive solution volumes and negligible dissolved $CaCO_3$. The net equation is $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$.

Calcium amount is $0.120 \times 0.0250 = 0.00300$ mol; carbonate is $0.0500 \times 0.0400 = 0.00200$ mol. Carbonate limits, giving $0.00200 \times 100.09 = 0.20018$ g precipitate, reported as 0.200 g. Remaining calcium amount is 0.00100 mol. Its concentration in 0.0650 dm^3 is $0.00100/0.0650 = 0.0154$ mol dm^{-3}. The spectator ions remain dissolved; the volume used for the final concentration includes both mixed solutions.

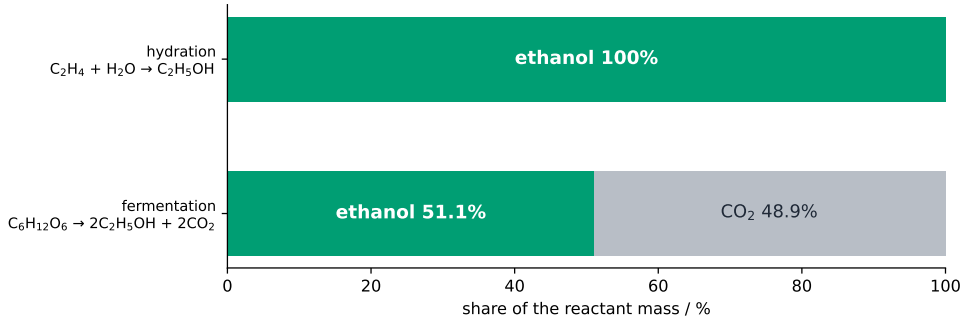
Atom economy

How much of the reactants ends up as product?

Atom economy 原子经济性 measures how much of the mass of the reactants ends up in the product you want.

$$\text{atom economy} = \frac{\text{molar mass of the desired product}}{\text{total molar mass of all reactants}} \times 100$$

Use the coefficients from the balanced equation in both totals.



The displayed hydration equation has ethanol as its only product, so its theoretical atom economy is 100%

Worked example: two routes to ethanol

- Hydration: $C_2H_4 + H_2O \rightarrow C_2H_5OH$. Every atom ends up in ethanol: atom economy 100%.
- Fermentation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. Atom economy $= 2 \times 46.08/180.18 \times 100 = 51.1\%$.

A high atom economy means a larger fraction of the stoichiometric reactant mass is allocated to the desired product. It does not measure solvent use, energy demand, toxicity, actual conversion, product isolation or overall cost; compare those separately. It is not the same as percentage yield: a reaction can have a 100% atom economy but a poor yield.

Practice

1. Balance: $Al + O_2 \rightarrow Al_2O_3$. Also balance the charge and atoms for calcium carbonate precipitation from $Ca^{2+}(aq)$ and $CO_3^{2-}(aq)$.
2. Balance: $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$.
3. Calculate the mass of magnesium oxide made by burning 6.08 g of magnesium: $2Mg + O_2 \rightarrow 2MgO$.
4. Calculate the mass of oxygen needed to burn 11.0 g of propane completely (equation in the handout).
5. Calculate the volume of hydrogen at STP made when 0.654 g of zinc reacts with excess acid: $Zn + 2HCl \rightarrow ZnCl_2 + H_2$.
6. 25.00 cm^3 of hydrochloric acid needs 18.40 cm^3 of 0.150 mol dm^{-3} sodium hydroxide for neutralization. Calculate the concentration of the acid.
7. Titres of 24.30, 23.80, 23.70 and 23.75 cm^3 were recorded; the first was the rough titration. Calculate the mean titre to use.
8. Explain why the conical flask is rinsed with distilled water but the burette is rinsed with the solution it holds.
9. 4.00 g of hydrogen reacts with 16.0 g of oxygen: $2H_2 + O_2 \rightarrow 2H_2O$. Find the limiting reactant and the mass of water made.
10. 10.0 g of $CaCO_3$ is heated and 4.80 g of CaO is collected. Calculate the percentage yield.
11. Calculate the atom economy for making hydrogen from methane: $CH_4 + H_2O \rightarrow CO + 3H_2$.
12. Give two reasons why the actual yield of a reaction is often less than the theoretical yield.
13. In the invented precipitation case above, find the limiting reactant, dry $CaCO_3$ mass and remaining Ca^{2+} concentration. Explain why the original 25.0 cm^3 is not the volume for that final concentration. Then find the total gas volume for the 40.0 cm^3 H_2/30.0 cm^3 O_2 case at the stated 400 K, 100 kPa after complete reaction.

14. An invented 1.25 g impure limestone sample produces 0.227 dm^3 dry CO_2 at STP with excess acid. Assume only $CaCO_3$ produces gas and reaction/collection are complete. Calculate $CaCO_3$ percentage purity. Explain how loss of CO_2 would bias this inferred purity, and why collecting the gas wet would require considering its water-vapour contribution.

Answers.

1. $4Al + 3O_2 \rightarrow 2Al_2O_3$; $Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)$.
2. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$.
3. $n(Mg) = 6.08/24.31 = 0.250$ mol, so 0.250 mol MgO; $m = 0.250 \times 40.31 = 10.1$ g.
4. $n(C_3H_8) = 11.0/44.11 = 0.249$ mol; $n(O_2) = 5(11.0/44.11) = 1.24688\ldots$ mol; $m = 1.24688\ldots \times 32.00 = 39.9$ g.
5. $n(Zn) = 0.654/65.38 = 0.0100$ mol, so 0.0100 mol H_2; $V = 0.0100 \times 22.7 = 0.227$ dm^3 (227 cm^3).
6. $n(NaOH) = 0.150 \times 0.01840 = 2.76 \times 10^{-3}$ mol; ratio 1 : 1; $c(HCl) = 2.76 \times 10^{-3}/0.02500 = 0.110$ mol dm^{-3}.
7. Concordant titres 23.80, 23.70, 23.75; mean 23.75 cm^3.
8. Water in the flask does not change the amount of solute it holds. Water left in the burette would dilute the solution and make the titre too large.
9. $n(H_2) = 4.00/2.02 = 1.98$ mol, $\div 2 = 0.990$; $n(O_2) = 16.0/32.00 = 0.500$ mol, $\div 1 = 0.500$. Oxygen limits. $n(H_2O) = 1.00$ mol; $m = 1.00 \times 18.02 = 18.0$ g.
10. $n(CaCO_3) = 10.0/100.09 = 0.0999$ mol; theoretical CaO $= 0.0999 \times 56.08 = 5.60$ g; yield $= 4.80/5.60 \times 100 = 85.7\%$.
11. Reactants $16.05 + 18.02 = 34.07$; desired product $3 \times 2.02 = 6.06$; atom economy $= 6.06/34.07 \times 100 = 17.8\%$.
12. Any two: the reaction is reversible; side reactions; product lost in transfer, filtering or purification; the reaction does not go to completion.
13. Carbonate limits at 0.00200 mol. Dry precipitate: $0.00200 \times 100.09 = 0.200$ g to three significant figures. Excess calcium: $0.00300 - 0.00200 = 0.00100$ mol; divide by the combined $0.0250 + 0.0400 = 0.0650$ dm^3 to obtain 0.0154 mol/dm^3. In the separate hot-gas case, 40.0 cm^3 H_2 consumes 20.0 cm^3 O_2, forming 40.0 cm^3 steam with 10.0 cm^3 O_2 remaining: total 50.0 cm^3 at the same conditions.
14. Dry CO_2 amount $0.227/22.7 = 0.0100$ mol equals $CaCO_3$ amount. Reacting $CaCO_3$ mass is $0.0100 \times 100.09 = 1.0009$ g; purity $1.0009/1.25 \times 100 = 80.1\%$. CO_2 loss gives too small an inferred amount and purity. For wet gas, the total pressure includes water vapour, so the CO_2 partial pressure is smaller than the total.

Exam tips

- Balance the equation before any calculation, and change only the coefficients.
- Show the mole ratio as a separate line so that the stoichiometric step can be checked.
- Divide cm^3 by 1000 before using $c = n/V$, and use 22.7 dm^3 only at STP.
- Average only concordant titres, and leave out the rough titration.
- For the limiting reactant, divide moles by the coefficient; never compare masses.
- Percentage yield compares masses of product; atom economy compares molar masses in the equation.

How fast? The rate of chemical change

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 2.2, How fast? The rate of chemical change, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: concentration and moles from Structure 1.4, enthalpy changes and energy profiles from Reactivity 1.1, and drawing tangents to curves.

Measuring the rate of reaction

Why does food last longer in a fridge?

Cooling slows many reactions involved in food deterioration; storage life depends on the food and conditions, rather than a universal two-day or one-week clock. A firework burns in a second, iron rusts over months. Chemists need to know not only what forms but how fast, and how to make a reaction faster or slower.

What rate means

The **rate of reaction** 反应速率 is the change in the amount or concentration of a reactant or product per unit time.

$$\text{rate} = \frac{\Delta[\text{product}]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\text{reactant}]}{\Delta t}$$

The unit is usually mol dm^{-3} s^{-1}. If you follow something else, such as a gas volume, the unit follows it: cm^3 s^{-1} or g s^{-1}.

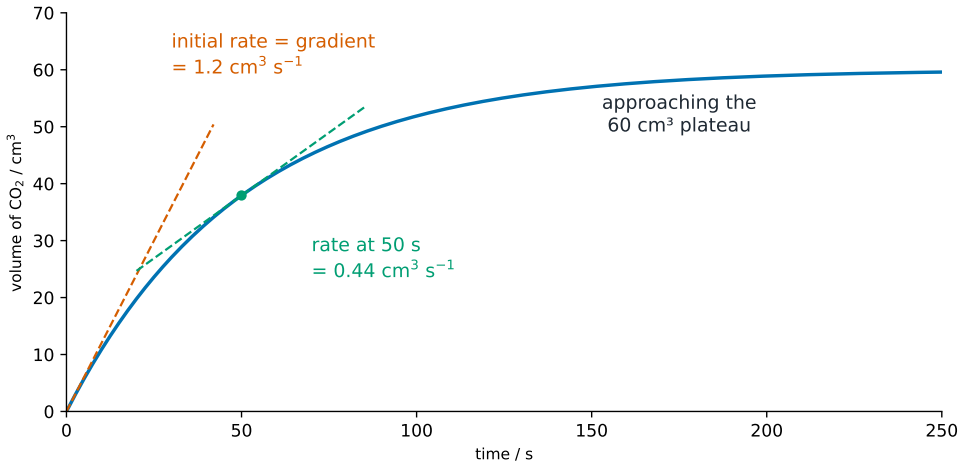
Ways to follow a reaction

What changes	Method	Example
gas is given off	collect the gas in a gas syringe; read the volume every 10 s	$CaCO_3$ + HCl
gas escapes	stand the flask on a balance; read the mass loss	$CaCO_3$ + HCl
colour	colorimeter: measure how much light passes through	bromine reacting with methanoic acid
ions form or are used	conductivity or pH meter	ester hydrolysis
a precipitate forms	time until a cross under the flask disappears	sodium thiosulfate + HCl



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

Reading a rate from a graph

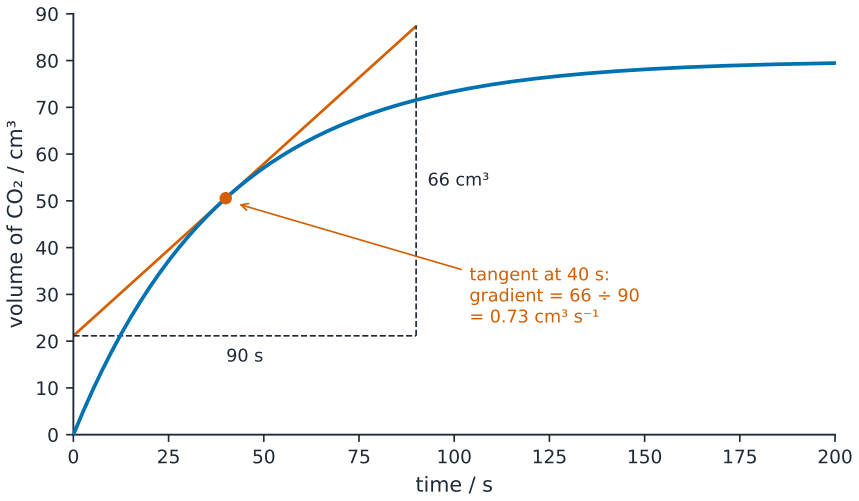


Invented gas-collection curve: the tangent gradient estimates the instantaneous volume-production rate.

- The rate at any time is the gradient of the curve at that time. Draw a **tangent** 切线 and find its gradient.
- In this illustrative consumption experiment, the curve is steepest at the start. This is not universal: induction periods or autocatalysis can give a later maximum. The **initial rate** 初始速率 is the gradient of the tangent at $t = 0$.
- The rate falls as reactants are used up. A flat measured trace means no detectable net change in that observable. Check for completion, dynamic equilibrium, leaks or a sensor limitation before claiming all reaction has stopped.

Choose a slope and specify the species

For a 20–60 s interval, an invented gas-volume rise from 10.0 to 34.0 cm^3 gives mean rate $(34.0 - 10.0)/(60 - 20) = 0.600$ cm^3/s. A tangent through chosen points (30 s, 22 cm^3) and (70 s, 46 cm^3) also has gradient 0.600 cm^3/s, but those must be points on the drawn tangent, not merely two widely separated points on the curve. A tangent estimates an instantaneous rate; a secant averages an interval. A decreasing mass or reactant trace has a negative slope, so define a positive disappearance rate with a minus sign.



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

For $2A \rightarrow B$ at fixed volume, A disappears twice as quickly as B forms. If $-\Delta[A]/\Delta t = 0.0060$ $mol/dm^3/s$, B forms at 0.0030 $mol/dm^3/s$. A normalized reaction rate divides each species rate by its coefficient. State which rate the data and rate constant use rather than switching conventions mid-calculation.

Select a defensible experimental signal

A gas syringe needs gas-tight connections and a consistent start; delayed fitting can lose the early, fastest gas production. A mass-loss experiment needs escaping gas and must account for evaporation or spray. For comparisons, control temperature, reagent amount and concentration, gas pressure and the solid's exposed surface as appropriate. Change only the intended factor and repeat to estimate variability.

gas syringe: gas-tight joints, fit at once (early gas is fastest)	**mass loss**: gas must escape; account for evaporation and spray
colorimeter: calibrate; fixed wavelength, path, working range	**pH or conductivity**: pH is logarithmic; all ions conduct

change one factor, control the rest, repeat to estimate variability

Four ways to follow a rate, and what each needs

A colorimeter can follow concentration through absorbance only with an appropriate calibration, wavelength, path length and working range. Conductivity reflects

contributions from all mobile ions; pH is logarithmic, so a pH–time slope is not directly a concentration–time slope. A disappearing-cross time gives an approximate relative-rate proxy $1/t$ only when the same observable threshold corresponds to the same amount of change, with comparable path length and observation conditions. It is not automatically an instantaneous rate.

Collision theory

Three conditions for a reaction

In the school **collision theory** 碰撞理论 model for collision-activated reactions, only some encounters lead to products. A successful collision needs:

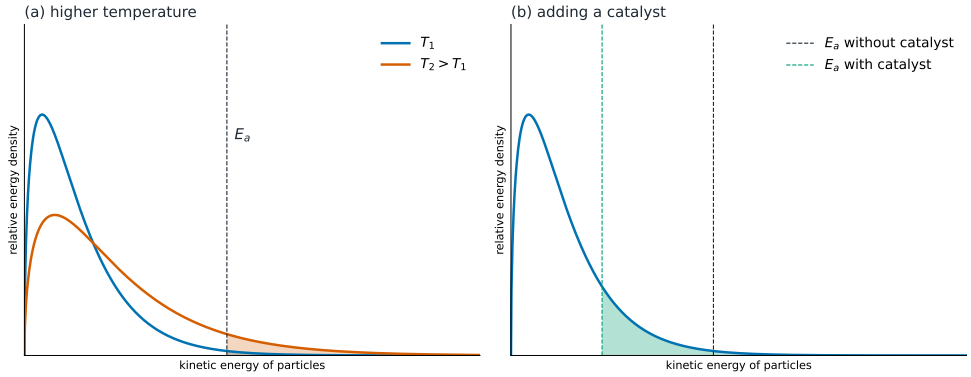
1. A collision: the particles must meet.
2. Enough energy: the collision energy must be at least the **activation energy** 活化能, E_a, the minimum energy needed for a reaction.
3. The right orientation: the reacting parts of the particles must meet.

The rate depends on how many successful collisions happen each second.

Factors that affect the rate

The Maxwell–Boltzmann distribution

The particles in a gas or solution do not all have the same energy. The **Maxwell–Boltzmann distribution** 麦克斯韦-玻尔兹曼分布 shows how many particles have each energy.

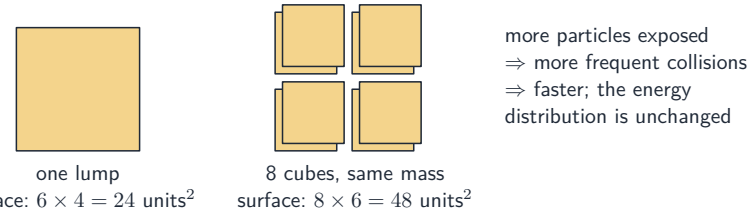


The shaded areas are the particles with at least enough energy to react

- The ideal energy-distribution density starts at zero at the origin. The vertical axis represents numbers per energy interval, not the energy of a single particle.
- The ideal curve has an unbounded tail that approaches zero as energy increases. A finite drawn window does not show the entire distribution.
- The area under the curve is the total number of particles. At a higher temperature the area stays the same, so the peak moves right and falls.
- The shaded tail represents particles above the model energy threshold; sufficient energy is necessary, but appropriate orientation and pathway still matter.

Concentration, pressure and surface area

Change	Effect on collisions	Effect on rate
higher reactant concentration at fixed temperature	more frequent relevant encounters in the simple model	often faster; infer dependence from evidence
compression raising reactant partial pressure at fixed temperature	more reactant particles per volume	often faster
smaller pieces of a solid (larger **surface area** 表面积)	more particles exposed, so more frequent collisions	faster



Cutting a solid doubles its exposed surface here

At fixed temperature and with the same pathway, these changes do not themselves raise the thermal-energy distribution or lower its threshold. Increasing pressure by adding an inert gas at constant volume does not increase the ideal reactant partial pressures. Concentration, surface saturation and complex mechanisms can give behaviours beyond the simplest collision-frequency explanation.

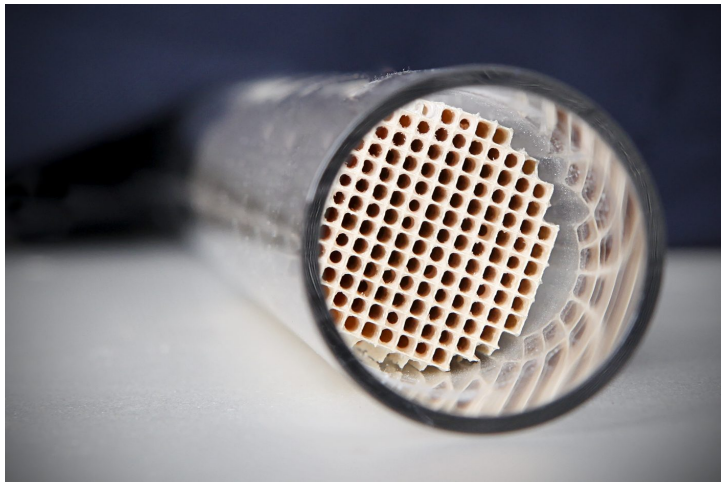
Temperature

A 10 K rise sometimes gives a roughly twofold increase near room temperature, but this is an empirical approximation, not a universal law. Two effects add together:

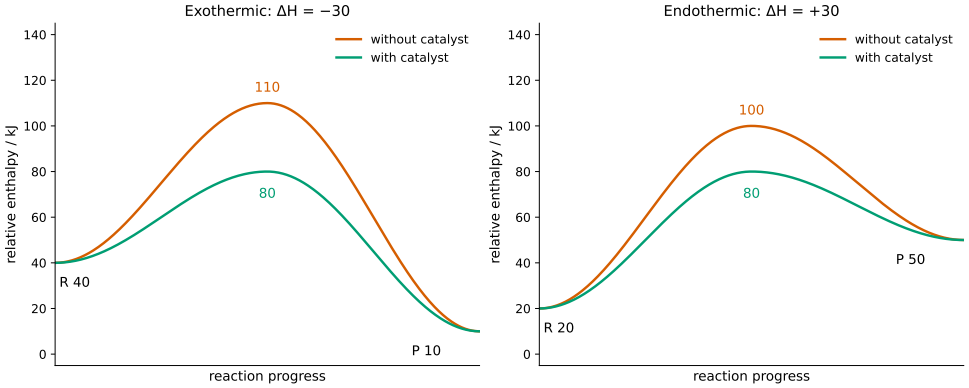
1. Mean translational kinetic energy is proportional to absolute temperature in kelvin; particles move faster, so collisions are a little more frequent. For 20 to 40 degrees Celsius, the mean-energy factor is $313.15/293.15 \approx 1.068$, not two.
2. Much more important: more particles have energy at least E_a (panel (a) above), so a much larger fraction of collisions succeeds.

Catalysts

A **catalyst** 催化剂 increases the rate through participation in a pathway and is regenerated overall. A catalyst can nevertheless be lost, poisoned or deactivated in practice. It gives an **alternative reaction pathway** 替代反应途径 with a lower activation energy.



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



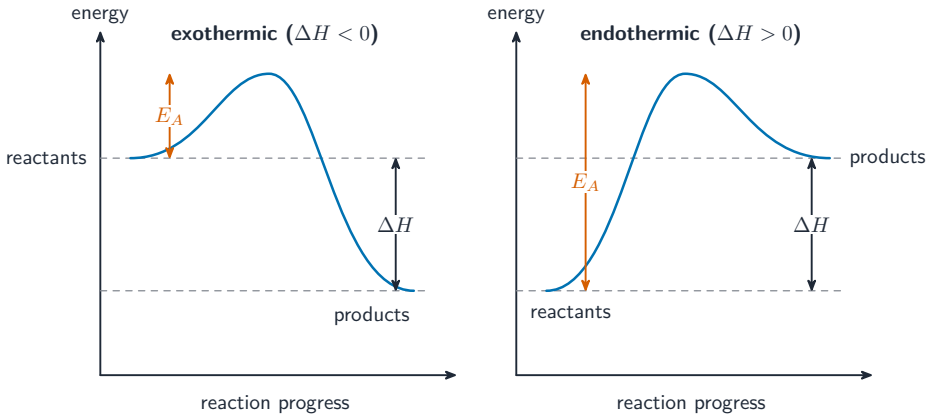
A catalyst lowers E_a but does not change ΔH

- With a lower E_a, more particles have enough energy (panel (b) above), so more collisions succeed.
- A catalyst does not change ΔH, and it does not change the position of an equilibrium.

- Examples: iron in the Haber process, MnO_2 for the decomposition of hydrogen peroxide, enzymes in living cells.

Read either an exothermic or an endothermic profile

The two-panel figure includes invented energy levels in kJ per stated reaction amount. For the endothermic example, reactants are at 20, products at 50 and the uncatalysed peak at 100. Thus $\Delta H = +30$, forward barrier $100 - 20 = 80$ and reverse barrier $100 - 50 = 50$. A catalysed peak at 80 gives barriers 60 and 30, while the endpoints and ΔH remain unchanged.



Exothermic reactions end lower than the reactants; endothermic end higher

At the same temperature a catalyst does not heat the sample or change its Maxwell–Boltzmann distribution: it provides another, lower-threshold pathway. It accelerates approach to the same equilibrium composition in a closed system at fixed conditions. In a simple complete reaction with the same limiting amount and no competing pathways, powdering a solid or adding a catalyst can change the time to a plateau without changing that final amount. Different side reactions, deactivation, leaks or collection conditions can invalidate that comparison.

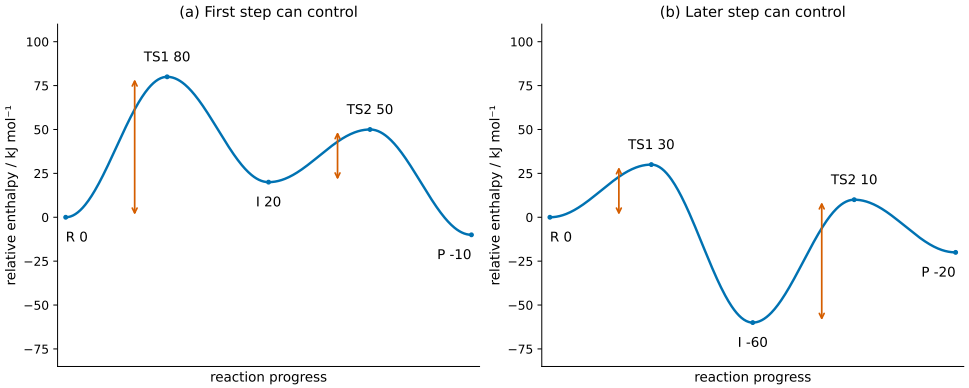
AHL: Rate equations

Elementary steps and mechanisms

Most reactions happen in a series of simple steps called **elementary steps** 基元步骤. The list of steps is the **reaction mechanism** 反应机理.

- The **molecularity** 分子数 of an elementary step is the number of reacting particles participating in that event: unimolecular (1), bimolecular (2) or, rarely, termolecular (3).

- An **intermediate** 中间体 is made in one step and used up in a later step. It does not appear in the overall equation.
- In a mechanism with a strongly dominant bottleneck, the **rate-determining step** 决速步骤 limits the overall flux. It need not be the first step. Compare a forward barrier with the energy of the state immediately before that step, not automatically with the original reactants.



Invented profiles compare local activation barriers. With comparable prefactors and suitable intermediate populations, the second step can control the flux even when its absolute peak is lower.

A transition state is a fleeting high-energy configuration represented by a peak; it is not a stable intermediate. An intermediate is a species between steps and corresponds to a local minimum. For an invented profile with reactants at 0, first peak at 30, intermediate at −60 and second peak at 10, local forward barriers are 30 and 70 kJ/mol. The later step can be the bottleneck even though its absolute peak is lower. Dominance also depends on kinetic prefactors, concentrations and reversibility; the energy sketch alone does not prove a mechanism.

The rate equation

For a reaction A + B → products, experiments give a **rate equation** 速率方程 of the form:

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

- m and n are the **orders** 级数 with respect to A and B. The assessed examples use integer orders such as 0, 1 and 2. Determine the overall rate law experimentally rather than copying coefficients from the overall equation; a proposed elementary step can then be tested against that evidence.
- The overall order is $m + n$.

- k is the **rate constant** 速率常数. For a specified reaction model, medium and catalyst, it is independent of the reactant concentrations over the range where that law applies. In the simple positive-activation-energy Arrhenius model it increases with temperature.

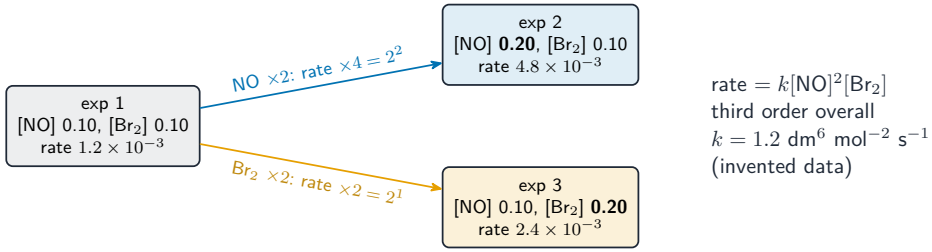
Units of k

Work out the units from rate = $k\times$ concentrations:

Overall order	Units of k
0	mol dm^{-3} s^{-1}
1	s^{-1}
2	dm^3 mol^{-1} s^{-1}
3	dm^6 mol^{-2} s^{-1}

Finding orders from initial rates

Invented teaching rates. For $2\text{NO(g)} + \text{Br}_2\text{(g)} \rightarrow 2\text{NOBr(g)}$:



Reading orders from initial rates (invented data)

Experiment	[NO] / mol dm^{-3}	[Br$_2$] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	4.8×10^{-3}
3	0.10	0.20	2.4×10^{-3}

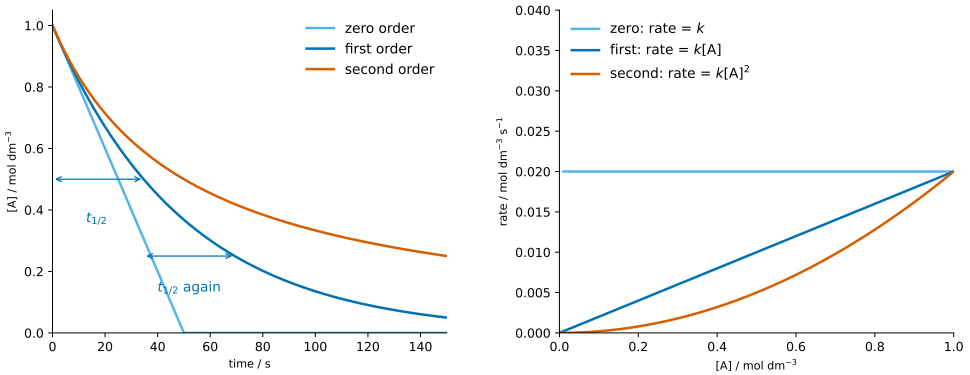
1. Experiments 1 and 2: [NO] doubles, [Br$_2$] is the same, and the rate goes up 4 times $= 2^2$. Second order in NO.
2. Experiments 1 and 3: [Br$_2$] doubles and the rate doubles $= 2^1$. First order in Br$_2$.
3. Rate $= k[\text{NO}]^2[\text{Br}_2]$, third order overall.
4. $k = \dfrac{1.2 \times 10^{-3}}{(0.10)^2 \times 0.10} = 1.2$ dm^6 mol^{-2} s^{-1}.

Here the tabulated rate is defined consistently by bromine disappearance, equivalent to half the NO disappearance rate. A different species-rate convention rescales k while

leaving the inferred concentration exponents unchanged.

Graphs of each order

These single-reactant models use the disappearance rate $-\mathrm{d[A]/dt}$ at constant conditions. Rate constants for different orders have different units, even when their numerical values happen to coincide.



Invented single-reactant disappearance models under constant conditions. The concentration and rate plots correspond to the listed laws.

- **Zero order:** for a single-reactant disappearance law, [A] falls linearly until the reactant is exhausted or the regime changes. A constant positive rate cannot continue when no A remains.
- **First order:** for $-d[\mathrm{A}]/dt = k[\mathrm{A}]$ under constant conditions, the disappearance rate is proportional to [A]. The **half-life** 半衰期, the time for [A] to halve, is constant: $t_{1/2} = \dfrac{0.693}{k}$.
- **Second order:** the rate–concentration graph is a curve; doubling [A] makes the rate four times faster.

Linking the rate equation and the mechanism

A rate law can reflect both the bottleneck and preceding steps. Eliminating an intermediate may introduce concentrations of species that formed it; do not simply read exponents from the overall equation.

step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ **slow** → rate $= k[NO_2]^2$

step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ **fast**

from the slow step's reactants, not the overall equation

overall: $NO_2 + CO \rightarrow NO + CO_2$

NO_3 is an intermediate: made in step 1, used in step 2

The rate law comes from the slow step of the mechanism

Illustrative supplied model, not a claim of measured data. Suppose $NO_2 + CO \rightarrow NO + CO_2$ has rate $= k[NO_2]^2$. A proposed slow-first mechanism consistent with this supplied law is:

$$\text{step 1 (slow): } 2NO_2 \rightarrow NO_3 + NO$$

$$\text{step 2 (fast): } NO_3 + CO \rightarrow NO_2 + CO_2$$

- The slow step involves two NO_2, so the rate is second order in NO_2.
- CO only appears in the fast step after it, so it is zero order and is not in the rate equation.
- NO_3 is an intermediate. The steps add up to the overall equation.

A mechanism must agree with the rate equation and add up to the overall equation. Agreement makes it possible, not proven.

A later slow step after a fast pre-equilibrium

Consider an invented proposed mechanism: A + B ⇌ I is a fast equilibrium, then I + B → P is slow. The overall equation is A + 2B → P. The intermediate I is formed and then consumed; it cancels from the overall equation. The slow step is bimolecular, involving I and B.

If the preceding equilibrium gives $[\mathrm{I}] = K[\mathrm{A}][\mathrm{B}]$, then the slow-step model gives $r = k_2[\mathrm{I}][\mathrm{B}] = k_2K[\mathrm{A}][\mathrm{B}]^2$. The observed overall order is three, although slow-step molecularity is two. The concentration relation requires the stated fast-equilibrium assumption. Kinetic agreement and atom balance make a mechanism possible; they do not establish it uniquely.

