Course Companion

Pearson Edexcel · International A-Level · Chemistry

Every topic handout in one volume

exercises.lol

Contents

1. 1 · Structure, Bonding and Introduction to Organic Chemistry 2

2. 2 · Energetics, Group Chemistry, Halogenoalkanes and Alcohols 17

3. 3 · Practical Skills in Chemistry I 31

4. 4 · Rates, Equilibria and Further Organic Chemistry 38

5. 5 · Transition Metals and Organic Nitrogen Chemistry 55

6. 6 · Practical Skills in Chemistry II 70

1 · Structure, Bonding and Introduction to Organic Chemistry

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From particles to a chemical prediction

Why can a tiny mass of a gas fill a large flask? Why does solid sodium chloride not carry current, while its solution does? Unit 1 links particle counting, electronic structure and bonding to observable behaviour, then uses the same ideas to explain organic reactions.

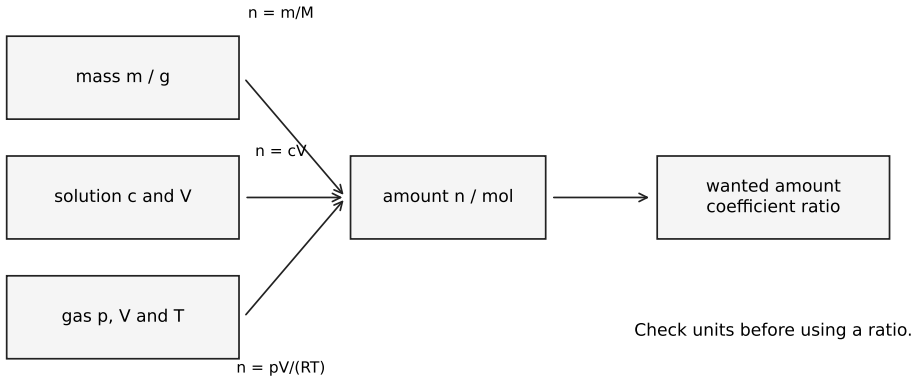
Use this reference with sheets 1.1–1.5 and their narrower skill companions. You need simple algebra, powers of ten and balanced equations. Topics 1–5 of the Pearson specification define this unit. Kinetics and equilibrium belong to Unit 2; they are not prerequisites for these sheets.

Count particles, then use the equation

An **atom** is one particle of an element . An element contains only one type of atom, defined by proton number. An **ion** has an electrical charge because its electron count differs from its proton count. A **molecule** is a discrete group of covalently bonded atoms. A compound contains different elements chemically combined. An empirical formula gives the simplest whole-number atom ratio; a molecular formula gives actual atom numbers in one molecule. Ionic lattices have formula units, not separate molecules.

The **mole** is the unit of amount of substance. The particle count is $N = nL$, where $L = 6.02 \times 10^{23}\ \text{mol}^{-1}$. Thus one mole contains 6.02×10^{23} of the specified entities. Always say whether you count atoms, molecules, ions or formula units. A mole of methane molecules contains five moles of atoms.

Relative atomic mass , A_r, compares the abundance-weighted mean atom mass with one-twelfth of a carbon-12 atom's mass. Relative molecular mass , M_r, adds the relative atomic masses in a molecule. Relative formula mass applies the same sum to a formula unit, including giant structures. Both are ratios without units. **Molar mass** , M, is mass per mole, in $\text{g}\,\text{mol}^{-1}$.



Choose the route to amount.

Use $n = m/M$ for a mass, $n = cV$ for a solution with V in $\mathrm{dm^3}$, and $pV = nRT$ for a gas with pressure in Pa, volume in $\mathrm{m^3}$ and temperature in K. A stated molar gas volume can replace the gas equation only under its stated conditions. At the usual classroom RTP approximation, use $24\ \mathrm{dm^3\,mol^{-1}}$. Divide $\mathrm{cm^3}$ by 1000 to obtain $\mathrm{dm^3}$.

Worked reacting-mass method. The equation is $\mathrm{Mg + 2HCl \rightarrow MgCl_2 + H_2}$. There is excess acid and 0.480 g magnesium, with $M(\mathrm{Mg}) = 24.0\ \mathrm{g\,mol^{-1}}$.

$$n(\mathrm{Mg}) = \frac{m}{M} = \frac{0.480\ \mathrm{g}}{24.0\ \mathrm{g\,mol^{-1}}} = 0.0200\ \mathrm{mol}$$

The coefficient ratio is $\mathrm{Mg{:}H_2} = 1{:}1$, so $n(\mathrm{H_2}) = 0.0200$ mol. At the stated RTP approximation:

$$V = nV_m = 0.0200\ \mathrm{mol} \times 24\ \mathrm{dm^3\,mol^{-1}} = 0.48\ \mathrm{dm^3}$$

If both reactant amounts are given, compare amount divided by coefficient. The smaller value identifies the **limiting reagent**. Do not compare masses alone.

Mass concentration is m/V in $\mathrm{g\,dm^{-3}}$; amount concentration is n/V in $\mathrm{mol\,dm^{-3}}$. Divide mass concentration by molar mass to convert between them. Parts per million, ppm, is a fraction multiplied by 10^6; state whether it is a mass fraction or, for gases at the same temperature and pressure, a volume fraction.

Formulae and experimental checks

To find an **empirical formula**, divide each element's mass by its A_r and divide the resulting amounts by the smallest amount. Multiply the whole ratio if necessary to obtain integers. Do not round 1.5 to 2: multiply all ratios by 2. To find a molecular formula, divide measured M_r by empirical-formula mass and multiply every subscript by this integer.

Worked check. A compound contains 2.40 g carbon and 0.600 g hydrogen. Carbon amount is $n = m/M = 2.40/12.0 = 0.200$ mol; hydrogen atom amount is $n = m/M = 0.600/1.00 = 0.600$ mol. C:H = 1:3, so the empirical formula is $\mathrm{CH_3}$. If $M_r = 30.0$, the factor is $30.0/15.0 = 2$, giving $\mathrm{C_2H_6}$. The element masses add to the sample mass, 3.00 g.

Balance full equations without changing substance formulae, and include states: (s), (l), (g), (aq). For a precipitation, $\mathrm{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)}$ omits spectator ions. For an acid and carbonate, $\mathrm{CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)}$ conserves both atoms and charge. A precipitate or gas is an observation; an equation explains the change. Zinc in copper(II) sulfate gives a reddish copper deposit while the blue solution fades: $\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$. Magnesium in dilute acid dissolves with hydrogen bubbles: $\mathrm{Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)}$. An acid with a soluble base can warm without gas or precipitate: $\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)}$. Match each equation to the actual observation rather than treating every acid reaction as gas formation.

Percentage yield compares actual with theoretical product amount. For a theoretical 4.00 g and actual isolated dry 3.20 g, yield = $3.20/4.00 \times 100\% = 80.0\%$.

Atom economy compares the balanced desired-product mass with all balanced product masses. Include equation coefficients. A high atom economy does not guarantee a high experimental yield.

$$\text{yield} = \frac{\text{actual product mass}}{\text{theoretical product mass}} \times 100\%$$

$$\text{atom economy} = \frac{\text{desired product molar mass} \times \text{coefficient}}{\sum(\text{product molar mass} \times \text{coefficient})} \times 100\%$$

In the molar-gas-volume practical, use a known limiting amount and collect the gas under measured conditions. Account for leaks, gas dissolving, incomplete reaction and dead space. A leak lowers measured gas volume and therefore the calculated molar volume. To confirm a formula by reaction with oxygen, heat to constant mass, cool before weighing and explain how loss of solid or incomplete oxidation changes the inferred ratio. Practical reasoning remains part of this theory unit.

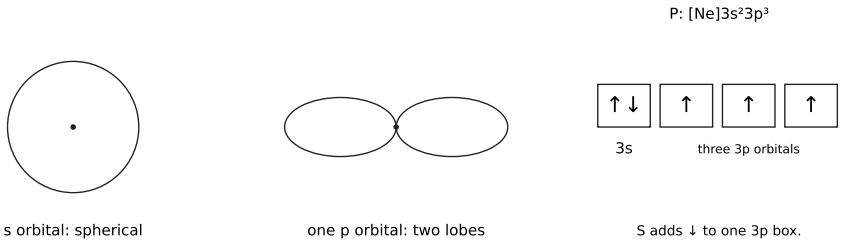
Electronic structure is evidence about the atom

Protons and neutrons are in the nucleus; electrons occupy orbitals around it. Relative particle masses are approximately 1, 1 and 1/1836; charges are +1, 0 and −1. Atomic number Z counts protons; mass number A counts protons plus neutrons. Thus neutrons $= A - Z$. A positive ion has fewer electrons than protons. **Isotopes** have the same proton number but different neutron numbers.

A mass spectrometer forms gaseous positive ions, separates them by mass-to-charge ratio , m/z, and detects relative abundance , the proportion of the sample contributing each ion type. Vaporisation, ionisation, acceleration, separation and detection have distinct roles. In magnetic separation at a given accelerating potential, a lower m/z ion bends more; a higher charge lowers m/z, rather than making bending smaller. A doubly charged mass-40 ion appears at $m/z = 20$.

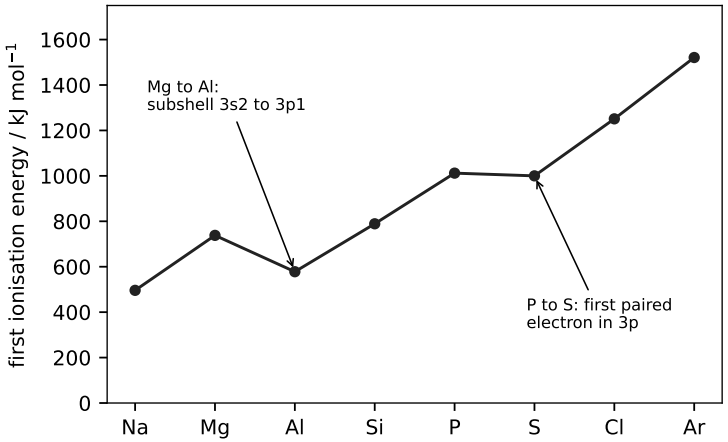
Worked isotope mean. For 60% mass-69 and 40% mass-71 gallium, $A_r = (69 \times 60 + 71 \times 40)/100 = 69.8$. The mean lies between the isotope masses, closer to the more abundant isotope. Molecular-ion peaks can identify M_r when charge is known. With chlorine isotope proportions 3:1, Cl_2 molecular-ion peaks at 70, 72 and 74 have probabilities 9/16, 6/16 and 1/16: the middle combination occurs in two orders.

An **orbital** holds at most two electrons with opposite spins. An s orbital is spherical; a p orbital has two lobes. There are 1, 3 and 5 orbitals in s, p and d subshells, holding at most 2, 6 and 10 electrons. Fill equal-energy orbitals singly before pairing. The first four quantum shells have maximum capacities 2, 8, 18 and 32 electrons. Their available subshells are 1s; 2s/2p; 3s/3p/3d; and 4s/4p/4d/4f. An f subshell has seven orbitals and holds fourteen electrons. The periodic table has s, p and d blocks according to the subshell receiving the differentiating electron. Write configurations through krypton, including the chromium and copper exceptions: Cr is $[Ar]3d^5 4s^1$ and Cu is $[Ar]3d^{10} 4s^1$. For their positive ions, remove 4s electrons before 3d electrons. Electron-box notation must show both occupancy and spin.



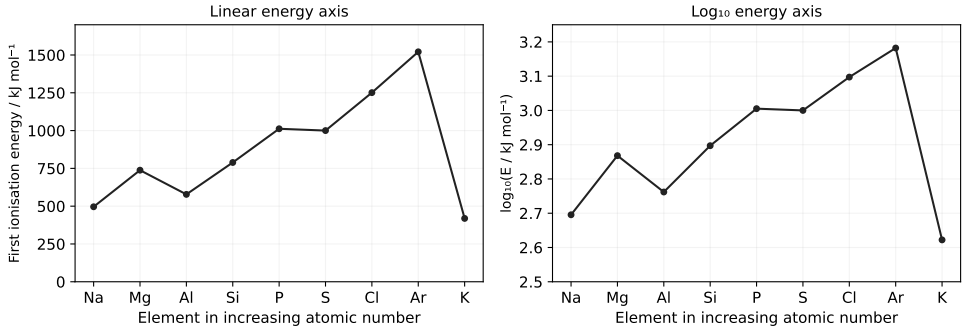
Orbital shapes and the singly occupied 3p orbitals in phosphorus.

First ionisation energy is the energy per mole for $X(g) \rightarrow X^+(g) + e^-$. Second ionisation removes an electron from $X^+(g)$; third ionisation is $X^{2+}(g) \rightarrow X^{3+}(g) + e^-$. All ionisation steps are endothermic. Greater nuclear charge strengthens attraction; more shielding and greater electron distance weaken it. A large successive-energy jump reveals that all outer-shell electrons have been removed. This identifies the main-group outer electron count but does not alone count every occupied shell.



First ionisation energies across Period 3 with the magnesium-to-aluminium subshell drop and the phosphorus-to-sulfur pairing dip annotated.

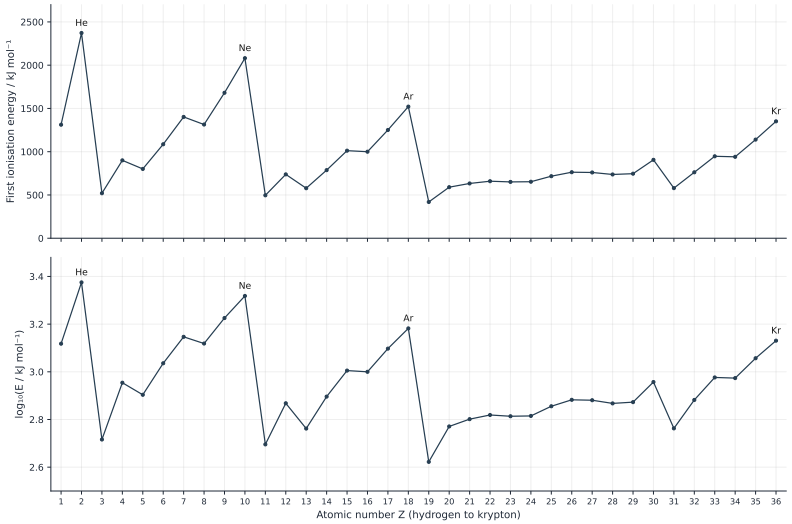
Across Period 3, nuclear charge rises while inner-shell shielding changes little, giving a broad first-ionisation increase. Al loses a higher-energy 3p electron more easily than Mg loses a 3s electron. S has a paired 3p electron with greater repulsion than the singly occupied 3p orbitals in P. Down a group, increased distance and shielding outweigh increased nuclear charge. Recurring trends across periods are **periodicity** ; use labelled axes, and interpret a logarithmic axis as ratios rather than equal energy increments.



The same ionisation data on linear and logarithmic axes; potassium starts the next period.

The supplied first-36-element graphing task on sheet 1.2.2 tests both ordinary and logarithmic axes. Noble-gas peaks are followed by decreases when a new outer shell starts; subshell and pairing effects produce additional dips within a period. The transition series does not form one perfectly smooth rising line. Helium belongs to

the s block by $1s^2$ despite its noble-gas column.

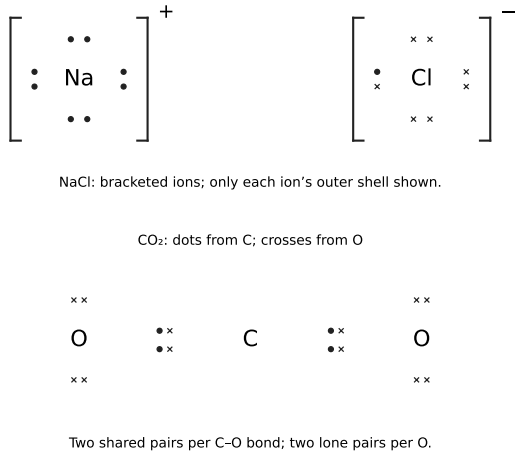


First ionisation energies through krypton on linear and logarithmic axes.

Bonding, shape and bulk properties

An **ionic bond** is the net electrostatic attraction between oppositely charged ions throughout a giant lattice. Electron transfer forms ions; the attraction is the bond. Conductivity when molten or dissolved, ion migration and electron-density evidence support the ionic model. Coloured cations move toward the negative electrode in solution. Electron-density maps show electron distribution around nuclei; compare the distribution with the ion model, rather than assuming a contour directly records the history of electron transfer. Ionic solids lack mobile ions. Smaller ions and higher charges usually strengthen lattice attraction. In an isoelectronic series, greater proton number pulls the same electron population closer: the radius decreases from N^{3-} toward Al^{3+}. Down a group, extra occupied shells increase radius.

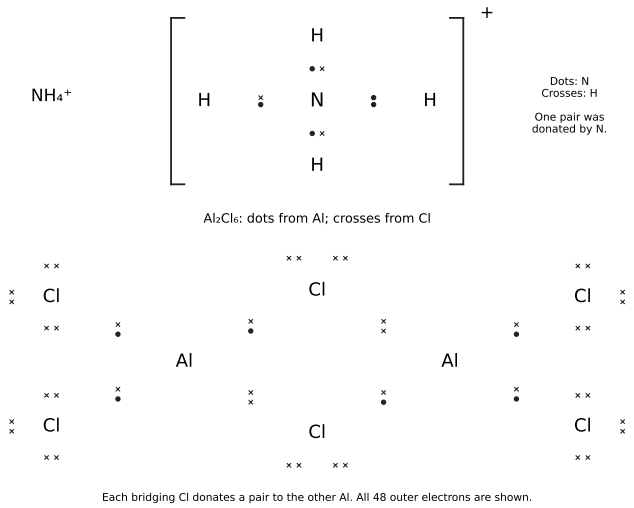
A **covalent bond** is attraction between two nuclei and a shared electron pair. Dot-and-cross diagrams identify electron origin. Include lone pairs and brackets/charge for ions. A coordinate bond uses a shared pair initially supplied by one atom, as when NH_3 donates a pair to H^+ to form NH_4^+. Aluminium chloride can form Al_2Cl_6 with two chloride bridges and coordinate bonding; electron diagrams must account for every outer electron.



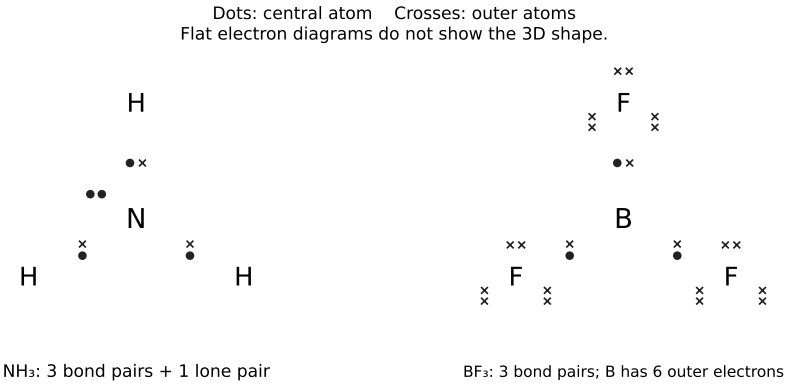
Ionic and multiple-bond outer-electron diagrams.



A triple bond and two lone pairs account for every outer electron of nitrogen.



Complete donor-pair diagrams for ammonium and aluminium chloride dimer.



Completed outer-electron diagrams.

Electron pairs around a central atom repel and arrange apart. Lone pairs repel more strongly than bonding pairs, but there is no universal fixed angle reduction per lone pair. Count regions around the central atom; a multiple bond occupies one region. Bond length is the distance between nuclei; bond angle is the angle between adjacent bonds.

Regions	Example	Shape and typical angle
2	$BeCl_2$, CO_2	linear, 180°
3	BCl_3	trigonal planar, 120°
4	CH_4, NH_4^+	tetrahedral, 109.5°
3 bonds + lone pair	NH_3	pyramidal, about 107°
2 bonds + 2 lone pairs	H_2O	bent, about 104.5°
5	gaseous PCl_5	trigonal bipyramidal, 90°/120°
6	SF_6	octahedral, 90°

Each carbon in ethene has three regions and a planar arrangement, with angles about 120°. **Electronegativity** is attraction for a bonding electron pair. Different electronegativities produce polar bonds. A molecule is polar only if its bond dipoles do not cancel: CO_2 is non-polar; H_2O is polar. Ionic and covalent bonding are ends of a continuum. Polarising power describes a cation's ability to distort another ion's electron cloud; polarisability describes how readily that cloud is distorted. A small, highly charged cation strongly distorts an anion's electron cloud; large anions are easier to polarise. Do not use one melting point alone as proof of structure.

Small molecular substances usually melt or boil by overcoming intermolecular attractions rather than breaking bonds inside molecules. Diamond has four covalent bonds per atom in a giant network; graphite has three per atom in layers and mobile delocalised electrons; graphene is a single layer. Diamond is hard and insulating; graphite layers can slide and conduct along them; graphene combines strength and conductivity. Metals contain positive ions attracted to delocalised electrons, which carry current in solid and molten metal.

The Period 2/3 melting trend follows changing structures: metallic elements, then giant covalent carbon/silicon, then small molecular non-metals and monatomic noble gases. In Period 2, lithium and beryllium are metallic; boron and carbon form giant covalent structures, then nitrogen, oxygen and fluorine are molecular and neon is monatomic. Molecular electron count and attractions help explain differences among the non-metals. A smooth nuclear-charge explanation alone cannot explain the whole melting trend. Stronger metallic attraction, involving ionic charge, ion size and the number of delocalised electrons, usually raises melting temperature; the detailed metal structure also matters. Heating a metal to melt it does not remove all its electrons.

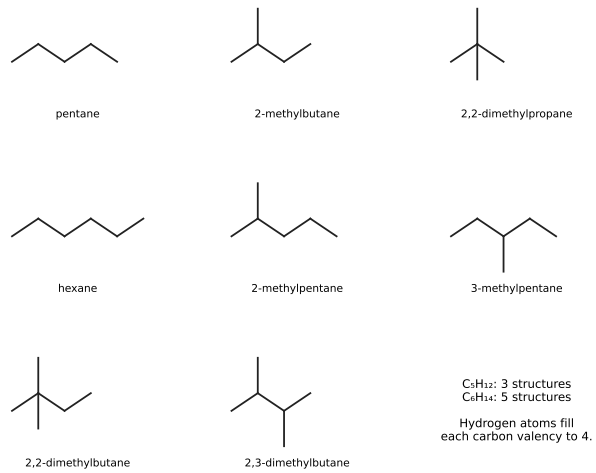
Organic formulae, fuels and radicals

A **functional group** gives characteristic reactions. A **homologous series** shares a functional group and general formula, with successive members differing by CH_2. Structural isomers have the same molecular formula but different atom connectivity. In displayed formulae show every atom and bond; in skeletal formulae each unlabelled end or corner is carbon, with enough implied H atoms for four bonds. Show heteroatoms and their attached hydrogen explicitly.

Use meth-, eth-, prop-, but-, pent-, hex-, hept-, oct-, non-, dec- for one to ten carbon

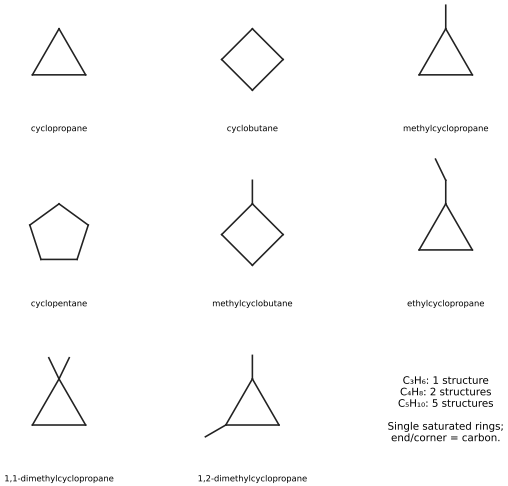
atoms. Choose a parent containing the relevant functional group and number to give its required lowest locant, then locate substituents. Acyclic alkanes have formula C_nH_{2n+2}; single-ring cycloalkanes have C_nH_{2n}. Both are saturated: they contain only carbon–carbon single bonds. C_nH_{2n} alone does not prove an alkene because a cycloalkane can share it.

Generate structural isomers systematically: keep the formula fixed, change the longest chain or ring size, distribute the remaining carbon atoms, then remove rotated or renumbered duplicates. Pentane has three chain isomers; hexane has five. A different drawing direction alone does not make a new structure.

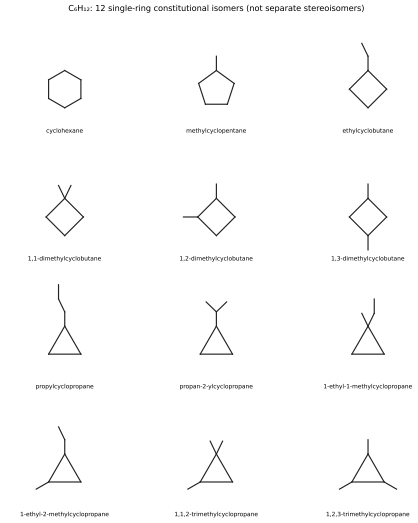


Complete chain-isomer formulae for pentane and hexane.

For saturated single rings, begin with the largest ring and shorten it while moving carbons into substituents. There is one C_3H_6 ring structure, two C_4H_8 and five C_5H_{10} structures. The C_6H_{12} set has twelve constitutional structures; distinct cis/trans forms are not counted again as structural isomers.



Complete single-ring structures for three, four and five total carbon atoms.



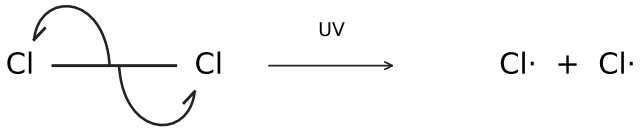
Complete single-ring structures for six total carbon atoms.

Fractional distillation separates crude oil into fractions with different boiling ranges. Cracking converts larger hydrocarbons to smaller products, including alkenes; reforming can change straight chains to branched or cyclic structures. Balance atoms in every proposed equation. Complete combustion of a hydrocarbon forms CO_2 and water. Incomplete combustion can form toxic CO or carbon particulates; CO reduces blood oxygen transport by binding haemoglobin. Fuel sulfur and high-temperature

nitrogen/oxygen reactions can produce acidic oxides. Carbon particulates harm air quality; unburned hydrocarbons can contribute to photochemical pollution. Removing fuel sulfur does not prevent nitrogen oxides formed from hot air. Carbon neutrality means no net carbon dioxide increase over the stated life-cycle boundary. Bioethanol's growth can take up CO_2, but processing and transport emissions prevent automatic carbon-neutral claims. Hydrogen makes water at use; its production method still matters.

A **hazard** is a potential source of harm; risk considers its likelihood and severity under actual conditions. Use the school's risk assessment, small quantities, ventilation and controls specific to flammability or toxicity. A safer alternative can reduce risk without pretending the original substance has no hazard.

A **free radical** has an unpaired electron. Homolytic fission gives one electron to each fragment; heterolytic fission gives both to one fragment, forming ions. UV light starts chlorine substitution by breaking Cl_2 homolytically: $Cl_2 \rightarrow 2Cl\cdot$. Use single-headed curly arrows for individual electrons.



Homolysis: one electron from the bond goes to each chlorine atom.
Each curly half-arrow tracks one electron.

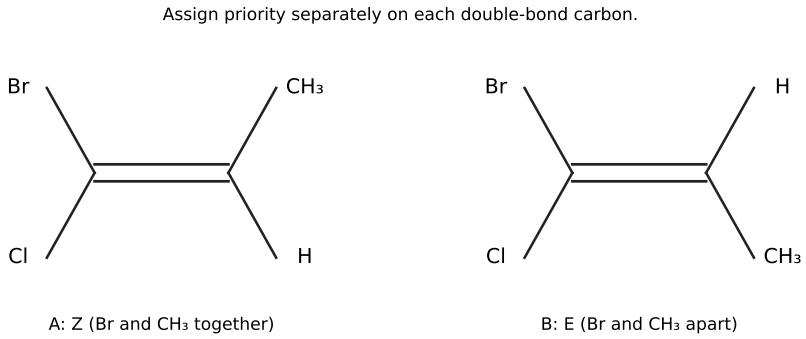
UV initiation uses two single-electron half-arrows.

Propagation: $Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$, then $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$. One radical is regenerated, so the chain continues. Termination joins two radicals, for example $2CH_3\cdot \rightarrow C_2H_6$. Further substitution and multiple possible positions produce mixtures, limiting the method's value for making one pure product.

Alkenes: follow the electron pair

An acyclic alkene with one C=C has formula C_nH_{2n}. A cycloalkene with one ring and one double bond has C_nH_{2n-2}: the ring removes another two hydrogens. A double bond consists of a sigma bond σ from head-on orbital overlap and a pi bond π from sideways p-orbital overlap. Rotating one carbon would break pi overlap, so rotation is restricted. **E/Z isomerism** requires two different groups on each double-bond carbon. Rank the directly attached atoms by atomic number; if tied, compare the next atoms. Compare priorities separately on the two carbons. Higher-priority groups together give Z, opposite give E. Cis/trans is insufficient where

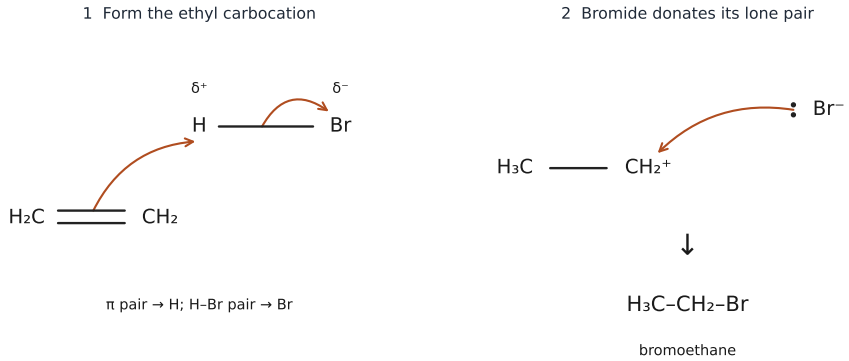
no suitable identical substituents can be compared.



Assign E/Z from the priorities on each carbon.

An **electrophile** accepts an electron pair. In HBr addition, a curly arrow begins at the pi bond and ends at H, while another begins at the H–Br bond and ends at Br. This forms a carbocation and Br^-; a bromide lone pair then forms the new carbon–bromine bond. Propene mainly gives 2-bromopropane because its route forms a secondary rather than primary carbocation. Tertiary carbocations are generally more stable than secondary, which are more stable than primary, under these conditions.

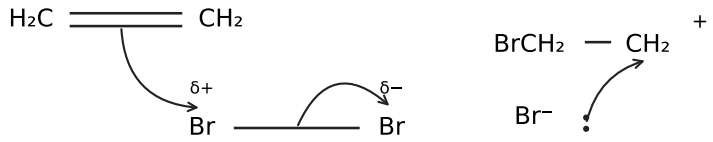
For **ethene**, the two double-bond carbons are equivalent. Proton addition in either direction makes the same ethyl carbocation, $CH_3CH_2^+$. Bromide donates a lone pair to its positive carbon, giving bromoethane; there are no two different constitutional products to choose between.



Complete electron-pair mechanism for ethene and hydrogen bromide.

Bromine is polarised by the electron-rich double bond and adds across it; ethene forms 1,2-dibromoethane. Bromine decolourisation supports unsaturation in an appropriate organic test but does not identify one unique alkene. Avoid unrequired claims about

stereochemical product mixtures.

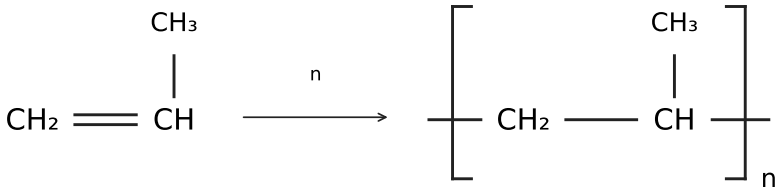


Product: $BrCH_2–CH_2Br$

Simple electrophilic-addition model: π pair → Brδ⁺; Br–Br pair → Brδ⁻.
A bromide lone pair supplies the second C–Br bond.