AHL: The Arrhenius equation

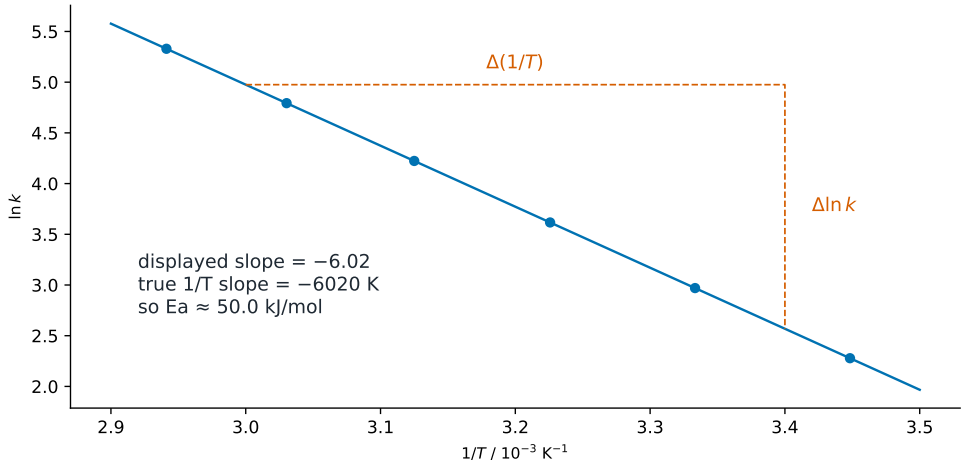
How k depends on temperature

$$k = Ae^{-E_a/RT} \qquad \ln k = -\frac{E_a}{RT} + \ln A$$

- A is the **frequency factor** 频率因子 (also called the pre-exponential factor). It takes account of how often particles collide and with the right orientation. It has the same units as k; it is not always a simple collision count per second. Treat it as approximately constant over the fitted temperature range.
- The exponential factor $e^{-E_a/RT}$ describes the strong thermal dependence in this Arrhenius model. It is not an exact integral of the three-dimensional Maxwell–Boltzmann energy tail. It rises steeply with T.
- $R = 8.31$ J K^{-1} mol^{-1} and T is in kelvin, so E_a must be in J mol^{-1}.

Finding E_a from a graph

A graph of $\ln k$ against $1/T$ is a straight line. The gradient is $-E_a/R$ and the y-intercept is $\ln A$.



The true $1/T$ gradient is $-Ea/R$. Here one horizontal tick unit represents 10^{-3} K^{-1}, so convert the displayed slope before calculating Ea.

Here the gradient is -6.02×10^3 K, so $E_a = 6.02 \times 10^3 \times 8.31 = 5.00 \times 10^4$ J mol^{-1} $= 50.0$ kJ mol^{-1}.

Two temperatures

With rate constants at two temperatures, use the data booklet form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Worked example. The rate constant doubles from 298 K to 308 K. Find E_a.

1. $k_2 = 2k_1$, so $\ln \dfrac{k_2}{k_1} = \ln 2 = 0.693$.
2. $\dfrac{1}{298} - \dfrac{1}{308} = 1.0895 \times 10^{-4}$ K^{-1} (keep all the digits).
3. $E_a = \dfrac{8.31 \times 0.693}{1.0895 \times 10^{-4}} = 5.29 \times 10^4$ J mol^{-1} $= 52.9$ kJ mol^{-1}.

The twofold result is compatible with an activation energy near 50 kJ/mol around room temperature. Another barrier or temperature range gives a different factor; do not extrapolate a fixed doubling rule indefinitely.

Read the plotted axis scale and recover A

If the horizontal coordinate is $x = 1000$ K$/T$, its numerical slope is $-E_a/(1000R)$, not $-E_a/R$. In the figure a displayed slope near -6.02 corresponds to -6020 K per unit $1/T$ and hence about 50.0 kJ/mol. Converting the tick difference 0.40 into 0.40×10^{-3} K^{-1} prevents a factor-of-1000 error.

For an invented first-order fit $\ln(k/\text{s}^{-1}) = 25.0 - 6.00x$, $E_a = 6.00 \times 1000 \times 8.31 = 49\,860$ J/mol, or 49.9 kJ/mol. The intercept gives $A = e^{25.0} = 7.20 \times 10^{10}$ s^{-1}. Use the same units for every k before taking numerical logarithms; the prefactor inherits those units. An extrapolated intercept is model-dependent, especially if the mechanism or prefactor changes across the temperature range.

Practice

1. In an experiment, 0.050 mol dm^{-3} of a reactant is used up in 25 s. Calculate the mean rate in mol dm^{-3} s^{-1}.
2. Describe how to follow the rate of the reaction between magnesium ribbon and hydrochloric acid.
3. State the three conditions for a successful collision.
4. Use collision theory to explain why powdered calcium carbonate reacts faster with acid than the same mass of lumps.
5. Sketch Maxwell–Boltzmann curves at two temperatures and use them to explain why a small rise in temperature gives a large rise in rate.
6. Explain how a catalyst increases the rate, with reference to an energy profile and a Maxwell–Boltzmann curve.

7. From the gas–time graph in this handout, explain why the rate at 50 s is lower than the initial rate.
8. For 2A → B, A concentration falls by 0.030 mol/dm^3 in 5.0 s at fixed volume. Find positive A disappearance rate, B formation rate and the coefficient-normalized reaction rate.
9. An invented gas trace rises from 10.0 to 34.0 cm^3 between 20 and 60 s. Find its mean rate. A tangent through (30 s, 22 cm^3) and (70 s, 46 cm^3) estimates an instantaneous rate: calculate it and explain what must be checked about the chosen points.
10. Explain why adding inert gas at fixed temperature and volume need not increase reaction rate. Two disappearing-cross times are 40 s and 25 s under comparable fixed-threshold conditions: find the relative 1/t rate factor and give a limitation of the comparison.
11. For the invented endothermic profile with reactants 20, products 50 and peak 100 kJ per reaction amount, find ΔH and both activation barriers. Repeat for a catalysed peak at 80. Explain what happens to the thermal-energy distribution at the same temperature.
12. **AHL.** For A + 2B → C, rate = k[A][B]^2. State the overall order and the units of k, and the factor by which the rate changes when [B] is tripled. Initial-rate data for X + Y → Z: [X] 0.10, [Y] 0.10, rate 2.0×10^{-4}; [X] 0.30, [Y] 0.10, rate 6.0×10^{-4}; [X] 0.10, [Y] 0.20, rate 2.0×10^{-4}. Deduce the rate equation and calculate k. A first-order reaction has $k = 0.0231$ s^{-1}. Calculate its half-life. State the single-reactant disappearance-law assumption behind the half-life formula.
13. **AHL.** For an illustrative alkaline hydrolysis model, 2-bromo-2-methylpropane has rate = k[$(CH_3)_3CBr$]. Suggest a two-step mechanism and identify the rate-determining step and the intermediate. For the fast A+B⇌I followed by slow I+B→P model above, deduce the overall equation and rate law under the stated pre-equilibrium assumption. Distinguish intermediate from transition state.
14. **AHL.** k is 3.0×10^{-4} s^{-1} at 300 K and 1.2×10^{-3} s^{-1} at 320 K. Calculate E_a. State what the gradient and the intercept of a $\ln k$ against $1/T$ graph represent. For the invented first-order fit ln(k/s^{-1})=25.0−6.00x with x=1000 K/T, find Ea and A.

Answers.

1. $0.050/25 = 2.0 \times 10^{-3}$ mol dm^{-3} s^{-1}.
2. Collect the hydrogen in a gas syringe and read the volume every 10 s (or measure the mass loss on a balance); keep the temperature, acid concentration and volume the same.
3. The particles collide, with energy at least equal to E_a, and with the correct orientation.
4. Powder has a larger surface area, so more particles are exposed and collisions with acid particles are more frequent.
5. At the higher temperature the curve is lower and broader with the same area; the area beyond E_a is much larger, so a much larger fraction of collisions has enough energy.
6. It gives an alternative pathway with a lower E_a (a lower peak on the profile, the same ΔH). On the Maxwell–Boltzmann curve the lower E_a line has more particles beyond it, so more collisions succeed.
7. Reactants have been used up, so their concentration is lower and collisions are less frequent; the tangent is less steep.
8. A disappearance: $0.030/5.0 = 0.0060$ mol/dm^3/s. Divide by two for B formation and the normalized reaction rate: each is 0.0030 mol/dm^3/s.
9. Mean: $(34.0-10.0)/(60-20) = 0.600$ cm^3/s. Tangent: $(46-22)/(70-30) = 0.600$ cm^3/s. The two latter points must lie on the tangent, not simply on the curve. Equality here is a supplied coincidence, not a general equivalence of mean and instantaneous rates.
10. At constant volume and temperature, ideal reactant partial pressures remain unchanged when inert gas is added. Relative proxy factor $(1/25)/(1/40) = 1.6$. The same opacity threshold, optical path and comparable observation conditions are needed; 1/t is not automatically an instantaneous rate.
11. ΔH = 50−20 = +30 kJ. Uncatalysed barriers: forward 100−20 = 80 and reverse 100−50 = 50 kJ. Catalysed barriers: 80−20 = 60 and 80−50 = 30 kJ. The distribution at fixed temperature stays the same; the alternative pathway has a lower threshold.
12. **AHL.** Third order; dm^6 mol^{-2} s^{-1}; $3^2 = 9$ times faster. Tripling [X] triples the rate: first order in X. Doubling [Y] has no effect: zero order in Y. Rate = k[X]; $k = 2.0 \times 10^{-4}/0.10 = 2.0 \times 10^{-3}$ s^{-1}. $t_{1/2} = 0.693/0.0231 = 30.0$ s. The half-life expression assumes −d[A]/dt=k[A] with k constant.
13. **AHL.** Step 1 (slow, rate-determining): $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$. Step 2 (fast): $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$. The intermediate is the carbocation $(CH_3)_3C^+$. For the separate proposed model, A+2B→P and rate=k_2K[A][B]^2; the second, bimolecular step is slow. I is an intermediate at a local energy minimum; a transition state is a fleeting peak configuration. Agreement with the data does not prove uniqueness.
14. **AHL.** $\ln(1.2\times10^{-3}/3.0\times10^{-4}) = \ln 4 = 1.386$. $1/300 - 1/320 = 2.08\times10^{-4}$ K^{-1}. $E_a = 8.31 \times 1.386/2.08 \times 10^{-4} = 5.53 \times 10^4$ J mol^{-1} = 55.3 kJ mol^{-1}. Gradient $= -E_a/R$; intercept $= \ln A$. For the scaled fit, Ea=6.00×1000×8.31=49.9 kJ/mol and A=e^{25}=7.20×10^{10} s^{-1}.

Exam tips

- Rate is measured from the gradient of a tangent; draw the tangent long and read two far-apart points.

- At fixed temperature, reactant concentration and exposed surface can change encounter frequency. Heating changes the energy distribution; a catalyst changes the pathway threshold.
- Sketch the ideal Maxwell–Boltzmann density from the origin with a tail approaching zero; keep total area constant for the same particle count.
- A catalyst does not change ΔH or the equilibrium position.
- **AHL.** Orders come from experiments, never from the balanced equation.
- **AHL.** In the Arrhenius equation, use T in K and E_a in J mol^{-1}; divide by 1000 at the end.

How far? The extent of chemical change

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 2.3, How far? The extent of chemical change, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: concentration in mol dm^{-3} from Structure 1.4, exothermic and endothermic reactions from Reactivity 1.1, and rates and catalysts from Reactivity 2.2.

Dynamic equilibrium

Why does a sealed bottle of cola stay fizzy?

In a sealed bottle at constant temperature, carbon dioxide exchanges between the drink and the gas above it. At equilibrium its dissolution and escape rates are equal. Opening the bottle lowers the CO_2 partial pressure above the drink; dissolved CO_2 is then lost overall. The drink approaches a different state in contact with the atmosphere, rather than preserving the original high-pressure equilibrium.

Many chemical reactions behave the same way. They do not go to completion; their net composition settles to a mixture of reactants and products while both reactions continue.

Reversible reactions

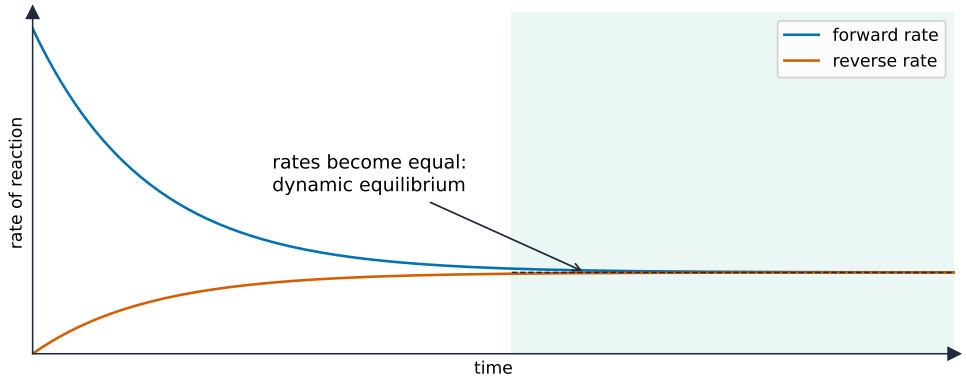
A **reversible reaction** 可逆反应 can go in both directions. The sign $\rightleftharpoons$ shows this.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

- The **forward reaction** goes from left to right; the **reverse reaction** goes from right to left.
- If initially only H_2 and I_2 are present, the forward reaction starts first. Once HI is present, the reverse reaction can occur too.

What dynamic equilibrium means

A **dynamic equilibrium** 动态平衡 is reached in a **closed system** 封闭系统 when the rate of the forward reaction equals the rate of the reverse reaction.



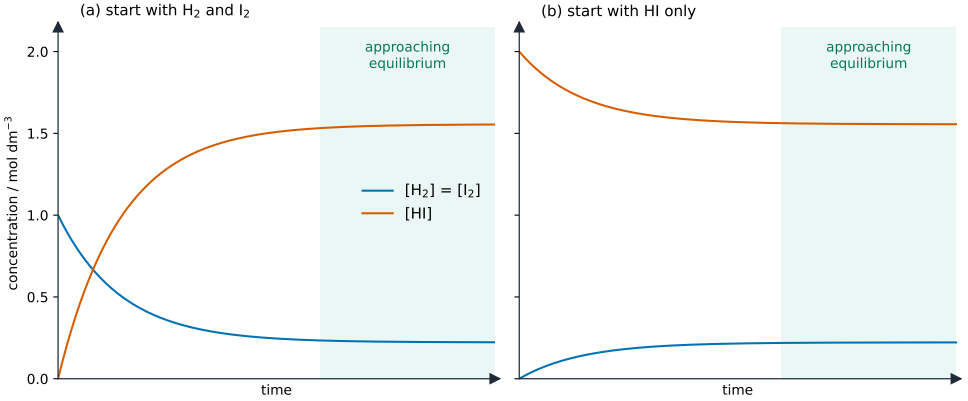
equal forward and reverse rates; constant composition at fixed conditions

At equilibrium the two rates are equal, but neither is zero

- **Dynamic:** both reactions keep going. Particles still react, but the forward and reverse changes cancel.
- **Constant concentrations:** at fixed temperature and volume, the macroscopic concentrations no longer change, although particles continue reacting.
- **Not equal concentrations:** "constant" does not mean "the same". At equilibrium a mixture can be mostly products or mostly reactants.
- **Closed system:** no matter enters or leaves; heat can still pass through its boundary. A closed system is not necessarily thermally isolated. Conditions must remain stable for its equilibrium composition to remain unchanged.

The same equilibrium from both sides

For the supplied classroom model at 700 K, take $K_c = 49$. Starting with 1.00 mol dm^{-3} each of H_2 and I_2 gives [HI] $= 14/9 \approx 1.56$ and [H_2] = [I_2] $= 2/9 \approx 0.222$ mol dm^{-3}. Starting with 2.00 mol dm^{-3} HI alone at the same temperature and volume conserves the same hydrogen and iodine inventories and gives the same final mixture. Different initial elemental amounts generally give different concentrations, even when K_c is unchanged. The plotted relaxation curves illustrate the approach; they are not measured kinetic data.



The same conserved amounts of each element, temperature and volume give the same equilibrium mixture in this model

Evidence that equilibrium is dynamic. A proposed tracer test introduces a trace amount of D_2, containing a heavier **isotope** 同位素 of hydrogen. Detecting DI subsequently would show continuing molecular exchange even if the bulk composition appeared unchanged within measurement resolution. Adding an appreciable amount would disturb the mixture, and isotope effects mean exactly unchanged concentrations must not be assumed. Constant colour alone cannot establish that reactions have stopped.

Physical equilibria

Equilibrium is not only for reactions. In a closed flask of bromine, liquid evaporates and vapour condenses at equal rates, so the brown colour of the vapour stays constant:

$$\mathrm{Br_2(l)} \rightleftharpoons \mathrm{Br_2(g)}$$

The equilibrium constant

The equilibrium law

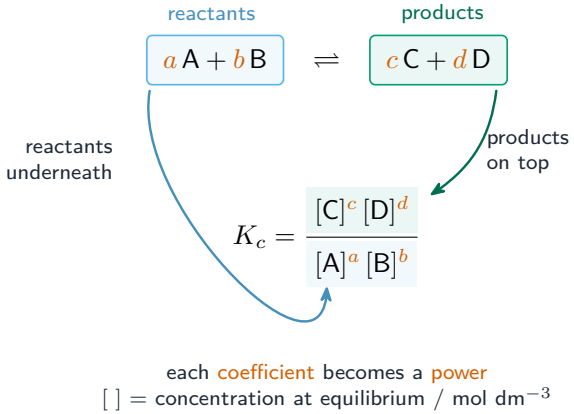
For a balanced homogeneous reaction, the equilibrium law relates the concentrations through a ratio. Use the coefficients as powers rather than multiplying the concentrations by those coefficients. For the general reaction

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

the **equilibrium constant** 平衡常数 K_c is

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

- Square brackets mean concentration in mol dm^{-3} **at equilibrium**.
- Products go on top, reactants underneath.
- Each concentration is raised to the power of its coefficient in the balanced equation.
- For a fixed equation and concentration convention in the ideal/dilute model, K_c has the same value at a given temperature, whatever the starting amounts. Among the disturbances studied here, only temperature changes it. Reversing or rescaling the equation changes the constant being defined.



Building K_c: products on top, reactants underneath, coefficients as powers, concentrations at equilibrium.

Worked example: calculating K_c

At 700 K the equilibrium mixture for $H_2 + I_2 \rightleftharpoons 2HI$ contains $[H_2] = [I_2] = 0.020$ mol dm^{-3} and $[HI] = 0.14$ mol dm^{-3}.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.14^2}{0.020 \times 0.020} = \frac{0.0196}{0.00040} = 49$$

Keep the stated concentration convention when comparing numerical K_c values. The thermodynamic equilibrium constant uses activities relative to standard states; it is dimensionless. A raw concentration quotient can carry concentration powers when the two sides have different total coefficients. Do not change concentration units halfway through a calculation.

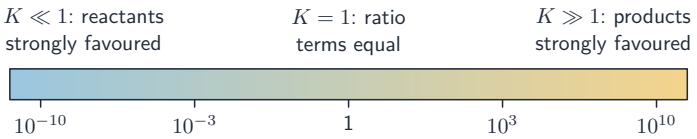
Writing K_c for other equations

Equation	K_c
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$\frac{[NH_3]^2}{[N_2][H_2]^3}$
$2SO_2 + O_2 \rightleftharpoons 2SO_3$	$\frac{[SO_3]^2}{[SO_2]^2[O_2]}$
$2HI \rightleftharpoons H_2 + I_2$ (reverse of the example)	$\frac{[H_2][I_2]}{[HI]^2} = \frac{1}{49} = 0.020$

- Reversing an equation gives $1/K_c$.
- Doubling every coefficient squares K_c: for $2H_2 + 2I_2 \rightleftharpoons 4HI$, $K_c = 49^2 = 2401$.

What the size of K tells you

The **position of equilibrium** 平衡位置 says whether the mixture is mainly reactants or mainly products.



for A ⇌ 2B, $K = 1$ means $[B]^2/[A] = 1$, not $[A] = [B]$; K alone is not a percentage yield

What the size of K says about the position of equilibrium

Value of K	What the equilibrium expression requires
$K \gg 1$	a large product-to-reactant activity ratio; products strongly favoured
$K > 1$	product side favoured in this expression, less strongly than when $K \gg 1$
$K = 1$	numerator and denominator equal; individual concentrations need not be equal
$K < 1$	reactant side favoured in this expression
$K \ll 1$	a very small product-to-reactant ratio; reactants strongly favoured

The initial inventory and the exponents still matter. For A ⇌ B, $K = 1$ means [A]=[B]. For A ⇌ 2B, it means $[B]^2/[A] = 1$ in the chosen convention, not [A]=[B]. A constant alone does not specify a universal percentage yield or a reaction rate.

K tells you **how far** a reaction goes, not **how fast**. A reaction with a huge K can still be very slow, for example the burning of a diamond at room temperature.

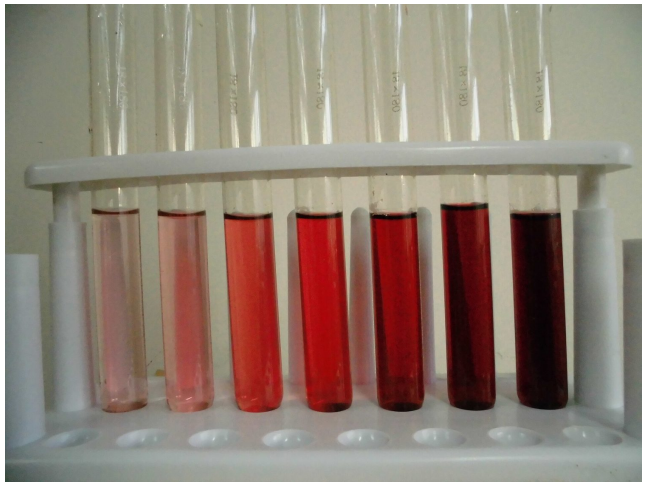
Le Chatelier's principle

The principle

Le Chatelier's principle 勒夏特列原理: when a system at equilibrium is disturbed, the position of equilibrium shifts to partly counteract the effect of the change. It does not generally restore every original concentration.



An ammonia plant: industrial equilibria like Haber's process are driven by pressure, temperature and catalysts



Cobalt chloride changes colour as its equilibrium shifts.

To predict a shift, first write the balanced equation with state symbols and the sign of ΔH for the forward reaction.

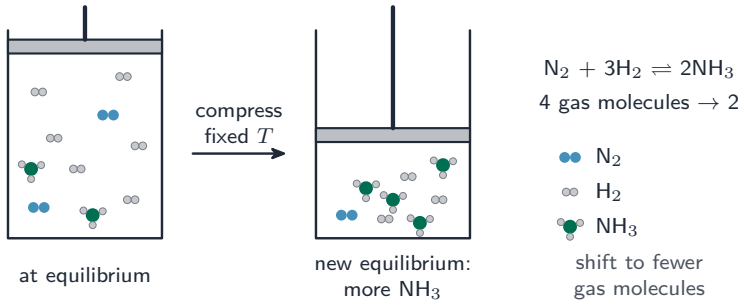
Changing a concentration

Add more of a reactant: the system uses some of it up, so the equilibrium shifts to the right and more product forms. Remove a product: the system makes more of it, again a shift to the right.

K_c does **not** change. The concentrations rearrange until the fraction in the K_c expression has its old value again.

Changing the pressure

For the ideal gas equilibria here, first specify **compression or expansion at fixed temperature**. Compression increases all reactant partial pressures; it is not equivalent to every rise in total pressure. Count the gaseous coefficients in the balanced equation.



Compression at fixed temperature shifts the mixture towards the side with fewer gas molecules (particle counts schematic).

- Compress at fixed temperature: the equilibrium shifts to the side with **fewer** gas molecules, which lowers the pressure.
- Expand at fixed temperature: the equilibrium shifts to the side with **more** gas molecules.
- Same number on both sides, as in $H_2 + I_2 \rightleftharpoons 2HI$ (2 and 2): compression has no effect on equilibrium mole fractions. All concentrations still rise immediately when volume falls.

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ there are 4 gas molecules on the left and 2 on the right, so a higher pressure shifts the equilibrium to the right and gives more ammonia. Adding an inert gas at fixed volume and temperature instead leaves the reacting gas concentrations and partial pressures unchanged: there is no ideal-gas equilibrium shift. At fixed total pressure, inert-gas addition expands the mixture and can favour the side with more gas. State which condition is controlled.

Heterogeneous and physical equilibria

For $CO_2(g) \rightleftharpoons CO_2(aq)$, raising the CO_2 partial pressure at fixed temperature drives more gas into solution. Lowering it, as when a carbonated bottle is opened, favours escape. The gas and solution are different phases; the rule still concerns a dynamic balance. Dissolved gas is not a pure solid or pure liquid phase and must not be omitted merely because it is in a liquid.



less $CaCO_3$ more $CaCO_3$

same temperature and volume: same p_{CO_2} while both solids remain; $K_p = p_{CO_2}$

Adding solid does not change the equilibrium CO_2 pressure

In $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, pure solid activities are constant while both solid phases remain. They are omitted from the usual expression, leaving the CO_2 term. Adding more $CaCO_3$ at the same temperature and vessel volume does not change the equilibrium CO_2 level while both solids are present. More surface may speed the approach. If a solid phase is exhausted, that two-solid equilibrium condition no longer applies. Pure liquid phases are similarly omitted, but components of a homogeneous liquid mixture generally are not.

Changing the temperature

For the same balanced equation and convention, temperature is the only disturbance in this unit that changes K.

the equilibrium shifts to *oppose* the change you make

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

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

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

- Raise the temperature: the equilibrium shifts in the **endothermic** direction, which takes in heat.
- Lower the temperature: it shifts in the **exothermic** direction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

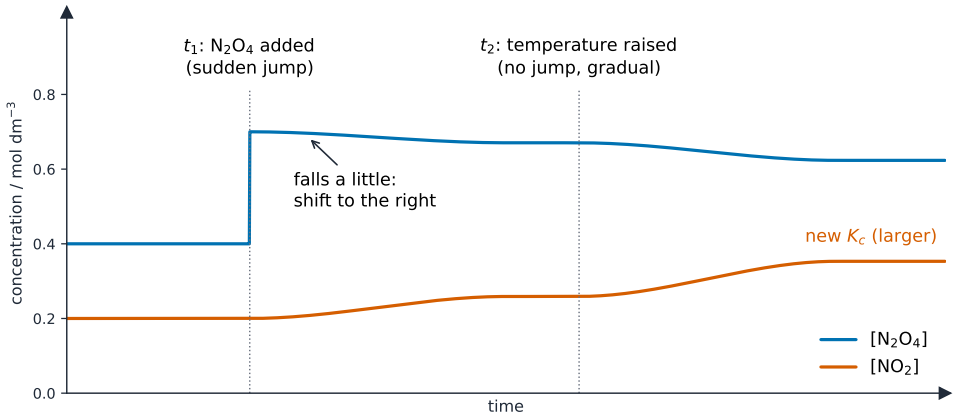
N_2O_4 is colourless and NO_2 is brown. The forward reaction is endothermic, so heating the gas shifts the equilibrium to the right: the gas turns darker brown and K_c becomes larger. Cooling within the gas-phase range favours colourless N_2O_4. Use a rigid cell with a fixed optical path when interpreting colour; changing volume or a phase change would complicate the comparison.

For an exothermic forward reaction the opposite is true: a higher temperature gives a smaller K and less product.

Adding a catalyst

A catalyst accelerates approach through an alternative pathway consistent with the same forward/reverse equilibrium. Equilibrium is reached sooner, but the position of equilibrium and K do not change.

Summary



$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, forward endothermic · fixed volume; invented data

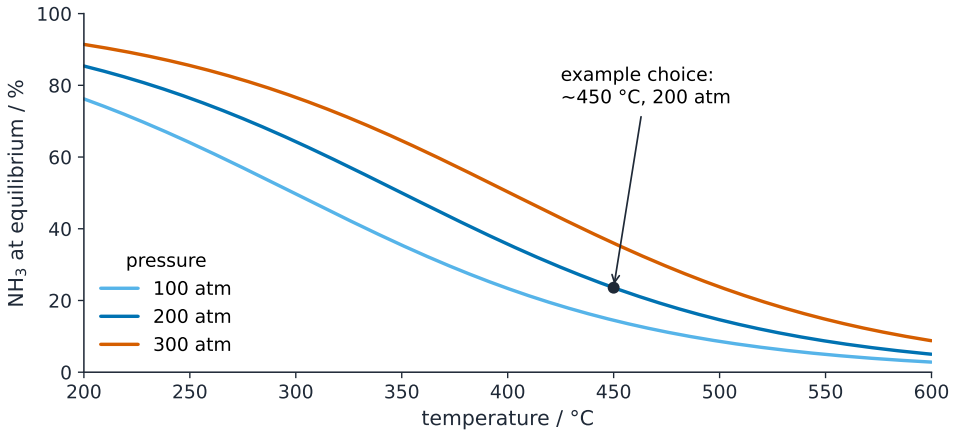
Invented fixed-volume data: adding N_2O_4 changes one concentration immediately; later heating changes the equilibrium constant. Curves show idealized relaxation, not measured rates.

Change	Shift in position	Effect on K
add a reactant or remove a product	to the right	none
compress at fixed temperature (gases)	to the side with fewer gas molecules	none
raise the temperature	in the endothermic direction	changes
add a catalyst	none; equilibrium is reached sooner	none

Industry: making ammonia

The Haber process makes ammonia for fertilizers:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$



invented illustrative trends; not measured equilibrium yields

Invented illustrative trends, not measured plant yields: lower temperature and higher pressure favour ammonia. The marked conditions are a classroom operating example.

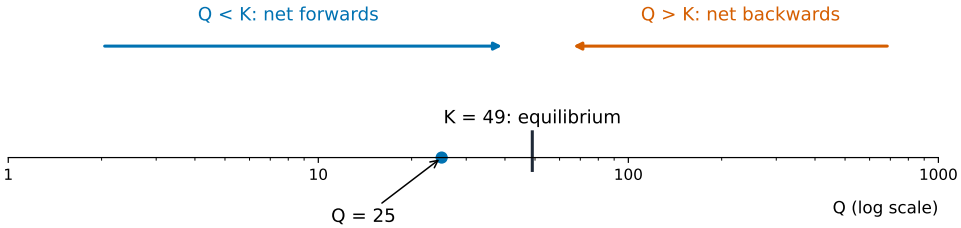
- **Illustrative pressure about 200 atm.** Fewer gas molecules on the right, so high pressure gives a higher **yield** 产率. Increasing pressure brings equipment and energy costs; the practical optimum depends on the plant.
- **Illustrative temperature about 450 °C.** The forward reaction is exothermic, so a low temperature gives a higher yield, but the reaction would be far too slow. This illustrates a **compromise** 折中 between yield and rate, not a unique operating temperature for every plant.
- **Iron catalyst.** It makes the reaction faster; it does not change the yield.
- **Ammonia is removed** by cooling it to a liquid, and unreacted N_2 and H_2 are recycled. Removing the product keeps shifting the equilibrium to the right.

AHL: The reaction quotient

This extension uses Gibbs energy from Reactivity 1.4 and natural logarithms.

Q for a mixture that is not at equilibrium

The **reaction quotient** 反应商 Q has the same expression as K, but uses the concentrations at any moment, not only at equilibrium.



Compare Q with K to see which way the mixture will react

- $Q < K$: the net change is forwards; products form until $Q = K$. This does not mean the forward rate keeps increasing.
- $Q > K$: the net change is backwards until $Q = K$.
- $Q = K$: the mixture is already at equilibrium.

Worked example: which way?

At 700 K, $K_c = 49$ for $H_2 + I_2 \rightleftharpoons 2HI$. A flask contains $[H_2] = [I_2] = 0.10$ mol dm^{-3} and $[HI] = 0.50$ mol dm^{-3}.

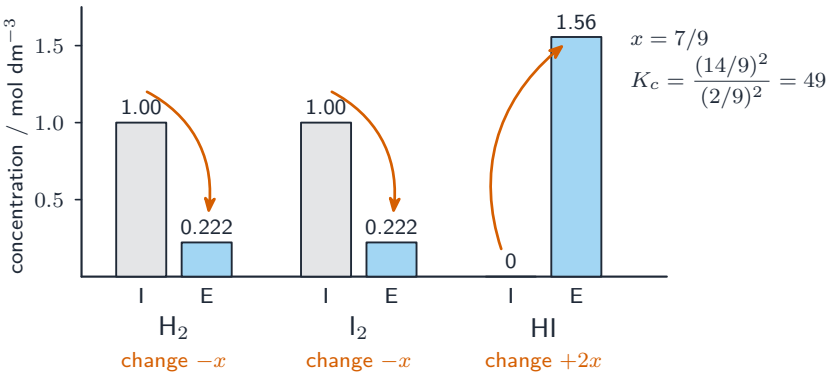
$$Q = \frac{0.50^2}{0.10 \times 0.10} = \frac{0.25}{0.010} = 25$$

Q (25) is less than K (49), so the mixture is not at equilibrium. It reacts forwards: [HI] rises and $[H_2]$ and $[I_2]$ fall until Q reaches 49.

AHL: Equilibrium calculations

The ICE table

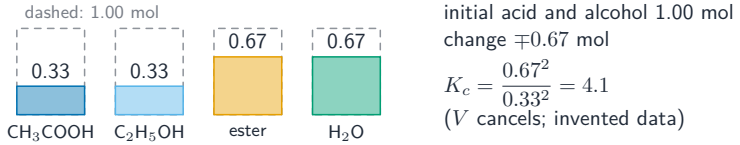
To find equilibrium amounts, use an **ICE** table: **I**nitial amounts; **C**hange in the balanced mole ratio; **E**quilibrium = initial + change. Use a single concentration unit throughout each table and reject negative concentrations.



The ICE table as bars: the changes follow the 1 : 1 : 2 ratio of the equation.

■ Worked example: finding K_c

Invented data for an idealized homogeneous liquid mixture: initially 1.00 mol ethanoic acid, 1.00 mol ethanol and negligible ester or water. A dry acid catalyst adds negligible water. At equilibrium 0.67 mol ester is present. All four mixture components enter the concentration expression; liquid state symbols do not make them separate pure liquid phases.



Equilibrium amounts for the esterification: Kc = 4.1 (invented)

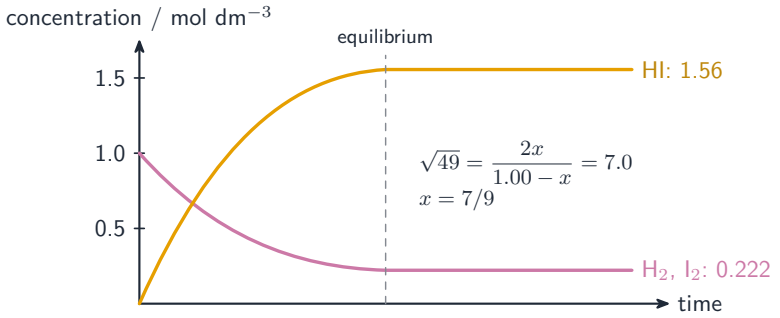
	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial / mol	1.00	1.00	0	0
Change / mol	−0.67	−0.67	+0.67	+0.67
Equilibrium / mol	0.33	0.33	0.67	0.67

The volume V is the same for every substance, and there are 2 particles on each side, so V cancels:

$$K_c = \frac{(0.67/V)(0.67/V)}{(0.33/V)(0.33/V)} = \frac{0.67^2}{0.33^2} = 4.1$$

■ Worked example: finding equilibrium concentrations

At 700 K, $K_c = 49$ for $H_2 + I_2 \rightleftharpoons 2HI$. Start with 1.00 mol dm^{-3} each of H_2 and I_2 and no HI. Let x mol dm^{-3} of H_2 react.



H_2 + I_2 ⇌ 2HI at 700 K reaching equilibrium

	H_2	I_2	HI
Initial	1.00	1.00	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$1.00 - x$	$1.00 - x$	$2x$

$$49 = \frac{(2x)^2}{(1.00 - x)^2}$$

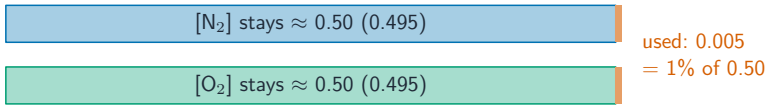
Both sides are perfect squares, so take the square root:

$$7.0 = \frac{2x}{1.00 - x} \quad \Rightarrow \quad 7.0 - 7.0x = 2x \quad \Rightarrow \quad x = 7/9 \approx 0.7778$$

Keep $x = 7/9$ until substitution: $[HI] = 14/9 \approx 1.56$ and $[H_2] = [I_2] = 2/9 \approx 0.222$ mol dm^{-3}. Substituting the unrounded values returns 49 exactly. Rounding x too early to 0.78 would give a different quotient.

■ When K is very small

A small K can permit a small-depletion approximation, but initial amounts and stoichiometry must also be checked. Tentatively take the equilibrium reactant concentrations as their initial values, then check that the calculated depletion is small relative to each relevant initial concentration. This **approximation** 近似 avoids solving a quadratic.



$[NO]^2 \approx 4.0 \times 10^{-4} \times 0.50 \times 0.50 = 1.0 \times 10^{-4}$, so $[NO] = 0.010$
check: depletion small relative to each initial value, so the approximation holds

A small K: check that the depletion is small

At a high temperature, $K_c = 4.0 \times 10^{-4}$ for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$. Start with $[N_2] = [O_2] = 0.50$ mol dm^{-3}.

$$K_c = \frac{[NO]^2}{[N_2][O_2]} \approx \frac{[NO]^2}{0.50 \times 0.50} = 4.0 \times 10^{-4}$$

$$[NO]^2 = 1.0 \times 10^{-4} \quad \Rightarrow \quad [NO] = 0.010 \text{ mol dm}^{-3}$$

Only 0.005 mol dm^{-3} of N_2 was used, 1% of 0.50, so the approximation was fair. State the assumption in your answer.

A small numerical K alone is insufficient: for $A \rightleftharpoons 2B$ with $K_c = 1.6 \times 10^{-5}$ and initial $[A] = 10^{-8}$ mol dm^{-3}, treating [A] as unchanged predicts $[B] = 4.0 \times 10^{-7}$ mol dm^{-3}. That exceeds the conservation limit 2.0×10^{-8}; reject the approximation. No quadratic solution is required to detect its failure. The main examples below are solvable by square roots or justified approximations.

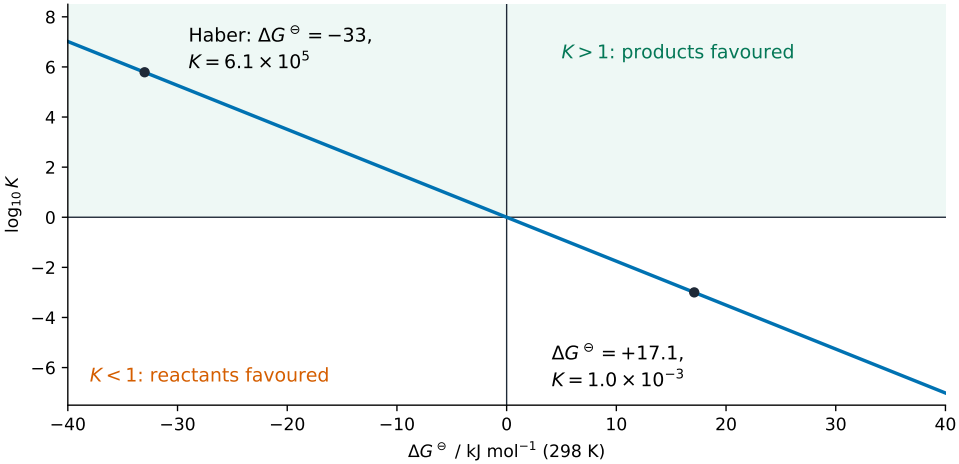
AHL: Equilibrium and Gibbs energy

■ Linking $\Delta G^{\ominus}$ and K

The standard **Gibbs energy** 吉布斯能 change of a reaction and its equilibrium constant are linked (data booklet):

$$\Delta G^{\ominus} = -RT \ln K$$

$R = 8.31$ J K^{-1} mol^{-1}, T in K, $\Delta G^{\ominus}$ in J mol^{-1}. Here K is the dimensionless **thermodynamic** constant using activities relative to standard states. For gases with unequal total coefficients, it must not silently be identified with a raw concentration quotient.



A negative $\Delta G^{\ominus}$ means $K > 1$; a positive $\Delta G^{\ominus}$ means $K < 1$

$\Delta G^{\ominus}$	K	**Equilibrium mixture**
negative	greater than 1	products favoured in the activity ratio
zero	1	equal numerator and denominator, not necessarily equal concentrations
positive	less than 1	reactants favoured in the activity ratio

At fixed temperature and pressure, the total Gibbs energy has a minimum at equilibrium subject to the conserved inventories. The reaction Gibbs energy under the **actual mixture conditions**, $\Delta_r G$, is zero there; $\Delta G^{\ominus}$ need not be zero. A positive standard value does not prohibit forward reaction from a sufficiently reactant-rich mixture.

As an explanatory extension, $\Delta_r G = \Delta G^{\ominus} + RT \ln Q$, using thermodynamic activities. For supplied $\Delta G^{\ominus} = +5.00$ kJ mol^{-1} at 298 K and $Q = 0.0100$, this gives $5000 + (8.31)(298)\ln(0.0100) = -6404$ J mol^{-1} ≈ -6.40 kJ mol^{-1}. Forward change is favoured even though the standard value is positive. Here $K = e^{-5000/(8.31\times298)} \approx 0.133$; when Q reaches K, actual $\Delta_r G = 0$ while the standard value remains +5.00 kJ mol^{-1}.

■ **Worked example: K from $\Delta G^\ominus$**

Using a supplied rounded standard value of $\Delta G^\ominus = -33$ kJ mol^{-1} for the Haber equation at 298 K:

$$\ln K = \frac{-\Delta G^\ominus}{RT} = \frac{33\,000}{8.31 \times 298} = 13.3259\ldots \quad \Rightarrow \quad K \approx 6.1 \times 10^5$$

At room temperature the equilibrium lies far to the right. Industry still heats the gases, because at 298 K the reaction is far too slow.

■ **Worked example: $\Delta G^\ominus$ from K**

A reaction has $K = 1.0 \times 10^{-3}$ at 298 K.

$$\Delta G^\ominus = -(8.31)(298)\ln(1.0 \times 10^{-3}) \approx +17\,100 \text{ J mol}^{-1}$$

This is +17.1 kJ mol^{-1}. The positive sign agrees with $K < 1$.

Practice

All numerical scenarios are supplied teaching data.

1. State two features of a dynamic equilibrium.
2. Calcium carbonate and calcium oxide are heated in a vessel while CO_2 is continuously swept away below its equilibrium partial pressure. Explain why the original decomposition equilibrium cannot be maintained.
3. Write the K_c expression for $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$.
4. For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the equilibrium concentrations are $[PCl_5] = 0.040$, $[PCl_3] = 0.020$ and $[Cl_2] = 0.080$ mol dm^{-3}. Calculate K_c.
5. $K_c = 2.5 \times 10^{-31}$ for a reaction at 298 K. Describe the equilibrium mixture.
6. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, $\Delta H = -91$ kJ mol^{-1}. Predict the effect on the yield of methanol of (a) compressing the gases at fixed temperature, (b) raising the temperature, (c) adding a catalyst.
7. A rigid sealed transparent cell containing gaseous N_2O_4 and NO_2 is warmed, at fixed optical path and within the gas-phase range. State and explain the colour change.
8. Explain the rate/yield compromise in the illustrative 450 °C Haber operating choice.
9. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, explain (a) why adding $CaCO_3$ does not shift an established equilibrium while both solids remain and (b) why the argument fails if all $CaCO_3$ is consumed.
10. For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, compare (a) compression and (b) adding inert gas at fixed volume, both at fixed temperature. Does either operation change K?
11. For A $\rightleftharpoons$ B, two equilibrium mixtures at the same temperature have ([A],[B]) = (0.20,0.60) and (0.40,1.20) mol dm^{-3}. Calculate both constants and explain whether different concentrations imply a contradiction.
12. **AHL.** (a) For $H_2 + I_2 \rightleftharpoons 2HI$, $K_c = 49$. A mixture has $[H_2] = [I_2] = 0.050$ and $[HI] = 0.60$ mol dm^{-3}. Calculate Q and state the direction of change. (b) 2.00 mol of SO_2 and 1.00 mol of O_2 are mixed in a 1.00 dm^3 flask. At equilibrium, 1.60 mol of SO_3 is present. Calculate K_c for $2SO_2 + O_2 \rightleftharpoons 2SO_3$.
13. **AHL.** (a) $K_c = 4.0$ for $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$. Starting with 1.00 mol of acid and 1.00 mol of ethanol, calculate the amount of ester at equilibrium. (b) For $A(g) \rightleftharpoons 2B(g)$, $K_c = 1.6 \times 10^{-5}$. The initial [A] is 0.10 mol dm^{-3}. Use an approximation to find [B] at equilibrium, and state the assumption.
14. **AHL.** (a) Calculate K at 298 K for a reaction with $\Delta G^\ominus = -11.4$ kJ mol^{-1}. (b) For supplied $\Delta G^\ominus = +5.00$ kJ mol^{-1} and thermodynamic $Q = 0.0100$ at 298 K, calculate actual $\Delta_r G$ and predict direction. Use $R = 8.31$ J mol^{-1} K^{-1}.

Worked answers.

1. In a closed system at fixed conditions, forward and reverse rates are equal and nonzero. At fixed volume, concentrations are constant, not necessarily equal.
2. Sweeping away CO_2 keeps its pressure below the two-solid equilibrium value. Decomposition proceeds overall while $CaCO_3$ remains, preventing the original closed-vessel equilibrium.
3. $K_c = \dfrac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$
4. $K_c = \dfrac{0.020 \times 0.080}{0.040} = 0.040.$
5. Reactants are strongly favoured: the product/reactant expression is extremely small. Exact concentrations or percentage conversion require the equation and initial inventory.
6. (a) Yield increases: compression favours the right, with one gaseous coefficient versus three. (b) Yield decreases: heating favours the endothermic reverse direction; K falls. (c) Equilibrium yield is unchanged; approach is faster.
7. Darker brown: heating favours the endothermic forward reaction, $N_2O_4(g) \rightarrow 2NO_2(g)$, increasing brown NO_2 in the fixed-volume gas cell.
8. Lower temperature favours ammonia in this exothermic reaction but gives a slower rate. The illustrative 450 °C choice trades some equilibrium yield for faster production.
9. (a) Pure solid activities remain constant while both phases remain, so extra bulk solid leaves equilibrium CO_2 unchanged; surface can affect rate. (b) Exhaustion removes a required phase.
10. (a) Compression favours ammonia: four gaseous coefficients become two. (b) Inert gas at fixed volume leaves reacting partial pressures unchanged: no shift. Neither changes K at fixed temperature.

11. $K_c = 0.60/0.20 = 3.0$ and $1.20/0.40 = 3.0$. Both satisfy the same ratio; individual concentrations also depend on the conserved inventory.
12. **AHL.** $Q = 0.60^2/(0.050 \times 0.050) = 0.36/0.0025 = 144$. $Q > K$, so the mixture reacts backwards: [HI] falls, [H_2] and [I_2] rise. (b) Change: SO_3 +1.60, SO_2 −1.60, O_2 −0.80. Equilibrium: SO_2 0.40, O_2 0.20, SO_3 1.60 mol dm^{-3}. $K_c = 1.60^2/(0.40^2 \times 0.20) = 2.56/0.032 = 80$.
13. **AHL.** $4.0 = x^2/(1.00 - x)^2$, so $2.0 = x/(1.00 - x)$, $x = 2.0 - 2.0x$, $x = 2/3 \approx 0.67$ mol of ester. (b) Assume [A] stays 0.10. $[B]^2 = 1.6 \times 10^{-5} \times 0.10 = 1.6 \times 10^{-6}$, $[B] = 1.3 \times 10^{-3}$ mol dm^{-3}. A depletion is half [B], 6.3×10^{-4} mol dm^{-3}, or 0.63%: the unchanged-A approximation is justified.
14. **AHL.** (a) $\ln K = 11400/(8.31 \times 298) = 4.60349\ldots$, so $K = 99.83\ldots \approx 1.0 \times 10^2$. Keep guard digits. (b) $\Delta_r G = 5000 + (8.31)(298)\ln(0.0100) = -6404$ J mol^{-1} $\approx$ −6.40 kJ mol^{-1}, so net forward change is favoured. At equilibrium actual $\Delta_r G = 0$; the standard value remains +5.00 kJ mol^{-1}.

Exam tips

- Dynamic equilibrium means equal nonzero rates and constant concentrations at fixed volume, not equal concentrations.
- Use equilibrium concentrations and coefficient powers. For the fixed equation and convention, temperature alone among these disturbances changes K.
- State ΔH before predicting heating effects; count gaseous coefficients for compression at fixed temperature. Inert-gas conditions matter. Catalysts do not change K.

Reactivity 3.1 · Proton transfer reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.1, Proton transfer reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: amount of substance and concentration from Structure 1.4, equilibrium and K from Reactivity 2.3, and logarithms to base 10. Use the stated temperature and K_w value. Numerical examples below use the dilute-solution concentration model at 298 K unless stated otherwise; they are supplied teaching data.

Brønsted–Lowry acids and bases

What do vinegar, stomach acid and cleaning ammonia have in common?

Vinegar and stomach acid both turn blue litmus red, and ammonia solution turns red litmus blue. One idea explains all three: in every Brønsted–Lowry acid–base reaction a **proton** 质子, an H^+ ion, moves from one particle to another.



Vinegar is a dilute solution of ethanoic acid, a carboxylic acid

Acids donate, bases accept

- A **Brønsted–Lowry acid** 布朗斯特-劳里酸 is a proton donor.
- A **Brønsted–Lowry base** 布朗斯特-劳里碱 is a proton acceptor. Ammonia and water accept a proton using an available lone pair. The general definition is proton acceptance, rather than a requirement that every possible base be one of these molecules.

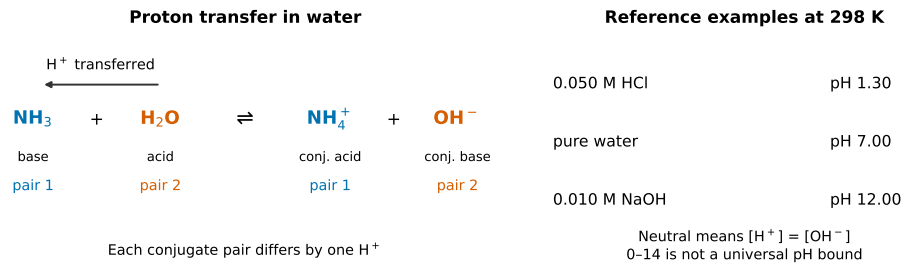
In aqueous solution a proton is hydrated rather than present as a bare isolated particle. The oxonium representation is H_3O^+. Writing $H^+(aq)$ is a short form for $H_3O^+(aq)$.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Conjugate acid–base pairs

When an acid donates a proton, what is left can accept a proton back: it is a base. A **conjugate acid–base pair** 共轭酸碱对 is two species that differ by one proton.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



A Brønsted–Lowry acid donates H^+ and a base accepts it; $pH = -\log[H^+]$

Here NH_3 (base) and NH_4^+ (its conjugate acid) are one pair; H_2O (acid) and OH^- (its conjugate base) are the other.

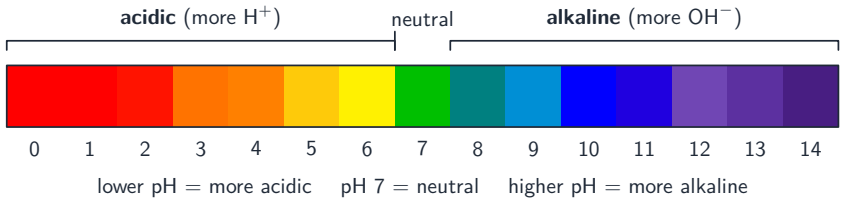
Water acts as a base with HCl and an acid with NH_3. Such proton donors/acceptors are **amphiprotic** 两性的; other examples include HCO_3^-, HSO_4^- and $H_2PO_4^-$. Show both roles: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$, and $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$. Check atoms and charge. Conjugate partners differ by one H^+ and one charge unit; reacting partners are not automatically conjugates.

A **base** can neutralize an acid; an **alkali** is a base that produces an alkaline aqueous solution. CuO is a basic oxide but not a soluble alkali. Aqueous ammonia is an alkali even though NH_3 contains no OH group: it accepts a proton from water, producing OH^-.

pH and the ionic product of water

The pH scale

The **pH** scale expresses hydrogen-ion activity logarithmically. For the dilute solutions in these calculations, use the numerical hydrogen-ion concentration in mol dm^{-3}:



Universal indicator is red at low pH, green near neutral pH 7 at 298 K, and purple at high pH; colour depends on pH, not acid/base strength alone.

$$pH = -\log_{10}[H^+] \qquad [H^+] = 10^{-pH}$$

- A decrease of one pH unit means $[H^+]$ is **ten times** larger.
- pH has no units. Give it to the same number of decimal places as the significant figures in $[H^+]$.

Worked example: $[H^+] = 0.050$ mol dm^{-3} gives $pH = -\log(0.050) = 1.30$. A solution of pH 3.40 has $[H^+] = 10^{-3.40} = 4.0 \times 10^{-4}$ mol dm^{-3}.

Measuring and comparing pH

Universal indicator mixes indicators for approximate chart-based pH. Sample colour and lighting can interfere; it cannot justify two-decimal-place accuracy. A probe needs suitable buffer calibration, rinsing between samples, stabilization and temperature control. Display resolution alone does not establish accuracy.



pH paper estimates the pH of a solution from the colour it turns

On ordinary linear axes, pH against $[H^+]$ is a decreasing logarithmic curve, not a straight line. Invented $[H^+]$ values 0.0010, 0.010 and 0.10 mol dm^{-3} give pH 3.00, 2.00

and 1.00. Equal tenfold concentration factors give equal pH intervals. Values outside 0–14 are possible; 0–14 is a familiar range for dilute aqueous examples, not a universal bound.

Water ionizes a little

Pure water contains a tiny amount of ions:

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

The **ionic product of water** 水的离子积, K_w, is

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

In pure water $[H^+] = [OH^-] = 1.00 \times 10^{-7}$, so the pH is 7.00. A solution is **neutral** when $[H^+] = [OH^-]$, acidic when $[H^+] > [OH^-]$ and alkaline when $[H^+] < [OH^-]$.

The ionization of water is endothermic, so K_w increases with temperature. At 50 °C pure water has a pH of about 6.6, but it is still neutral, because $[H^+]$ and $[OH^-]$ are still equal.

pH of strong acids and bases

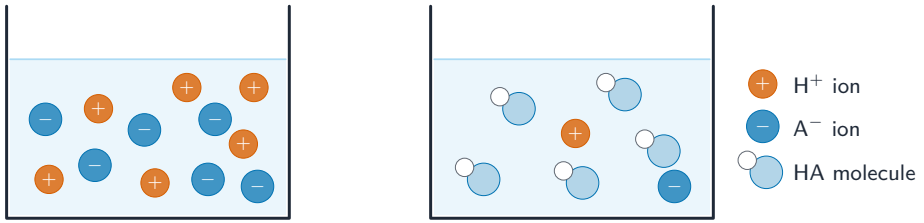
For a fully ionized monoprotic strong acid well above the water contribution, $[H^+]$ is approximately its analytical concentration. A fully dissociated soluble hydroxide supplies OH^- according to its formula: one per NaOH, two per dissolved $Ba(OH)_2$. Do not automatically set every acid concentration equal to $[H^+]$ regardless of proton count or dilution. Water ionization matters for extremely dilute solutions.

- 0.020 mol dm^{-3} HCl: $[H^+] = 0.020$, pH = 1.70.
- 0.010 mol dm^{-3} NaOH: $[OH^-] = 0.010$, so $[H^+] = K_w/0.010 = 1.0 \times 10^{-12}$, pH = 12.00.

Strong and weak acids and bases

Full and partial ionization

- A **strong acid** 强酸 ionizes completely in water: HCl, HNO_3, H_2SO_4 (first proton). A **strong base** ionizes or dissociates completely: group 1 hydroxides and $Ba(OH)_2$.
- A **weak acid** 弱酸 ionizes only partly; the equilibrium lies to the left: ethanoic acid and other carboxylic acids, carbonic acid. A **weak base** accepts protons only partly: ammonia and amines.



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

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

For the supplied ethanoic-acid model with $K_a = 1.74 \times 10^{-5}$, approximately 1.3% of a 0.10 mol dm^{-3} solution is ionized. The fraction depends on concentration and temperature; it is not a fixed percentage for every ethanoic-acid solution.

Do not confuse **strong** with **concentrated**. Strength is about how far the acid ionizes; concentration is how much acid is dissolved in each dm^3. A dilute solution of a strong acid can have a higher pH than a concentrated solution of a weak acid.

For conjugate pairs in the same solvent at the same temperature, the stronger the acid, the weaker its conjugate base: Cl^- has almost no tendency to accept a proton, while CH_3COO^- accepts one easily.

Acid–base equilibrium favours the weaker acid and weaker base. For $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$, compare the two acids and their conjugates, not simply whether the substances are on the left or right. Proton transfer towards the less strongly donating acid is favoured under the corresponding equilibrium model.

Telling them apart

Compare solutions of the **same concentration** at the same temperature:

Test	0.10 **mol dm^{-3} HCl (strong)**	0.10 **mol dm^{-3} CH_3COOH (weak)**
pH	1.0	about 2.9
electrical conductivity	high (many ions)	low (few ions)
rate with magnesium or $CaCO_3$	fast bubbling	slow bubbling

Equal volumes of these equal-concentration monoprotic acids contain equal acid

amounts and need equal hydroxide amounts for complete neutralization. With excess magnesium, complete reaction and matched collection conditions, they give the same final gas amount despite different initial rates. More weak acid ionizes as H^+ is consumed. Control solid surface when comparing rates; leaks or limiting solid can change observed totals.

Neutralization and pH curves

Neutralization

Proton-transfer neutralization forms a salt; water is formed when hydroxide or a basic oxide takes up the proton. Ammonia and amines can form salts **without producing water**. For dilute strong acid with hydroxide, the net ionic equation is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H \approx -57 \text{ kJ mol}^{-1}$$

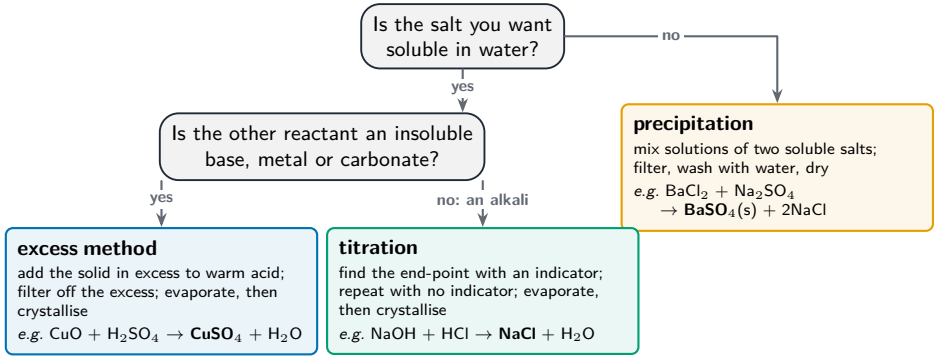
The usual dilute hydroxide **neutralization** 中和 releases heat.

Other acid reactions:

- with a metal carbonate or hydrogencarbonate: salt, water and carbon dioxide;
- with a reactive metal and a suitable dilute non-oxidizing acid such as HCl: salt and hydrogen; oxidizing acids need separate treatment;
- with a metal oxide or hydroxide: salt and water.

Balance the products and identify a salt's parents

Useful patterns include the following; state symbols and charge balance make the chemistry explicit.



Choosing a salt preparation: solubility of the salt first, then whether the other reactant is insoluble or an alkali.

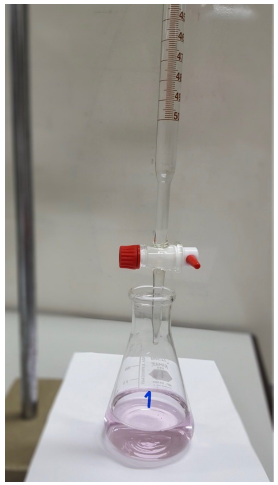
- $CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)$: oxide consumes two protons per oxide ion.
- $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$: an organic acid also neutralizes hydroxide.
- $Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$.
- $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$.
- $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$, and $CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3Cl(aq)$: no water product is needed.

For ammonium nitrate, a possible parent acid is HNO_3 and parent base is NH_3. For sodium ethanoate they are CH_3COOH and NaOH. The cation and anion identify useful parent choices; a salt name alone does not imply the solution is neutral.

To prepare a soluble salt from acid and an insoluble basic oxide, add oxide until some remains unreacted, filter off the excess, concentrate the filtrate carefully and allow crystals to form. Wash and dry the crystals as appropriate. For two soluble reactants, a titration can establish the reacting amounts; repeat those amounts without indicator before concentrating, to avoid indicator contamination. Do not evaporate every hydrate to dryness as a universal preparation method.

Titration technique and concentration

Wear appropriate eye protection. Rinse the burette with its titrant and the pipette with the solution it transfers; rinse the conical flask with distilled water. Read the meniscus at eye level, swirl over a white tile and add titrant dropwise near the endpoint. The titre is the final burette reading minus the initial reading. Exclude the rough trial and average careful titres meeting the stated concordance rule.



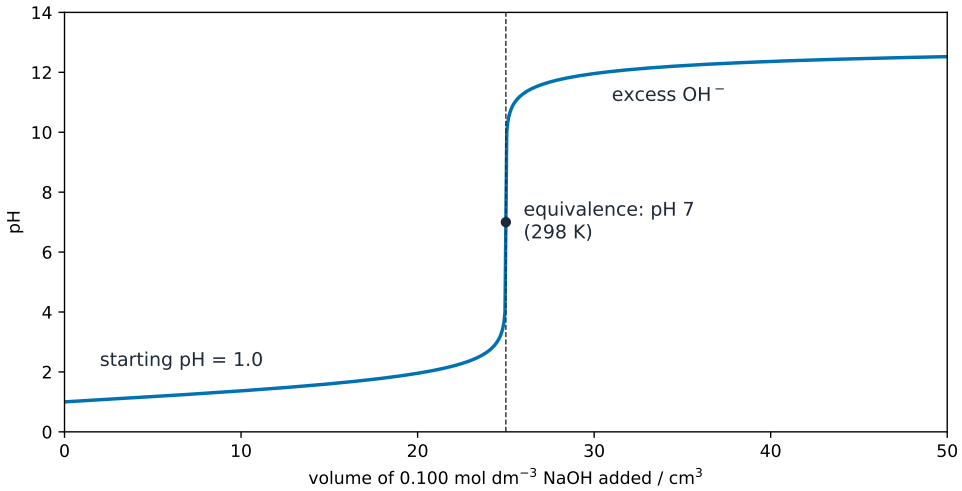
A titration setup: reacting volumes from a burette find the concentration of an unknown solution

For an invented HCl/NaOH titration, 25.00 cm^3 of HCl needs 0.150 mol dm^{-3} NaOH. Careful titres of 18.35, 18.40 and 18.45 cm^3 meet a stated maximum range of 0.10

cm^3; their mean is 18.40 cm^3. HCl + NaOH → NaCl + H_2O gives a 1:1 ratio. First find the known amount: $n(\text{NaOH}) = cV = 0.150(18.40/1000) = 0.00276$ mol. Hence $n(\text{HCl}) = 0.00276$ mol, and $c(\text{HCl}) = n/V = 0.00276/0.02500 = 0.110$ mol dm^{-3} to three significant figures. Both volumes must be in dm^3 when calculating amounts or concentrations this way.

The pH curve of a strong acid and a strong base

A **pH curve** 滴定曲线 shows how the pH changes as one solution is added to another in a titration.

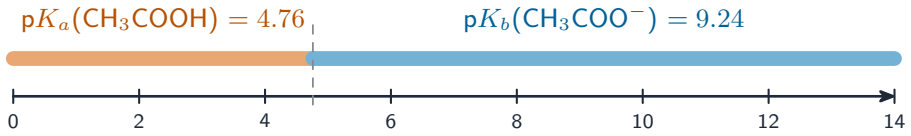


This 298 K example reaches equivalence at 25.0 cm^3 and pH 7.00.

- The **equivalence point** 化学计量点 is where the amounts of acid and base match the equation. For dilute strong acid and strong base at 298 K it is at pH 7.00. Equal amounts mean the balanced reacting ratio, not necessarily equal solution volumes.
- Near equivalence in this supplied 0.100 mol dm^{-3} example, a small addition causes a steep pH rise. The size of the rise depends on concentration, volume and the increment added. This steep section is why an indicator can show the end point sharply.
- The starting pH comes from the acid concentration; with a large excess of titrant, pH approaches that of the alkali. During titration, mixing dilutes both solutions. Add smaller measured increments near the steep region, mix and allow the pH reading to settle.

AHL: pOH, K_a and K_b

This extension uses dissociation constants and their base-ten logarithms from the data booklet. Keep the conjugate partner and the temperature explicit.



$pK_a + pK_b = 14.00$ for a conjugate pair at 298 K

smaller pK_a: stronger acid, so its conjugate base is weaker (larger pK_b)

For a conjugate pair at 298 K, pKa + pKb = 14.00

pOH

The same logarithm works for hydroxide ions:

$$\text{pOH} = -\log_{10}[\text{OH}^-] \qquad \text{pH} + \text{pOH} = 14.00 \text{ at } 298 \text{ K}$$

So for 0.010 mol dm^{-3} NaOH, pOH = 2.00 and pH = 12.00.

Acid and base dissociation constants

The extent of ionization of a weak acid is measured by its **acid dissociation constant** 酸解离常数, K_a:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \qquad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

For a weak base, $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$:

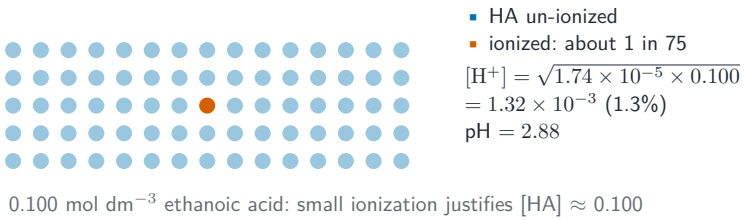
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

As with pH, $pK_a = -\log K_a$ and $pK_b = -\log K_b$. A **larger** K_a (smaller pK_a) means a **stronger** acid.