Electron-pair arrows for bromine addition to ethene in the simple carbocation model.

Other additions: hydrogen with nickel gives an alkane; steam with an acid catalyst gives an alcohol; cold, dilute acidified manganate(VII) oxidises C=C to a diol. State reagents and conditions, not only product names. In **addition polymerisation** , open each C=C into the polymer backbone, retain its side groups, and show brackets with bonds extending through them and n outside. A repeat unit is the smallest backbone segment whose repetition describes the chain, including its side groups. No small molecule is eliminated. Polymer disposal needs evidence: sorting/recycling, persistence, biodegradable alternatives and removal of toxic incineration gases have different advantages and costs.



Propene → poly(propene); continuation bonds cross the brackets.
Side groups stay attached; no small molecule is eliminated.

Propene polymerisation preserves the methyl side group and shows continuation bonds.

Independent checks

1. A mass-40 ion gives $m/z = 20$. Explain its charge.
2. An element's first three ionisation energies are relatively close; the fourth is much greater. State what you can infer and what you cannot infer from this jump alone.
3. A gas occupies 0.240 dm^3 at a molar volume of 24.0 $dm^3\ mol^{-1}$. A 0.480 g sample made this gas in a 1:1 reaction. Find the sample's molar mass and state one reason the experimental value could be too high.
4. Why can the same molecular formula describe an alkene and a cycloalkane?
5. Predict the product when HBr adds to $CH_2{=}C(CH_3)_2$, and explain the preferred carbocation.

Answers. 1 A 2+ ion has half the singly charged mass-to-charge ratio. 2 Three outer electrons, consistent with main Group 3/13; the jump alone does not establish period. 3 $n = V/V_m = 0.240/24.0 = 0.0100$ mol; $M = m/n = 0.480/0.0100 = 48.0\ g\,mol^{-1}$. A leak lowers measured gas amount and raises inferred molar mass. 4 One ring or one double bond each reduces H count by two relative to an acyclic alkane. 5 2-bromo-2-methylpropane; H adds to CH_2, forming a tertiary carbocation before Br^- supplies a pair to the positive carbon.

2 · Energetics, Group Chemistry, Halogenoalkanes and Alcohols

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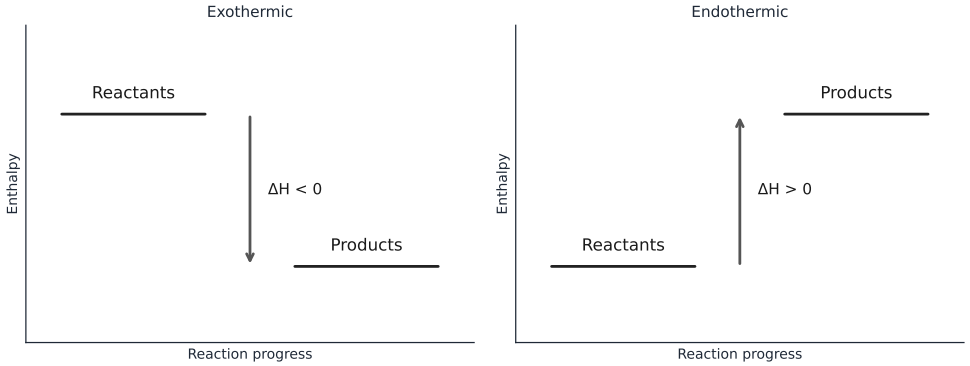
Choose a model before choosing an equation

A flask can get warmer while the reacting chemicals lose energy. A clear solution can form a white precipitate without any change in oxidation number. This unit connects observations to models: energy transfer, attractions, electron transfer, collisions and reaction pathways. Start by identifying which model explains the evidence.

Prerequisites: Unit 1 mole ratios, electronic configuration, bond polarity, structural formulae and electron-pair arrows. The scope is Pearson Topics 6–10. Core practicals 2–8 are taught where they support these topics; a reference cannot replace supervised practical experience. Follow the school risk assessment. Hazardous halogen, concentrated-acid and organic preparations require approved laboratory supervision.

Enthalpy: define the reaction, then follow the energy

An **enthalpy change** , ΔH, is the heat energy change at constant pressure. Standard conditions mean a pressure of 100 kPa and a stated temperature, usually 298 K. State symbols matter: making liquid water releases a different amount of energy from making water vapour. An exothermic reaction has $\Delta H < 0$; an endothermic reaction has $\Delta H > 0$. In an enthalpy-level diagram, put reactants and products on horizontal levels. The arrow runs from reactants to products; its vertical change gives ΔH.



Initial/final enthalpy levels and signs.

These definitions specify different reactions, each under standard conditions with substances in their standard states:

Change	What the equation must represent
Standard enthalpy of reaction	The reaction exactly as written, including its coefficients
Standard enthalpy of formation	Formation of **one mole** of compound from its elements
Standard enthalpy of combustion	Complete burning of **one mole** of substance in oxygen
Standard enthalpy of neutralisation	Formation of **one mole of water** by reaction of an acid and an alkali
Standard enthalpy of atomisation	Formation of **one mole of gaseous atoms** from the element

For example, $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ is an atomisation equation, whereas $Cl_2(g) \rightarrow 2Cl(g)$ describes twice that amount. The standard formation enthalpy of an element in its standard state is zero by convention, not because the element has no energy.

A complete calorimetry calculation

Mix 50.0 cm^3 of 1.00 mol dm^{-3} HCl with 50.0 cm^3 of 1.00 mol dm^{-3} NaOH. Both start at the same temperature; the corrected rise is 6.8 °C. Assume density 1.00 g cm^{-3}, specific heat capacity 4.18 J g^{-1} $°C^{-1}$ and negligible cup heat capacity.

$$m = \rho V = 1.00\ \text{g cm}^{-3} \times 100.0\ \text{cm}^3 = 100.0\ \text{g}$$

$$q_{\text{solution}} = mc\Delta T = 100.0\ \text{g} \times 4.18\ \text{J g}^{-1}\,°\text{C}^{-1} \times 6.8\ °\text{C} = 2842\ \text{J}$$

$$n(\text{H}_2\text{O}) = cV = 1.00\ \text{mol dm}^{-3} \times 0.0500\ \text{dm}^3 = 0.0500\ \text{mol}$$

$$\Delta H_{\text{neut}} = -\frac{q_{\text{solution}}}{n(\text{H}_2\text{O})} = -\frac{2.842\ \text{kJ}}{0.0500\ \text{mol}} = -56.8\ \text{kJ mol}^{-1}$$

The solution gains energy, so the reaction loses it. Use the **total heated mass**, but the limiting reacting amount. For unequal acid and alkali amounts, calculate both before finding the water amount. In a combustion experiment, water heated is not the fuel amount: obtain the latter from the burner's mass loss and the fuel molar mass.

Use a lid, insulation and stirring, and measure temperatures before and after mixing at regular times. Extrapolate the post-reaction cooling line to the mixing time when the method requires a cooling correction. Heat lost to the surroundings or absorbed by the cup makes an uncorrected exothermic result less negative. Incomplete combustion and fuel evaporation also make a combustion result less negative. Repeats help random variation; they do not remove these systematic effects. A large temperature rise reduces percentage thermometer uncertainty but must remain safe.

Hess cycles and bond enthalpies

Hess's law says that the enthalpy change depends on the initial and final states, not the route. Reverse an equation: reverse the sign. Multiply its coefficients: multiply its enthalpy. Add equations and cancel species, including their states, before adding the enthalpies.

For $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$, use $C + O_2 \rightarrow CO_2$, $\Delta H = -394$ kJ mol^{-1}, and the reverse of $CO + \frac{1}{2}O_2 \rightarrow CO_2$, whose forward $\Delta H = -283$ kJ mol^{-1}. The target is the sum, so $\Delta H = -394 - (-283) = -111$ kJ mol^{-1}. A cycle using formation data gives $\sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$, with coefficients included. A combustion cycle gives the reactant combustion sum minus the product combustion sum.

Core practical 2 compares dissolution/reaction routes to the same final solution. Match amounts and final states, account for each measured temperature change, and test whether experimental error explains disagreement. A cycle with unmatched final concentrations is not exactly the same thermodynamic route.

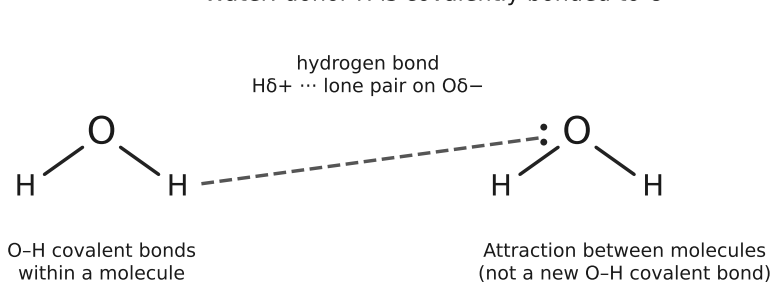
A **mean bond enthalpy** is the average energy needed to break one mole of a specified covalent bond in gaseous molecules. Bond breaking takes energy; bond formation releases it.

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

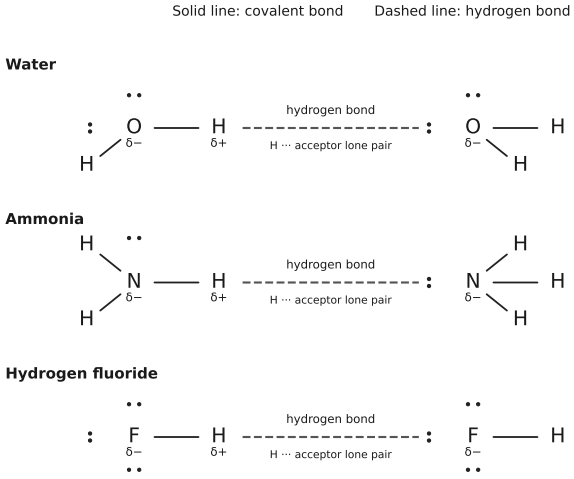
For $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, let H–H = 436, Cl–Cl = 243 and H–Cl = 431 kJ mol^{-1}. Then $\Delta H \approx 436 + 243 - 2(431) = -183$ kJ mol^{-1}. Conversely, if $\Delta H = -184$ kJ mol^{-1}, $E(\text{H} - \text{Cl}) = [436 + 243 - (-184)]/2 = 431.5$ kJ mol^{-1}. Mean values average different molecular environments and assume gas-phase bonds, so the estimate may differ from measured reaction enthalpy. A weak bond may break more readily, but reaction speed also depends on the whole activation pathway; ΔH alone does not predict rate.

Intermolecular forces: explain the particles that separate

All atoms and molecules have London forces , caused by instantaneous dipoles inducing dipoles in neighbouring particles. More electrons and a more polarisable electron cloud usually strengthen these forces. Permanent dipole–dipole attractions also occur between polar molecules . A **hydrogen bond** is an attraction between H bonded to N, O or F and a lone pair on N, O or F of another molecule. An O–H covalent bond within ethanol is not itself a hydrogen bond.



Hydrogen bonding between water molecules.



Complete hydrogen-bond pair answers; line drawings are schematic, not three-dimensional shape models.

Water, ammonia and hydrogen fluoride hydrogen-bond. Ethanol also has an O–H donor and oxygen lone pairs. An ether has oxygen lone pairs and can accept hydrogen bonds from water, but cannot hydrogen-bond to another ether molecule using an O–H donor. Use the actual structure rather than just finding oxygen in the formula.

Explain boiling by the attractions **between** molecules, not by breaking every covalent bond. Longer alkane chains usually have more electrons and stronger London forces, so boiling temperatures rise. For isomeric alkanes, branching makes molecules more compact and reduces effective contact, so boiling temperature usually falls. An alcohol has a higher boiling temperature than a similar-size alkane because additional hydrogen bonding requires more energy to overcome. From HCl to HBr to HI, larger electron

clouds strengthen London forces; HF is unusually high because it hydrogen-bonds.

Water has unusually high melting and boiling temperatures for its molecular size. Ice contains an open hydrogen-bonded arrangement. On melting, some of this arrangement collapses, bringing molecules closer; liquid water is denser than ice near the melting point. It is incorrect to explain floating ice by saying its molecules become larger.

Solubility depends on the balance between attractions broken and attractions formed. Water hydrates ions: the partially negative oxygen faces cations and partially positive hydrogens face anions. Small alcohols mix well with water because their O–H groups hydrogen-bond; a growing non-polar carbon chain reduces this advantage. Many halogenoalkanes have polar C–X bonds yet dissolve poorly in water: they cannot replace the water–water hydrogen-bond network effectively. A non-aqueous solvent with similar intermolecular attractions can be more suitable. "Polar dissolves polar" is a useful starting comparison, not a universal rule.

Redox and Groups 1 and 2: track electrons and charge density

An **oxidation number** is a bookkeeping value, written with a sign; the total equals the charge on the species. Elements have zero. Group 1 is usually +1 and Group 2 +2. Oxygen is usually −2, but −1 in peroxides; hydrogen is usually +1, but −1 in metal hydrides. Use the sum rule when a familiar rule has an exception. For example, in $Cr_2O_7^{2-}$, $2x + 7(-2) = -2$, so chromium is +6. Iron(III) oxide is Fe_2O_3 because two +3 and three −2 sum to zero.

Oxidation is electron loss and an increase in oxidation number. Reduction is electron gain and a decrease. An oxidising agent **gains** electrons and is reduced; a reducing agent loses electrons and is oxidised. To combine half-equations, multiply them until electrons lost equal electrons gained, then cancel electrons. For example, $Mg \rightarrow Mg^{2+} + 2e^-$ and $Cl_2 + 2e^- \rightarrow 2Cl^-$ give $Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$. Check both atoms and charge.

Down Groups 1 and 2, increasing radius and shielding reduce attraction to the outer electron despite increasing nuclear charge. First ionisation energy decreases and reaction by electron loss becomes easier. Group 1 metals Li to K and Group 2 metals Mg to Ba therefore become more reactive down their groups.

Reaction	Pattern and important conditions
Group 1 + water	$2M + 2H_2O \rightarrow 2MOH + H_2$; alkaline solution, increasingly vigorous down Li to K
Group 2 + water	$M + 2H_2O \rightarrow M(OH)_2 + H_2$; Mg reacts very slowly with cold water; steam gives MgO and H_2
Metals + chlorine	Group 1 gives MCl; Group 2 gives MCl_2; metals are oxidised and chlorine reduced
Metals + oxygen	Group 2 normally gives MO; lithium gives Li_2O, sodium commonly peroxide Na_2O_2, potassium commonly superoxide KO_2 in excess oxygen
Basic oxides + acid	$MO + 2H^+ \rightarrow M^{2+} + H_2O$ for Group 2
Oxides + water	Group 1 oxides give soluble hydroxides; Group 2 oxides give hydroxides with varying rate/solubility; MgO reacts slowly
Hydroxides + acid	Neutralisation; e.g. $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

Group 2 hydroxide solubility increases down the group; sulfate solubility decreases. Thus $BaSO_4$ is a useful insoluble precipitate, whereas $Ba(OH)_2$ is more soluble than $Mg(OH)_2$. Keep solubility distinct from strength: the dissolved Group 2 hydroxide supplies hydroxide ions, but a small dissolved amount limits concentration.

Small cations with high charge density strongly polarise large anions. Lithium and the smaller Group 2 cations therefore make their carbonates and nitrates less thermally stable. Stability increases down each group as cation size increases. Most Group 1 carbonates resist ordinary laboratory heating; Li_2CO_3 decomposes to $Li_2O + CO_2$. Group 2 carbonates give $MO + CO_2$. Group 1 nitrates except lithium give nitrite + oxygen, $2MNO_3 \rightarrow 2MNO_2 + O_2$. Lithium and Group 2 nitrates give oxide, brown NO_2 and oxygen; e.g. $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$. Compare equal amounts under controlled heating; do not confuse a faster gas-production rate with a directly measured decomposition temperature. NO_2 is toxic and acidic; use approved ventilation. CO_2 turns limewater milky; oxygen relights a glowing splint.