Multiplying $K_a = [H^+][A^-]/[HA]$ by the conjugate-base expression $K_b = [HA][OH^-]/[A^-]$ cancels the acid/base concentration factors. Thus, for that conjugate pair, $K_a \times K_b = K_w$, so $pK_a + pK_b = 14.00$ at 298 K. Ethanoic acid has $pK_a = 4.76$, so the ethanoate ion has $pK_b = 9.24$.

pH of a weak acid

Assume that only a little of the acid ionizes, so [HA] at equilibrium is about the starting concentration, and that $[H^+] \approx [A^-]$. This second approximation requires negligible water contribution and no appreciable other source of H^+ or A^-; it does not hold for an acid/salt buffer.



0.100 mol dm^{-3} ethanoic acid: small ionization justifies [HA] ≈ 0.100

Only about 1.3% of 0.100 mol dm^{-3} ethanoic acid ionizes

Worked example: the pH of 0.100 mol dm^{-3} ethanoic acid, $K_a = 1.74 \times 10^{-5}$.

- $K_a = \dfrac{x^2}{0.100}$, so $x^2 = 1.74 \times 10^{-6}$.
- $x = [H^+] = 1.32 \times 10^{-3}$ mol dm^{-3}.
- pH $= -\log(1.32 \times 10^{-3}) = 2.88$.

The assumption holds because only 1.3% of the acid has ionized. For a weak base, use $[OH^-] \approx \sqrt{K_b c}$ under the analogous assumptions, then $[H^+] = K_w/[OH^-]$. A small-depletion check is required in either case; a small numerical constant alone is insufficient.

Working backwards to K_a

A 0.0500 mol dm^{-3} solution of a weak acid has pH 3.10. Then $[H^+] = 10^{-3.10} = 7.94 \times 10^{-4}$, and

The acid remaining is $0.0500 - x$, not exactly 0.0500. With $x = 10^{-3.10}$:

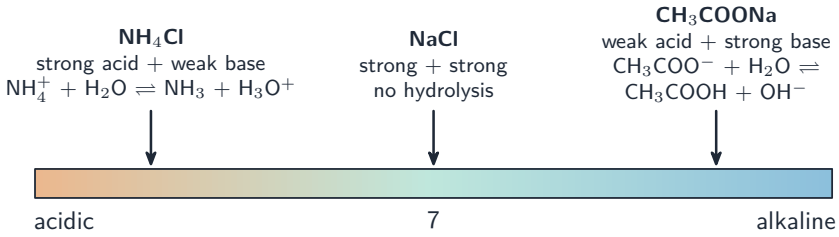
$$K_a = \frac{x^2}{0.0500 - x} \approx 1.28 \times 10^{-5}, \qquad pK_a \approx 4.89.$$

Neglecting depletion would give 1.26×10^{-5} and pKa 4.90. Label that as an approximation. Rounding the supplied pH also limits the justified precision.

AHL: Salts, pH curves and indicators

The pH of salt solutions

A salt solution is not always neutral. The ion from the weak partner reacts with water.



Salt solutions: acidic, neutral or alkaline by parent strength

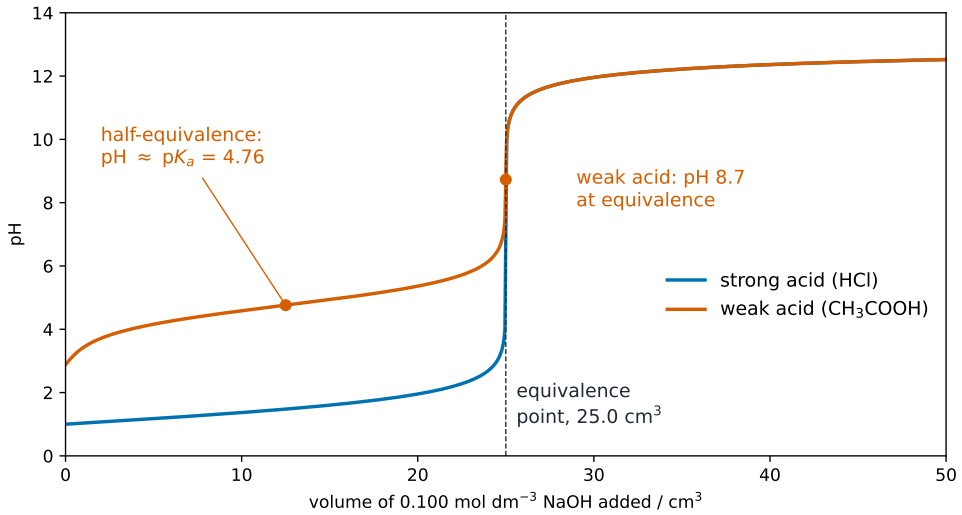
Salt made from	Example	Dilute solution at 298 K
strong acid + strong base	NaCl	neutral
weak acid + strong base	CH_3COONa	alkaline
strong acid + weak base	NH_4Cl	acidic

Ethanoate hydrolysis produces OH^-: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$. Ammonium produces H_3O^+: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$. Write the water explicitly when explaining proton transfer.

Hydrogencarbonate is amphiprotic, so consider **both** $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ and $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$. Supplied constants can show the base process dominates, making its salt solution alkaline. For example, using $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$, its base constant is $K_w/K_{a1} \approx 2.3 \times 10^{-8}$, larger than its acid constant K_{a2}. Do not classify every ion with hydrogen as necessarily acidic.

For a salt from a weak acid and weak base, both ions can hydrolyse; compare their acid and base constants. A blanket rule based only on one parent is insufficient. Hydrolysis of hydrated metal ions is outside the required Reactivity 3.1 scope here.

pH curves with weak acids and bases

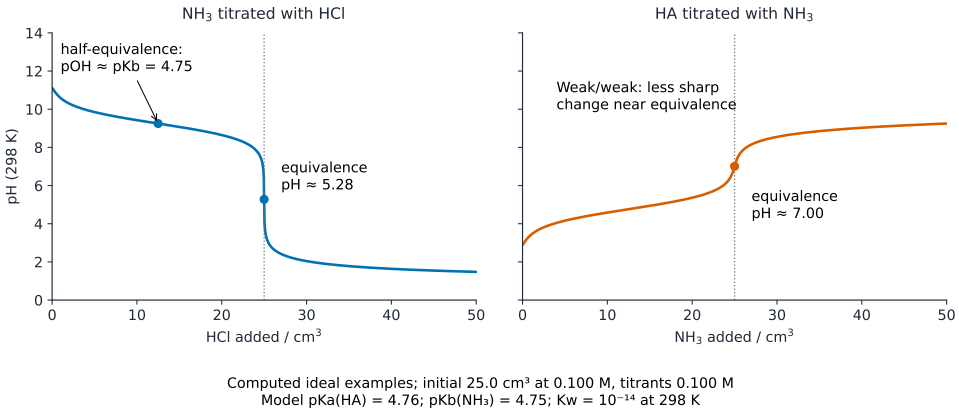


In the usual buffer approximation, a weak-acid titration has pH ≈ pKa at half-equivalence

Points to read from a pH curve:

- The **starting pH** is higher for a weak acid of the same concentration.
- The **equivalence point** is above 7 for a weak acid with a strong base (the salt is alkaline), below 7 for a strong acid with a weak base, and at 7 for the strong/strong case at 298 K. A weak/weak case generally has a less pronounced change and its equivalence pH depends on both constants.
- At the **half-equivalence point** half the acid has become A^-, so $[HA] = [A^-]$ and $K_a = [H^+]$: **pH** ≈ **p**K_a in the usual concentration/buffer approximation. This can estimate K_a from a well-resolved curve; it is not an exact identity for every concentration or activity convention.
- The gently sloping region before equivalence is a buffer region.

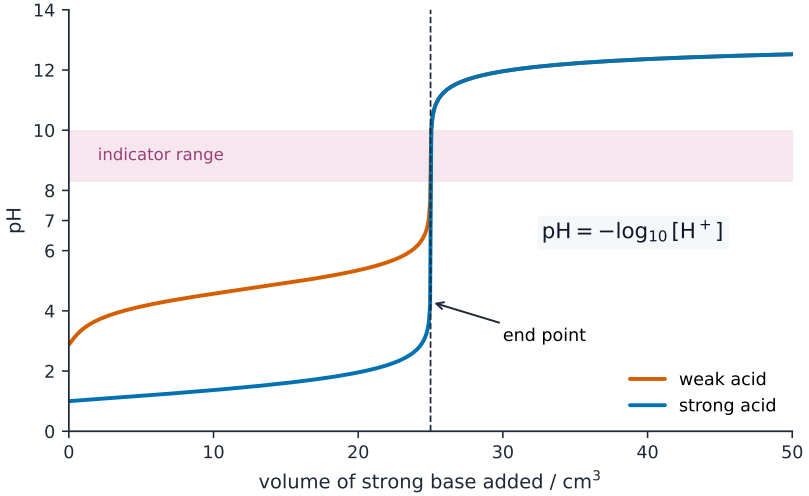
For a weak base such as NH_3 titrated with strong acid, the curve starts alkaline and falls. Before equivalence the NH_3/NH_4^+ mixture buffers the solution. At half-equivalence, approximately equal base/conjugate-acid amounts give pOH ≈ pKb, or pH ≈ pKa of NH_4^+. Equivalence is acidic because NH_4^+ hydrolyses. Reversing which solution is in the burette reverses the curve direction; identify the starting solution before sketching.



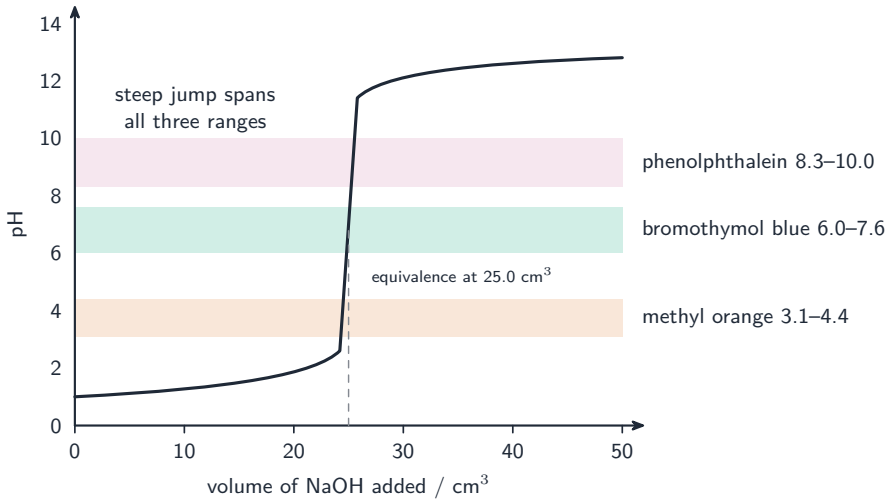
Original computed examples: all initial samples are 25.0 cm³ of 0.100 mol dm⁻³; titrants are 0.100 mol dm⁻³. Constants are supplied model values. These are not measured data.

Choosing an indicator

An acid–base **indicator** 指示剂 is a weak acid, HIn, whose molecule and conjugate base have different colours:



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



An indicator works when its colour-change range lies inside the steep part of the curve

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq) + In^-(aq)}$$

The colour changes over about two pH units centred on its pK_a (equal forms give the midpoint colour near pKa, not a universal operational endpoint). For $K_{\mathrm{In}} = [H^+][In^-]/[HIn]$, increasing $\mathrm{H^+}$ reduces $[In^-]/[HIn]$, favouring the acid colour. Added $\mathrm{OH^-}$ removes $\mathrm{H^+}$ and favours the base colour. The observed **endpoint** depends on the chosen visible criterion and need not be exactly equal indicator-form concentrations. The **equivalence point** instead follows stoichiometry. Choose a range inside the sufficiently steep part of the actual pH curve, near its equivalence pH.

Indicator	**pK_a**	**Colour change (acid → alkali)**	**Range**	**Use for**
methyl orange	3.7	red → yellow	3.1–4.4	strong acid + weak base
bromothymol blue	7.0	yellow → blue	6.0–7.6	strong acid + strong base
phenolphthalein	9.6	colourless → pink	8.3–10.0	weak acid + strong base

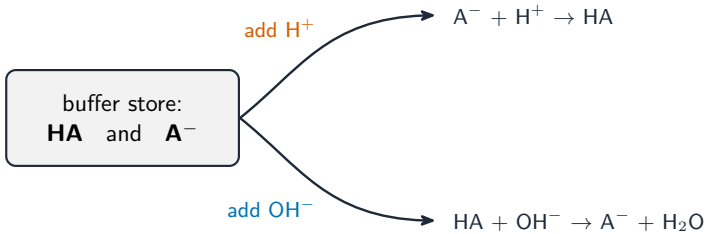
For the supplied 0.100 mol $\mathrm{dm^{-3}}$ strong/strong titration, the steep region can accommodate all three. This is not a concentration-independent rule: dilute titrations can have a much smaller jump. A weak/weak titration often has no satisfactory sharp colour endpoint; use an appropriate alternative measurement rather than forcing one of these indicator labels onto every curve. Universal indicator is a mixture giving a broad colour range, useful for approximate pH but usually unsuitable for a sharp titration endpoint.

AHL: Buffer solutions

What a buffer does

A **buffer solution** 缓冲溶液 resists a change in pH when small amounts of acid or alkali are added. It does not hold pH exactly constant or neutralize unlimited additions.

A buffer contains a weak acid and its conjugate base (or a weak base and its conjugate acid), both in appreciable amounts relative to the small added acid or base. For example: ethanoic acid with sodium ethanoate, or ammonia with ammonium chloride.



small additions: the component ratio changes only slightly

The large reserves of HA and A^- remove added H^+ or OH^-

- Add a little acid: $\mathrm{CH_3COO^- + H^+ \rightarrow CH_3COOH}$.
- Add a little alkali: $\mathrm{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$.

Because both reserves are large, the ratio $[\mathrm{A^-}]/[\mathrm{HA}]$ hardly changes, and so the pH hardly changes.

A buffer can also be made by part-neutralizing a weak acid with a strong base: adding 12.5 $\mathrm{cm^3}$ of NaOH to 25.0 $\mathrm{cm^3}$ of ethanoic acid in the pH curve above gives equal amounts of HA and $\mathrm{A^-}$.

The pH of a buffer

Rearranging K_a and taking logarithms:

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

- When $[\mathrm{A^-}] = [\mathrm{HA}]$, $\mathrm{pH} = \mathrm{p}K_a$.

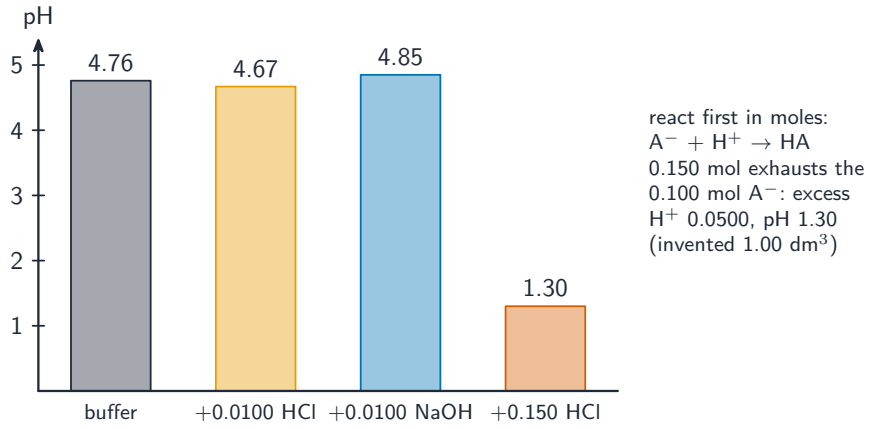
- To make a buffer of a chosen pH, pick an acid with pK_a close to that pH and adjust the ratio.
- **Diluting** a buffer ideally changes its pH very little while both components remain well above the water-ionization contribution: their ratio stays approximately the same. Real activities and very large dilution can change pH. At a fixed comparison volume, the diluted buffer has less acid/base capacity per volume; the entire enlarged batch still contains approximately the same total component amounts. Specify whether capacity refers to a fixed portion or the whole batch.

Worked example: a buffer contains 0.20 mol dm^{-3} CH_3COOH and 0.10 mol dm^{-3} CH_3COONa (p$K_a = 4.76$).

$$\mathrm{pH} = 4.76 + \log\frac{0.10}{0.20} = 4.76 - 0.30 = 4.46$$

■ Work in moles before recalculating the buffer ratio

For an invented 1.00 dm^3 buffer with 0.100 mol HA, 0.100 mol A^- and pKa 4.76, add 0.0100 mol HCl with negligible volume change. First react the added strong acid: $A^- + H^+ \rightarrow HA$. The new amounts are A^- 0.0900 mol and HA 0.110 mol, so pH $\approx 4.76 + \log(0.0900/0.110) = 4.67$. Adding the same amount of NaOH instead gives A^- 0.110 and HA 0.0900 mol, hence pH $\approx$ 4.85. The pH changes modestly because neither reserve is exhausted.



Small additions barely move a buffer; exhausting it does (invented)

Adding 0.150 mol HCl would consume the entire initial 0.100 mol A^- and leave 0.0500 mol excess strong acid. The buffer equation with a negative base amount would be meaningless. Excess H^+ dominates: at the stated unchanged volume, $[H^+] \approx 0.0500$ mol dm^{-3} and pH $\approx$ 1.30. This is a capacity limit, not a failure of stoichiometry. For a buffer prepared by partial neutralization, similarly react the strong acid or base first; use the **remaining** weak/conjugate amounts in the equilibrium expression.

Practice

Use supplied concentration-model values at 298 K unless stated otherwise.

1. Identify the two conjugate acid–base pairs in $HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+$.
2. Write equations to show that HCO_3^- is amphiprotic.
3. Calculate the pH of: (a) 0.0025 mol dm^{-3} HCl, (b) 0.050 mol dm^{-3} KOH.
4. A solution has pH 4.70. Calculate $[H^+]$ and $[OH^-]$.
5. Compare two tests of 0.10 mol dm^{-3} HCl and ethanoic acid. State expected results and controls.
6. Why can heated pure water have pH below seven while remaining neutral?
7. Sketch 0.100 mol dm^{-3} NaOH added to 20.0 cm^3 of 0.100 mol dm^{-3} HCl: mark starting pH and equivalence.
8. Classify CuO and aqueous NH_3 as bases/alkalis. Balance NH_3 + HCl and identify whether water forms.
9. Name parent acid/base choices for sodium ethanoate and ammonium nitrate. Outline salt crystallization from acid and insoluble oxide.
10. Compare universal indicator and a probe for resolving 0.05 pH unit. State two calibration/control requirements.
11. At a stated temperature $K_w = 4.00 \times 10^{-14}$. Find neutral $[H^+]$ and pH; explain why the solution is neutral.
12. **AHL.** (a) Calculate the pH of 0.050 mol dm^{-3} methanoic acid, p$K_a = 3.75$. State and check the small-depletion assumption; a supplied numerical equilibrium check gives $[H^+] = 0.002894$ mol dm^{-3}. (b) The pK_b of ammonia is 4.75. Calculate pK_a of the ammonium ion, and the pH of 0.10 mol dm^{-3} ammonia.
13. **AHL.** (a) Predict whether solutions of (a) KNO_3, (b) Na_2CO_3, (c) NH_4NO_3 are acidic, neutral or alkaline, and explain one of them with an equation. (b) Choose an indicator for titrating ethanoic acid with sodium hydroxide, and explain your choice. (c) Explain what happens at half-equivalence when strong acid titrates NH_3, and why a weak/weak titration may lack a sharp indicator endpoint.
14. **AHL.** (a) Calculate the pH of a buffer made from 0.050 mol NH_3 and 0.10 mol NH_4Cl in 1.0 dm^3 of solution (pK_a of $NH_4^+ = 9.25$). Explain how it resists a small addition of acid. (b) Add 0.010 mol HCl to that buffer with negligible volume change. Calculate its new pH. (c) Explain the limit of the claim that dilution does not change buffer pH.

Worked answers.

1. HNO_3 (acid) and NO_3^- (conjugate base); H_3O^+ (acid) and H_2O (conjugate base).

2. As an acid: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$. As a base: $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$.
3. (a) $-\log(0.0025) = 2.60$. (b) At 298 K, $[H^+] = 10^{-14}/0.050 = 2.0 \times 10^{-13}$ mol dm^{-3}, giving pH 12.70.
4. $[H^+] = 10^{-4.70} = 2.0 \times 10^{-5}$ mol dm^{-3}; $[OH^-] = 1.00 \times 10^{-14}/2.0 \times 10^{-5} = 5.0 \times 10^{-10}$ mol dm^{-3}. These values use $K_w = 1.00 \times 10^{-14}$ at 298 K.
5. Compare equal concentration, volume and temperature: HCl has lower pH and higher conductivity than ethanoic acid. With equal magnesium surface, HCl has faster initial bubbling.
6. Endothermic water ionization increases on heating, raising $[H^+]$ above 10^{-7} mol dm^{-3}. Water stays neutral because $[H^+]$=$[OH^-]$.
7. Start at pH 1.0; rise slowly, then steeply at 20.0 cm^3, with equivalence pH 7 at 298 K; approach the excess-NaOH pH beyond equivalence.
8. CuO is a basic oxide, not a soluble alkali. Aqueous NH_3 produces OH^- and is an alkali. $NH_3 + HCl \rightarrow NH_4Cl$; no water product.
9. Parents: CH_3COOH/NaOH; HNO_3/NH_3. Add excess oxide, filter, concentrate carefully, cool to crystallize, then wash and dry appropriately.
10. Use a suitably calibrated, stable pH probe, with buffer standards and temperature control. Rinse between samples. Universal indicator lacks this precision; display resolution alone does not prove accuracy.
11. $[H^+] = [OH^-] = \sqrt{K_w} = 2.00 \times 10^{-7}$ mol dm^{-3}; pH $\approx$ 6.70. Equal ion concentrations establish neutrality.
12. **AHL.** (a) $K_a = 10^{-3.75} = 1.78 \times 10^{-4}$; the shortcut gives $[H^+] \approx \sqrt{K_a c} = 2.98 \times 10^{-3}$ and pH $\approx$ 2.53. Estimated ionization is 5.96%, so depletion is not negligible for a tight-accuracy calculation. The supplied checked concentration gives pH $\approx$ 2.54. Do not present 2.53 as an exact solution. (b) $pK_a = 14.00 - 4.75 = 9.25$. $K_b = 10^{-4.75} \approx 1.78 \times 10^{-5}$; $[OH^-] \approx \sqrt{10^{-4.75} \times 0.10} = 1.3335 \times 10^{-3}$, pOH $\approx$ 2.875, pH $\approx$ 11.13 using the small-depletion approximation. Retaining depletion instead gives about 11.12; the approximation can affect the last reported decimal.
13. **AHL.** (a) neutral (strong acid, strong base). (b) alkaline: $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$. (c) acidic: $NH_4^+ \rightleftharpoons NH_3 + H^+$. (b) Phenolphthalein. The equivalence point is about pH 8.7 and the steep section runs from about pH 7 to 11; phenolphthalein changes colour between 8.3 and 10.0, inside this range. Methyl orange would change far too early. (c) Near half-equivalence, equal NH_3/NH_4^+ amounts give pOH $\approx$ pKb, or pH $\approx$ pKa of NH_4^+. A weak/weak curve has a less pronounced change and may not put an indicator range in a sufficiently steep interval.
14. **AHL.** pH $= 9.25 + \log(0.050/0.10) = 9.25 - 0.30 = 8.95$. Added H^+ reacts with the large reserve of ammonia, $NH_3 + H^+ \rightarrow NH_4^+$, so the ratio $[NH_3]/[NH_4^+]$ and the pH change very little. (b) HCl consumes 0.010 mol NH_3: remaining base 0.040 mol, conjugate acid 0.110 mol. pH $\approx 9.25 + \log(0.040/0.110) = 8.81$. (c) The unchanged-ratio approximation requires sufficiently concentrated components; extreme dilution and activity changes can affect pH. At fixed comparison volume, dilution lowers capacity per volume; it does not remove the original batch's component moles.

Exam tips

- Identify donor/acceptor and conjugate pairs. Compare strength at matched concentration; state temperature for K_w. Show logarithms and match precision to the data and measuring method.
- **AHL.** Check weak-acid depletion; use the conjugate partner in $K_a K_b = K_w$. Half-equivalence relations are buffer approximations.
- **AHL.** Choose indicators from the actual curve; react added strong acid/base before using a buffer ratio, and check neither reserve is exhausted.

Electron transfer reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.2, Electron transfer reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: ions and ionic formulas from Structure 2.1, alcohols and other functional groups from Structure 3.2, and amounts in moles from Structure 1.4. Numerical examples use supplied classroom data. Use the stated conditions rather than assuming every predicted reaction must be rapid or observable.

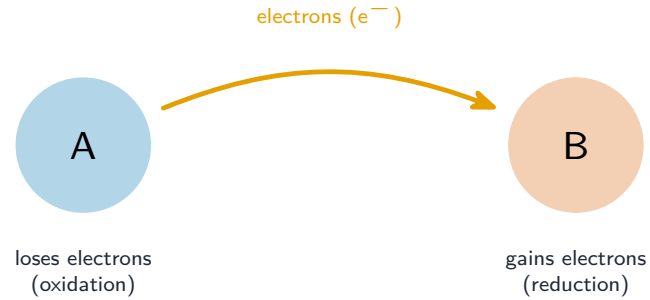
Oxidation and reduction

What do rusting, batteries and breathalysers share?

An iron nail rusts, a phone battery powers a screen, and a traditional chemical breath-test example uses an orange-to-green dichromate change. Modern instruments need not use that reaction. Redox involves electron transfer or a change in formal oxidation states; covalent reactions need not release free electrons into the solution. These are **redox** reactions: **red**uction and **ox**idation always happen together.



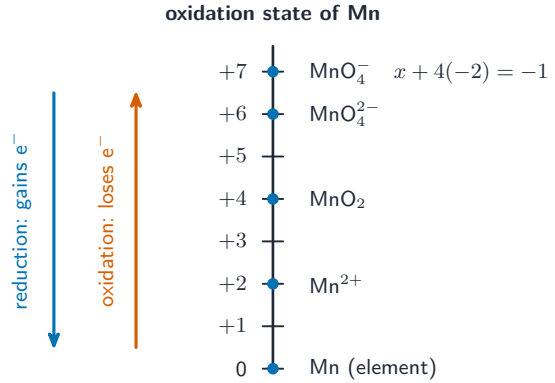
Rusting is the oxidation of iron by oxygen.



Electrons pass from the substance that is oxidised (loses them) to the one that is reduced (gains them) – the two always happen together

Electrons and oxidation states

- **Oxidation** 氧化 is loss of electrons, or an increase in oxidation state.
- **Reduction** 还原 is gain of electrons, or a decrease in oxidation state.



Up the ladder is oxidation (electrons lost); down is reduction (electrons gained)

A memory aid: OIL RIG, "oxidation is loss, reduction is gain" of electrons.

The **oxidation state** 氧化态 of an atom is the charge it would have if all its bonds were ionic. Use these rules in order:

1. An element on its own is 0 (Fe, O_2, Cl_2).
2. A simple ion has its charge (Na^+ is +1, O^{2-} is −2).
3. The oxidation states in a compound add up to 0; in an ion they add up to the charge.

4. F is -1 in its compounds; elemental F_2 follows rule 1. O is usually -2 (but -1 in peroxides). H is usually $+1$ (but -1 in metal hydrides such as NaH).

Worked example. Find the oxidation state of Mn in MnO_4^- and of Cr in $Cr_2O_7^{2-}$.

- MnO_4^-: $x + 4(-2) = -1$, so $x = +7$.
- $Cr_2O_7^{2-}$: $2x + 7(-2) = -2$, so $2x = +12$ and $x = +6$.

Oxidation states are written with the sign first (+7), and they appear in names as Roman numerals: manganate(VII), dichromate(VI), iron(III) chloride.

Oxidation state is a formal electron-accounting model, not necessarily the actual atomic charge. In H_2O the hydrogen oxidation state is $+1$, but the molecule does not contain two free H^+ ions bonded to an O^{2-} ion. For a non-metal with several atoms in different environments, a formula can give an average rather than every atom's individual state.

Oxygen gain and hydrogen loss often indicate oxidation; oxygen loss and hydrogen gain often indicate reduction. The electron/oxidation-state definition is more general. Carbon has oxidation states -4, -2, 0, $+2$ and $+4$ respectively in CH_4, CH_3OH, HCHO, HCOOH and CO_2. This connects organic functional-group changes to the same accounting used for metal ions. $FeCl_2$ and $FeCl_3$ contain iron(II) and iron(III); sulfur has $+4$ in SO_2 and $+6$ in $SO_4{}^{2-}$. Do not assume main-group non-metals have only one oxidation state.

Oxidizing and reducing agents

- An **oxidizing agent** 氧化剂 oxidizes another substance, so it is itself reduced. It gains electrons.
- A **reducing agent** 还原剂 reduces another substance, so it is itself oxidized. It loses electrons.

In $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, zinc is oxidized (0 to +2) and is the reducing agent; Cu^{2+} is reduced (+2 to 0) and is the oxidizing agent.

Half-equations

Splitting a redox reaction

A **half-equation** 半反应方程式 shows the oxidation or the reduction on its own, with the electrons written in.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad \text{(oxidation)}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{(reduction)}$$

Balancing half-equations in acid

For ions such as MnO_4^-, balance in this order:

1. Balance the atoms other than O and H.
2. Add H_2O to balance O.
3. Add H^+ to balance H.
4. Add electrons to balance the charge.

Worked example. MnO_4^- is reduced to Mn^{2+} in acid.

1. Mn is balanced.
2. Four O on the left, so add $4H_2O$ on the right.
3. Eight H on the right, so add $8H^+$ on the left.
4. Charge on the left: $-1 + 8 = +7$. On the right: $+2$. Add $5e^-$ on the left.

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

1 atoms besides O, H	$MnO_4^- \rightarrow Mn^{2+}$
2 O with H_2O	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
3 H with H^+	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
4 charge with e^-	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ charge check: $(-1) + (+8) + (-5) = +2$ on the left; $+2$ on the right

Balancing a half-equation in acid: atoms, then O with water, H with H^+, charge with electrons

Combining half-equations

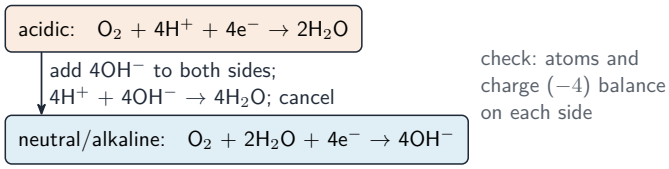
Multiply the half-equations so the electrons lost equal the electrons gained, then add them and cancel. With iron(II), $Fe^{2+} \rightarrow Fe^{3+} + e^-$, multiply by 5:

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

Check: the charges are equal on both sides (+17 and +17).

■ Half-equations when the medium is not acidic

Do not leave a large net supply of H^+ in an equation intended for neutral or alkaline conditions. An oxygen-reduction example is:



Rewrite a half-equation for neutral or alkaline conditions

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$

Atoms balance (O_4H_4 on each side) and charge is -4 on each side. It can be obtained from $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ by adding $4OH^-$ to both sides, forming water and cancelling. Calling the starting bulk solution neutral does not mean local pH stays seven: electrode reactions can produce OH^- or H^+ nearby.

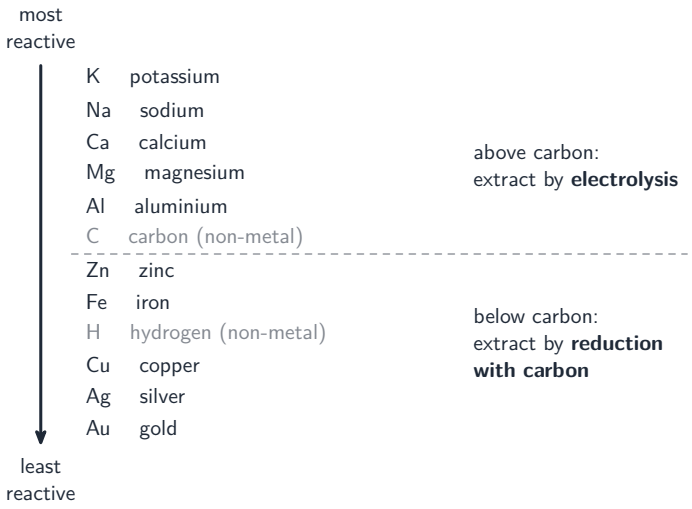
For the supplied neutral/alkaline reduction product MnO_2, the half-equation is $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$. The same element can have a different reduction product in a different medium. State the product and conditions before balancing. When adding half-equations, cancel electrons completely; they cannot remain in the final overall equation for a closed redox reaction.

In an acidified manganate(VII)/iron(II) titration, purple MnO_4^- is consumed while Fe^{2+} remains. A small excess gives a persistent faint colour, so the reagent can act as its own indicator. This is an observed endpoint, not a new definition of equivalence. Such demonstrations follow the school's approved procedure.

The activity series

■ Which metal gives up electrons more easily?

Metals react by losing electrons, so a more reactive metal is a stronger reducing agent. Use supplied displacement observations to infer an **activity series** 活动性顺序 for the metals being compared. An illustrative subset is Mg > Zn > Fe > Cu > Ag. The syllabus supplies appropriate metal/ion data; a long memorized list is not a substitute for interpreting them.



An activity series: a metal higher in the list is more easily oxidized and can displace a metal below it from a solution of its ions

A metal displaces a less active metal from a solution of its ions. In this **displacement** 置换 reaction the more active metal is oxidized:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The blue colour fades and a brown-pink coating of copper forms on the zinc. Copper does not displace zinc from zinc sulfate under this simple aqueous model. A protective oxide film or slow kinetics can hide a thermodynamically favoured change; no visible reaction alone is not a universal proof of relative potential.

■ Halogens

Halogens react by gaining electrons, so they are oxidizing agents. Their strength falls down the group: $Cl_2 > Br_2 > I_2$. A halogen displaces a less reactive halogen from its halide ions:

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Formation of dissolved bromine gives an orange/yellow-brown colour under the stated aqueous conditions. Colour intensity also depends on concentration and solvent. Down group 17, halogens generally become less readily reduced; the halide ions show the opposite trend as reducing agents. In main-group metals, electron loss generally becomes easier down a group, but observed water-reaction rates and aqueous standard potentials are not identical rankings.

Metals and acids

Suitable reactive metals with dilute non-oxidizing acids such as HCl or dilute H_2SO_4 can form a salt and hydrogen. Oxide passivation and kinetics can affect the observation; oxidizing acids such as nitric acid need separate predictions. The metal is oxidized and H^+ is reduced:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Metals below hydrogen, such as copper and silver, do not react with dilute HCl or H_2SO_4.

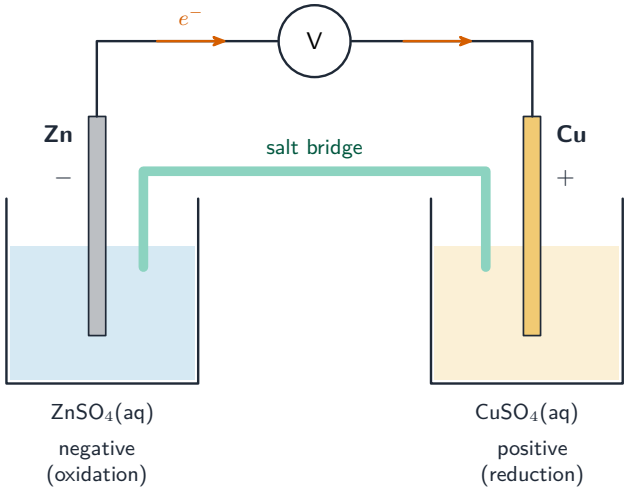
Primary and secondary cells

Turning a redox reaction into a current

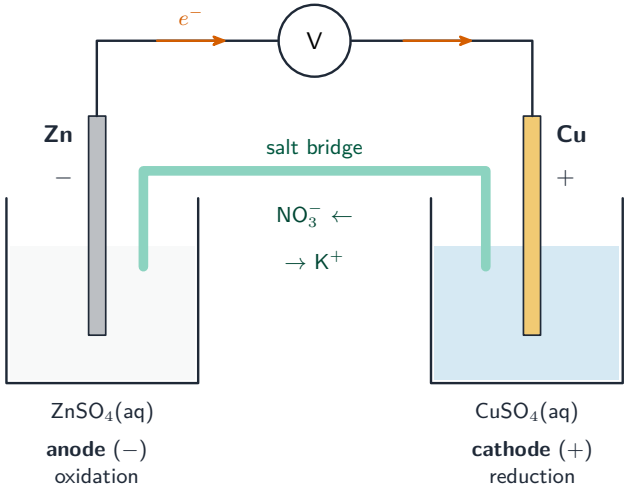
When zinc directly contacts copper(II) sulfate, the coupled redox reaction releases energy largely as heat rather than useful electrical work. A **voltaic cell** separates the half-reactions and provides an external conducting path: chemical energy can supply electrical work. A **primary cell** 一次电池 is designed for discharge without routine recharging; a rechargeable secondary cell is also voltaic while discharging.



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



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)



Electrons flow through the wire from the anode to the cathode

- At the **anode** 阳极, oxidation happens: $Zn \rightarrow Zn^{2+} + 2e^-$. In a primary cell the anode is the negative electrode.
- At the **cathode** 阴极, reduction happens: $Cu^{2+} + 2e^- \rightarrow Cu$. In a primary cell the cathode is the positive electrode.

- Electrons flow through the external wire from anode to cathode.
- The **salt bridge** 盐桥, for example filter paper soaked in $KNO_3(aq)$, lets ions move between the solutions. Without it, charge builds up and the current stops. In this Zn/Cu cell, nitrate anions move towards the zinc compartment as Zn^{2+} accumulates; potassium cations move towards the copper compartment as Cu^{2+} is removed. This maintains approximate **bulk electrical neutrality**, not necessarily pH seven. Electrons travel in the external metallic path, not through the salt bridge. Choose bridge ions that do not significantly react with either solution.

For the simple metal/metal-ion displacement cells here, the more readily oxidized metal is the anode under the stated conditions. A ranking alone does not give a numerical voltage or make an equal number of list positions correspond to equal voltage intervals. A high-resistance voltmeter measures the potential difference with very little current; appreciable energy delivery requires a conducting load. During sustained Zn/Cu discharge, zinc loses mass, copper gains mass and Cu^{2+} concentration decreases in the simple model.

■ Secondary cells

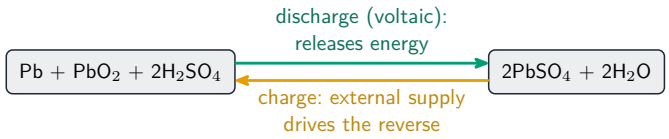
A **secondary cell** 二次电池 is rechargeable. During discharge it operates in voltaic mode; its rechargeable design does not change it into a primary cell. To recharge it, an external supply pushes current the other way and reverses the reactions.

Cell	Used in	Note
lead–acid	cars	heavy; lead is toxic; sulfuric acid is corrosive
lithium-ion	phones, laptops, electric cars	light, stores a lot of energy; Li^+ ions move between the electrodes
nickel–metal hydride	rechargeable AA cells	energy density and performance depend on the particular design

A **fuel cell** 燃料电池 is different: it is fed continuously with fuel (such as hydrogen) and oxygen, so it is not recharged. The ideal hydrogen/oxygen cell's net chemical product is water; the source of the hydrogen and electricity used to produce it still affects wider environmental impacts.

■ Reverse a supplied secondary-cell reaction

For an illustrative lead–acid discharge model:



oxidation defines the anode in each mode, so the anode electrode swaps when the reaction reverses

A lead-acid cell: discharge and charge are the same equation reversed

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O.$$

Charging reverses that overall equation. Reversing each supplied half-equation swaps its electrons between reactant and product sides. Oxidation still defines the anode in each operating mode; the physical electrode undergoing oxidation changes when the reaction is reversed. An external charging source must provide a suitable potential and practical energy losses are unavoidable. Do not infer that every primary-cell chemistry can be recharged safely simply because a balanced equation can be reversed on paper.

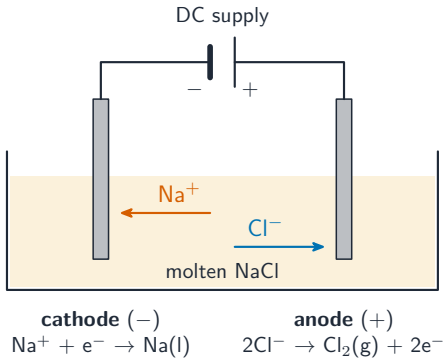
Primary cells are convenient without charging equipment but need replacement after their useful discharge. Secondary cells can reduce repeated replacement and be used for many cycles, but require charging infrastructure and deteriorate. Fuel cells continue while reactants are supplied, but need fuel storage, delivery and suitable catalysts. Compare the actual application rather than assigning an unconditional "safest" or "best" label to every battery type.

For an ideal acidic hydrogen fuel cell, anode $2H_2 \rightarrow 4H^+ + 4e^-$ and cathode $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ combine to $2H_2 + O_2 \rightarrow 2H_2O$. Hydrogen is oxidized, oxygen reduced; external electrons flow from fuel anode to oxygen cathode. An alkaline version uses different half-equations but has the same net equation.

Electrolytic cells

■ Using electricity to force a reaction

An **electrolytic cell** 电解池 uses electrical energy to drive a redox reaction that would not happen on its own. This is **electrolysis** 电解. The **electrolyte** 电解质 must contain mobile ions. In the molten/aqueous examples studied here, melting or dissolving allows ion migration; other technologies can use ion-conducting membranes or solids.



In electrolysis the cathode is negative and the anode positive

The names follow the same rule as in every cell: oxidation at the anode, reduction at the cathode. But the signs are reversed: in an electrolytic cell the cathode is negative because the power supply pushes electrons onto it.

For molten sodium chloride:

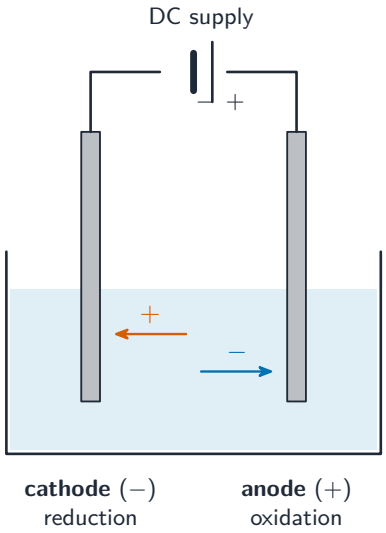
$$\text{cathode } (-): \quad \mathrm{Na^+ + e^- \rightarrow Na(l)}$$

$$\text{anode } (+): \quad \mathrm{2Cl^- \rightarrow Cl_2(g) + 2e^-}$$

Molten lead(II) bromide gives lead at the cathode and bromine at the anode. Electrons travel through the wires and power supply; ions carry charge through the electrolyte. Individual $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions do not carry electrons across the liquid as free electronic charge carriers. Predict products on paper; chlorine and bromine demonstrations remain teacher-controlled under the school procedure.

■ Predict products and use an approved setup

A molten salt contains its own ions. In an aqueous electrolyte, water-related species also compete: hydrogen or oxygen may form instead of a metal or halogen. Specify the electrolyte, its concentration and the electrode material before predicting products; an electrode can itself react. For example, $\mathrm{CuSO_4(aq)}$ with an inert anode gives oxygen there, whereas a copper anode can dissolve to $\mathrm{Cu^{2+}}$.



Electrolysis: the DC supply drives positive ions to the cathode (reduction) and negative ions to the anode (oxidation)

Use a low-voltage direct-current supply and approved electrodes under the school risk assessment. Collect gases only by an approved method. Chlorine and bromine demonstrations remain teacher-controlled; do not generate these gases independently.

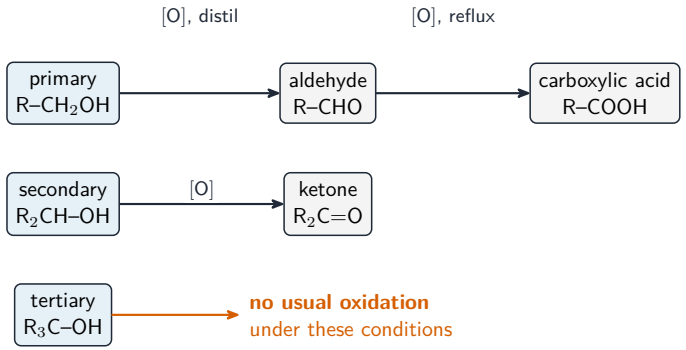
	Primary cell	**Electrolytic cell**
Energy change	chemical → electrical	electrical → chemical
Reaction	spontaneous	not spontaneous
Anode	negative, oxidation	positive, oxidation
Cathode	positive, reduction	negative, reduction

Redox in organic chemistry

The required syllabus focus is functional-group changes, equations, distillation/reflux and the role of hydride ions. The named reagents below give useful laboratory examples; memorizing particular oxidizing/reducing reagent names and their mechanisms is not required for these objectives.

■ Oxidation of alcohols

The usual oxidizing agent is acidified potassium dichromate(VI). It changes from orange ($\mathrm{Cr_2O_7^{2-}}$) to green ($\mathrm{Cr^{3+}}$) as it oxidizes the alcohol. In equations we write [O] for the oxygen it supplies.



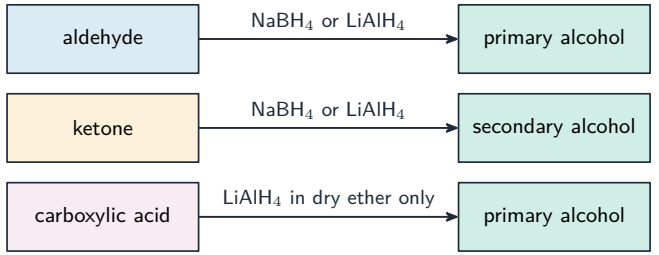
What an alcohol oxidizes to depends on its class

- A primary alcohol gives an aldehyde. To stop there, **distillation** 蒸馏 removes the aldehyde as soon as it forms: $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$.
- Heating under **reflux** 回流 keeps the aldehyde in the flask, so it is oxidized further to a carboxylic acid: $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$.
- A secondary alcohol gives a ketone: propan-2-ol gives propanone.
- A tertiary alcohol has no H on its C–OH carbon, so it is not oxidized by the usual mild alcohol-oxidation conditions. Harsh oxidation can break carbon–carbon bonds; "never oxidized" is too broad. In the stated dichromate test it does not give the usual orange-to-green alcohol reaction.

Distillation directs vapour through a condenser into a separate receiver, removing the more volatile aldehyde as it forms under suitable controlled conditions. Reflux uses a vertical condenser to return condensed vapour to the same flask, allowing sustained heating with excess oxidant for the acid product. Neither arrangement is a sealed pressure vessel; cooling water enters the condenser at the lower connection and leaves at the upper one. "Heat" alone does not specify which product is being collected.

Reduction of carbonyl compounds

Reducing reagents can transfer **hydride**, H^-: a hydrogen nucleus with two electrons. In a simple aldehyde/ketone reduction, hydride supplies an electron pair to the electron-deficient carbonyl carbon; subsequent protonation gives an alcohol. This is not adding bare H^+ alone or transferring a single radical electron. The [H] notation below is a stoichiometric reducing equivalent, not an assertion that free hydrogen atoms are bottled reagents.



hydride (H^-) attacks the carbonyl carbon, then protonation gives the alcohol; from the acid, the aldehyde forms on the way but is not isolated

Which reducing agent, which alcohol

- A carboxylic acid is reduced to a primary alcohol by lithium aluminium hydride, $LiAlH_4$, in dry ether. The aldehyde forms on the way but cannot be isolated.
- An aldehyde is reduced to a primary alcohol, and a ketone to a secondary alcohol, by sodium borohydride, $NaBH_4$, or by $LiAlH_4$.

$$CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$$

For example, $CH_3COOH + 2[H] \rightarrow CH_3CHO + H_2O$ and $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$ sum to $CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$. Count four reducing hydrogen equivalents for acid-to-alcohol, versus two for aldehyde/ketone-to-alcohol.

Hydrogenation

Hydrogenation 氢化 adds hydrogen across a C=C or C≡C bond, using an appropriate metal catalyst and stated conditions. A common classroom example uses nickel with heating; exact conditions depend on the substrate and catalyst. An alkyne gives an alkene and then an alkane:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad C_2H_4 + H_2 \rightarrow C_2H_6$$

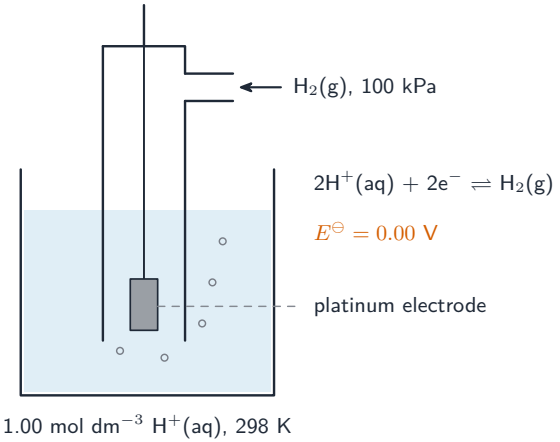
Hydrogenation can make oils more saturated and raise their melting range. Partial hydrogenation can also produce mixtures and cis/trans changes; there is no universal one-step product for every oil. One H_2 equivalent removes one degree of unsaturation: an alkyne requires two H_2 equivalents for complete conversion to the alkane. An alkene need not be cleanly isolated during an unrestricted alkyne hydrogenation.

AHL: Electrode potentials

This extension uses standard Gibbs energy from Reactivity 1.4 and reduction-potential data from the booklet.

The standard hydrogen electrode

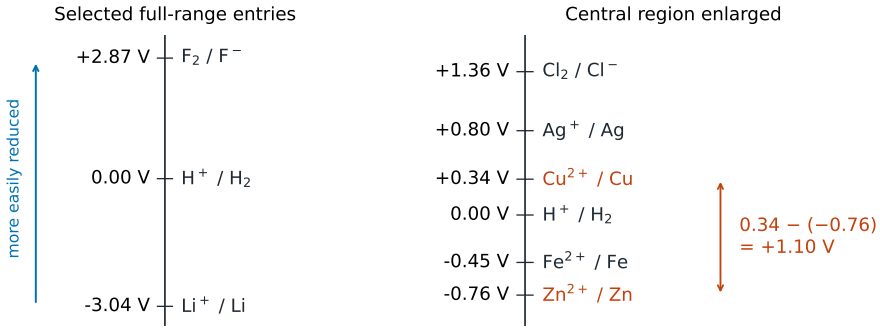
We cannot measure the potential of one half-cell on its own, only the difference between two. So every half-cell is measured against one reference: the **standard hydrogen electrode** 标准氢电极, which is defined as 0.00 V.



The reference half-cell: hydrogen gas over platinum in 1.00 mol dm^{-3} acid

The **standard electrode potential** 标准电极电势, $E^{\ominus}$, of a half-cell is the voltage it gives when joined to the standard hydrogen electrode at a specified temperature with standard activities and gas pressure 100 kPa. Booklet examples commonly use 298 K and approximate unit ionic activities by concentrations of 1.00 mol dm^{-3}; actual activities can differ from raw concentrations. Pure solids have unit activity. Standard state does not mean every measurement at any temperature must equal the 298 K tabulated number. Values are listed as reductions, in the data booklet.

Reading the series



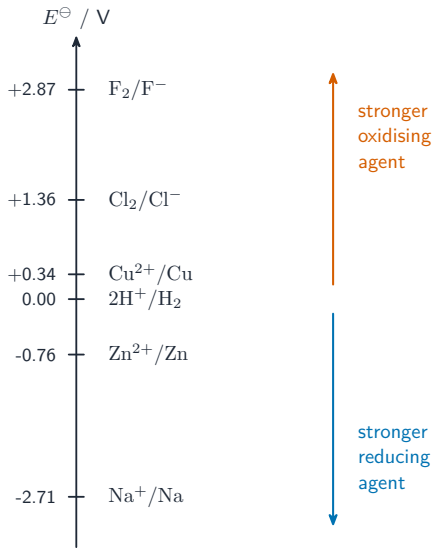
The more positive $E^{\ominus}$, the more easily the oxidized form is reduced

- A more positive $E^{\ominus}$ means the oxidized form (left side) gains electrons more easily: it is a stronger oxidizing agent. F_2 is the strongest oxidizing agent among the species listed in this figure.
- A more negative $E^{\ominus}$ means the reduced form (right side) loses electrons more easily: it is a stronger reducing agent. Li is the strongest reducing agent among the reduced forms listed. Its very negative aqueous potential does not mean an aqueous lithium-metal electrode can ignore lithium's reaction with water.

Match the exact half-equation: Fe^{2+}/Fe at a supplied -0.45 V is not Fe^{3+}/Fe^{2+} at $+0.77$ V. They connect different oxidation states.

Cell potentials

In a cell, the half-cell with the more positive $E^{\ominus}$ is reduced (the cathode). The **cell potential** 电池电势 is:



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

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

For the Zn/Cu cell: $E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10$ V.

A reaction is **spontaneous** 自发的 under standard conditions if $E^\ominus_{\text{cell}}$ is positive. Do not multiply $E^\ominus$ values when you multiply a half-equation: they do not depend on the amount.

> **Worked example.** Will Cl_2 oxidize Fe^{2+} to Fe^{3+}? $E^\ominus(Cl_2/Cl^-) = +1.36$ V and $E^\ominus(Fe^{3+}/Fe^{2+}) = +0.77$ V.

1. Cl_2 is reduced (cathode), Fe^{2+} is oxidized (anode).
2. $E^\ominus_{\text{cell}} = 1.36 - 0.77 = +0.59$ V.
3. Positive, so the forward reaction is thermodynamically favoured under the stated standard conditions: $Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$.

A positive standard cell potential predicts thermodynamic direction at standard activities, not reaction speed. Non-standard concentrations and gas pressures can alter the actual cell potential; passivation and kinetic barriers can prevent an obvious reaction. Conversely, a negative standard value is not a proof that no forward reaction is possible under every composition. Distinguish a thermodynamic prediction from an observed rate.

Linking $E^\ominus$ and $\Delta G^\ominus$

$$\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$$

Here n is the number of moles of electrons transferred in the equation and F is the **Faraday constant** 法拉第常量, 9.65×10^4 C mol^{-1}. A positive $E^\ominus_{\text{cell}}$ gives a negative $\Delta G^\ominus$: both mean the reaction is spontaneous.

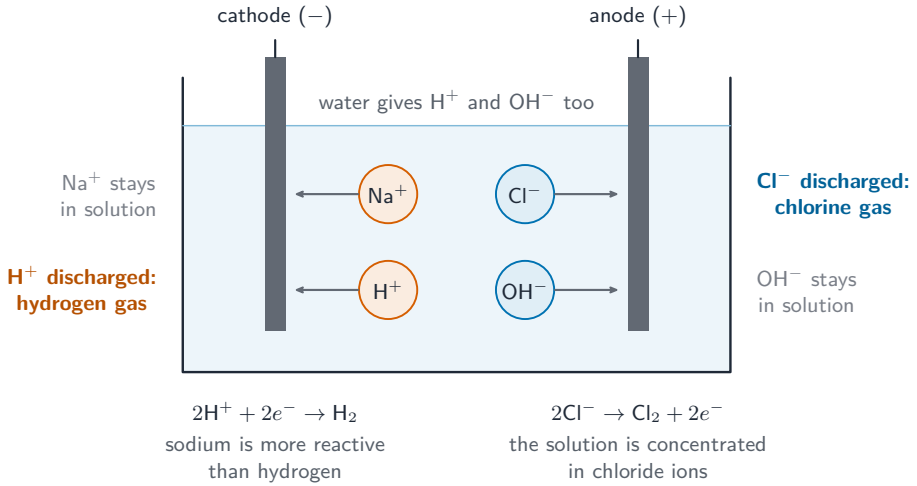
For the Zn/Cu cell, $n = 2$: $\Delta G^\ominus = -2 \times 96\,500 \times 1.10 = -2.12 \times 10^5$ J mol^{-1} $= -212$ kJ mol^{-1}.

Doubling every coefficient doubles n and ΔG°, but leaves E° unchanged. Thus 2Zn + 2Cu^{2+} $\rightarrow$ 2Zn^{2+} + 2Cu has $n = 4$ and ΔG° ≈ -425 kJ per mole of the doubled equation. Potential is intensive; reaction energy is extensive.

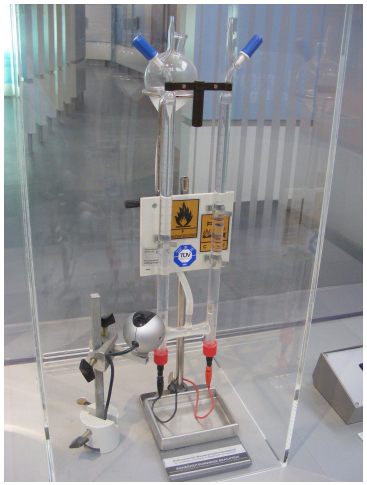
AHL: Electrolysis of aqueous solutions

Water competes

In an aqueous solution, water-related species compete with dissolved ions. The following two tabulated standard half-reactions use **different reference pH conditions**:



In concentrated sodium chloride solution, H^+ is discharged instead of Na^+, and Cl^- instead of OH^-



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

$$\text{cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^\ominus = -0.83 \text{ V}$$

$$\text{anode: } 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\ominus = +1.23 \text{ V (for the reduction)}$$

The -0.83 V reduction assumes unit OH^- activity; $+1.23$ V is for oxygen **reduction** at unit H^+ activity, opposite to the displayed anode direction. These unmatched pH references do not imply a universal 2.06 V minimum. At matched pH and standard gas activities, the equilibrium gap is about 1.23 V at 298 K. Practical overpotentials and resistance require extra voltage. No Nernst calculation is needed here.

- At the cathode, compare reduction potentials under consistent conditions as a thermodynamic starting point. Cu^{2+} ($+0.34$ V) and Ag^+ ($+0.80$ V) are reduced to metal. Na^+ (-2.71 V) and K^+ are not: hydrogen forms instead.
- At an inert anode, oxygen can form from water-related species. Concentrated chloride can instead give chlorine: concentration affects the potential and competing reaction rates, and electrode kinetics matter. These common predictions are not obtained reliably from unmatched standard numbers alone.

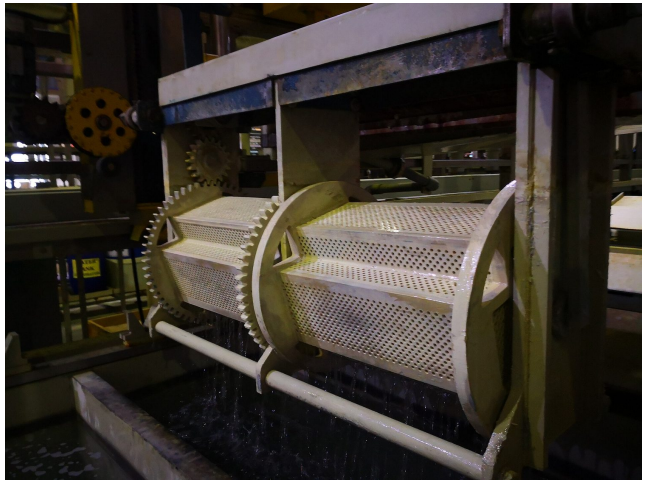
Electrolyte (inert electrodes)	Cathode	Anode
concentrated NaCl(aq)	H_2	Cl_2
dilute NaCl(aq)	H_2	mainly O_2
$CuSO_4$(aq)	Cu	O_2
dilute H_2SO_4(aq)	H_2	O_2

An **inert electrode** 惰性电极 conducts without being a main stoichiometric reactant in the model. Its surface still affects rates and overpotential; graphite can sometimes be consumed. A copper anode in $CuSO_4$ commonly dissolves by $Cu \rightarrow Cu^{2+} + 2e^-$ instead of giving O_2. Specify electrode material, electrolyte and concentration.

For acidic water electrolysis at inert electrodes, cathode $4H^+ + 4e^- \rightarrow 2H_2$ and anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ give $2H_2O \rightarrow 2H_2 + O_2$. Gas volumes are 2:1 at matched temperature/pressure without loss or side reactions. Pure water conducts poorly; an appropriate electrolyte carries charge without necessarily being a net reactant.

Electroplating

In **electroplating** 电镀 a thin layer of metal is put on an object by electrolysis.



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

- The object is the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$.
- The anode is the plating metal, which dissolves: $Cu \rightarrow Cu^{2+} + 2e^-$.
- The electrolyte supplies metal ions, for example $CuSO_4$(aq). Matching Cu dissolution and deposition transfer equal Cu^{2+} amounts per charge: well-mixed bulk concentration stays approximately constant at fixed volume. Side reactions and poor mixing can change this. With an inert anode, dissolved metal ions need replenishment.

Practice

Use supplied idealized conditions; state any extra assumption.

1. Give the oxidation state of: (a) S in H_2SO_4 (b) N in NH_4^+ (c) Cl in ClO_3^- (d) O in H_2O_2.
2. In $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$, identify the oxidizing agent and the reducing agent, with oxidation states.

3. Balance the half-equation for $Cr_2O_7^{2-}$ being reduced to Cr^{3+} in acid.
4. Combine your answer to 3 with $Fe^{2+} \rightarrow Fe^{3+} + e^-$ to give the overall equation.
5. Predict whether a reaction happens, and write an ionic equation if it does: (a) Mg + $FeSO_4$(aq) (b) Cu + $ZnSO_4$(aq) (c) Br_2(aq) + KI(aq).
6. For aqueous Mg/Mg^{2+} and Cu^{2+}/Cu half-cells, identify anode/cathode, write their half-equations and give external electron-flow direction.
7. Explain the role of the salt bridge.
8. Compare the cell in question 6 with molten $PbBr_2$ electrolysis: energy direction and electrode signs.
9. Name the product when each is treated under the usual alcohol-oxidation conditions with acidified $K_2Cr_2O_7$: (a) propan-1-ol, distilled (b) propan-1-ol, under reflux (c) butan-2-ol (d) 2-methylpropan-2-ol.
10. State the reducing agent and the product when propanone is reduced.
11. Reverse $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$ for charging. Does discharge make a secondary cell primary?
12. **AHL.** (a) Calculate $E^{\ominus}_{cell}$ for a cell made from Ag^+/Ag (+0.80 V) and Zn^{2+}/Zn (−0.76 V). Write the overall equation. (b) Calculate $\Delta G^{\ominus}$ for the silver/zinc cell in (a). (c) Use $E^{\ominus}$ values to decide whether I_2 (+0.54 V) can oxidize Fe^{2+} to Fe^{3+} (+0.77 V). State the conditions and a kinetic limitation.
13. **AHL.** (a) Predict the products at each electrode for concentrated KCl(aq) and $AgNO_3$(aq), using inert electrodes. (b) For $CuSO_4$(aq), contrast inert and copper anodes. (c) Explain why the −0.83 and +1.23 V water half-cell values cannot be combined without considering their pH references.
14. **AHL.** (a) Describe how to silver-plate a spoon. (b) Give half-equations for water electrolysis and predict the gas-volume ratio under matched collection conditions.

Worked answers

1. (a) +6 (b) −3 (c) +5 (d) −1.
2. Fe goes from +3 to 0, so Fe_2O_3 is reduced: it is the oxidizing agent. C goes from +2 to +4, so CO is oxidized: it is the reducing agent.
3. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$.
4. $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$.
5. (a) Yes: $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$. (b) No: Cu is less active than Zn. (c) Yes: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$.
6. Anode: $Mg \rightarrow Mg^{2+} + 2e^-$. Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. External electrons flow Mg → Cu.
7. The salt bridge carries ions to maintain bulk electrical neutrality and complete the circuit; it does not carry electrons.
8. Electrolysis: electrical → chemical, anode +/cathode −. Voltaic discharge: chemical → electrical, anode −/cathode +. Both oxidize at the anode.
9. (a) propanal (b) propanoic acid (c) butanone (d) no usual alcohol oxidation under these conditions.
10. $NaBH_4$ (or $LiAlH_4$); propan-2-ol.
11. Charging: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$. Discharge is voltaic operation; the design remains secondary.
12. **AHL.** $E^{\ominus}_{cell} = 0.80 - (-0.76) = +1.56$ V. $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$. (b) $n = 2$: $\Delta G^{\ominus} = -2 \times 96\,500 \times 1.56 = -3.01 \times 10^5$ J mol^{-1} = −301 kJ mol^{-1}. (c) I_2 would be reduced: $E^{\ominus}_{cell} = 0.54 - 0.77 = -0.23$ V. Thus Fe^{2+} oxidation by I_2 is unfavoured under standard conditions; reverse Fe^{3+} oxidation of I^- is favoured. Actual conditions can alter direction; kinetic barriers can slow a favoured reaction.
13. **AHL.** (a) KCl: cathode H_2, anode Cl_2. $AgNO_3$: cathode Ag, anode O_2. (b) $Cu^{2+} + 2e^- \rightarrow Cu$ occurs at the cathode; an inert anode gives O_2, a copper anode dissolves to Cu^{2+}. (c) −0.83 V assumes unit OH^- activity, +1.23 V unit H^+ activity: unmatched pH references.
14. **AHL.** (a) Spoon: cathode; silver: anode; $AgNO_3$(aq) electrolyte, direct current. (b) Cathode $4H^+ + 4e^- \rightarrow 2H_2$; anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Net $2H_2O \rightarrow 2H_2 + O_2$. H_2:O_2 = 2:1 by volume at matched temperature/pressure without loss or side reactions.

Exam tips

- Balance atoms, charge and electrons; define agents and electrodes by their reactions. State organic reaction conditions.
- **AHL.** $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$; never multiply $E^{\ominus}$ by the coefficients.
- **AHL.** $\Delta G^{\ominus} = -nFE^{\ominus}$ gives J mol^{-1}; divide by 1000 for kJ.