For a controlled thermal comparison, use comparable measured molar amounts, particle size and apparatus with the same heating rate. Record sample temperature at the same agreed detectable onset or extent of decomposition. Bubble time alone also depends on heating and gas collection, so it does not directly measure thermal stability. Record the apparatus and detection limit; decomposition need not occur at one universal sharp temperature.

Flame colours arise when excited electrons fall to lower energy levels and emit photons of characteristic energies. Li is crimson, Na yellow, K lilac, Ca brick-red, Sr crimson-red and Ba apple-green; Mg has no characteristic flame-test colour. Clean the wire with hydrochloric acid and heat until no colour remains according to the approved method.

Use separate samples and keep the flame region and loading method consistent; avoid sodium contamination. White burning magnesium is not a diagnostic magnesium-ion flame colour.

Ion tests and volumetric analysis

Use separate aliquots so one test's reagent cannot contaminate the next.

Ion	Test and observation	Ionic reasoning
Carbonate/hydrogencarbonate	Add dilute acid; gas turns limewater milky	$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$; $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$
Sulfate	Acidify with dilute HCl, then add $BaCl_2$(aq); white precipitate	$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$(s); acid removes carbonate interference
Ammonium	Add NaOH(aq), warm gently; gas turns damp red litmus blue and gives white fumes with HCl	$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; $NH_3 + HCl \rightarrow NH_4Cl$
Halide	Acidify with dilute HNO_3, then add $AgNO_3$(aq)	$Ag^+ + X^- \rightarrow AgX$(s); do not introduce chloride with HCl

AgCl is white and dissolves in dilute ammonia. AgBr is cream, insoluble in dilute ammonia but dissolves in concentrated ammonia. AgI is yellow and insoluble in both. These tests identify halide ions already in solution; a covalently bonded halogen in a halogenoalkane first needs hydrolysis .

A **standard solution** has an accurately known concentration. For core practical 4, accurately weigh a suitable solid acid, dissolve it in deionised water, transfer quantitatively to a volumetric flask , rinse the vessel/funnel into the flask, make to the mark at eye level and mix by repeated inversion. Choose its concentration using mass, molar mass and flask volume. Do not make to the mark before the solid has dissolved and reached room temperature.

For core practicals 3 and 4, rinse the burette with its titrant and the pipette with the solution it will transfer; rinse the conical flask with deionised water. Remove the filling funnel, ensure the jet is filled, read the meniscus at eye level and record final minus initial readings. Swirl and add drops near the endpoint over a white tile. Use a rough titre to locate the endpoint, then obtain concordant accurate titres. Do not average the rough titre with accurate ones. Methyl orange is yellow in alkali and red in acid; phenolphthalein is pink in alkali and colourless in acid. Select an indicator whose colour change lies in the sharp endpoint region.

■ Amount ratio before concentration

25.00 cm^3 of 0.0500 mol dm^{-3} Na_2CO_3 needs 24.60 cm^3 of HCl. The equation is $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$.

$$n(Na_2CO_3) = cV = 0.0500 \times 0.02500 = 0.001250 \text{ mol}$$

$$n(HCl) = 2n(Na_2CO_3) = 0.002500 \text{ mol}$$

$$c(HCl) = \frac{n}{V} = \frac{0.002500 \text{ mol}}{0.02460 \text{ dm}^3} = 0.1016 \text{ mol dm}^{-3}$$

Mass concentration is cM in g dm^{-3}. If each burette reading has uncertainty ± 0.05 cm^3, the maximum uncertainty in a titre is ± 0.10 cm^3; here $100(0.10/24.60) = 0.41\%$. Add relevant percentage uncertainties for a product/quotient as a maximum estimate. A larger appropriate titre lowers relative reading uncertainty. Repeating an endpoint does not correct a wrongly prepared standard.

Halogens: oxidising power and disproportionation

Chlorine is a pale green gas, bromine a red-brown liquid and iodine a grey-black solid at room temperature; iodine vapour is purple. Down Cl_2, Br_2, I_2, larger electron clouds strengthen London forces, raising melting and boiling temperatures. Electronegativity decreases as increasing radius and shielding weaken attraction for a shared bonding electron pair. Oxidising power also decreases: attraction for an incoming electron becomes weaker. Distinguish the bonding-pair definition from electron gain in redox; the electron-gain argument also differs from Group 1 electron loss.

Chlorine displaces bromide and iodide; bromine displaces iodide; iodine displaces neither. For example, $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$. Bromide loses electrons and is the reducing agent. In water, chlorine is pale green, bromine orange/brown and iodine brown; in the stated inert non-polar organic solvent, chlorine is pale yellow-green, bromine orange and iodine violet. State the solvent when using colour as evidence. Predict fluorine to be a stronger oxidant and astatine a weaker oxidant from the trend; do not invent a safe school test for either.

In **disproportionation** , the same element in one species is both oxidised and reduced. Chlorine with water gives $Cl_2 + H_2O \rightleftharpoons HCl + HClO$: Cl goes from 0 to -1 and $+1$. Chlorine water disinfects because chlorine-containing oxidants destroy microorganisms. Balance the benefit against toxicity and harmful by-products rather than claiming it is risk-free.

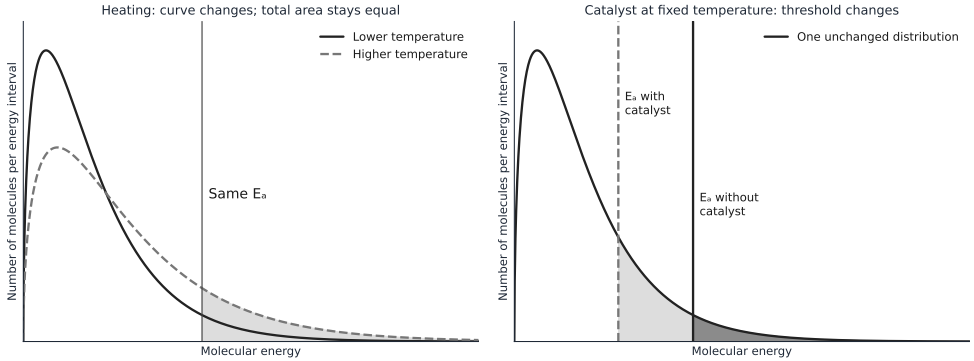
Cold dilute alkali gives $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$, the basis of hypochlorite bleach. Hot concentrated alkali gives $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$; chlorine becomes -1 and $+5$. Analogous bromine and iodine equations follow the same atom/charge accounting under the specified conditions.

With concentrated H_2SO_4, solid chloride salts undergo acid–base reaction to release HCl; chloride is not a sufficiently strong reducing agent to reduce the acid under these conditions. Bromide first gives HBr, which can reduce sulfur from $+6$ to $+4$ in SO_2 while forming Br_2: $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$. Iodide is a stronger reducing agent and can give sulfur and H_2S as well as SO_2, with iodine formed. The sulfur routes include $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$ and $6HI + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$. For H_2S: $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$. These are hazardous supervised demonstrations, not instructions for independent gas generation. Hydrogen halides dissolve in water to form acids and react with ammonia to form ammonium halides: $HX + NH_3 \rightarrow NH_4X$.

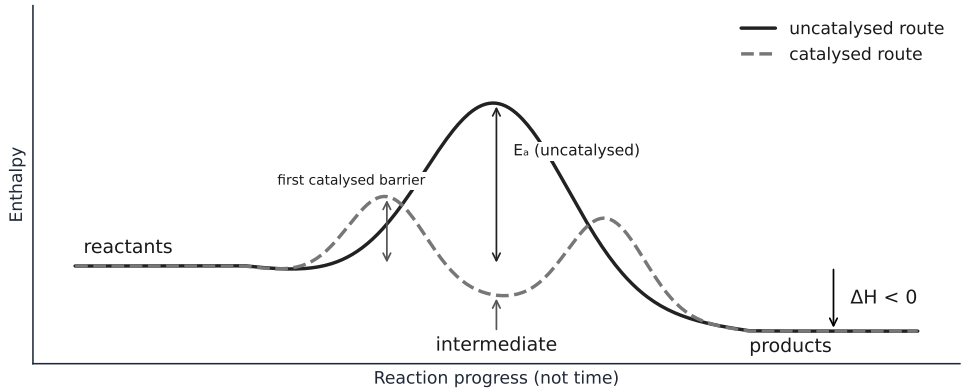
Rates and equilibria: separate speed from final composition

Reaction needs collisions with sufficient energy to overcome the **activation energy** and a suitable orientation. Greater concentration, gas pressure or exposed solid surface increases collision frequency. Higher temperature increases collision frequency and, more importantly, the fraction with energy at least E_a.

On a Maxwell–Boltzmann energy distribution, temperature increase makes the peak lower and shifts it to higher energy; the area stays the same for the same number of molecules. The high-energy area beyond E_a increases. A catalyst provides another pathway with lower activation energy. At the same temperature it does **not** change the distribution, but moves the energy threshold left so more collisions can react. A catalysed reaction profile may have two peaks separated by an intermediate; neither the reactant/product levels nor ΔH changes.



Heating changes distribution; catalyst changes threshold at fixed temperature.



Catalysed and uncatalysed energy routes.

For a fixed visible endpoint, $1/t$ is a comparative rate measure in s^{-1}, provided each trial reaches the same extent of reaction. It is not automatically a rate in mol dm^{-3} s^{-1}. On a gas-volume–time graph, average rate is $\Delta V/\Delta t$; instantaneous rate is a tangent gradient. If a tangent passes through (10 s, 12 cm^3) and (50 s, 36 cm^3), its gradient is $(36 - 12)/(50 - 10) = 0.60$ cm^3 s^{-1}. Use points on the tangent, not two nearby curve points. A faster reaction need not make more final product if the limiting amount is unchanged.

Dynamic equilibrium requires a closed system. Forward and reverse reactions continue at equal rates; concentrations remain constant but need not be equal. Increasing a reactant concentration shifts equilibrium toward its consumption. Increasing pressure favours the side with fewer **gas** moles; if gas coefficients are equal, there is no composition shift. Increasing temperature favours the endothermic direction. A catalyst speeds both directions and reaches the same equilibrium sooner.

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, with exothermic forward reaction, high pressure and low temperature favour ammonia yield. Low temperature slows reaction; very high pressure raises energy, equipment and safety costs. Industrial conditions balance rate, yield, separation/recycling and cost. A catalyst permits an adequate rate at lower temperature; it does not itself increase the equilibrium yield. More selective catalysts can also improve atom economy by reducing unwanted pathways, but this is a different claim from shifting equilibrium.

Halogenoalkanes: choose substitution or elimination

A **nucleophile** donates an electron pair to form a covalent bond. The polar C–X bond has a partially positive carbon. A curly arrow starts at a lone pair or bond, not at a positive charge. Heterolytic breaking gives both bond electrons to one atom, producing ions. A mechanism shows electron movement, not just an overall equation.

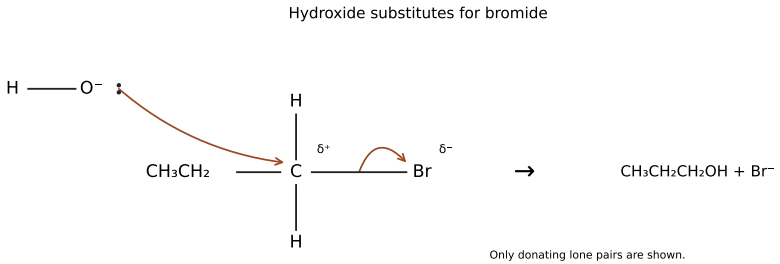
Classify a halogenoalkane by the number of carbon groups attached to the carbon bearing X: one primary, two secondary, three tertiary. This is not the position number in its name. 1-bromobutane is primary; 2-bromobutane is secondary; 2-bromo-2-methylpropane is tertiary.

Reagent and conditions	Main change	Example carbon-count check
Aqueous KOH, warm/reflux	Substitution; OH^- is a nucleophile	$CH_3CH_2Br \rightarrow CH_3CH_2OH$; 2 C remain 2 C
Ethanolic KOH, heat	Elimination; OH^- acts as a base	$CH_3CH_2Br \rightarrow CH_2{=}CH_2 + HBr$ removed overall
Excess alcoholic NH_3, heat under pressure	Substitution to an amine	$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$
Alcoholic KCN, heat/reflux	Substitution to a nitrile	$CH_3CH_2Br \rightarrow CH_3CH_2CN$; 2 C become 3 C
Water with $AgNO_3$ in ethanol	Hydrolysis; water is the nucleophile	Halide released forms AgX(s); ethanol helps mix reactants

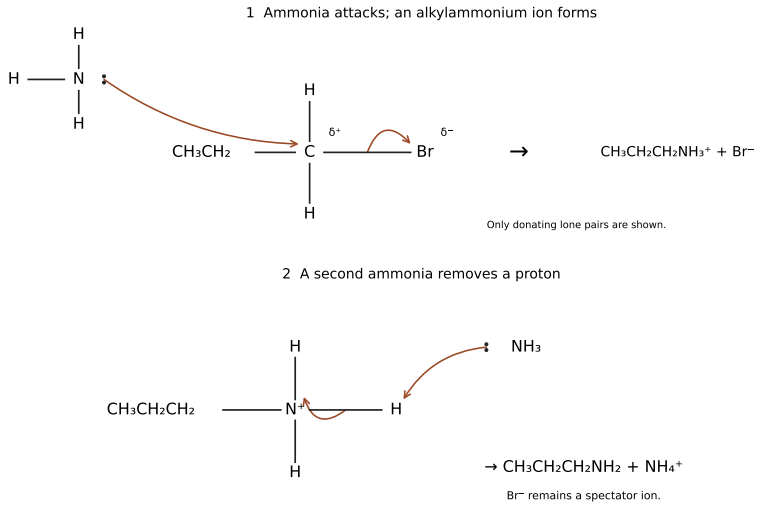
For primary bromoethane and OH^-, draw one arrow from an oxygen lone pair to the carbon bearing Br and another from the C–Br bond to Br. Products are ethanol and Br^-. For ammonia, the same electron-pair attack gives $CH_3CH_2NH_3^+$ and Br^-; a second ammonia removes H^+ to give $CH_3CH_2NH_2$ and NH_4^+. Include this proton-transfer step and charges. Detailed S_N1/S_N2 kinetics are Unit 4 material.

■ Complete primary substitution drawings

The following original example uses **1-bromopropane**, so count three carbons throughout. The hydroxide mechanism gives propan-1-ol; the ammonia route gives propan-1-amine after proton transfer. Only the donating lone pairs are drawn. The first ammonia stage produces a positively charged nitrogen with four bonds; the second restores three bonds and a lone pair. Bromide remains present while the second ammonia becomes ammonium.



Primary hydroxide substitution with electron-pair arrows.



Both ammonia substitution stages including proton transfer.

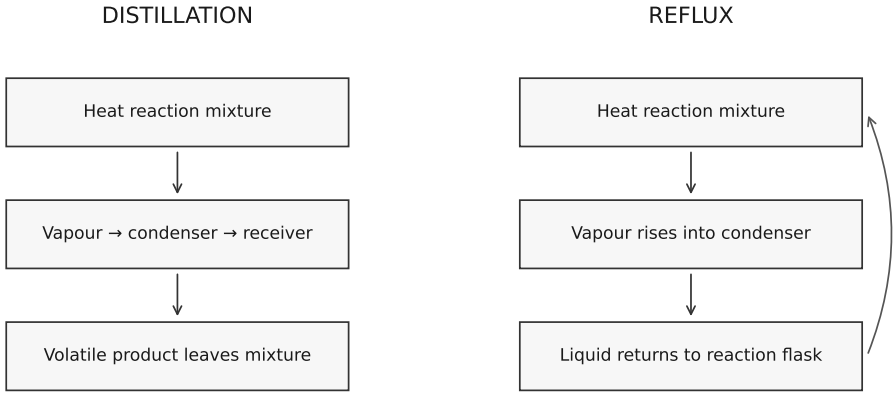
In core practical 5, compare equal concentrations/volumes of halogenoalkanes with the same silver nitrate/ethanol mixture at controlled temperature. Time formation of a comparable precipitate. Iodoalkanes hydrolyse faster than bromoalkanes, which hydrolyse faster than chloroalkanes, because C–I is weaker than C–Br and C–Cl. C–F is strongest and least easily broken. Do not use C–X polarity alone to predict this order. In the specified aqueous/ethanolic hydrolysis comparison, tertiary halogenoalkanes generally react faster than secondary, then primary. Solvent, concentration and detection conditions must be matched; precipitate appearance is an indirect rate measure.