Reactivity 3.3 · Electron sharing reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.3, Electron sharing reactions, for the course first assessed in 2025. This topic is the same at Standard Level and Higher Level.

Prerequisites: covalent bonds and electronegativity from Structure 2.2, alkanes and structural formulas from Structure 3.2, and bond enthalpies from Reactivity 1.2. You will use bond enthalpy values from the data booklet.

Radicals

Why does sunlight matter?

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

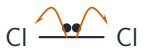
Free-radical substitution in three steps: initiation makes radicals, propagation carries the chain, and termination ends it

At room temperature, a methane/chlorine mixture can show little reaction in the dark. Suitable light can initiate a rapid chain reaction. Chloromethane is not the only possible organic product: further substitution can give CH_2Cl_2, $CHCl_3$ and CCl_4 as well. One kind of particle explains all of this: the radical.

What a radical is

- A **free radical** 自由基, usually just called a radical, is a particle with an **unpaired electron** 未成对电子.
- We show the unpaired electron with a single dot: Cl•, Br•, •CH_3, •OH.
- A radical can be a single atom, such as Cl•, or a group of atoms, such as the methyl radical •CH_3.

homolytic fission



$Cl^{\bullet} + {}^{\bullet}Cl$

one electron each
⇒ two **radicals**

heterolytic fission



$R^+ + :Br^-$

both electrons to one
⇒ two **ions**

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

The radicals in these mechanisms are reactive intermediates: they are formed and consumed during the reaction. A collision still needs a suitable pathway and enough energy. An unpaired electron does not mean that every collision reacts, or that every radical has the same lifetime.

Radical character and electrical charge answer different questions. Do not identify a radical from charge alone. Cl• has 17 electrons and no charge; the chloride ion Cl^- has 18 electrons and a full outer shell, so it is not a radical.

A radical can also be an ion

Charge records an excess or shortage of electrons relative to the nuclei. A radical dot records an unpaired electron. A species can therefore have both a dot and a charge.

Cl•	NO•	$CH_4^{\bullet+}$	$O_2^{\bullet-}$
charge 0	charge 0	charge +1	charge −1
17 electrons	15 electrons	9 electrons	17 electrons

an odd electron total needs an unpaired electron; a species can carry both a dot and a charge

A dot means an unpaired electron; a charge means an electron excess or shortage

Example	Charge	Electron count and interpretation
Cl•	0	17 electrons: an atomic radical
NO•	0	$7 + 8 = 15$: a neutral molecular radical
$CH_4^{\bullet+}$	+1	$6 + 4 - 1 = 9$: a molecular radical cation
$O_2^{\bullet-}$	−1	$2(8) + 1 = 17$: a molecular radical anion

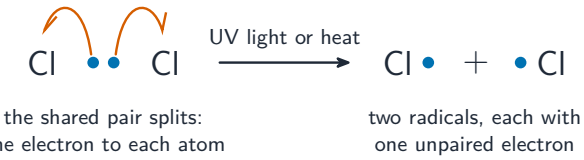
These odd electron totals require at least one unpaired electron. For known closed-shell examples such as chloride or hydroxide, all electrons are paired. A charge alone cannot tell you which situation applies. The molecular-ion example connects this unit to electron-impact mass spectrometry; radical ions are not the neutral chain carriers in methane chlorination.

Homolytic fission

Breaking a bond evenly

A covalent bond is a shared pair of electrons. When the bond breaks so that each atom keeps one electron of the pair, the break is called **homolytic fission** 均裂. For the closed-shell single-bond examples here, each fragment receives one electron and two radicals form.

$$Cl_2 \rightarrow Cl\bullet + Cl\bullet$$



In homolytic fission each atom takes one electron of the shared pair

A **single-barbed arrow** 单钩箭头 (also called a fishhook arrow) shows the movement of ONE electron. A normal double-barbed arrow shows a PAIR of electrons; you will use it in Reactivity 3.4.

Draw electron movement rather than particle movement

Start each fishhook at one electron in the shared bond and finish at the atom receiving that electron. Two fishhooks are needed for Cl–Cl homolysis: one electron goes to each Cl. The large straight reaction arrow only separates reactants and products; it does not replace the fishhooks. The reverse process combines two radicals: their two unpaired electrons make a shared pair and a covalent bond.

In a propagation step, one new bond forms as another breaks. Follow both atoms and the unpaired electron. A dot is not a negative charge, and an arrow starting from a bare positive nucleus does not show an electron source. Full electron-pair arrows belong to the next unit; do not replace a single-electron arrow with a double-headed one.

What supplies the energy?

Breaking a bond is endothermic, so homolytic fission needs energy from **ultraviolet light** 紫外线 or from heat. The halogens split most easily because their bonds are weak:

Bond	Bond enthalpy / kJ mol^{-1}
Br–Br	193
Cl–Cl	242
C–C	346
C–H	414

In the usual methane/chlorine photochemical reaction, light absorbed by chlorine produces Cl radicals. The lower Cl–Cl bond enthalpy helps explain this initiation route. Which bond light breaks also depends on absorption and wavelength; the weakest bond is not a universal rule for all photochemistry.

Alkanes and radical substitution

Why alkanes are unreactive

Alkanes such as methane do not react with acids, alkalis or most other polar reagents. There are two reasons:

1. **Strong bonds.** C–C (346 kJ mol^{-1}) and C–H (414 kJ mol^{-1}) need a lot of energy to break.
2. **Almost no polarity.** The electronegativities of C (2.6) and H (2.2) are close, so C–H bonds are almost **non-polar** 非极性的. Alkanes lack a strongly electron-rich or electron-poor functional-group centre for the usual ionic reactions.

Combustion and radical substitution are important alkane reactions. Cracking is another possible reaction under suitable conditions, so this is not a complete list.

Connect substitution to other organic reaction types

A **functional group** 官能团 is an atom or group of atoms responsible for characteristic reactions, such as the OH group in an alcohol. Identify the reacting bonds and keep four bonds at each carbon in a structural formula.

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

- Substitution replaces a group: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ under suitable UV light replaces C–H by C–Cl.
- Addition opens a multiple bond: $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$ with steam and a phosphoric-acid catalyst adds H and OH across C=C.
- Oxidation changes the alcohol group: $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$ with excess acidified dichromate under reflux makes a carboxylic acid.
- Addition polymerization joins many monomers: $nCH_2{=}CH_2 \rightarrow [-CH_2{-}CH_2-]_n$ under suitable initiator, temperature and pressure conditions. C=C bonds become C–C links; no small molecule is lost.

A linked synthesis is ethene → ethanol → ethanoic acid: use steam/phosphoric acid first, then excess acidified dichromate under reflux. Each organic molecule retains two carbon atoms in both steps. Reagents and conditions belong to their own arrow; UV chlorination conditions cannot replace hydration or oxidation conditions.

The chain reaction

Methane and chlorine react in UV light by **radical substitution** 自由基取代: a chlorine atom takes the place of a hydrogen atom. It is a **chain reaction** 链反应 with three stages.

1. Initiation

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

Light absorbed by chlorine makes radicals.

2. Propagation

$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

One radical enters; another leaves each step.

3. Termination

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

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6$$

Each combination removes two radicals.

Initiation makes radicals, propagation passes them on, termination removes them

1. **Initiation** 引发: UV light splits chlorine molecules into radicals.

$$Cl_2 \rightarrow 2Cl\bullet$$

2. **Propagation** 链增长: each step uses one radical and makes another, so the chain keeps going.

$$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$$

$$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

The Cl• made in the second step starts the first step again. One initiation can lead to thousands of propagation cycles.

3. **Termination** 终止: two radicals join, so the chain stops.

$$Cl\bullet + Cl\bullet \rightarrow Cl_2 \qquad \bullet CH_3 + Cl\bullet \rightarrow CH_3Cl \qquad \bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$$

The overall equation is the sum of the two propagation steps:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

In the first propagation step, chlorine abstracts hydrogen: H transfers directly from methane into HCl. A free hydrogen radical is not a product in this mechanism. The products of propagation are HCl and $\bullet CH_3$, never CH_3Cl and •H.

Counting steps from equations

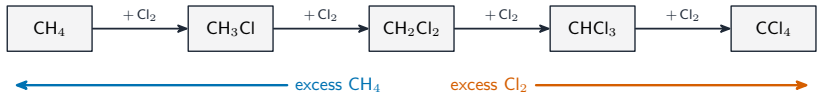
To decide which stage an equation is:

Radicals on the left	Radicals on the right	Stage
0	2	initiation
1	1	propagation
2	0	termination

A mixture of products

Further substitution

Chloromethane still has C–H bonds, so a Cl• radical can attack it too:



each product still has C–H bonds (until CCl_4), so substitution continues: a mixture forms (light starts the radical chain)

Radical substitution keeps going while C–H bonds remain: the reactant ratio steers the mixture

$$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$$

$$\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$$

The same can happen again to give $CHCl_3$ and finally CCl_4. Termination also adds products such as ethane. Radical substitution commonly gives a **product mixture**

产物混合物. Which products are detectable depends on conditions and conversion. A useful organic product may need separation, for example by distillation when boiling points permit.

To get more of...	Use...
CH_3Cl	a large excess of methane, so Cl• usually meets CH_4
CCl_4	a large excess of chlorine

Evidence for the chain model

- A low dark rate and a higher rate under suitable light support photochemical initiation. This observation alone does not establish every proposed intermediate.
- A short burst of light causes a lot of reaction: each radical is passed on many times.
- Ethane formation is consistent with methyl radicals combining. Together with light dependence and chain amplification, this supports the mechanism; a single product is not unique proof of every step.

What conditions can change

Excess methane increases the chance that a chlorine radical meets methane rather than a partly chlorinated molecule. It can improve the proportion of chloromethane without making all side reactions impossible. Limiting conversion can also reduce repeated substitution. Excess chlorine and longer reaction progress can favour more highly chlorinated products. These are qualitative controls, not a guarantee of a pure product or a fixed percentage.

For complete monochlorination only, one mole of alkane consumes one mole of chlorine and makes one mole of HCl. Further substitution uses more chlorine. If a sample consumes 0.060 mol Cl_2, you cannot report 0.060 mol chloromethane unless you know that every chlorine molecule was used in that single-substitution route.

Larger alkanes

Ethane reacts in the same way:

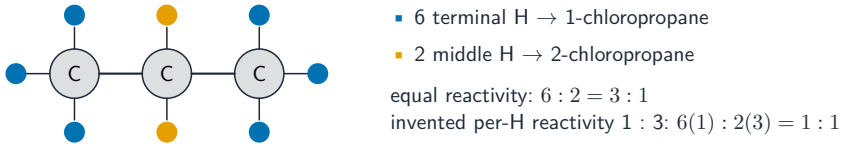
$$C_2H_6 + Cl\bullet \rightarrow \bullet C_2H_5 + HCl \qquad \bullet C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl\bullet$$

In propane, a chlorine radical can remove a hydrogen atom from an end carbon or from the middle carbon, so two different monochloro products form: 1-chloropropane and 2-chloropropane.

Bromination follows the same type of chain mechanism. Under comparable conditions it is commonly slower and more selective than chlorination; do not infer exact product percentages from that statement.

Symmetry and amounts of products

The two end carbons of propane are equivalent. Removing H from either end gives the same constitutional product, 1-chloropropane; removing H from the middle gives 2-chloropropane. Do not count left and right drawings as different compounds. Similarly, butane gives two constitutional monochloro products, 1-chlorobutane and 2-chlorobutane. Optical isomers of the latter are not an extra substitution position.

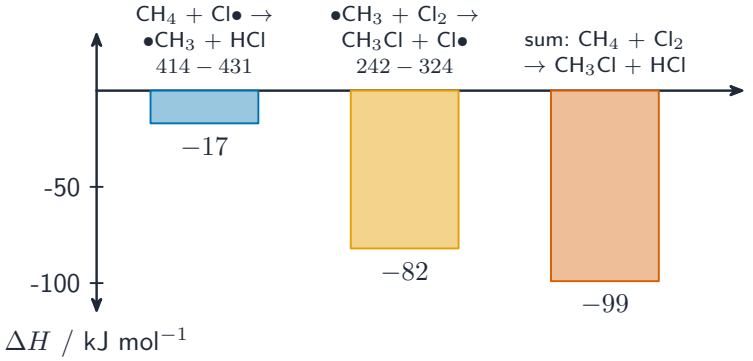


Counting equivalent hydrogens in propane

There are six terminal H atoms and two middle H atoms in propane. If every H had equal reactivity, a deliberately simplified model would predict 6 : 2 = 3 : 1 amounts of 1- to 2-chloropropane. Real sites need not have equal reactivity. With *invented* per-H relative reactivities of 1 for terminal and 3 for middle H, the weighted amounts are 6(1) : 2(3) = 1 : 1. Neither invented model is a universal experimental ratio. Use supplied selectivity data; do not treat the number of H atoms as the whole explanation.

Energy changes in the chain

Use the supplied mean bond enthalpies to estimate the propagation energy changes. These values are approximate gas-phase averages; a negative enthalpy change is not a measured activation energy.



Both propagation steps are exothermic: −17 and −82 kJ mol^{-1}

Bond	C–H	Cl–Cl	H–Cl	C–Cl	H–Br
Bond enthalpy / kJ mol^{-1}	414	242	431	324	366

Worked example. Find ΔH for each propagation step of the chlorination of methane.

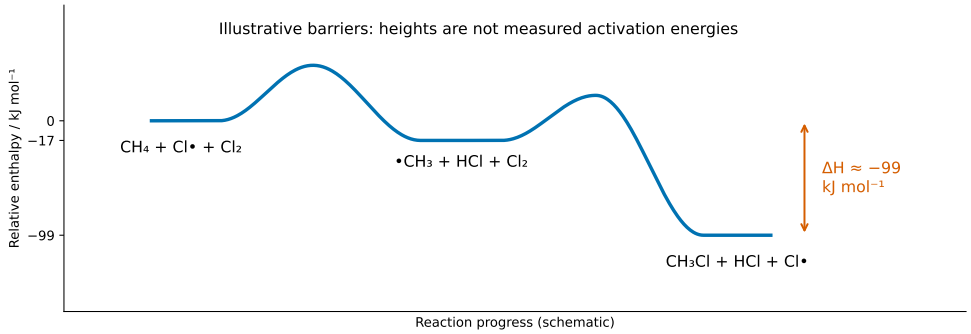
1. $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$: break C–H, form H–Cl. $\Delta H = 414 - 431 = -17$ kJ mol^{-1}.
2. $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$: break Cl–Cl, form C–Cl. $\Delta H = 242 - 324 = -82$ kJ mol^{-1}.
3. Add the two steps: $\Delta H = -99$ kJ mol^{-1} for $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

Both estimated propagation changes are exothermic. The observed rate also depends on activation barriers, temperature, reactant concentrations and radical loss. Exothermic does not by itself mean fast.

For bromine the first estimate is $414 - 366 = +48$ kJ mol^{-1}. Hydrogen abstraction by bromine commonly has a higher barrier than by chlorine under comparable conditions. Its endothermicity helps interpret the difference, but enthalpy alone does not calculate a rate.

Kinetic stability is compatible with energy release

A fuel/oxygen mixture may release energy when it burns but remain little changed at room temperature because the initiation pathway has a large activation barrier. It is kinetically resistant under those conditions even though combustion products are thermodynamically favoured. Specify the proposed reaction: an alkane is not simply thermodynamically unstable relative to every possible chemical change.



Illustrative barriers; endpoint differences use the supplied mean bond enthalpies. The intermediate lies between two transition states.

UV supplies initiation energy; it is not a substance consumed once for every propagation cycle. Adding the propagation equations cancels both Cl• and •CH$_3$, leaving the net substitution equation. By contrast, adding initiation to every cycle incorrectly predicts that two new chlorine radicals are needed for each product molecule.

Radicals in the atmosphere

How CFCs destroy ozone

Chlorofluorocarbons 氯氟烃 (CFCs), such as CCl_2F_2, were used in fridges and spray cans. They are unreactive near the ground, so they drift up into the **stratosphere** 平流层. There, strong UV light breaks the C–Cl bond (324 kJ mol^{-1}), which is weaker than the C–F bond (492 kJ mol^{-1}):



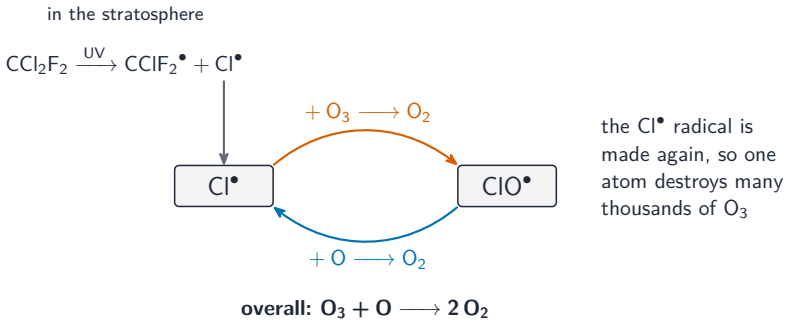
Chlorofluorocarbons were once common aerosol propellants; in the stratosphere UV light splits off chlorine radicals that destroy ozone

$$CCl_2F_2 \rightarrow \bullet CClF_2 + Cl\bullet$$

The chlorine radical then destroys **ozone** 臭氧 in two propagation steps:

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$

$$ClO\bullet + O \rightarrow Cl\bullet + O_2$$

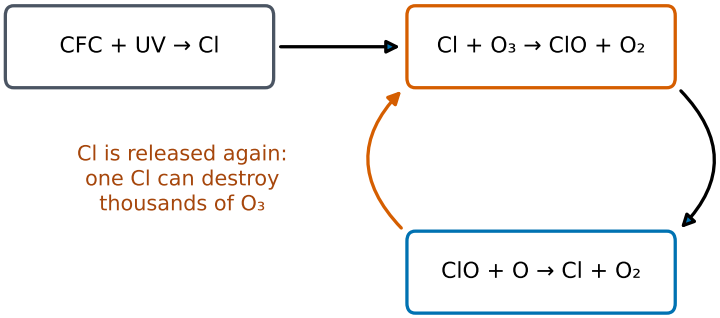


The chlorine radical is made again at the end of each cycle

Overall: $O_3 + O \rightarrow 2O_2$. The chlorine radical is made again, so one Cl atom can destroy many thousands of ozone molecules before a termination step removes it. The Montreal Protocol, agreed in 1987, established controls leading to the phase-out of ozone-depleting substances including CFCs; it was not an instant worldwide removal of every CFC.

■ Limits of the simple ozone cycle

The written two-step model consumes one ozone molecule and one oxygen atom, not two ozone molecules. $Cl\bullet$ is regenerated and acts as a catalyst for the overall change; $ClO\bullet$ is an intermediate. Atomic oxygen is available through atmospheric photochemistry. The actual atmosphere has other coupled pathways and radical reservoirs; this simplified cycle does not represent every polar ozone-loss mechanism. The number of molecules destroyed by one chlorine atom is not a fixed constant: it depends on how long the chain survives before chlorine is removed into other species.



the Montreal Protocol phased out CFCs; the ozone layer is slowly recovering

A chlorine atom from a CFC destroys ozone in a repeating cycle

Methane/chlorine and ozone chemistry are explanatory models here, not instructions for unsupervised experiments. Chlorine, UV exposure and potentially vigorous reactions require approved teacher-controlled demonstrations and the school risk assessment.

Practice

1. Which of these are radicals: Cl^-, $Cl\bullet$, $\bullet CH_3$, CH_4, $\bullet OH$, OH^-? Explain your choice.
2. Write an equation for the homolytic fission of bromine. State the condition needed.
3. Draw single-barbed arrows to show the homolytic fission of the C–Cl bond in CH_3Cl.
4. Give two reasons why alkanes are unreactive with acids and alkalis.
5. Ethane reacts with chlorine in UV light. Write equations for the initiation step, the two propagation steps and a termination step that forms butane.
6. State whether each step is initiation, propagation or termination: (a) $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$ (b) $CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$ (c) $Br_2 \rightarrow 2Br\bullet$.
7. Explain why the reaction of methane with chlorine gives a mixture of products. Suggest how to make chloromethane the main product.
8. Use bond enthalpies (C–H 414, H–Br 366, Br–Br 193, C–Br 285 kJ mol^{-1}) to find ΔH for each propagation step in the bromination of methane, and for the overall reaction.
9. How many different monochloro products form when propane reacts with chlorine in UV light? Name them.
10. Explain, with equations, how one chlorine atom from a CFC can destroy many ozone molecules.
11. Given atomic numbers H 1, C 6, N 7 and O 8, calculate the electron totals in $NO\bullet$, $CH_4\bullet^+$ and $O_2\bullet^-$. Explain why both radical and ion can describe one species.
12. State the two constitutional monochloro products of butane. For propane, use the invented relative per-H reactivities 1 (terminal) and 3 (middle) to calculate percentages of 1- and 2-chloropropane among monochloro products.
13. Invented model: 0.0020 mol Cl_2 initiates; each $Cl\bullet$ completes 40 propagation cycles. Find propagation CH_3Cl amount and explain amplification. Assume ample reactants, no side products.
14. Repair these claims: (a) a negative propagation enthalpy proves a zero activation energy; (b) a radical is always neutral; (c) the ozone cycle shown consumes two O_3 molecules; (d) every absorbed photon produces exactly one molecule of chloromethane.

Answers.

1. $Cl\bullet$, $\bullet CH_3$ and $\bullet OH$: each has an unpaired electron. Cl^-, OH^- and CH_4 have all electrons paired.

2. $Br_2 \rightarrow 2Br\bullet$, in UV light (or heat).
3. One single-barbed arrow from the bond to C and one from the bond to Cl, giving $\bullet CH_3 + Cl\bullet$.
4. Strong C–C/C–H bonds and the lack of a strongly polar functional-group centre make the usual ionic reaction pathways difficult. This is kinetic resistance, not a claim that no reagent can ever react.
5. $Cl_2 \rightarrow 2Cl\bullet$; $C_2H_6 + Cl\bullet \rightarrow \bullet C_2H_5 + HCl$; $\bullet C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl\bullet$; $2\bullet C_2H_5 \rightarrow C_4H_{10}$.
6. (a) termination (b) propagation (c) initiation.
7. Chloromethane still has C–H bonds, so $Cl\bullet$ substitutes it further to CH_2Cl_2, $CHCl_3$ and CCl_4; termination adds ethane. Use a large excess of methane.
8. Step 1: $414 - 366 = +48$ kJ mol^{-1}. Step 2: $193 - 285 = -92$ kJ mol^{-1}. Overall: -44 kJ mol^{-1}.
9. Two: 1-chloropropane and 2-chloropropane.
10. UV gives $Cl\bullet$ from the CFC; $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$; $ClO\bullet + O \rightarrow Cl\bullet + O_2$. The $Cl\bullet$ is made again, so the cycle repeats thousands of times until termination.
11. $NO\bullet$ has $7 + 8 = 15$ electrons; $CH_4\bullet^+$ has $6 + 4 - 1 = 9$; $O_2\bullet^-$ has $2(8) + 1 = 17$. Each odd count requires an unpaired electron. The last two also have a net charge, so they are radical ions. A chloride ion is an ion without radical character.
12. The butane products are 1-chlorobutane and 2-chlorobutane. For the invented propane model, terminal sites contribute $6 \times 1 = 6$ and middle sites $2 \times 3 = 6$. Each therefore gives $6/(6+6) \times 100 = 50\%$. Equal per-H reactivity would instead give 75% and 25%; neither assumption is universal.
13. Initiation: $2 \times 0.0020 = 0.0040$ mol $Cl\bullet$. Propagation: $0.0040 \times 40 = 0.16$ mol CH_3Cl, consuming a further 0.16 mol Cl_2 and methane. Radical regeneration does not regenerate reactant molecules. Cycle count and absent side reactions are model assumptions.
14. (a) Enthalpy compares endpoints; activation energy measures a barrier. (b) Radicals may be neutral or charged. (c) Cancel $Cl\bullet$/$ClO\bullet$ to obtain $O_3 + O \rightarrow 2O_2$. (d) Initiation can support many cycles; radical loss and side reactions affect amplification.

Exam tips

- Put the dot on the radical atom; distinguish an unpaired electron from charge. A fishhook moves one electron, a full curly arrow a pair.
- First propagation gives $HCl + \bullet CH_3$, not a free $H\bullet$. Classify the whole equation: combination termination removes two radicals.
- Explain mixtures through repeated substitution and radical combination. Count equivalent positions and use supplied site-reactivity data before predicting proportions.
- Name the reaction and conditions: thermodynamic favourability does not establish speed, and bond-enthalpy differences do not give activation energies.

Reactivity 3.4 · Electron-pair sharing reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.4, Electron-pair sharing reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: covalent and coordination bonds and electronegativity from Structure 2.2, functional groups and classes of compounds from Structure 3.2, and homolytic fission and radicals from Reactivity 3.3.

Nucleophiles and electrophiles

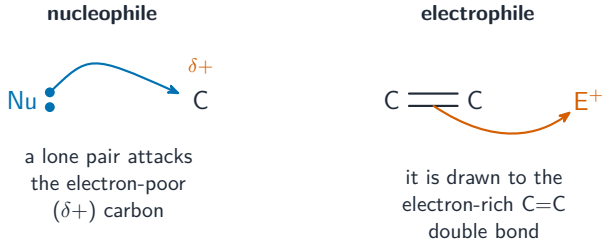
Why does bromoethane react with alkali, but ethane does not?

Warm aqueous hydroxide can substitute Br in bromoethane to form ethanol; ethane shows little reaction under the same conditions. The polar C–Br bond provides a reacting centre. Here a whole electron pair moves, rather than splitting into single electrons as in homolysis.

Two kinds of reagent

- A **nucleophile** 亲核试剂 is a reactant that forms a new bond by giving both electrons of the bond. The common examples here donate a lone pair and are neutral or negative: OH^-, H_2O, NH_3, CN^-, Cl^-.
- An **electrophile** 亲电试剂 is a reactant that forms a new bond by accepting both electrons of the bond. It has an electron-pair-accepting centre and can be charged or neutral: H^+, NO_2^+, Br_2 near a C=C bond, the H of HBr.

"Nucleophile" means "nucleus-loving": it is attracted to a positive centre. "Electrophile" means "electron-loving": it is attracted to a region of high electron density.



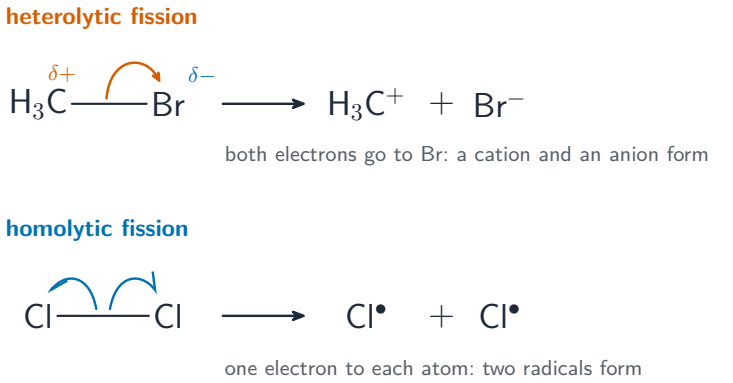
A nucleophile gives an electron pair; an electrophile takes one

Heterolytic fission and curly arrows

Breaking a bond unevenly

When a covalent bond breaks and **both** bonding electrons go to one atom, the break is **heterolytic fission** 异裂. The atom that takes the pair is usually the more electronegative one. For the neutral closed-shell molecules illustrated here, it gives a positive and a negative ion. It does not split the pair into two unpaired electrons.

$$CH_3Br \rightarrow CH_3^+ + Br^-$$

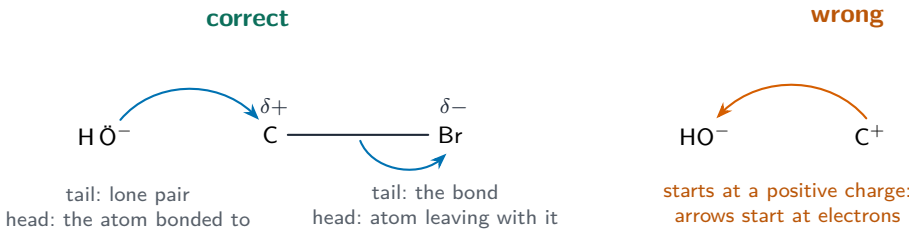


A curly arrow moves an electron pair; a single-barbed arrow moves one electron

$CH_3Br \rightarrow CH_3^+ + Br^-$ illustrates electron allocation, not proof that a free methyl carbocation readily forms in water. Primary substitution can form and break bonds together; detailed mechanisms are treated at Higher Level.

Drawing curly arrows

A **curly arrow** 弯箭头 (with a full, double-barbed head) shows the movement of an electron PAIR.



Arrows start at electrons

- The tail starts at the donating electron pair: show the relevant lone pair or bond. A minus sign identifies charge, not the physical position of an electron pair.
- The head points to where the pair goes: an atom (to form a new bond) or an atom that leaves with the pair.
- Every curly arrow starts at electrons, not at a positive charge or a nucleus. Check the resulting bond count and formal charges as well as the arrow direction.

Nucleophilic substitution

Halogenoalkanes have a polar bond

In a **halogenoalkane** 卤代烷, such as bromoethane, the halogen is more electronegative than carbon (Br 3.0, C 2.6). The C–Br bond is polar, so the carbon is $\delta+$. A nucleophile attacks this $\delta+$ carbon.

The reaction

In **nucleophilic substitution** 亲核取代, a nucleophile gives an electron pair to form a new bond as another bond breaks. The group that leaves with the old bonding pair is the **leaving group** 离去基团.

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

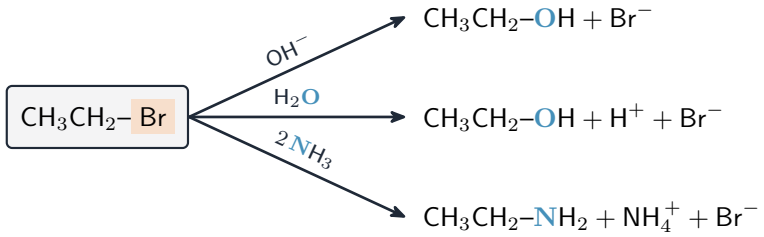
Here OH^- is the nucleophile and Br^- is the leaving group. Conditions: warm, with aqueous sodium hydroxide.

Two curly arrows describe the change:

1. From a lone pair on the O of OH^- to the $\delta+$ carbon: the new C–O bond forms.
2. From the C–Br bond to Br: the bonding pair leaves with Br as Br^-.

Predict a product by tracing the reacting atom

Hydroxide donates at oxygen, replacing Br by OH without changing the carbon skeleton. Water can also donate at oxygen: an initially protonated organic product must lose H^+ to give the neutral alcohol. Ammonia donates at nitrogen and can give an amine after proton transfer. Do not simply copy the whole nucleophile formula into a neutral product without checking its charge and bond count.



the donor atom replaces Br; the carbon skeleton is unchanged

The nucleophile's donor atom replaces Br on the same carbon skeleton; water and ammonia products then lose H^+.

For an illustrative overall ammonia reaction:

$$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+ + Br^-.$$

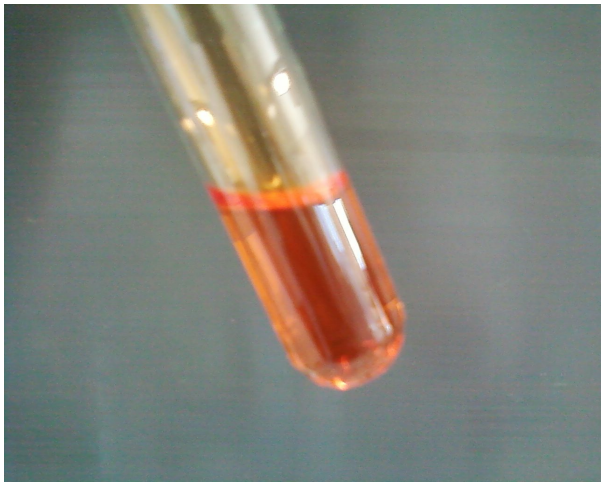
One NH_3 supplies nitrogen to the organic product; another accepts a proton. The net equation conserves atoms and charge.

Worked common example. 0.0200 mol of 1-bromopropane reacts by substitution with excess aqueous hydroxide. The equation RBr + OH^- → ROH + Br^- gives a 1:1 mole ratio. The maximum propan-1-ol amount is therefore 0.0200 mol; actual isolated yield may be lower. A three-carbon substrate does not make three moles of alcohol per mole reacted.

Electrophilic addition to alkenes

Why alkenes attract electrophiles

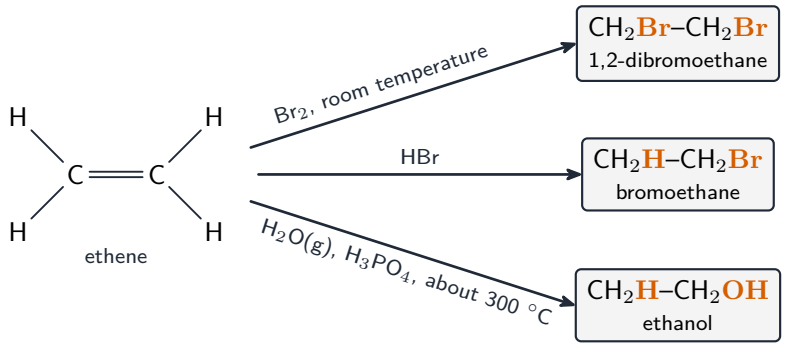
The C=C double bond in an alkene has four electrons between two carbon atoms: a region of high electron density. Electrophiles are attracted to it. In **electrophilic addition** 亲电加成 the double bond opens and two new single bonds form, so one molecule adds across the C=C.



Orange bromine water: shaken with an alkene it decolourises, as bromine adds across the C=C double bond

Three additions to learn

Reagent	Illustrative conditions	Product from ethene
Br_2	room temperature, suitable medium	1,2-dibromoethane
HBr	usual ionic addition conditions	bromoethane
H_2O (steam)	H_3PO_4 catalyst, about 300 °C	ethanol



C=C becomes C–C; one added atom or group on each carbon

Electrophilic addition: the C=C opens and one atom or group adds to each carbon.

The corresponding net equations are:

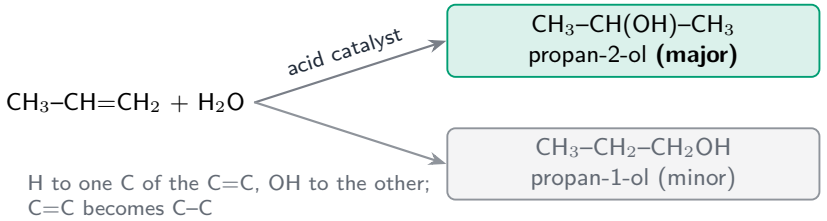
$$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$$
$$C_2H_4 + HBr \rightarrow CH_3CH_2Br$$
$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

In a suitable comparison, cyclohexene rapidly decolourizes orange bromine water while cyclohexane shows no rapid change in the dark. Keep light, temperature and reagent amounts comparable. Decolourization is evidence consistent with unsaturation, not unique proof of an alkene: other reacting substances can consume bromine.

Catalytic addition of steam to ethene is one industrial route to ethanol; fermentation is another. The water reagent and the acid catalyst play different roles. A catalyst is regenerated overall, whereas one water molecule is incorporated per ethene molecule in the net equation.

Track the double bond, atoms and conditions

In addition the two carbon atoms remain joined: the C=C becomes C–C and each gains a new bond. For HBr, add H to one double-bond carbon and Br to the other; for hydration add H and OH, not a new oxygen atom with no hydrogens. But-2-ene + Br_2 gives $CH_3CHBrCHBrCH_3$, named 2,3-dibromobutane. Carbon numbering follows the product connectivity.



Two orientations; one major product

For unsymmetrical alkenes such as propene, two constitutional orientations can be drawn. Under the usual acid-catalysed hydration conditions propan-2-ol is the major product. Detailed carbocation mechanisms are Higher Level content.

Worked amount example. In a stated single-addition model, 0.0120 mol but-2-ene needs 0.0120 mol Br_2. With Br_2 molar mass 159.8 g/mol, mass = amount × molar mass = 0.0120 × 159.8 = 1.9176 g, or **1.92 g** to three significant figures. This is a calculated requirement, not a recommended experimental dose.

Compare the two reaction patterns

Feature	Substitution	Addition
Organic starting point	a suitable C–leaving-group bond	C=C in an alkene
Change in skeleton	one group replaces another	two new bonds form across C=C
Example	bromoethane → ethanol	ethene → bromoethane

Specify reagent and conditions: HBr addition to ethene and aqueous OH^- substitution of bromoethane use different reacting bonds. Concentrated acids, bromine and halogenoalkanes require approved teacher-controlled procedures.

Functional groups, oxidation and polymerization

A **functional group** 官能团 is an atom or group of atoms responsible for characteristic reactions: an alcohol contains OH and a carboxylic acid contains COOH. Structural formulas must retain four bonds at each carbon.

Oxidation is another reaction pattern: $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$ with excess acidified dichromate under reflux converts the alcohol group into a carboxylic acid group. It does not replace Br by OH or add a reagent across C=C.

In addition polymerization, $nCH_2{=}CH_2 \rightarrow [-CH_2{-}CH_2-]_n$: many ethene molecules join as their C=C bonds become C–C links. Suitable initiator, temperature and pressure conditions are required. Each repeat unit retains both monomer carbons and no small molecule is lost. Trace bonds to distinguish substitution, addition, oxidation and polymerization before selecting reagents.

AHL: Lewis acids and bases

A wider definition

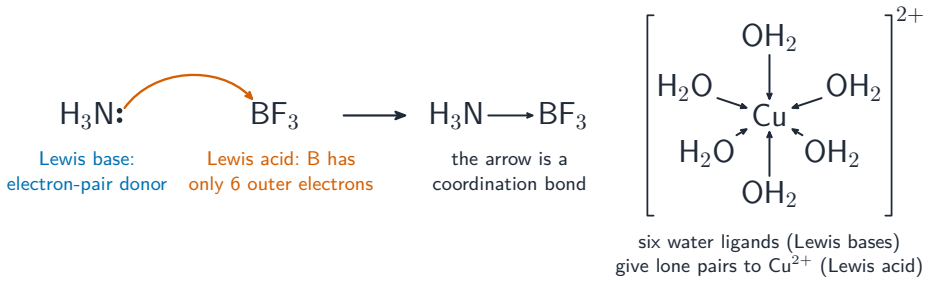
- A **Lewis acid** 路易斯酸 is an electron-pair acceptor.
- A **Lewis base** 路易斯碱 is an electron-pair donor.

Every Brønsted–Lowry base is a Lewis base: to accept a proton, it donates an electron pair to H^+. But the Lewis definition also covers reactions with no proton at all.

When a Lewis base reacts with a Lewis acid, the bond that forms is a **coordination bond** 配位键: both shared electrons come from the same atom.

$$NH_3 + BF_3 \rightarrow H_3N{\rightarrow}BF_3$$

Boron in BF_3 has only six outer electrons, so it can accept a pair.



A Lewis base gives a lone pair; a Lewis acid accepts it

Complex ions

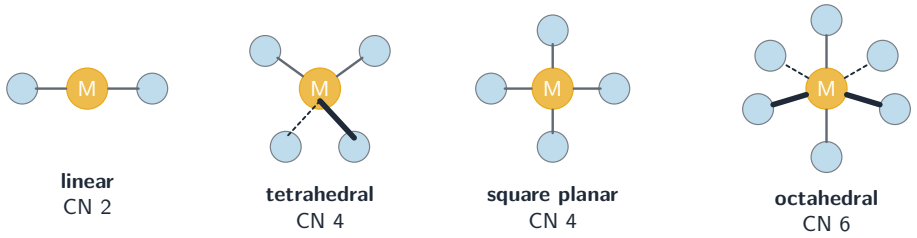
Transition element ions are Lewis acids. Molecules or ions with a lone pair, called **ligands** 配体, form coordination bonds to the metal ion and give a **complex ion** 配离子:

$$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$$

Water, ammonia, Cl^- and CN^- are common ligands. The number of coordination bonds to the metal ion is its **coordination number** 配位数; it is 6 here.

Calculate complex-ion charge rather than ligand count alone

The complex charge is metal-ion charge plus the sum of ligand charges. Neutral H_2O and NH_3 contribute zero; each Cl^- or CN^- contributes -1. Thus $[Cu(NH_3)_4]^{2+}$ has charge $+2$, while $[Fe(CN)_6]^{4-}$ contains iron with $x + 6(-1) = -4$, giving Fe(II). For $[Co(NH_3)_5Cl]^{2+}$, $x - 1 = +2$, so cobalt is $+3$.



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

Coordination number counts donor atoms bonded to the metal, not simply the complex charge. Six monodentate cyanide ligands give coordination number six. For a multidentate ligand, one ligand can provide several donor atoms. The donor origin of a coordination bond does not make it a separate class of weak bond after formation.

$NH_3 + H^+ \rightarrow NH_4^+$ illustrates both definitions: NH_3 accepts a proton as a Brønsted–Lowry base and donates its lone pair as a Lewis base. $BF_3 + NH_3$ needs no proton, showing the wider Lewis scope. Draw the donor pair on N and the curly arrow to electron-deficient B; a coordination arrow in a product records donor origin, whereas the curly arrow records pair movement.

Linking the ideas

Nucleophiles are Lewis bases: they give an electron pair. Electrophiles are Lewis acids: they accept one. So all of this unit's mechanisms are Lewis acid–base reactions.

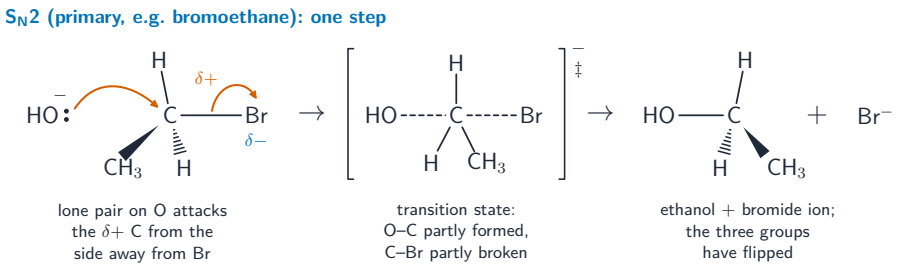
AHL: S_N1 and S_N2 mechanisms

Two routes for nucleophilic substitution

How the halogenoalkane reacts depends on how many carbon atoms are bonded to the carbon that carries the halogen.

Halogenoalkane	Example	Main mechanism
primary 伯: one alkyl group on the C–X carbon	bromoethane	S_N2
secondary: two alkyl groups	2-bromopropane	both
tertiary 叔: three alkyl groups	2-bromo-2-methylpropane	S_N1

S_N2: one step



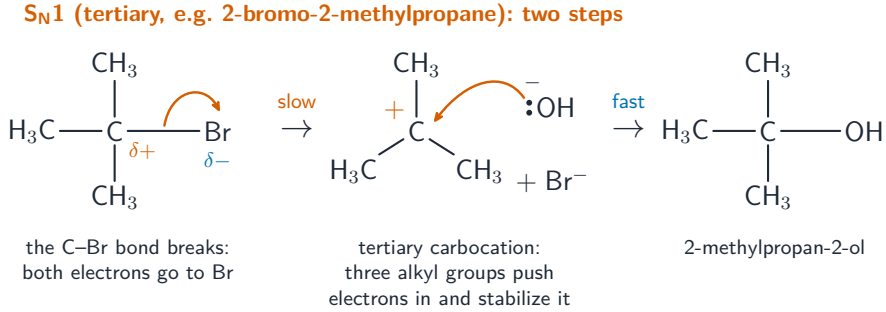
The incoming O pair and departing C–Br pair move in one concerted event.

S_N2 means substitution, nucleophilic, bimolecular. The nucleophile attacks the carbon from the side opposite the halogen while the C–X bond breaks, all in one step (see the bromoethane figure above).

- In the **transition state** 过渡态 C–O is partly formed and C–Br partly broken; the system carries an overall negative charge in this OH^-/neutral-halide example. Dotted bonds mean partial bonding, not exactly half a bond or an isolable intermediate.
- Two particles are in the only step, so rate = k[RBr][OH^-].
- Backside attack gives **inversion of configuration** 构型翻转 at the reacting carbon: the three remaining groups turn over. S_N2 is **stereospecific** 立体专一的. A chiral starting halogenoalkane gives a product with inverted spatial arrangement; the alcohol is not the other enantiomer of the halogenoalkane, because their compositions differ. R/S labels also depend on priority assignments.
- Primary halogenoalkanes react this way because the back of the carbon is open to attack.

S_N1: two steps

S_N1 means substitution, nucleophilic, unimolecular.



The slow first step makes a carbocation; the nucleophile then attacks fast

1. Slow: the C–Br bond breaks heterolytically to give a **carbocation** 碳正离子 and Br^-.
2. Fast: the nucleophile attacks the positive carbon.

- The slow first step is the **rate-determining step** 决速步骤. Only the halogenoalkane is in it, so rate = k[RBr].
- The carbocation centre is planar, so attack can occur from either face. If that centre becomes chiral in the product, both product enantiomers can form. This simple model allows racemization but does not guarantee an exactly 50:50 experimental ratio; ion pairing can affect access.
- Tertiary halogenoalkanes react this way because three alkyl groups push electrons towards the positive carbon and make the carbocation stable enough to form. The bulky groups also block back attack.

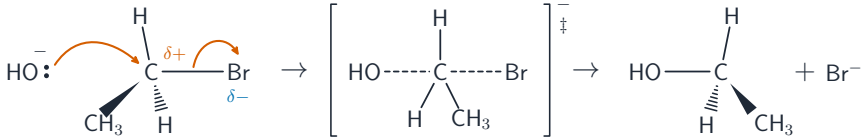
Keep the comparison within its scope

The primary/tertiary distinction gives the syllabus mechanism models; secondary substrates can use either route. Real rates and competing pathways depend on the reaction conditions. Detailed solvent and mechanism effects on the leaving-group rate comparison are not assessed in this objective. Compare otherwise similar substrates under matched conditions rather than turning the mechanism table into an unconditional rate ranking.

Use rate data as a test of the model

For invented data, let [RBr] = 0.020 mol/dm^3 and [OH$^-$] = 0.100 mol/dm^3 give rate 4.0×10^{-5} mol/(dm^3 s). Doubling either concentration separately doubles the rate. The observations support rate = k[RBr][OH$^-$] over the tested range. Here $k = 4.0 \times 10^{-5}/(0.020 \times 0.100) = 0.020$ dm^3/(mol s).

S$_N$2 (primary, e.g. bromoethane): one step

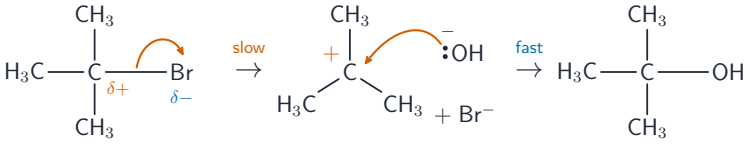


lone pair on O attacks the $\delta+$ C from the side away from Br

transition state: O–C half-formed, C–Br half-broken, charge spread

ethanol + bromide ion; the three groups have flipped

S$_N$1 (tertiary, e.g. 2-bromo-2-methylpropane): two steps



the C–Br bond breaks: both electrons go to Br

tertiary carbocation: three alkyl groups push electrons in and stabilise it

2-methylpropan-2-ol

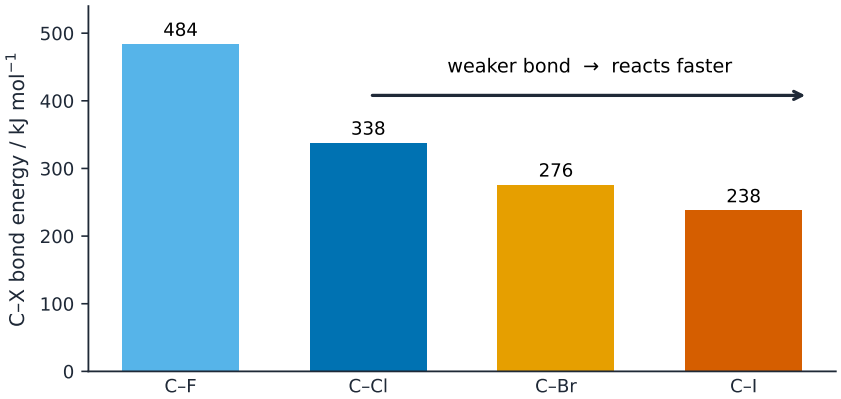
S_N2 is a single step through a charged transition state; S_N1 is a slow step to a carbocation, then a fast attack

For a separate invented S$_N$1 example, doubling [RBr] doubles the rate but doubling [OH$^-$] leaves it unchanged under the stated conditions. This supports rate = k[RBr], not the absence of hydroxide from the overall reaction. Zero order in a species is a kinetic statement, not a claim that it is chemically irrelevant.

A one-step S$_N$2 profile has one transition-state peak. The two-step S$_N$1 model has two peaks and a carbocation intermediate in the valley between them. A transition state is not a bottleable intermediate. Neither overall stoichiometry nor substrate class alone proves an experimentally unique pathway.

The leaving group

The rate of substitution depends on the halogen. Iodoalkanes react fastest:



rate: RI > RBr > RCl (weaker C–X ⇒ faster)

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

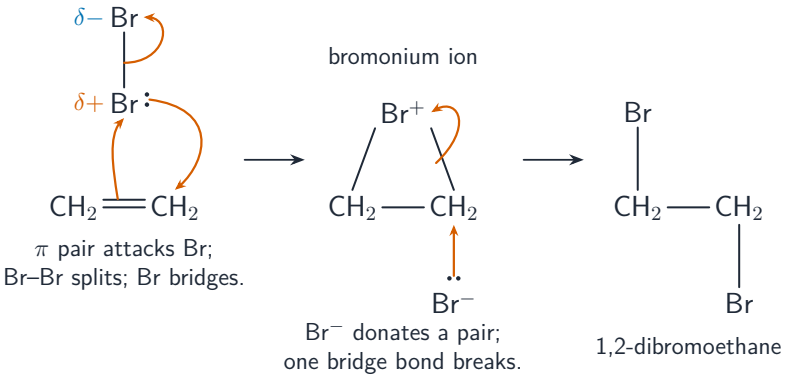
Bond	C–Cl	C–Br	C–I
Bond enthalpy / kJ mol^{-1}	324	285	228
Relative rate	slowest		fastest

For otherwise comparable halogenoalkanes under the stated substitution conditions, C–I is weaker than C–Br and C–Cl, so iodo compounds commonly react faster. Iodide is a better leaving group than chloride. The polarity order alone predicts the wrong trend. These mean homolytic bond enthalpies support a qualitative comparison; they are not numerical activation energies for heterolytic substitution.

AHL: Electrophilic addition mechanisms

Bromine and ethene

A Br$_2$ molecule is non-polar, but the electron-rich C=C bond repels the electrons in Br–Br as it gets close. This induces a dipole: the near Br becomes $\delta+$.



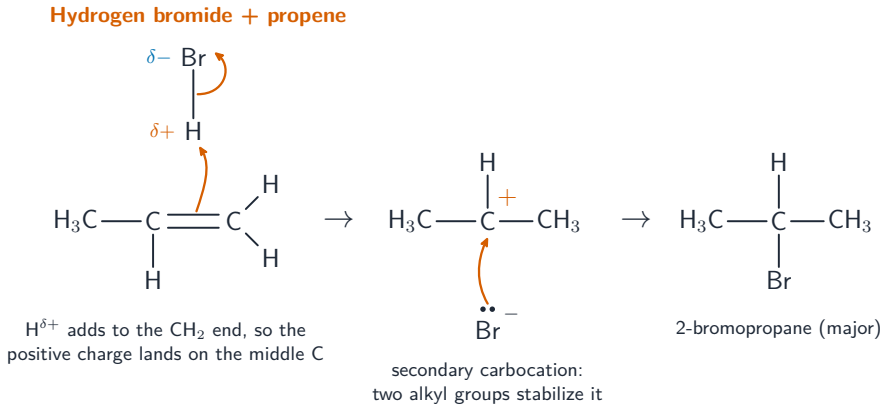
The bridged bromonium ion accounts for the usual bromine-addition pathway.

1. The π pair attacks the nearer Br, the Br–Br pair moves to the departing Br, and a lone pair on the nearer Br bonds to the other carbon. A positively charged **bridged bromonium ion** and Br^- form.
2. Br^- donates a lone pair to a carbon from the opposite side as the corresponding C–Br bridge bond breaks back towards Br. This gives 1,2-dibromoethane. A free open carbocation is an oversimplification of this bromination mechanism.
3. In aqueous bromine, water can compete as a nucleophile and bromohydrin products can form. The classroom decolourization observation alone does not identify every organic product; specify a Br_2 addition model when predicting the dibromide.

■ Hydrogen halides and acid-catalysed hydration

HBr is already polar. The π pair forms a bond to H, the H–Br pair goes to Br, then Br^- attacks the carbocation. For acid-catalysed hydration, π electrons first accept H^+ to form a carbocation. Water then donates an O lone pair to the positive carbon, giving an oxonium ion. Loss of H^+ gives an alcohol and regenerates the acid catalyst.

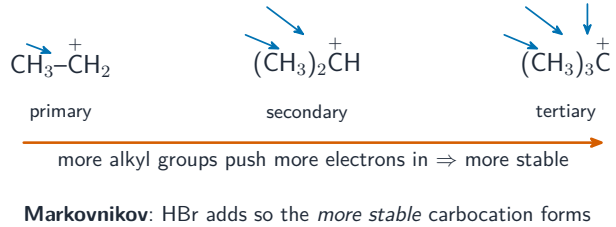
For ethene: $CH_2{=}CH_2 + H^+ \rightarrow CH_3CH_2^+$; then $+ H_2O \rightarrow CH_3CH_2OH_2^+$; loss of H^+ gives CH_3CH_2OH. Check that the intermediate attached oxygen has three bonds and positive charge. Adding OH^- directly to a carbocation describes a different reagent situation from acid-catalysed hydration, where water is the available nucleophile.



HBr addition uses a carbocation model; bromination is distinguished above.

■ Unsymmetric alkenes: Markovnikov's rule

When HBr adds to propene, two products are possible: 1-bromopropane and 2-bromopropane. The major product is 2-bromopropane.



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

More alkyl groups on C^+ make the carbocation more stable

- The H adds to the end carbon so the positive charge is on the middle carbon. That is a secondary carbocation, which is more stable than the primary one.
- Alkyl groups push electron density towards the positive carbon, which spreads out the charge. Stability: tertiary > secondary > primary.
- Under the usual ionic addition conditions, the pathway through the more stable carbocation is favoured, so its product predominates. This is not a rule for every radical or rearranging addition reaction.

Markovnikov's rule 马氏规则 says this in short form: the H atom adds to the carbon of the C=C that already has more H atoms.

AHL: Electrophilic substitution of benzene

■ Why benzene substitutes instead of adding

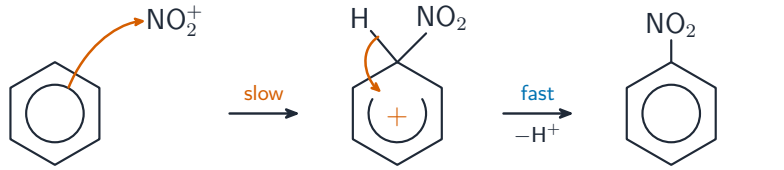
Benzene has six **delocalized** 离域的 π electrons above and below its plane. Electrophilic attack temporarily disrupts aromatic delocalization. Loss of H^+ then restores it, giving **electrophilic substitution** 亲电取代. Addition would leave the final product without the original aromatic system; it is less favoured under the substitution conditions, not impossible under every possible condition.

■ Nitration as an example

The required mechanism can start with a supplied charged electrophile E^+; formation of that electrophile is not assessed. Nitration illustrates the same ring attack and restoration of aromaticity.

As contextual chemistry, benzene can be warmed to about 50 °C with a mixture of concentrated nitric and sulfuric acids. The acids form the electrophile, the **nitronium ion** 硝鎓离子:

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$



The ring attacks NO_2^+, then loses H^+ to get its delocalization back

1. A curly arrow from the delocalized ring to the N of NO_2^+. This is slow: the intermediate has lost its delocalization and carries a positive charge, shown by a broken ring (horseshoe) with + inside.
2. A curly arrow from the C–H bond into the ring. H^+ leaves and the delocalized ring is restored. HSO_4^- takes the H^+, so H_2SO_4 is a catalyst.

Overall: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$.

Practice

Use the stated reaction conditions. New numerical data below are invented teaching examples, not results from real papers.

1. Classify OH^-, NH_3, H_2O, H^+, NO_2^+ and Br_2 approaching an alkene as electron-pair donors or acceptors. Explain why the sign of the charge alone is insufficient.
2. Contrast homolysis of Cl_2 with the formal heterolysis $CH_3Br \rightarrow CH_3^+ + Br^-$. Give electron destinations and arrow types. Does the latter equation prove that a free methyl carbocation is an intermediate in ordinary substitution?
3. Write the overall equation for 1-bromopropane with warm aqueous OH^-. Identify the nucleophile, attacked atom, leaving group and organic product.
4. Explain C–Br polarity and specify the start and end of both electron-pair arrows for replacing Br with OH. Explain why a curly arrow beginning at $C\delta^+$ points the wrong way for nucleophilic attack.
5. Give structural formulas and names of the main organic products when propene reacts with (a) Br_2 in a stated dibromide-addition model, (b) HBr under usual ionic conditions, (c) acid-catalysed water. Describe the carbon–carbon bond change.
6. Compare cyclohexene and cyclohexane using bromine water in the dark. State the observation, two controlled conditions and one limitation of identifying an unknown from this test alone.
7. Use $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+ + Br^-$ to explain the two ammonia roles. For water as nucleophile, explain why an initial product with oxygen bonded to two H atoms and the organic group must lose a proton to give an alcohol.
8. A substitution consumes 0.0200 mol 1-bromopropane with excess OH^-. Find maximum propan-1-ol amount. If isolated yield is 68.0%, find actual amount. Does the carbon count change the 1:1 mole ratio?
9. In a single-addition model, find Br_2 amount and mass required for 0.0120 mol but-2-ene, using $M(Br_2) = 159.8$ g/mol. Name the dibromide.
10. Plan the two-step route ethene → bromoethane → ethanol. Give reagents, suitable conditions and the reaction pattern of each step; write both net equations.
11. Repair these claims: (a) every nucleophile is negative; (b) a curly arrow can start at a positive charge; (c) steam is the catalyst for ethene hydration; (d) bromine decolourization proves the unknown is ethene.
12. **AHL.** (a) Explain $BF_3 + NH_3$ and $H^+ + NH_3$ using Lewis roles and electron-pair arrows. Which also uses the Brønsted–Lowry definition? (b) Find metal oxidation states and coordination numbers for $[Fe(CN)_6]^{4-}$ and $[Co(NH_3)_5Cl]^{2+}$, assuming all ligands monodentate. (c) Explain why a coordination bond is not necessarily weaker than another covalent bond.
13. **AHL.** (a) Compare primary bromoethane S_N2 with tertiary 2-bromo-2-methylpropane S_N1: steps, arrows, rate expressions and energy-profile features. (b) Invented rates double when either [RBr] or $[OH^-]$ doubles separately. At 0.020 mol/dm^3 RBr and 0.100 mol/dm^3 OH^-, rate is 4.0×10^{-5} mol/(dm^3 s). Deduce k and predict the rate if both concentrations double. (c) Describe the spatial result of a stated S_N2 conversion of chiral 2-bromobutane to butan-2-ol; explain why calling it "the other enantiomer of the starting compound" is wrong. (d) Compare otherwise matched 1-iodobutane and 1-chlorobutane substitution rates.

14. **AHL.** (a) Describe electron-pair movements for Br_2 addition to ethene using a bridged intermediate. (b) Give all three stages of acid-catalysed ethene hydration, including the charged oxygen intermediate and catalyst regeneration. (c) Explain the major product of HBr + propene and distinguish the carbocation model from bromination. (d) Starting from a supplied electrophile E^+, describe benzene substitution and restoration of aromaticity. Identify the role of each curved arrow; do not assume electrophile formation is required.

■ Worked answers

1. OH^-, NH_3 and H_2O donate electron pairs: nucleophiles. H^+, $NO_2{}^+$ and the polarized Br_2 reactant accept pairs: electrophiles. Neutral molecules can fill either role depending on the available donating pair or accepting centre.
2. $Cl_2 \rightarrow 2Cl\bullet$: one electron to each Cl, shown with two fishhooks. $CH_3Br \rightarrow CH_3{}^+ + Br^-$: the full C–Br pair goes to Br, shown with one full curly arrow. The latter is formal electron allocation, not evidence for a free methyl carbocation pathway.
3. $CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$. OH^- donates at O to the carbon bonded to Br; Br^- leaves; the alcohol is propan-1-ol.
4. Br attracts the bonding electrons more strongly than C, leaving $C\delta^+$. Draw the O lone pair → attacked C, and C–Br bond pair → Br. Starting the first arrow at positive carbon would show electrons coming from the electron-poor site rather than from hydroxide.
5. (a) $CH_3CHBrCH_2Br$, 1,2-dibromopropane; (b) $CH_3CHBrCH_3$, 2-bromopropane; (c) $CH_3CH(OH)CH_3$, propan-2-ol, the major hydration product. Each addition replaces C=C by C–C and gives one new bond to each carbon. The carbon skeleton retains three atoms.
6. Cyclohexene rapidly decolourizes the orange reagent; cyclohexane has no rapid change in the dark. Match temperature, reagent amount and other conditions, keeping light exposure controlled. Other substances can consume bromine, so decolourization is not unique proof of an alkene or of ethene.
7. One NH_3 donates its N lone pair to form the organic C–N bond; another accepts H^+, giving $NH_4{}^+$. The net equation has eleven H atoms on each side and total charge zero. A water-derived intermediate R–$OH_2{}^+$ has three O bonds and +1 charge; deprotonation gives R–OH without losing the oxygen-containing group.
8. The balanced substitution is 1:1, so maximum alcohol amount = 0.0200 mol. Actual amount = theoretical amount × fractional yield = $0.0200 \times 0.680 = 0.0136$ mol. Three carbon atoms stay together within each product molecule; they do not multiply the number of molecules produced.
9. The alkene/Br_2 ratio is 1:1, so $n(Br_2) = 0.0120$ mol. Mass $m = nM = 0.0120 \times 159.8 = 1.9176$ g, giving **1.92 g**. The product is $CH_3CHBrCHBrCH_3$, 2,3-dibromobutane.
10. First, HBr adds to ethene under usual ionic addition conditions: $CH_2{=}CH_2$ + HBr → CH_3CH_2Br. Then warm aqueous OH^- substitutes Br: $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$. Step one is electrophilic addition; step two nucleophilic substitution. Neither requires changing the two-carbon skeleton.
11. (a) NH_3 and H_2O are neutral nucleophiles. (b) Start at a donating pair or bond, not positive charge. (c) Water is the net reagent; acid is regenerated as catalyst. (d) The observation shows bromine consumption and is consistent with unsaturation; it does not uniquely identify ethene.
12. **AHL.** (a) NH_3 donates its N lone pair: arrow N pair → B in BF_3, or → H^+. NH_3 is the Lewis base; BF_3/H^+ the Lewis acid. $H^+ + NH_3 \rightarrow NH_4{}^+$ also involves proton acceptance, so it is Brønsted–Lowry acid–base chemistry. $BF_3 + NH_3$ involves no proton transfer. (b) Fe: $x + 6(-1) = -4$, so +2; coordination number six. Co: $x + 5(0) - 1 = +2$, so +3; coordination number six. (c) Donor origin describes how the shared pair formed, not a separate universal bond-strength class.
13. **AHL.** (a) S_N2: O pair → C and C–Br pair → Br in one concerted step; rate = k[RBr][OH^-], one transition-state peak and no carbocation intermediate. S_N1: slow C–Br pair → Br creates the carbocation, then fast O pair → C; rate = k[RBr] in the simple model, two peaks with an intermediate valley. A tertiary centre supports the carbocation and obstructs backside attack. (b) First order in each reactant, second order overall: $k = r/([RBr][OH^-]) = 0.020$ dm^3/(mol s). Doubling both gives a factor four: 1.6×10^{-4} mol/(dm^3 s). (c) Backside attack inverts the arrangement at the reacting carbon. Butan-2-ol and 2-bromobutane differ in composition, so they cannot be enantiomers of each other; reassess R/S priorities rather than assuming the label always flips. (d) Matched iodobutane commonly reacts faster: C–I is weaker and I^- a better leaving group. Bond polarity alone is not the correct explanation.
14. **AHL.** (a) The π pair attacks Brδ^+; Br–Br pair goes to the departing Br and a near-Br lone pair bonds to the other carbon, making a bromonium ion. Br^- then donates a pair to a carbon while its bridge C–Br pair returns to Br, opening the ring to give the dibromide. (b) π pair → H^+ gives $CH_3CH_2{}^+$; H_2O O pair → C gives $CH_3CH_2OH_2{}^+$; base-assisted H^+ loss returns the O–H pair to O, giving ethanol and regenerating acid. (c) Propene protonation favouring a secondary carbocation leads mainly to 2-bromopropane after Br^- attack. Bromination instead uses the bridged bromonium model. (d) A ring π pair → E^+ creates a C–E bond and a positively charged non-aromatic intermediate. A C–H pair returns into the ring as a base removes H^+; aromaticity is restored in C_6H_5E. Addition would not restore that original aromatic system.

Exam tips

- Start a full curly arrow at an electron pair or bond, then check the new bonds and charges. A minus sign records charge; it does not locate a pair.
- Identify the reacting carbon, donor atom and leaving group. Keep carbon skeletons and atom counts consistent; distinguish addition from substitution.
- State reagents, conditions and evidence limits. Bromine consumption is consistent with unsaturation but does not uniquely identify an alkene; "colourless" describes colour, while "clear" describes transparency.
- **AHL.** Distinguish a transition state from an intermediate. Use rate data, not overall coefficients, to test a rate expression; compare leaving groups under matched conditions.
- **AHL.** Explain spatial inversion without calling different-composition reactant and product enantiomers. Hydration needs water attack and deprotonation; benzene substitution must restore aromaticity.