Core practical 6 converts 2-methylpropan-2-ol to 2-chloro-2-methylpropane using concentrated HCl. Explain substitution of OH by Cl, separation of organic/aqueous layers, removal of acidic impurities, drying and purification. A separating funnel must be vented as specified by the approved method; identify layers using density/evidence, not an assumption that all organic liquids float. No naked flame near flammable organics.

Alcohols, purification and spectral evidence

Classify alcohols by the carbon attached to OH, not by counting all OH groups. Primary propan-1-ol oxidises with potassium dichromate(VI) in dilute sulfuric acid. Distil the aldehyde as it forms to limit further oxidation: $CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$. Heat under reflux with excess oxidant to make the acid: $CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$. Secondary propan-2-ol gives propanone: $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$. Tertiary alcohols resist oxidation under these conditions because the OH-bearing carbon lacks

H. Orange dichromate turns green on reduction.



Distillation and reflux process comparison.

Aldehydes give a brick-red precipitate with warm Fehling's or Benedict's solution; ordinary ketones do not. Carboxylic acids react with carbonate/hydrogencarbonate to release CO_2. These distinguish products of core practical 7; do not identify an unknown from the dichromate colour alone.

Alcohol combustion produces CO_2 and H_2O when oxygen is sufficient. PCl_5 converts an alcohol to a chloroalkane, producing $POCl_3$ and HCl fumes: $ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$. The fumes support an OH-group test but are not unique proof of an alcohol. KBr with 50% concentrated sulfuric acid supplies HBr for conversion to a bromoalkane; red phosphorus and iodine supply a reagent for an iodoalkane. Heating with concentrated phosphoric acid eliminates water to make an alkene. Distinguish dehydration from oxidation and substitution; state conditions on the arrow.

Reflux heats the mixture while a condenser returns vapour; distillation collects vapour after condensation and separates by volatility. Water enters the condenser at the bottom and leaves at the top. Solvent extraction partitions a product between immiscible layers. Use a suitable anhydrous drying agent to remove residual water, then decant/filter it before final distillation. A narrow boiling range near a reference value supports purity but is not conclusive identification; pressure and thermometer position affect the measurement.

The molecular-ion peak in a mass spectrum gives molecular mass for a singly charged ion. It need not be the largest peak. Fragment ions help suggest structures: loss of CH_3 corresponds to 15 mass units, but a single fragment rarely proves one isomer. Distinguish isotope peaks from fragments. In an IR spectrum, compare absorption positions with the **provided** data: C=O, O–H, N–H, C=C, C–H and C–X can identify possible functional groups. Alcohol O–H is broad; acid O–H is very broad and appears with C=O. Both aldehydes and ketones have C=O, so combine IR with formula, mass spectrum and chemical tests. An absent strong expected absorption can rule out a proposal, subject to spectrum quality. Core practical 8 combines ion tests and organic tests using clean separate aliquots and a recorded chain of evidence.

Independent transfer checks

Attempt before reading the guidance. These original checks are not official past-paper questions.

1. A solution warms but a student reports a positive molar enthalpy. Explain the sign error and two distinct quantities needed besides temperature change.
2. Two isomeric alkanes have the same electron count. Explain why their boiling temperatures can differ without invoking hydrogen bonding.
3. An unknown salt gives a white solid with $BaCl_2$ after acidification and a gas turning red litmus blue with warm NaOH. Identify both ions and give two ionic equations.
4. Raising temperature increases rate but lowers equilibrium product yield. What does this imply about the forward enthalpy, and why does a catalyst not solve the yield change directly?
5. A primary bromide gives a three-carbon nitrile. Identify the bromide, its reagent/conditions, and the product of subsequent substitution using aqueous KOH on the original bromide.
6. An unknown C_3H_6O has a C=O absorption and reduces Fehling's solution. Give its structure and explain one rejected isomer.

Guidance: (1) Energy gained by the solution is lost by the reaction; heated mass/specific heat capacity and limiting reacting amount are needed. (2) Branching changes contact and London attractions. (3) Sulfate and ammonium; $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$, $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$. (4) Forward reaction is exothermic; a catalyst changes rates, not equilibrium composition at a fixed temperature. (5) Bromoethane; alcoholic KCN with heat gives CH_3CH_2CN; aqueous KOH gives ethanol. (6) Propanal, CH_3CH_2CHO; propanone has the formula and carbonyl but does not reduce Fehling's solution under the stated test.

3 · Practical Skills in Chemistry I

Pearson Edexcel · International A-Level · Chemistry

The chemist's bench, in writing

A white solid, a colourless liquid, a gas that smells of swimming pools: WCH13 asks what you would *do* with them. Which test separates lithium from strontium, why the drying agent sits where it does, whether the metal was in excess, and why your enthalpy value is smaller than the data book's. Every question reaches back to the bench work of Units 1 and 2 – reactions you ran, measurements you took, and the judgement behind each step.

WCH13/01 Practical Skills in Chemistry I is the third IAS unit: 1 hour 20 minutes, 50 marks, all compulsory, a minimum of 6 mathematical marks. The specification names four assessed abilities – independent thinking in a practical context, use of scientific methods, numeracy (graphs, significant figures, accuracy and precision), and use of apparatus (selection, range and resolution, health and safety). Questions may go beyond the eight **core practicals** to unfamiliar situations built from the same techniques.

The eight IAS core practicals

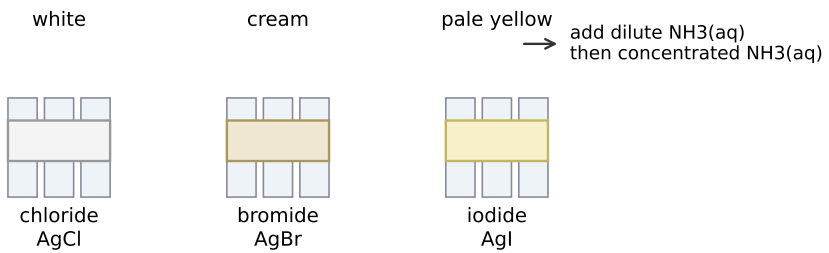
Core practical	What it does	Key skill
1 Molar volume of a gas	Known mass of metal reacts with excess acid; gas collected and volume measured	$V_m = V/n$ with the gas syringe read at room conditions
2 Enthalpy by Hess's law	Temperature rises from two related reactions combined into a cycle	$q = mc\Delta T$, then per mole; sources of error
3 Finding HCl concentration	Titration against a standard base with an indicator	Burette technique, concordant titres, mean
4 Standard solution + NaOH	Weigh a solid acid, make up to volume as a **standard solution**, titrate the unknown	Quantitative transfer, volumetric flask
5 Halogenoalkane hydrolysis rates	Time to precipitation with aqueous ethanol–silver nitrate at controlled temperature	Timing a **clock reaction**, comparing rates
6 Chlorination of 2-methylpropan-2-ol	Tertiary alcohol + concentrated HCl gives 2-chloro-2-methylpropane	Separating, drying and weighing an organic product
7 Oxidation of propan-1-ol	Distil to keep propanal; reflux to reach propanoic acid	Choosing **distillation** vs **reflux** for the product wanted
8 Inorganic and organic unknowns	The full qualitative scheme	Observations stated as colours and precipitates

Qualitative analysis: say what you see

Flame tests: clean a nichrome or platinum wire with concentrated hydrochloric acid, dip the sample, and hold it in the hottest non-luminous (roaring blue) flame. Lithium crimson, sodium yellow, potassium lilac, calcium brick-red, strontium red, barium pale green, copper blue-green. Two reds collide – lithium and strontium – so confirm chemically: add sulfate ions (dilute sulfuric acid or a soluble sulfate); **strontium sulfate** precipitates, lithium sulfate stays dissolved. Potassium is lilac, rubidium red-violet – say the exact words, not "purple".

Halide anions: acidify with dilute nitric acid, add silver nitrate – chloride **white**,

bromide **cream**, iodide **pale yellow precipitate** . Confirm with ammonia: AgCl dissolves in *dilute* $NH_3(aq)$, AgBr only in *concentrated* $NH_3(aq)$, AgI in neither.



AgCl dissolves in dilute ammonia; AgBr only in concentrated

ammonia; AgI is insoluble in both

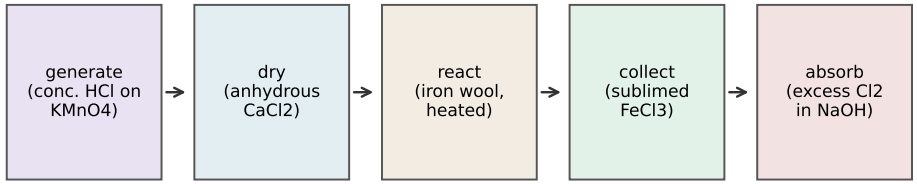
Three halide precipitates with the ammonia-solubility confirmation that separates them.

Organic functional groups: phosphorus(V) chloride on an alcohol or carboxylic acid steams – the gas is **hydrogen chloride** (misty fumes, not "hydrochloric acid"). Acidified dichromate(VI) turns **orange to green** when a primary or secondary alcohol (or an aldehyde) is oxidised. Combine tests with a molecular ion: two C_3H_8O isomers give Mr 60; the strongest peak at m/z 31 (CH_2OH^+) marks the primary alcohol, at 45 (CH_3CHOH^+) the secondary – propan-1-ol and propan-2-ol.

Ions move – an experiment you can read

Filter paper soaked in **tap water** (deionised water barely conducts – it has almost no ions), with drops of silver nitrate and potassium chromate(VI): when the current flows, **Ag^+ ions migrate towards the cathode** and **CrO_4^{2-} towards the anode**, meeting as a red precipitate – $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4$. The demonstration is evidence that both salts are **ionic** . A green spot of copper(II) chromate splits: blue Cu^{2+} streams to the cathode, yellow chromate to the anode.

Synthesis: justify every stage



heat the iron only after the air is flushed out;

every junction dry; toxic exit gas absorbed, never released

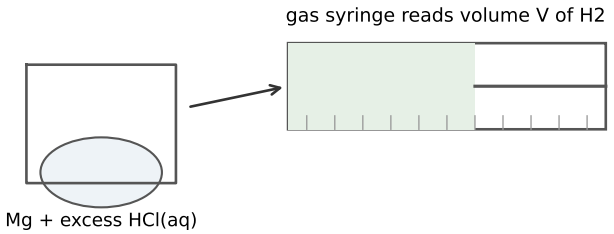
A gas synthesis train: generate chlorine, dry it, react it over heated iron, collect the product, absorb excess gas.

The anhydrous iron(III) chloride synthesis pays a mark for each stage's reason. Concentrated HCl on potassium manganate(VII) is a **redox** reaction: chloride ions lose electrons ($2Cl^- \rightarrow Cl_2 + 2e^-$) while manganate(VII) is reduced. Anhydrous calcium chloride **dries** the chlorine (a **drying agent** , not a "dehydrating agent"); ceramic wool holds it in place. The iron is heated only after half a minute so the **air is flushed out** first – otherwise iron meets oxygen before chlorine. Sodium hydroxide at the exit **absorbs the excess toxic chlorine**. The product sublimes into the receiver and is sealed quickly because it is **deliquescent** – it absorbs water to form hydrates, which is why a weighed product can be *heavier* than the calculated maximum.

Worked check. From 2.00 g of iron: $n = 2.00/55.8 = 0.0358$ mol. $M_r(FeCl_3) = 55.8 + 3 \times 35.5 = 162.3$. Maximum mass $= 0.0358 \times 162.3 = 5.82$ g – and 5.80 is rejected for under-claiming the figures the data support.

Measurements: range, resolution, technique

Choose apparatus by what the measurement needs: a **burette** (± 0.05 cm^3 per reading, 50 cm^3 range) for titres, a **volumetric flask** for making up solutions, a **gas syringe** for gas volumes, a thermometer graduated to 0.1–1 °C for temperature changes. Weigh by difference; read the bottom of the **meniscus** at eye level; take titres to **concordant** agreement (within 0.10 cm^3) before averaging – the rough titre never enters the mean. Quote significant figures the data support, and state **uncertainty** as ± half a division per reading, doubling for a difference of two readings.



A gas syringe collecting hydrogen from magnesium and acid for the molar-volume calculation.

Calorimetry and its honest errors

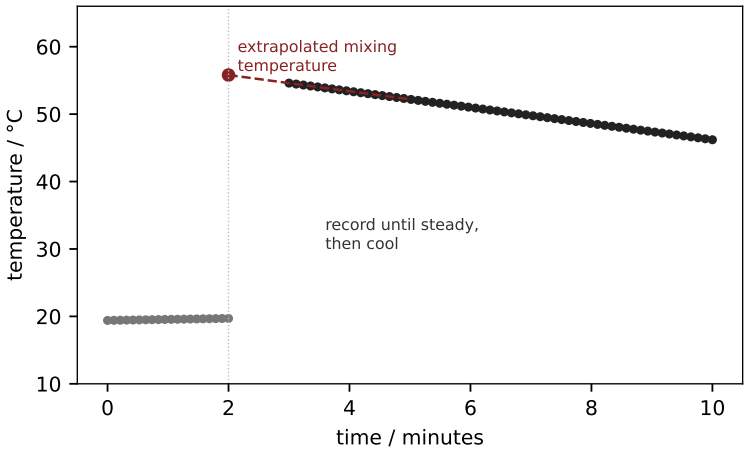
Magnesium **displaces** zinc: measure the temperature change of a known mass of solution and convert to an **enthalpy change** per mole.

Worked check (the 2025 data). $n(\mathrm{Zn^{2+}}) = 0.0500 \times 1.00 = 0.0500$ mol; $n(\mathrm{Mg}) = 2.20/24.3 = 0.0905$ mol – magnesium is in excess. $\Delta T = 55.2 - 19.4 = 35.8$ °C.

$$q = mc\Delta T = 50.0 \times 4.18 \times 35.8 = 7482 \text{ J}$$

$$\Delta H = -q/n = -7.482/0.0500 = -150 \text{ kJ mol}^{-1}$$

Divide by the moles **of the limiting reagent in the solution** (the zinc ions), not by the magnesium. A smaller experimental value than the data book means **heat loss** – the classic answer. Improvements the scheme credits: an insulated container (polystyrene cup), a lid, temperature readings every 30 seconds or a data logger, a *lower* concentration so less heat is lost per second, and a cooling-curve graph extrapolated back to mixing time. "Use a pipette" and "repeat and average" are explicitly ignored here – better glassware does not stop heat loss.



A cooling curve extrapolated back to the time of mixing for the true temperature change.

What written practice cannot do

This paper examines written practical understanding. Full marks do not show that you titrated to a sharp endpoint, transferred a solid quantitatively, or handled concentrated HCl behind a screen – those manipulations are built in class through the eight core practicals and their companions.

Check yourself

1. Describe a flame test on an unknown solid, including how the wire is cleaned.
2. State the precipitate colours for chloride, bromide and iodide with silver nitrate, and how ammonia confirms each.
3. Lithium and strontium both flame red. Give a chemical test that distinguishes their nitrates, with observations.
4. In the filter-paper migration experiment, why must the paper be soaked in tap rather than deionised water, and which ion in tap water could give a white precipitate near the silver nitrate?
5. Write the half-equation for chlorine formation from concentrated hydrochloric acid and potassium manganate(VII), and justify "redox".
6. 2.00 g of iron gives iron(III) chloride. Calculate the maximum mass, and explain why a real product could weigh more.
7. 50.0 $\mathrm{cm^3}$ of 1.00 mol $\mathrm{dm^{-3}}$ $\mathrm{ZnSO_4}$ reacts with 2.20 g Mg. Show which reagent is in excess.

8. Temperatures 19.4 °C and 55.2 °C for 50.0 g of solution (c = 4.18 J g^{-1} $°C^{-1}$). Calculate ΔH with sign and unit.
9. Give three scheme-credited improvements to the calorimetry, and one common suggestion the scheme ignores.
10. A C_3H_8O isomer's mass spectrum peaks strongly at m/z 45 rather than 31. Which isomer is it, and what ion is m/z 45?