Experimental programme

International Baccalaureate · IB Diploma · Chemistry · HL

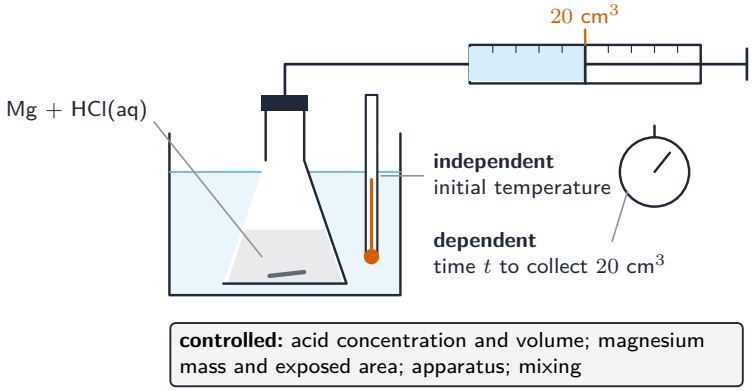
Scope and prerequisites

This handout teaches experimental planning, chemical measurement, uncertainty, graph interpretation and evaluation for the IB Chemistry experimental programme. Use these methods throughout supervised practical work. Sections marked **AHL** are for Higher Level only.

Prerequisites: mole and concentration calculations, balanced equations and straight-line graphs. All numerical datasets and investigations below are original, invented teaching examples. They illustrate methods rather than reporting real measurements.

Design a question that measurements can answer

A useful research question specifies the independent variable, dependent variable and chemical system. "How does temperature affect chemistry?" is too broad. "How does initial temperature affect the time for a specified magnesium strip to produce 20 cm^3 of hydrogen in hydrochloric acid of fixed concentration?" identifies quantities that can be measured. Temperature is the independent variable; elapsed time is the dependent variable. For the same collected volume, $1/t$ can compare average rates, but it is not automatically an initial rate.



A measurable research question names what you change, what you measure and what you keep the same.

Identify control variables and explain their effects: acid concentration and volume, magnesium mass and exposed area, apparatus geometry and mixing. "Keep everything the same" gives neither a method nor a reason. Select a range wide enough to reveal

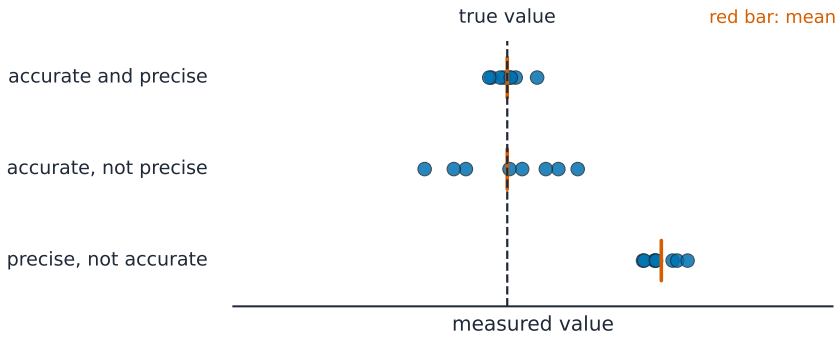
a trend while keeping the process measurable and the apparatus within approved limits. A pilot trial can reveal a reaction too fast to time or gas leakage before the full investigation.

Use repeated trials at each condition to estimate scatter and judge reliability. Randomizing the order of conditions can reduce the influence of drift, such as gradual room-temperature change. Repeats at one concentration do not replace a range of concentrations. Continuous variables can take intermediate values; a discrete variable such as the number of identical pieces takes separate countable values.

A risk assessment connects a hazard, exposure route and control: acid splashes → eye/skin exposure → appropriate eye protection and controlled handling; flammable solvent → ignition → suitable heating and removal of flames. Follow the teacher's apparatus limits and disposal instructions. Plan waste minimization and any environmental or ethical issues before collecting data.

Choose and use measuring equipment

Choose the instrument for the quantity and required precision, not merely the nearest container.



A systematic error shifts every reading; random error scatters them. Repeats help only with scatter

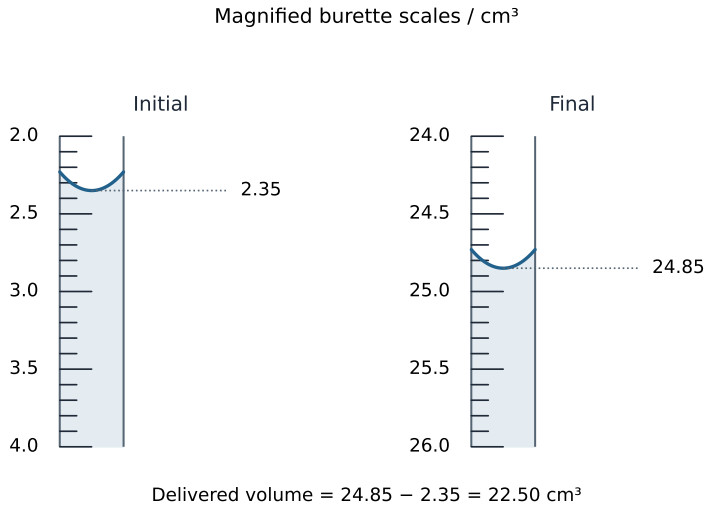
- **Mass:** tare a stable balance; keep the vessel dry and record its displayed precision. Weighing by difference subtracts the final container mass from its initial mass.
- **Volume:** a volumetric pipette delivers one specified volume; a burette delivers a variable volume by subtracting readings; a volumetric flask contains a specified total volume at its mark. A beaker is normally unsuitable for precise concentration preparation.
- **Time, temperature and length:** define the start/finish event, immerse a temperature probe consistently without touching the vessel, and avoid parallax when reading a scale. A fast sensor can still have a calibration offset or response lag.
- **pH:** calibrate an appropriate probe using suitable buffers, rinse between samples and allow stabilization. A pH reading is not a direct measurement of acid concentration for every chemical system.
- **Electrical quantities:** an ammeter measures current in series; a voltmeter measures potential difference in parallel. Choose a suitable range and account for electrode/contact conditions when comparing cells.

A **systematic error** 系统误差 shifts measurements consistently, for example a calibration offset. Random error produces unpredictable scatter. Repetition can reduce uncertainty in a mean caused by random variation, but it does not remove a shared offset. A gas leak or heat loss may create a directional bias without being a simple constant zero error.

Accuracy concerns agreement with the appropriate reference; precision concerns the spread or resolution of measurements. Closely agreeing repeats can all be inaccurate. A reference comparison must use matching conditions and a trustworthy reference value.

■ Read a burette as a difference

For a clear aqueous solution with a concave meniscus, read the bottom at eye level. Burette values increase downwards. Record initial and final readings to the precision supported by the scale and stated method; do not assume the initial reading is zero. Check that the tip is filled and free of air bubbles before starting.



Delivered volume = final reading minus initial reading; read the meniscus consistently at eye level.

For the invented readings 2.35 ± 0.05 and 24.85 ± 0.05 cm^3,

$$V = 24.85 - 2.35 = 22.50 \text{ cm}^3,$$

$$u_V = 0.05 + 0.05 = 0.10 \text{ cm}^3.$$

The conservative result is 22.50 ± 0.10 cm^3. The uncertainty values are given for this example; consult the apparatus specification and method rather than assuming every burette has this uncertainty.

Chemical techniques: purpose and critical detail

Make a known concentration

A **standard solution** has a reliably known concentration. Calculate the solute amount and mass using $n = cV$ and $m = nM$. Dissolve the solid, transfer it quantitatively into a suitable volumetric flask, rinse the original vessel into the flask, then add solvent to the mark and mix thoroughly. Make the final adjustment at the appropriate temperature. Purity, hydration and the suitability of the solute as a standard matter; an accurately weighed impure or water-absorbing sample does not automatically give an accurate concentration.



A separating funnel: two immiscible liquid layers are run off separately, for example to recover an organic product



Heating under reflux: vapour condenses in the vertical condenser and drips back, so a mixture can be heated for a long time without losing volatile substances

For dilution, use $c_1V_1 = c_2V_2$ because solute amount is conserved, provided there is no reaction or loss. Transfer the aliquot with a pipette and dilute **to** the final flask volume, not by adding that entire volume of solvent. Never pipette by mouth.

In a titration, rinse a burette with its titrant and a pipette with the solution it will deliver; use a clean conical flask, normally rinsed with deionized water. Swirl, approach the endpoint dropwise and choose an indicator whose change occurs in the appropriate steep region. The observed endpoint is not the definition of the stoichiometric equivalence point. Acid–base and redox titrations both require a balanced equation; some redox systems are self-indicating. Keep a rough titre separate from the carefully obtained concordant trials and state the selection rule.

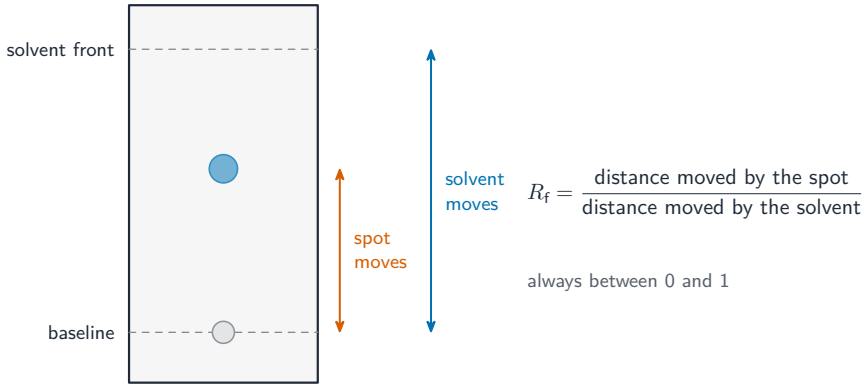
Separate, purify and characterize

- **Filtration** separates an insoluble solid from a liquid; it does not remove dissolved salt. A separating funnel separates suitable immiscible liquid layers.
- **Recrystallization** uses a suitable solvent in which the product is much more soluble hot than cold. Cool to crystallize, collect and wash with a little cold solvent; too much solvent can reduce recovery.
- **Drying to constant mass** means repeating a suitable heat–cool–weigh cycle until successive masses agree within the stated criterion. Cool before weighing; constant mass does not prove chemical purity or justify heating a decomposing compound more strongly.
- **Distillation** vaporizes and condenses a component for collection, using volatility differences. **Reflux** returns condensed vapour to the reaction vessel, allowing prolonged heating with less volatile material lost. Neither setup should be sealed during ordinary atmospheric heating.

- **Paper/TLC chromatography** compares movement of substances under specified conditions. Keep the sample above the initial solvent level; mark the solvent front promptly. R_f is distance moved by the spot from the baseline divided by distance moved by the solvent front from the same baseline. Matching R_f alone does not prove identity.
- **Melting-point determination** can support a purity assessment: impurities often depress and broaden a melting range, but comparison requires suitable heating and a relevant reference. A single melting point is not a complete structural identification.



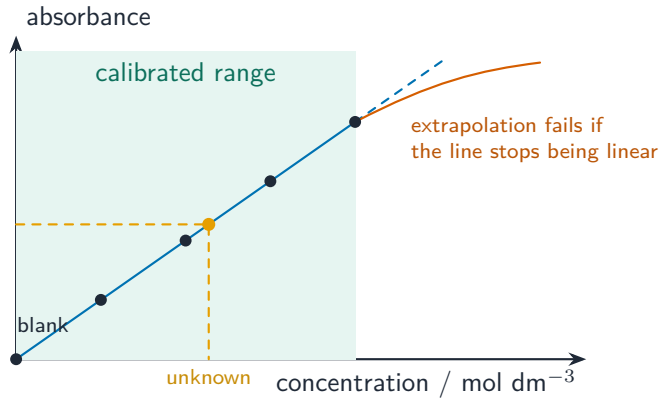
A rotary evaporator removes solvent under reduced pressure – the step after the reaction



Thin-layer chromatography: the R_f value is how far the spot moved divided by how far the solvent front moved

Measure chemical behaviour

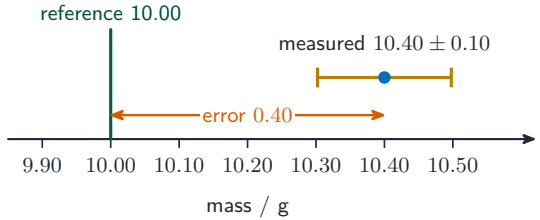
- **Calorimetry:** measure temperature change and the mass being heated; use insulation and account for apparatus heat capacity and heat exchange where relevant. The reaction and surroundings have opposite heat signs.
- **Electrochemical cells:** keep electrode surfaces, electrolyte conditions and temperature consistent; a high-resistance voltmeter reduces current drawn during a potential-difference measurement.
- **Colorimetry/spectrophotometry:** choose a suitable wavelength, use a blank and consistent clean cuvettes, and build a calibration using known concentrations. A calibration range must be justified; extrapolation outside it can fail if the relationship ceases to be linear.
- **Physical/digital molecular models:** use them to investigate connectivity and geometry, stating model assumptions and limitations. A ball-and-stick bond is a representation, not a rigid stick physically joining atoms.



Read unknowns inside the calibration range

Record raw data and propagate uncertainty

Keep original readings, units, apparatus uncertainties and qualitative observations. Put units and common uncertainties in column headings; use consistent decimal places for an instrument. Record unexpected changes and failed trials honestly. Preserve raw data before calculations or spreadsheet transformations. For database work, retain the source, conditions, units and any filtering choices; for sensors, record calibration and sampling settings.



$$\text{\% uncertainty} = 100 \times \frac{0.10}{10.40} = 0.96\% \quad \text{(divide by the measured value)}$$

$$\text{\% error} = 100 \times \frac{|10.40 - 10.00|}{10.00} = 4.0\% \quad \text{(divide by the reference)}$$

Percentage uncertainty divides by the measured value; percentage error divides by the reference

An **uncertainty** 不确定度 quantifies a limitation on the result. Absolute uncertainty has the measured quantity's unit; fractional uncertainty is $u_x/|x|$, and percentage uncertainty is that fraction multiplied by 100. These are not the same as percentage disagreement with a reference.

Choose a percentage calculation by asking what is being compared. If an invented measurement is 10.40 ± 0.10 g and its accepted reference is 10.00 g, percentage uncertainty is $100(0.10/10.40) = 0.96\%$, while the magnitude of percentage error is $100|10.40 - 10.00|/10.00 = 4.0\%$. The reference is the error calculation's denominator; the measured value is the uncertainty calculation's denominator. Neither calculation is the uncertainty of the reference itself.

If a value rises from 10.00 to 10.40 g, percentage change uses the initial value and is +4.0%. If two comparable measurements, 10.00 and 10.40 g, have neither an initial/reference role, one common percentage-difference convention uses their mean: $100|10.40 - 10.00|/[(10.40 + 10.00)/2] = 3.92\%$. State the convention; some questions specify a different comparison denominator. A small percentage uncertainty does not prove small percentage error.

For the conservative maximum-uncertainty method used here:

- In addition or subtraction, add absolute uncertainties: $u_{a\pm b} = u_a + u_b$.
- In multiplication or division, add fractional uncertainties: $u_y/|y| \approx u_a/|a| + u_b/|b|$ for $y = ab$ or a/b.
- A defined exact conversion or stoichiometric coefficient adds no measurement uncertainty. Multiplying a measured value by an exact coefficient scales its absolute uncertainty by the same factor, leaving its percentage uncertainty unchanged.

These are conservative first-order estimates for small uncertainties, not a claim that every error reaches its maximum simultaneously. Statistical combination of independent random standard uncertainties can instead use quadrature; do not switch between conventions halfway through an answer. Shared/correlated errors need separate treatment. Subtracting two readings from the same instrument can cancel a truly constant zero offset, even though the conservative reading-uncertainty sum is still used when requested.

■ **Worked example: titration concentration**

Use 25.00 ± 0.03 cm^3 of NaOH and a titre of 22.50 ± 0.10 cm^3 of HCl of concentration 0.1000 mol dm^{-3} with 0.20% uncertainty. The balanced reaction is 1:1.

$$c_{\mathrm{NaOH}} = \frac{c_{\mathrm{HCl}} V_{\mathrm{HCl}}}{V_{\mathrm{NaOH}}} = \frac{0.1000 \times 22.50}{25.00} = 0.09000 \text{ mol dm}^{-3}.$$

Volumes share the same units, so their ratio is dimensionless. Maximum percentage uncertainty is

$$100\frac{u_c}{c} = 0.20 + 100\frac{0.10}{22.50} + 100\frac{0.03}{25.00} \approx 0.76\%.$$

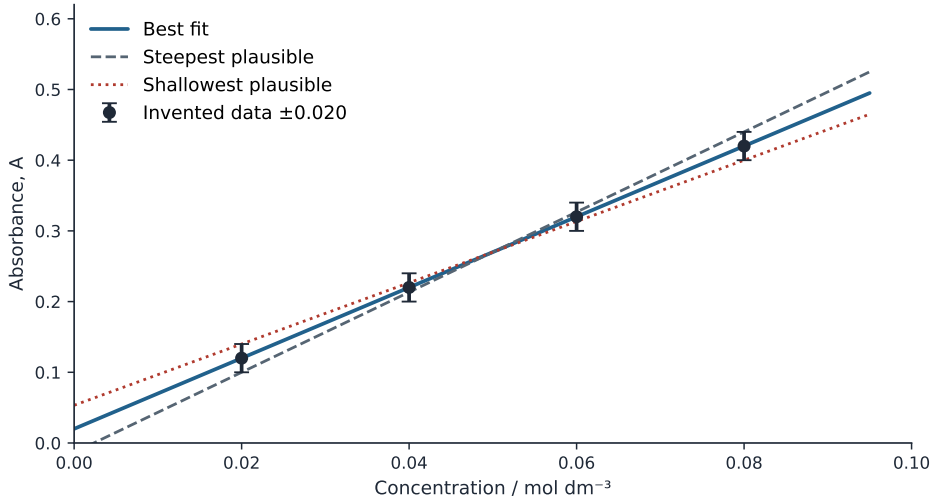
$$u_c = 0.09000 \times 0.00764 \approx 0.00069 \text{ mol dm}^{-3}.$$

A suitably rounded result is 0.0900 ± 0.0007 mol dm^{-3}. Keep guard digits until this final rounding; quote the value and absolute uncertainty to the same decimal place.

Graphs, gradients and model testing

Put the independent variable on the horizontal axis and the dependent variable on the vertical axis, with quantities and units. Use a readable scale covering the useful data range; a plotted axis need not always start at zero. A qualitative sketch has labelled but unscaled axes. Scatter plots suit paired continuous measurements; bar charts compare categories, and histograms describe a continuous distribution grouped into intervals.

Plot justified uncertainty bars and a best-fit line or curve. Do not join every noisy point with straight segments and call the changing slopes a physical model. A gradient is $\Delta y/\Delta x$ using two widely separated points on the fitted line, not necessarily two measured points. Its unit is vertical-axis unit divided by horizontal-axis unit. A tangent gives an instantaneous gradient; a chord gives an average gradient.



Treat the full set of uncertainty bars as constraints; endpoint choices alone do not guarantee a plausible line.

In the invented calibration, concentrations 0.020, 0.040, 0.060 and 0.080 mol dm^{-3} give absorbances 0.120, 0.220, 0.320 and 0.420, each with ±0.020 uncertainty; horizontal uncertainty is neglected. The best line is $A = 5.00c + 0.020$.

The steepest allowed line goes through $(0.020, 0.100)$ and $(0.080, 0.440)$; the shallowest through $(0.020, 0.140)$ and $(0.080, 0.400)$. Both also intersect the intervening bars:

$$m_{\max} = \frac{0.440 - 0.100}{0.080 - 0.020} = 5.67 \text{ dm}^3\,\text{mol}^{-1},$$

$$m_{\min} = \frac{0.400 - 0.140}{0.080 - 0.020} = 4.33 \text{ dm}^3\,\text{mol}^{-1}.$$

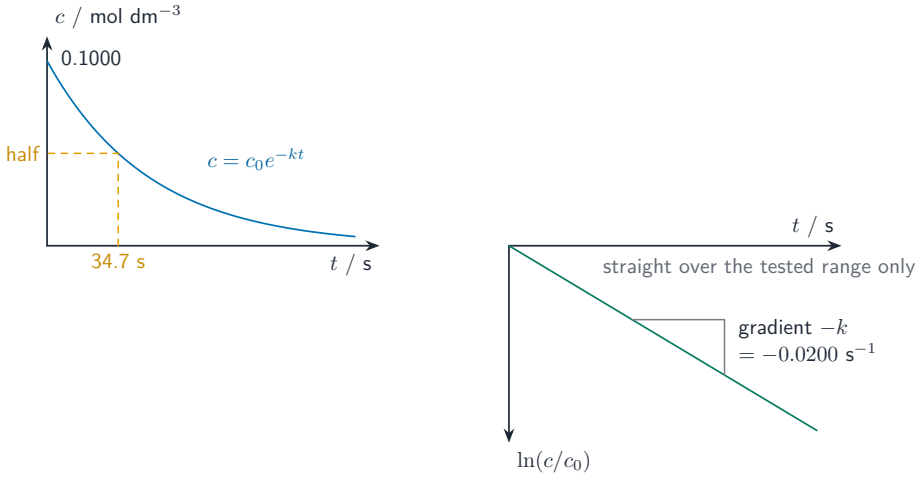
A symmetric gradient estimate is $m \approx (m_{\max} + m_{\min})/2 = 5.00$, with $u_m \approx (m_{\max} - m_{\min})/2 = 0.67$ dm^3 mol^{-1}. This graphical range describes the stated bars and straight-line model, not a formal statistical confidence interval.

A nonzero intercept may suggest a blank offset, a background signal or an incomplete model. Investigate it; do not automatically force the graph through the origin. An excellent R^2 describes how well a fitted model accounts for variation in the chosen response data; it does not prove accuracy, causation or the absence of systematic error. Even an exact line can contain a shared calibration bias. Inspect residuals, the data range and the chemistry too. Interpolation stays within the measured range; extrapolation extends beyond it and needs additional justification.

For an invented straight-line calibration fitted with an intercept, suppose $R^2 = 0.81$. The fit accounts for 81% of the variation in the measured response within this dataset; 19% remains in the residual variation. This does not mean 81% of readings are accurate or that concentration has caused 81% of the variation. A second model with $R^2 = 0.94$ accounts for more response variation in the same dataset, but still needs a physically justified form and a check of residuals and calibration bias. A higher value alone does not establish a better measurement method.

AHL: Powers and exponential models

For $y = x^n$ with an exact exponent and small uncertainty,



Linearise, then read k from the gradient

$$\frac{u_y}{|y|} \approx |n|\frac{u_x}{|x|}.$$

The magnitude matters: for $y = 1/x^2$, a 2% uncertainty in x gives about 4% in y, not −4%. Constants known exactly do not contribute. This first-order approximation becomes unreliable for very large fractional uncertainties or values near singularities.

An exponential model can be linearized. If $c = c_0 e^{-kt}$, then $\ln(c/c_0) = -kt$. Plotting the dimensionless logarithm against time gives gradient $-k$. For an invented $k = 0.0200$ s^{-1} and $c_0 = 0.1000$ mol dm^{-3}, at 30.0 s:

$$c = 0.1000e^{-0.0200(30.0)} = 0.0549 \text{ mol dm}^{-3}.$$

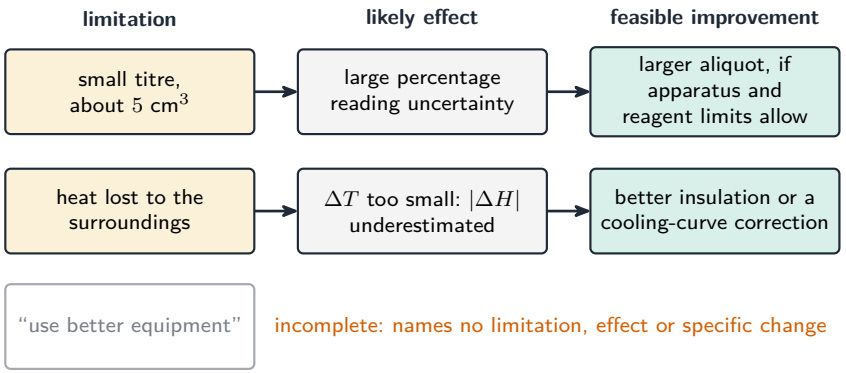
The half-time satisfies $1/2 = e^{-kt}$, so $t = \ln 2/k = 34.7$ s. An approximately straight transformed plot supports the model over the tested range; it does not independently establish a chemical mechanism.

Conclude and evaluate

Answer the research question using processed data and uncertainty. Separate observations from explanations: "the temperature rose" is an observation; "the reaction transferred heat to the solution" is an interpretation supported by a model. Compare relevant references under matching conditions, and distinguish accuracy, precision, reliability and validity.

Do not delete a point because it weakens the trend. Inspect the raw record, repeat where appropriate and give a defensible reason for including or excluding an anomalous trial. Retain the original value and the decision. A spreadsheet trend line or simulation produces an output from inputs and assumptions; check units and formulae, preserve provenance and test whether the model represents the chemical system.

An evaluation should link a limitation to its likely effect and a feasible improvement. "Use better equipment" is incomplete. For a small titre, a suitable larger aliquot can reduce percentage reading uncertainty without changing chemical stoichiometry, provided apparatus and reagent limits allow it. For heat loss, better insulation or time-series correction addresses the bias; repeating the same poorly insulated method does not remove it.



Limitation → likely effect → feasible improvement. A vague fix names none of the three.

Practice

Use conservative maximum uncertainty unless stated otherwise. All additional data are invented.

1. Turn "Does acid concentration affect reaction speed?" into a measurable research question. Identify independent/dependent variables and two justified controls.
2. A balance reads 6.237 ± 0.001 g before transfer and 2.104 ± 0.001 g after transfer. Find the transferred mass and its uncertainty.
3. A burette gives 2.35 ± 0.05 cm^3 initially and 24.85 ± 0.05 cm^3 finally. Calculate titre and percentage uncertainty. Explain why using only one reading uncertainty is wrong.
4. A temperature rises from 20.0 ± 0.1 °C to 26.0 ± 0.1 °C. Find the rise and percentage uncertainty. Does adding 273 to both readings change the rise?
5. A 0.2000 mol dm^{-3} stock has 0.50% uncertainty. Dilute 25.00 ± 0.03 cm^3 to 250.0 ± 0.15 cm^3. Calculate concentration and its maximum percentage uncertainty.
6. Use the titration worked example to calculate the NaOH concentration and uncertainty. What happens to the calculated concentration if an air bubble initially in the burette tip fills with titrant during the titre?
7. Identify a suitable technique to obtain an insoluble solid, purify a soluble crystalline solid, collect a volatile liquid, and heat a reacting mixture while returning vapour. Give one important distinction for each pair.
8. A calibration is $A = 5.00c + 0.020$, with c in mol dm^{-3}. Find the concentration for $A = 0.270$. Explain why dividing absorbance by 5.00 without the intercept is wrong.
9. Recalculate the steepest and shallowest gradients in the calibration above and estimate the gradient uncertainty. Why must the lines be checked against intermediate bars too?
10. A chromatography spot moves 3.6 cm and the solvent front 6.0 cm from the baseline. Find R_f. Explain why a matching R_f under different conditions does not prove identity.
11. Three titres are 22.45, 22.50 and 22.55 cm^3. Find mean and range. For an invented calibration fitted with an intercept, interpret $R^2 = 0.81$. Explain why close agreement and a higher R^2 do not prove accuracy, and give a justified approach to an anomalous fourth titre.
12. **AHL.** For a cube edge $x = 2.00 \pm 0.02$ cm, estimate volume and uncertainty using the small-uncertainty power rule. State its approximate nature.
13. **AHL.** For $c = c_0 e^{-kt}$ with $c_0 = 0.1000$ mol dm^{-3} and $k = 0.0200$ s^{-1}, calculate c at 30.0 s and the half-time. State the gradient and unit of a plot of $\ln(c/c_0)$ against time.
14. An invented mass result is 10.40 ± 0.10 g; the accepted reference is 10.00 g. Calculate percentage uncertainty and the magnitude of percentage error. Then treat 10.00 and 10.40 g as two comparable measurements and calculate their percentage difference using their mean. Explain the different denominators.

Worked answers

1. For example: how does HCl concentration over a specified safe range affect the time for a fixed magnesium strip to produce 20 cm^3 hydrogen at constant initial temperature? Independent: HCl concentration; dependent: elapsed time to that volume. Control magnesium mass/exposed area because reactive quantity and

surface affect the rate; control temperature because it affects reaction rate. State acid volume and apparatus too.

2. $m = 6.237 - 2.104 = 4.133$ g; $u_m = 0.001 + 0.001 = 0.002$ g. Report 4.133 ± 0.002 g.
3. $V = 24.85 - 2.35 = 22.50$ cm^3; $u_V = 0.10$ cm^3. Percentage uncertainty $= 100(0.10/22.50) = 0.44\%$. Delivered volume depends on both readings, so both reading uncertainties enter the conservative difference estimate.
4. $\Delta T = 6.0 \pm 0.2$ K; percentage uncertainty $= 100(0.2/6.0) = 3.3\%$. Converting both readings by adding the same Celsius-to-kelvin offset leaves their difference unchanged.
5. $c_2 = c_1V_1/V_2 = 0.2000(25.00/250.0) = 0.02000$ mol dm^{-3}. Maximum percentage uncertainty $= 0.50 + 100(0.03/25.00) + 100(0.15/250.0) = 0.68\%$. Absolute uncertainty is $0.02000(0.0068) = 0.000136$ mol dm^{-3}; with two uncertainty digits, report 0.02000 ± 0.00014 mol dm^{-3}.
6. $c = 0.1000(22.50/25.00) = 0.09000$ mol dm^{-3}; maximum uncertainty $\approx 0.76\%$, giving 0.0900 ± 0.0007 mol dm^{-3}. Filling an initial tip bubble makes the indicated titre exceed liquid delivered into the flask; the calculated amount of acid and hence NaOH concentration is too high in this model.
7. Insoluble solid: filtration. Soluble crystalline product: recrystallization followed by collection/drying; filtration alone cannot remove dissolved impurities. Volatile liquid collection: distillation; prolonged reaction with condensate returned: reflux. Reflux does not collect the distillate as product outside the reaction vessel.
8. $c = (A - 0.020)/5.00 = (0.270 - 0.020)/5.00 = 0.0500$ mol dm^{-3}. Ignoring the intercept assigns background absorbance to the analyte and overestimates concentration.
9. $m_{\max} = 0.340/0.060 = 5.67$; $m_{\min} = 0.260/0.060 = 4.33$ dm^3 mol^{-1}. Midpoint 5.00 and half-range 0.67 dm^3 mol^{-1}. An endpoint-extreme line might miss other bars; it must remain plausible for the whole dataset and model.
10. $R_f = 3.6/6.0 = 0.60$, dimensionless. Solvent, stationary phase and other conditions affect movement; different substances can also share an R_f. Compare under matched conditions with additional evidence.
11. Mean $= (22.45 + 22.50 + 22.55)/3 = 22.50$ cm^3; range $= 22.55 - 22.45 = 0.10$ cm^3. $R^2 = 0.81$ means the fitted model accounts for 81% of response variation in the stated dataset, not 81% accuracy or a causal percentage. A common calibration bias can preserve both precision and a strong linear fit. Inspect the fourth trial's raw observations and method, repeat if possible and justify any exclusion rather than deleting it because it weakens agreement.
12. **AHL.** $V = x^3 = 8.00$ cm^3; fractional uncertainty $u_V/V \approx 3(0.02/2.00) = 0.030$. Thus $u_V \approx 0.24$ cm^3, giving 8.00 ± 0.24 cm^3 with two uncertainty digits. This is a first-order estimate for small uncertainty, not exact evaluation of both cubed bounds.
13. **AHL.** $c = 0.1000e^{-0.0200(30.0)} = 0.0549$ mol dm^{-3}. $t_{1/2} = \ln 2/0.0200 = 34.7$ s. Since $\ln(c/c_0) = -kt$, gradient is -0.0200 s^{-1}.
14. Percentage uncertainty $= 100(0.10/10.40) = 0.96\%$. Magnitude of percentage error $= 100|10.40 - 10.00|/10.00 = 4.0\%$. Mean-denominator percentage difference $= 100(0.40/10.20) = 3.92\%$. Uncertainty compares a stated uncertainty with its measured value; error compares disagreement with a reference; the stated symmetric difference treats neither measurement as the reference.

Exam tips

- Distinguish a reading from a difference and an absolute uncertainty from a percentage. State which uncertainty convention you use.
- Record original values and units, then keep guard digits until final rounding. Precision of repeats is not proof of accuracy.
- A gradient needs units and a model; an intercept, residual pattern or anomaly needs investigation, not automatic deletion.
- Link each evaluation point to a direction or consequence and a specific feasible improvement. Answer the research question within the supported range.
- **AHL.** Multiply fractional uncertainty by the magnitude of an exact exponent; check the axes and sign when linearizing an exponential model.

Reference: IB Chemistry guide: tools and inquiry skills.