Answers: 1 clean the wire with concentrated HCl and heat; dip the sample into the hottest blue (non-luminous) flame and note the colour; 2 chloride white AgCl, bromide cream AgBr, iodide pale yellow AgI; AgCl dissolves in dilute ammonia, AgBr only in concentrated, AgI in neither; 3 add dilute sulfuric acid (or a soluble sulfate): a white precipitate ($SrSO_4$) means strontium, no precipitate means lithium; 4 deionised water has almost no ions so it does not conduct; chloride ions (or hydrogencarbonate) could form white AgCl on the silver side; 5 $2Cl^- \rightarrow Cl_2 + 2e^-$; chloride ions lose electrons (oxidised, oxidation number $-1 \rightarrow 0$) while manganate(VII) gains them (reduced); 6 $n = 2.00/55.8 = 0.0358$ mol; $0.0358 \times 162.3 = 5.82$ g; the deliquescent product absorbs water forming hydrates, adding water's mass; 7 $Zn^{2+} = 0.0500$ mol, Mg = 2.20/24.3 = 0.0905 mol – Mg in excess; 8 $\Delta T = 35.8$ °C; $q = 50.0 \times 4.18 \times 35.8 = 7482$ J; $\Delta H = -7.482/0.0500 = -150$ kJ mol^{-1}; 9 insulated (polystyrene) container; lid; temperature every 30 s or data logger; lower concentration; cooling-curve graph – ignored: pipette/burette, more accurate balance, repeats; 10 propan-2-ol; m/z 45 is CH_3CHOH^+ ($C_2H_5O^+$).

4 · Rates, Equilibria and Further Organic Chemistry

Pearson Edexcel · International A-Level · Chemistry

Fast, feasible and complete are different claims

A reaction can be thermodynamically possible yet too slow to observe. Another can happen quickly but stop with much reactant left. This unit separates three questions: how fast, in which direction, and how far? It then uses those models to explain organic reactions and analytical evidence.

Prerequisites: Units 1 and 2 mole ratios, enthalpy, collision theory, dynamic equilibrium, nucleophiles and organic functional groups. Pearson Topics 11–15 define this scope. Core practicals 9a, 9b, 10 and 11 support the theory. Use the approved supervised laboratory method; the models here do not replace practical experience or risk assessment.

Rate equations are measured, not copied from coefficients

The **rate equation** relates rate to concentrations at a specified temperature:

$$r = k[\mathrm{A}]^m[\mathrm{B}]^n$$

The **order** with respect to A is m; overall order is $m+n$. These powers are found experimentally. They need not match the balanced equation's coefficients. In this course, individual orders are 0, 1 or 2. The **rate constant** k depends on temperature and pathway, not the reactant concentrations in the stated model. Its units follow by rearranging the equation.

Trial	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.100	0.100	0.00200
2	0.200	0.100	0.00400
3	0.100	0.200	0.00800

Compare trials 1 and 2: only [A] doubles and rate doubles, so order in A is one. Compare 1 and 3: only [B] doubles and rate quadruples, so order in B is two. Therefore $r = k[\mathrm{A}][\mathrm{B}]^2$ and overall order is three.

$$k = \frac{r}{[\mathrm{A}][\mathrm{B}]^2} = \frac{0.00200\ \mathrm{mol\,dm^{-3}\,s^{-1}}}{0.100\ \mathrm{mol\,dm^{-3}}(0.100\ \mathrm{mol\,dm^{-3}})^2} = 2.00\ \mathrm{dm^6\,mol^{-2}\,s^{-1}}$$

Using trial 2 or 3 gives the same k. That is an internal check, not independent proof that the model works outside the measured range. With both concentrations doubled, the model predicts a factor $2 \times 2^2 = 8$ increase in initial rate.

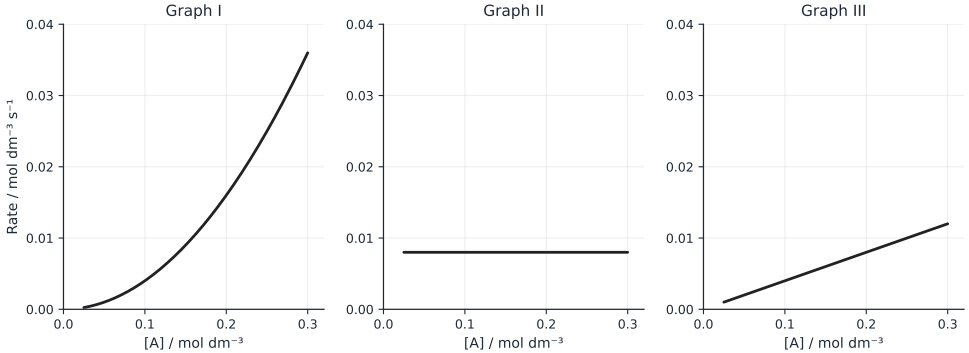
Graphs, half-life and method choice

A zero-order rate–concentration graph is horizontal; a first-order graph is a straight line through the origin; a second-order graph curves upward as concentration squared. A zero-order concentration–time graph falls linearly while the model remains valid. For first order, concentration falls exponentially and the **half-life** is constant: the time from 0.080 to 0.040 mol dm^{-3} equals that from 0.040 to 0.020. For second order, successive half-lives grow as concentration falls. Read half-life from the graph and show the concentration pair used; one interval alone cannot establish constant half-life.

Initial-rate experiments vary one concentration between separate trials and hold others and temperature constant. Continuous monitoring follows one trial over time. Select a measurement that changes with reaction progress: gas volume for a gas-forming reaction; mass loss for escaping gas; colorimetry for a suitable coloured species; or timed samples quenched and titrated. Mass loss is unsuitable if no material leaves the apparatus. Calibrate a colorimeter and control path length/wavelength. Account for sampling delay, gas leaks and temperature drift.

Conductivity can follow a reaction when ions with different mobilities replace each other: in ethyl ethanoate **hydrolysis** by NaOH, highly mobile OH^- is replaced by ethanoate. Calibrate the signal against composition and control temperature, probe geometry, mixing and solvent background. Gas volume or mass loss cannot follow this closed reaction because no gas is evolved.

A clock endpoint can approximate initial rate if the same small amount reacts before the endpoint in each trial. Then $1/t$ is proportional to the initial rate. Keep total volume, endpoint chemistry and temperature fixed. If a large changing fraction reacts before the endpoint, inverse time is not a valid initial-rate comparison.



Rate against [A]: Graph I curves upward (second order), Graph II is flat (zero order), Graph III is a straight line through the origin (first order)

Mechanisms must fit both kinetics and stoichiometry

The **rate-determining step** is the slow step controlling the overall rate under the stated conditions. A proposed mechanism must add to the overall equation and be consistent with the observed rate law. **Intermediates** are made in one step and consumed in another; a **catalyst** is consumed then regenerated. A rate equation supports a mechanism but rarely proves it uniquely.

For acid-catalysed iodination of propanone, rate is first order in propanone and H^+ and zero order in iodine under the usual measured conditions. Changing iodine concentration alone does not change the initial rate. This supports iodine reacting after the slow sequence; it does not mean iodine is absent from the overall reaction. In core practical 9a, follow iodine amount through appropriately quenched samples and titration, or use a calibrated colour method. Core practical 9b uses an iodine clock: justify the fixed-extent approximation before treating $1/t$ as rate.

A compatible simplified iodination sequence is fast $P + H^+ \rightleftharpoons PH^+$, slow $PH^+ \rightarrow E + H^+$, then fast $E + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. Here P is propanone, PH^+ its O-protonated form and E is $CH_3C(OH)=CH_2$. The **pre-equilibrium** gives $[PH^+] = K[P][H^+]$, so $r = k_2[PH^+] = k_2K[P][H^+]$, with zero iodine order. Cancelling intermediates gives $P + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. Acid is regenerated in the catalytic enol-forming sequence, while iodination also creates acid overall. This is a possible mechanism, not unique proof; early-rate comparisons must control acid concentration.

For primary **halogenoalkane** substitution by OH^-, an S_N2 model has one concerted step and rate depending on both reactants. Backside attack produces inversion at a suitable chiral carbon. For tertiary hydrolysis, an S_N1 model has slow C–X heterolysis forming a carbocation, then faster nucleophile attack. Its rate depends on halogenoalkane concentration but not nucleophile concentration under the stated conditions. A freely accessible planar carbocation permits attack from both sides, giving a racemic product in the ideal model. Solvent and substrate matter; do not apply either rate law to every substitution without evidence.

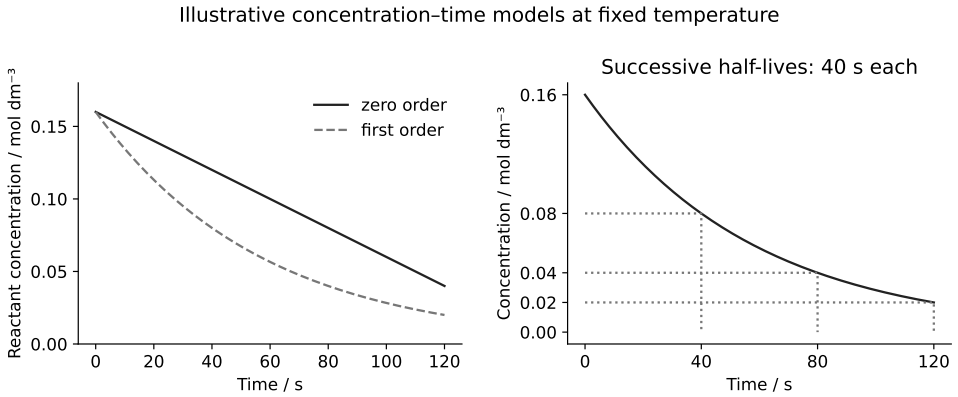
Temperature and catalysis

When supplied, use the Arrhenius relation $k = Ae^{-E_a/(RT)}$, or $\ln k = \ln A - E_a/(RT)$. On a graph of $\ln k$ against $1/T$, gradient $= -E_a/R$. Use kelvin and match energy units to $R = 8.31$ J mol^{-1} K^{-1}. A measured gradient of -6200 K gives:

$$E_a = -R \times \text{gradient} = -(8.31\ \text{J mol}^{-1}\ \text{K}^{-1})(-6200\ \text{K}) = 5.15 \times 10^4\ \text{J mol}^{-1} = 51.5\ \text{kJ mol}^{-1}$$

Core practical 10 measures comparable rates across controlled temperatures. Let the mixture reach the chosen temperature, measure the reacting mixture rather than only the water bath, and justify the same rate proxy at every temperature. A graph against $1000/T$ has a gradient smaller by a factor of 1000 than one against $1/T$; label the actual axis before using the equation.

A **homogeneous catalyst** is in the same phase as the reacting mixture; a **heterogeneous catalyst** is in another phase. A solid industrial catalyst can adsorb gaseous reactants onto its surface, weaken bonds/provide another pathway, then release products by desorption. Greater accessible surface gives more sites. A poison blocks sites. The catalyst lowers **activation energy** and changes rate, not the **equilibrium constant** at a fixed temperature.



Illustrative rate curves and successive half-lives.

Entropy and feasibility: include the surroundings

Entropy describes the random dispersal of particles and energy. For a substance, entropy generally rises with temperature and from solid to liquid to gas. A perfect crystal at zero kelvin has zero entropy. Gas spreading through a room is favoured because many more arrangements distribute its molecules through the larger volume.

The natural direction has positive **total entropy change** :

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}, \qquad \Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

Calculate system entropy using products minus reactants, with balanced coefficients. Standard molar entropy units are J mol^{-1} K^{-1}, so convert an enthalpy in kJ mol^{-1} to J mol^{-1} before dividing by kelvin.

Suppose a reaction has $\Delta S_{\text{system}} = +120$ J mol^{-1} K^{-1} and $\Delta H = +30.0$ kJ mol^{-1}. At 298 K:

$$\Delta S_{\text{surroundings}} = -\frac{30000\ \text{J mol}^{-1}}{298\ \text{K}} = -100.7\ \text{J mol}^{-1}\,\text{K}^{-1}$$

$$\Delta S_{\text{total}} = 120 - 100.7 = +19.3\ \text{J mol}^{-1}\,\text{K}^{-1}$$

The process is feasible despite being endothermic. Assuming the given enthalpy/entropy values stay approximately constant, the boundary is $T = \Delta H/\Delta S_{\text{system}} = 30000/120 = 250$ K; above 250 K total entropy is positive. At the boundary it is zero, not positive.

An exothermic reaction increases surroundings entropy. An endothermic one decreases it, but a sufficiently positive system change can outweigh that decrease. More gas moles often suggest a positive system entropy change; use data for a numerical conclusion. Dissolving an ionic solid disperses ions, but strong hydration can order surrounding water, so solution entropy is not automatically positive. Neither sign of system entropy alone decides feasibility.

Thermodynamic stability concerns the energetically/entropically favoured state under the stated conditions. **Kinetic stability** concerns a high activation barrier and slow reaction. A feasible reaction can remain imperceptibly slow. Increasing temperature changes both kinetics and total entropy; these are different explanations.

Lattice and solution cycles: declare the sign convention

Pearson defines **lattice energy** here as the exothermic formation of one mole of ionic solid from its gaseous ions. For NaCl, the equation is $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}$, so this lattice formation value is negative. Separating the lattice is the reverse and positive.

First **electron affinity** is the enthalpy change when one mole of gaseous atoms each gains one electron to form gaseous 1− ions. Write the gas states and electron: $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$. Second electron affinity adds an electron to an already negative gaseous ion and is usually endothermic because of repulsion.

A **Born–Haber cycle** - for NaCl separates formation from the elements into **atomisation** , ionisation, electron affinity and lattice formation. Using illustrative values in kJ mol^{-1}, $\Delta H_f = -411$, Na atomisation +108, Cl atomisation +121, Na ionisation +496 and Cl electron affinity −349:

$$\Delta H_f = \Delta H_{\text{at}}(\text{Na}) + \Delta H_{\text{at}}(\text{Cl}) + IE_1(\text{Na}) + EA_1(\text{Cl}) + \Delta H_{\text{latt}}$$

$$\Delta H_{\text{latt}} = -411 - [108 + 121 + 496 - 349] = -787\ \text{kJ mol}^{-1}$$

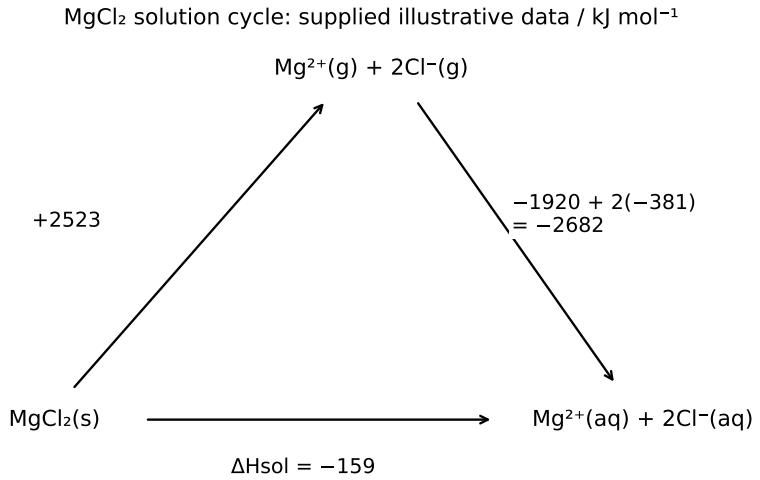
For $MgCl_2$, include two chlorine atomisations, two electron affinities and both Mg ionisation energies. The cycle must form the ions in the actual solid formula. A theoretical lattice value from a purely ionic model may differ from a Born–Haber value derived from experiment. A substantial extra stabilisation supports **covalent character** : a small highly charged cation polarises a large anion's electron cloud. Agreement supports the model but does not prove a bond is perfectly ionic.

Hydration enthalpy forms one mole of aqueous ions from gaseous ions, normally exothermically. Solution enthalpy dissolves one mole of solute in sufficient water that further dilution gives no enthalpy change, under the stated standard conditions. With the lattice **formation** convention:

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

If lattice formation is -780 and the total hydration enthalpy is -760 kJ mol^{-1}, solution enthalpy is $+780 - 760 = +20$ kJ mol^{-1}. Smaller ions and greater ionic charge usually make both lattice formation and hydration more negative. Because these effects compete, one trend alone cannot establish solubility. Combine solution enthalpy with entropy to assess dissolution. In Group 2 sulfate trends, changes in hydration and lattice terms differ in size; do not say every less exothermic hydration term necessarily makes every salt insoluble.

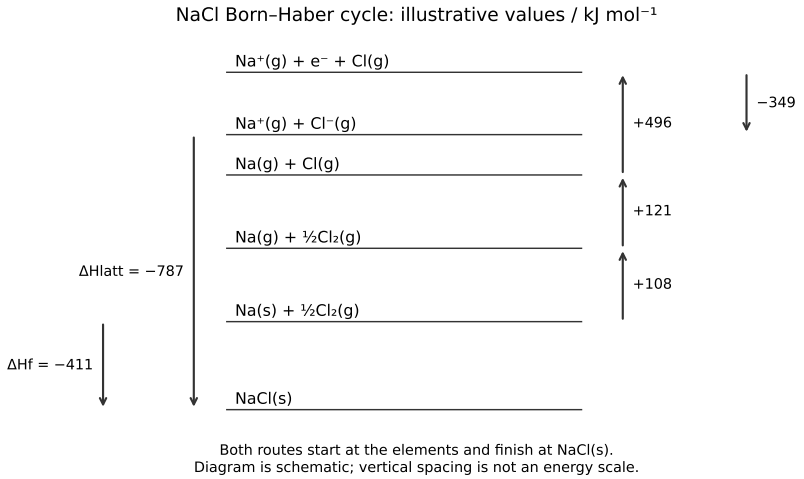
A complete solution cycle keeps ion counts and states. For illustrative $MgCl_2$ data, reverse lattice formation -2523 to give $+2523$ kJ mol^{-1}, then hydrate Mg^{2+} at -1920 and two Cl^- at -381 each. Thus total hydration is -2682 and solution enthalpy is -159 kJ mol^{-1}. The same solid and aqueous ions must start and finish both routes.



Complete original MgCl2 solution/hydration cycle with supplied illustrative data.

Down Group 2, larger cations have less exothermic hydration. For the large sulfate anion, the lattice-dissociation term changes comparatively little, so the loss of hydration stabilisation helps explain decreasing sulfate solubility. For hydroxides, the decrease in lattice-dissociation enthalpy is more important and can outweigh the less exothermic hydration, supporting increasing solubility. These explanations compare both terms within each family; a final numerical prediction also needs solution entropy

at the stated temperature.



NaCl energy cycle with illustrative data and the lattice-formation convention.

Equilibrium constants: calculate from equilibrium amounts

For $aA + bB \rightleftharpoons cC + dD$, an appropriate concentration expression is $K_c = [C]^c[D]^d/([A]^a[B]^b)$. Use **equilibrium** concentrations, not the amounts initially mixed. Omit pure solids and pure liquids in heterogeneous expressions; do not omit an aqueous solute simply because its formula contains no gas state.

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

With equilibrium concentrations 0.200, 0.100 and 0.300 mol dm^{-3} for NH_3, N_2 and H_2 respectively, $K_c = (0.200)^2/[0.100(0.300)^3] = 14.8$ dm^6 mol^{-2}. Derive the units from the expression rather than memorising one unit for all constants.

■ Use an amount table before the expression

For $A(g) + B(g) \rightleftharpoons C(g)$, initially 0.500 mol each of A and B and no C are in 2.00 dm^3. If 0.200 mol C forms, equilibrium amounts are 0.300, 0.300 and 0.200 mol. Concentrations are 0.150, 0.150 and 0.100 mol dm^{-3}, so:

$$K_c = \frac{0.100\ \text{mol}\,\text{dm}^{-3}}{(0.150\ \text{mol}\,\text{dm}^{-3})^2} = 4.44\ \text{dm}^3\,\text{mol}^{-1}$$

Using the mole amounts directly would give a different wrong result because the concentration powers do not cancel all volume factors.

For gases, **partial pressure** is **mole fraction** times total pressure: $p_i = (n_i/n_{\text{total}})P$. Pearson's K_p data use pressures in atm. For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = p(NO_2)^2/p(N_2O_4)$ with units atm. At total pressure 3.00 atm and equilibrium amounts 1.00 mol N_2O_4 and 2.00 mol NO_2, the partial pressures are 1.00 and 2.00 atm. Thus $K_p = 4.00$ atm. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = p(CO_2)$ while both solids are present; their amounts do not enter the expression.

Changing concentration or pressure changes composition as the system returns to the same constant at fixed temperature. A catalyst does not change the constant. For an exothermic forward reaction, raising temperature lowers K; for an endothermic forward reaction, it raises K. The change in K explains the new equilibrium composition. A very large K favours products in the stated expression but does not guarantee a fast reaction or literally zero reactant.

Where supplied, $\Delta S_{\text{total}} = R \ln K$ relates the entropy change and an appropriately standardised dimensionless equilibrium constant. Positive total entropy corresponds to $K > 1$; zero to $K = 1$; negative to $K < 1$. Use the defined constant and standard-state conventions. Do not take a logarithm of an unconverted dimensional pressure value or confuse this with a claim that all classroom Kc/Kp expressions have identical units.

Acid–base calculations: identify the model and check it

A Brønsted–Lowry **acid** donates a proton; a **base** accepts one. **Conjugate** acid–base partners differ by one H^+. In $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, the pairs are NH_4^+/NH_3 and H_2O/OH^-. A **strong acid** dissociates essentially completely in the specified dilute aqueous model; a **weak acid** only partly dissociates. Strength describes **dissociation**, whereas concentration describes amount per volume.

$$\text{pH} = -\log_{10}[\text{H}^+], \qquad [\text{H}^+] = 10^{-\text{pH}}$$

Use numerical hydrogen-ion concentration in mol dm^{-3} in this course expression. A 0.0200 mol dm^{-3} **monoprotic** strong acid has $\text{pH} = -\log_{10}(0.0200) = 1.70$. A pH of 3.40 gives $[H^+] = 3.98 \times 10^{-4}$ mol dm^{-3}. Do not automatically double a diprotic acid concentration unless the stated dissociation model justifies both protons being fully released.

For water, $K_w = [H^+][OH^-]$. At 298 K use $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}, when given. A strong base giving $[OH^-] = 0.0100$ mol dm^{-3} gives $[H^+] = K_w/[OH^-] = 1.00 \times 10^{-12}$ mol dm^{-3} and pH = 12.00. In general neutral means $[H^+] = [OH^-]$; pH 7 is neutral at this temperature, not a universal temperature-independent rule. $pK_a = -\log_{10} K_a$ and $pK_w = -\log_{10} K_w$ using the course's concentration conventions.

Weak acids and measured Ka

For $HA \rightleftharpoons H^+ + A^-$, $K_a = [H^+][A^-]/[HA]$. If water's H^+ contribution is too small to matter and dissociation x is small compared with initial concentration c, then $[H^+] \approx [A^-] = x$ and $[HA] \approx c$:

$$[\text{H}^+] \approx \sqrt{K_a c}$$

For $K_a = 1.80 \times 10^{-5}$ mol dm^{-3} and $c = 0.100$ mol dm^{-3}, $[H^+] \approx 1.34 \times 10^{-3}$ mol dm^{-3}, so pH ≈ 2.87. The fraction dissociated is 0.00134/0.100 = 1.34%, supporting the approximation. The specification does not require quadratic solutions; recognise when supplied data do not justify the simple approximation rather than hiding the issue.

Core practical 11 finds K_a from calibrated pH and known acid concentration. If pH = 2.90 for 0.100 mol dm^{-3} acid, $x = 10^{-2.90} = 1.26 \times 10^{-3}$ mol dm^{-3}. Then $K_a = x^2/(c - x) = 1.61 \times 10^{-5}$ mol dm^{-3}. If concentration is obtained from a weighed acid, first use $c = m/(MV)$ with the final solution volume. Calibrate the pH meter with suitable buffers, rinse the electrode between samples and control temperature.

For a tenfold dilution of an ideal strong acid in the appropriate concentration range, pH increases by one. For a weak acid obeying the small-dissociation approximation, $[H^+]$ falls by $\sqrt{10}$ and pH rises by about 0.5. Compare equimolar acid/base/salt measurements using dissociation and reaction of ions with water; a salt solution is not automatically neutral. Very dilute solutions need care because water's own ions matter.

Buffers, titration curves and indicators

A **buffer solution** resists small pH changes when small amounts of acid or alkali are added. A weak-acid buffer contains substantial HA and its conjugate base A^-. Added H^+ is consumed by A^-; added OH^- is consumed by HA. Both components must remain after any initial neutralisation. Buffer capacity is finite.

$$[\text{H}^+] \approx K_a \frac{[\text{HA}]}{[\text{A}^-]}, \qquad \text{pH} \approx \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

With $K_a = 1.80 \times 10^{-5}$, $[HA] = 0.200$ and $[A^-] = 0.100$ mol dm^{-3}, $[H^+] \approx 3.60 \times 10^{-5}$ mol dm^{-3} and pH ≈ 4.44. To make pH 5.00, the required ratio is $[A^-]/[HA] = K_a/[H^+] = 1.80$. If [HA] is 0.100 mol dm^{-3}, $[A^-]$ should be 0.180 mol dm^{-3} under the stated approximation.

For a required **final** total $[HA] + [A^-]$, solve the ratio and total together. At target pH 5.00 with $K_a = 2.00 \times 10^{-5}$ mol dm^{-3}, the ratio is 2.00. If the total is 0.120 mol dm^{-3}, final [HA] is 0.0400 and $[A^-]$ is 0.0800 mol dm^{-3}. For 250.0 cm^3 made using 40.0 cm^3 acid stock and 60.0 cm^3 salt stock, the stock concentrations must be

0.0400(250.0/40.0) = 0.250 and 0.0800(250.0/60.0) = 0.333 mol dm^{-3}. Make up to the final volume; do not add that entire volume of water.

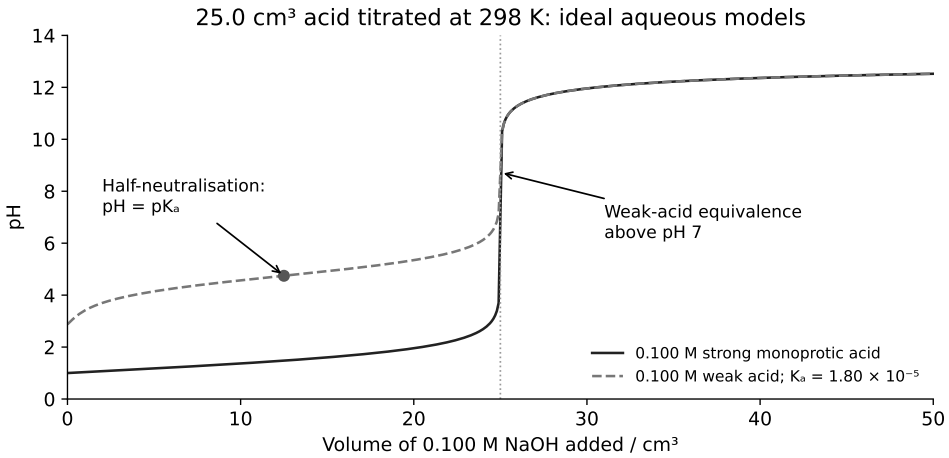
When a strong base is added to a weak acid, do the mole reaction first: $HA + OH^- \rightarrow A^- + H_2O$. Suppose 0.0100 mol HA initially meets 0.00400 mol OH^-. Afterwards HA = 0.00600 mol and A^- = 0.00400 mol, so use their 2:3 ratio; common final volume cancels in the ratio. Using the initial acid amount would be wrong. Beyond the **equivalence point** the excess strong base controls pH and the acid-buffer expression no longer applies.

On a **titration curve**, distinguish initial pH, buffer region, steep change, equivalence and excess **titrant**. Strong acid–strong base has equivalence near pH 7 at 298 K. Weak acid–strong base has equivalence above 7; strong acid–weak base below 7. Weak acid–weak base usually lacks a sharp enough vertical region for a simple colour **indicator**. Choose an indicator whose transition interval lies within the steep region shown by the actual curve; do not choose just because its midpoint matches the starting pH.

At **half-neutralisation** of a weak acid by strong base, [HA] = $[A^-]$, so pH = pKa. The analogous strong-acid/weak-base curve supports analysis of the conjugate weak-acid equilibrium when the species and direction are stated. For a diprotic acid, equivalence amounts reflect two proton equivalents, but two separate steep jumps are visible only when the dissociations are sufficiently distinct. Track each neutralisation stage before applying a buffer or excess-reagent formula.

For weak base B receiving strong acid, track $B + H^+ \rightarrow BH^+$. At half-equivalence equal B and BH^+ give pH ≈ pKa of $\mathbf{BH^+}$. If this pH is 9.25, its $K_a = 10^{-9.25} = 5.62 \times 10^{-10}$ mol dm^{-3}. The pair buffers added acid while both remain: B is converted into BH^+. This is a falling pH curve; beyond equivalence the excess strong acid controls pH.

Buffers in cells and blood help limit changes in enzyme conditions. For the carbonic acid/hydrogencarbonate pair, $HCO_3^- + H^+ \rightarrow H_2CO_3$ consumes added acid and $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ consumes added alkali. Each addition consumes a component: blood also needs respiratory and renal regulation, not unlimited permanent acid removal. Food buffers can reduce pH changes associated with microbial activity and deterioration. A buffer does not sterilise food or make unlimited acid addition harmless.



Strong and weak acid titration curves from ideal aqueous models.

Chirality and carbonyl reactions: use three-dimensional evidence

A **chiral centre** in these examples is a tetrahedral carbon attached to four different groups. Its two **enantiomers** are non-superimposable mirror images. Flat formulae can hide this difference; use wedge/dash bonds to show the three-dimensional arrangement. A pure enantiomer rotates **plane-polarised** monochromatic light; its partner gives the equal opposite rotation under identical conditions. A **racemic mixture** contains equal amounts of both, so their rotations cancel. Zero rotation alone does not prove a substance is racemic: an achiral substance is also inactive.

S_N2 attack at a chiral carbon gives inversion, whereas ideal S_N1 reaction through a planar carbocation allows attack from both sides. Use the stated starting material and observed optical activity to assess the mechanism. Do not infer the sign of optical rotation just by inspecting a wedge/dash drawing.

Aldehydes have a terminal –CHO group; **ketones** have C=O between two carbon groups. Propanal is CH_3CH_2CHO and propanone CH_3COCH_3. **Carbonyl** oxygen accepts hydrogen bonds from water. Simple aldehydes/ketones lack O–H/N–H/F–H donors, so their pure molecules do not form the alcohol-like hydrogen-bond network. Small ones are water-soluble; increasing the non-polar chain reduces solubility.

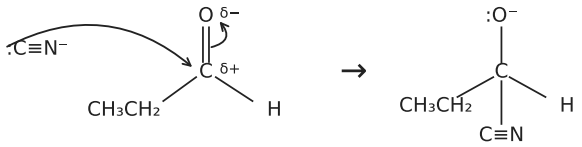
Reagent/test	Aldehyde	Ordinary ketone	Interpretation
Warm Fehling's/Benedict's	Brick-red Cu_2O precipitate	No such change	Aldehyde is oxidised
Tollens' reagent	Silver mirror/grey silver	No silver mirror	Distinguishes an aldehyde under the stated test
Acidified dichromate(VI)	Orange to green	Resists these conditions	Oxidation to carboxylic acid
2,4-DNPH	Yellow/orange precipitate	Yellow/orange precipitate	Carbonyl evidence; not an aldehyde/ketone distinction
$LiAlH_4$ in dry ether, then appropriate work-up	Primary alcohol	Secondary alcohol	Reduction of C=O

For example, $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$. Prepare derivatives with 2,4-DNPH by the approved method and compare their melting temperatures with supplied reference data. A sharp matching melting range supports identification; mixture contamination and reference overlap are limits. No derivative equation is required here. Tollens' reagent and cyanide chemistry require controlled laboratory handling and disposal; do not store or improvise these reagents.

HCN, with KCN providing CN^-, adds to a carbonyl by **nucleophilic addition**. A carbon lone pair in CN^- attacks the partially positive carbonyl carbon; the C=O π pair moves to oxygen. The O^- intermediate then gains H^+ from HCN, regenerating CN^-. Propanal gives $CH_3CH_2CH(OH)CN$. The planar carbonyl can be attacked from either face; with achiral conditions, the new chiral centre forms a racemic mixture. Propanone's product has two identical methyl groups, so it is not chiral for that reason.

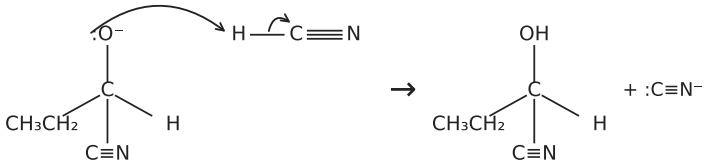
The full propanal mechanism includes the second electron-pair transfer: an O^- lone pair goes to the H of H–C≡N, and the H–C bond pair returns to cyanide carbon. The product $CH_3CH_2CH(OH)CN$ retains all four carbons, and CN^- is regenerated.

1 Carbon attack and movement of the C=O π pair



The negative charge is on oxygen; the new C–C bond retains the nitrile carbon.

2 Proton transfer from HCN regenerates CN^-



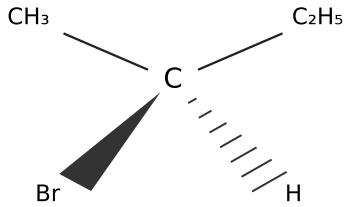
O lone pair → H; H–C bond pair → C. Product: $CH_3CH_2CH(OH)CN$.

Complete original two-stage HCN addition including cyanide regeneration.

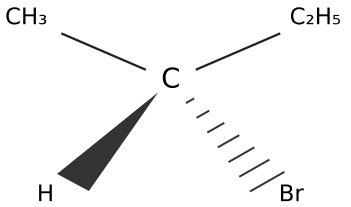
The **iodoform test** uses iodine in alkali: compounds with CH_3CO– give a yellow CHI_3 precipitate. Ethanal also fits this pattern with H as its other carbonyl substituent. Ethanol and secondary alcohols of type $CH_3CH(OH)R$ can first oxidise to a suitable carbonyl and also give a positive result. A positive test does not prove every unknown is propanone.

Swap two groups to obtain the other enantiomer

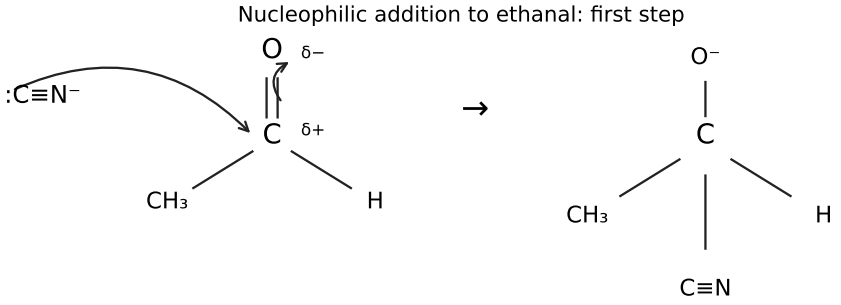
One enantiomer of 2-bromobutane



Opposite configuration



Opposite configurations of 2-bromobutane.



Electron-pair arrows in cyanide addition to ethanal.

Carboxylic acids, derivatives and condensation

A carboxylic acid has –COOH; name its carbonyl carbon as carbon 1. Hydrogen-bonded associations raise boiling temperatures. Small acids hydrogen-bond with water; a growing hydrocarbon part reduces solubility. Make acids by oxidation of primary alcohols/aldehydes or by **nitrile** hydrolysis with the stated aqueous acidic or alkaline conditions. The nitrile carbon becomes the acid/carboxylate carbon, so count it in the product chain.

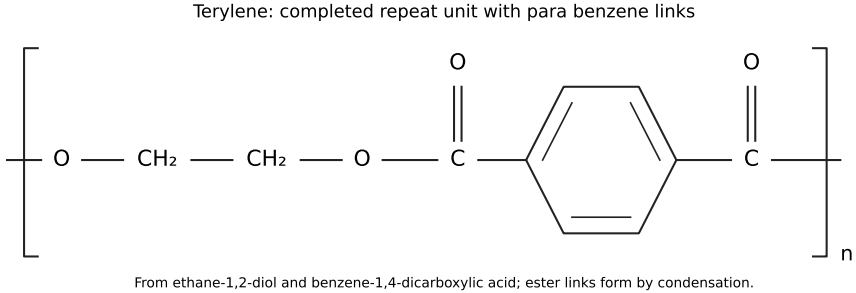
For propanenitrile, aqueous acid under **reflux** gives $CH_3CH_2CN + 2H_2O + H^+ \rightarrow CH_3CH_2COOH + NH_4^+$. Aqueous alkali under reflux gives $CH_3CH_2CN + H_2O + OH^- \rightarrow CH_3CH_2COO^- + NH_3$; acidify afterwards for the free acid. Both routes retain the nitrile carbon. Reducing propanoic acid uses $CH_3CH_2COOH + 4[H] \rightarrow CH_3CH_2CH_2OH + H_2O$, with $LiAlH_4$ in dry ether then work-up.

Carboxylic acids form salts with bases and release CO_2 with carbonate/hydrogencarbonate. $LiAlH_4$ in dry ether reduces RCOOH to RCH_2OH after the required work-up. PCl_5 converts RCOOH to the **acyl chloride** RCOCl, with $POCl_3$ and HCl also formed. Heating an acid with an alcohol and an acid catalyst establishes an **esterification** equilibrium: $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$. The product is ethyl ethanoate; the alcohol supplies the alkyl name and the acid supplies the carboxylate name.

Acyl chlorides react readily with nucleophiles. $RCOCl + H_2O \rightarrow RCOOH + HCl$; with R′OH they give RCOOR′ + HCl. With excess NH_3 they give $RCONH_2$ and NH_4Cl overall: $RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$. With a primary **amine** $R'NH_2$ they give an N-substituted **amide** ; a second amine molecule accepts HCl. Keep carbonyl carbon in the product and count the two nitrogen-reactant molecules in the overall equation.

Acid hydrolysis of an ester reversibly gives carboxylic acid and alcohol. Alkaline hydrolysis gives carboxylate salt and alcohol and is effectively driven to products by salt formation. Ethyl ethanoate + NaOH → sodium ethanoate + ethanol. Do not write a free carboxylic acid as the immediate product in alkaline solution.

A **polyester** forms by **condensation** between suitable bifunctional monomers, producing ester links and a small molecule. Terylene can use benzene-1,4-dicarboxylic acid and ethane-1,2-diol. Trace –O–CH_2–CH_2–O–CO–C_6H_4–CO– through the repeat unit, with open bonds crossing brackets. The para benzene arrangement matters. Do not use an alkene addition-polymer template: condensation links functional groups and releases water when a diacid and diol react.



Completed terylene repeat unit with ester links and open bonds.

Spectroscopy and chromatography: combine independent constraints

Accurate mass can distinguish formulae with the same nominal integer mass. With C = 12.0000, H = 1.0078 and O = 15.9949, C_2H_6O has mass $2(12.0000) + 6(1.0078) + 15.9949 = 46.0417$. Add the given precise atomic values before rounding; a nominal 46 alone does not establish this formula.

As a transfer comparison, C_3H_8O gives accurate relative mass 60.0573 and $C_2H_4O_2$ gives 60.0210 with the supplied atomic masses. Both have nominal 60. A measured 60.0210 selects the second formula; acid O–H/C=O evidence and two carbon-13 environments then support ethanoic acid over a formula-only guess.

Carbon-13 NMR gives one signal per distinct carbon environment in the simple spectra considered here. Symmetry can make different carbon atoms equivalent: propanone has two carbon environments, not three; propanal has three. Use supplied chemical-shift data to distinguish carbonyl, C–O and hydrocarbon environments. Signal count is not simply total carbon count.

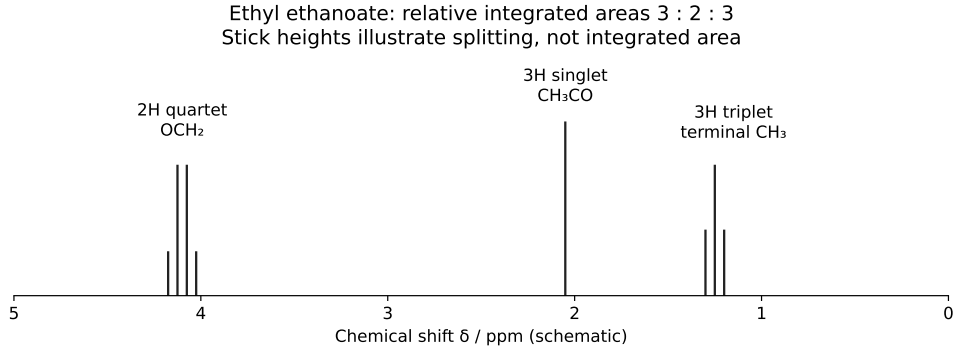
Proton NMR uses **chemical shifts** for environments, relative **integrated areas** for proton numbers, and **splitting** by neighbouring non-equivalent protons. For a simple set coupled to n equivalent neighbouring H atoms, the $n + 1$ rule predicts splitting. A CH_3CH_2– group often gives a 3H triplet and 2H

quartet. Exchangeable OH/NH signals may be broad and need not follow simple neighbouring-H splitting; use the stated spectrum. Ethyl ethanoate has a 3H singlet at the acyl methyl, a 2H quartet at OCH_2 and a 3H triplet at the terminal methyl, with three proton environments. Combine these with IR carbonyl evidence and molecular mass rather than treating one quartet as unique proof.

For butan-2-one, $CH_3COCH_2CH_3$, low-resolution proton NMR has three sets with areas 3:2:3. High resolution gives acyl-methyl singlet, CH_2 quartet and terminal-methyl triplet in the simple model. The two groups next to C=O lie in supplied 2.0–2.7 ppm data; the terminal methyl lies in 0.8–1.5 ppm. Carbon-13 has four environments, including a ketone carbonyl in the supplied 190–220 ppm range. Equivalent H in one methyl set do not split each other. Always use supplied shifts; these broad regions do not uniquely identify a compound.

Chromatography separates by different interactions with a **stationary phase** and a **mobile phase** . For paper/TLC, R_f = distance of spot/distance of solvent front, both from the baseline. A spot 3.6 cm from the baseline with a 6.0 cm solvent front has $R_f = 0.60$, without units. A lower Rf under the same conditions means relatively stronger retention by the stationary phase compared with transport by the mobile phase. Solvent and stationary-phase conditions affect the result; compare references under matched conditions. One spot can hide co-eluting substances.

HPLC and **gas chromatography** separate compounds through a column, giving different retention times under specified conditions. A matching **retention time** supports a candidate but is not unique proof. Coupling chromatography to **mass spectrometry** separates mixture components and gives mass/fragment evidence for each, useful in forensic work and drug testing in sport. Keep sampling provenance, standards, contamination controls and uncertainty in the interpretation.



Schematic splitting and assignments for ethyl ethanoate.

Independent transfer checks

These are original tasks; attempt before reading the guidance.

1. Doubling A doubles rate, doubling B changes nothing. Write the rate equation form and explain why B can still appear in the balanced reaction.
2. A reaction has $\Delta H = +24.0$ kJ mol^{-1} and $\Delta S(\text{system}) = +80.0$ J mol^{-1} K^{-1}. Find the feasibility temperature boundary and state the side that is favoured.
3. Lattice formation is -900 kJ mol^{-1} and total hydration is -930 kJ mol^{-1}. Find solution enthalpy and explain why this alone cannot prove high solubility.
4. A weak-acid buffer is made by adding 0.0030 mol OH^- to 0.0100 mol HA. Give the post-reaction A^-:HA ratio and explain why initial acid amount is unsuitable in the buffer expression.
5. A C_3H_6O sample has two carbon-13 signals and no Tollens' silver mirror. Propose a structure and predict whether its HCN-addition product is chiral.
6. An ester produces ethanol and sodium ethanoate with hot aqueous NaOH. Name the ester and predict its simple proton-NMR integration pattern.

Guidance: (1) $r = k[A]$ under the tested conditions; zero order in B supports its involvement after the slow sequence. (2) Boundary 300 K; above it total entropy is positive under the constant-data approximation. (3) $+900 - 930 = -30$ kJ mol^{-1}; entropy also matters. (4) 0.0030:0.0070 = 3:7; the OH^- has consumed some HA and made A^-. (5) Propanone; its addition product has two identical methyl groups and is achiral. (6) Ethyl ethanoate; three simple proton sets integrate 3:2:3, with singlet, quartet and triplet respectively.

5 · Transition Metals and Organic Nitrogen Chemistry

Pearson Edexcel · International A-Level · Chemistry

From a battery to a medicine

A battery transfers electrons through a wire. A metal catalyst changes a reaction pathway. An organic synthesis joins chosen carbon groups. In each case, success depends on identifying the particles and the conditions. This unit connects redox measurements, metal complexes and organic routes.

Prerequisites: oxidation numbers, half-equations, equilibrium, entropy, organic functional groups and Unit 4 analytical methods. This reference covers Pearson Topics 16–20 and the theory of core practicals 12–16. Separate practical Unit 6 requires practical-source preparation. Laboratory work needs the approved supervised procedure and its risk assessment.

Electrode potentials: compare reductions under the same conditions

A **half-cell** contains an oxidised/reduced pair in contact with a conducting electrode. A metal electrode can be the reacting solid. An inert platinum electrode carries electrons when the pair contains only solutions or a gas and solution. A **salt bridge** allows ions to move and completes the circuit without directly mixing the main solutions. Electrons flow through the wire, not the bridge.

An individual electrode potential cannot be measured alone. Connect it to a reference. The **standard hydrogen electrode** has hydrogen gas at 100 kPa, aqueous H^+ at 1.00 mol dm^{-3} and platinum, at 298 K. Its standard potential is defined as zero. The **standard electrode potential** of another couple is its potential relative to that reference under standard conditions. Other solutes have concentration 1.00 mol dm^{-3}; pure solids and liquids are in their standard states.

Write table entries as reductions. For example:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\circ = -0.76\ V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +0.34\ V$$

The more positive reduction is favoured at the positive electrode of the spontaneous cell. Zinc is oxidised at the negative electrode; Cu^{2+} is reduced at the positive electrode. The net equation is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$. Cancel equal electron amounts after multiplying half-equations, but **never multiply an electrode potential** by a coefficient.

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = +0.34 - (-0.76) = +1.10\ V$$

The cell diagram is Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s). A single line represents a phase boundary; the double line represents the salt bridge. State concentrations and conditions alongside the diagram. For an Fe^{3+}/Fe^{2+} solution half-cell, include Pt(s) as the inert contact. Species in one aqueous phase are separated by a comma, not an extra phase boundary.

In core practical 12, clean the metal surfaces and use a high-resistance voltmeter. Check electrode identity, solution concentration, temperature and good electrical contacts. Do not assume a smaller measured voltage disproves the table: actual conditions, oxide films and internal resistance affect measurements.

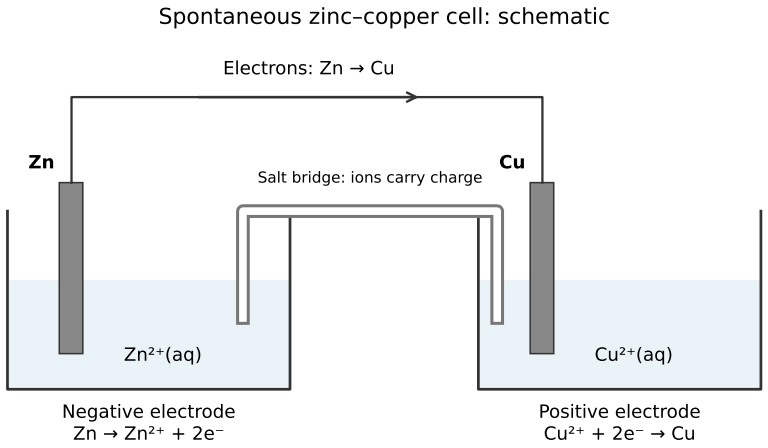
Feasibility has limits

A positive standard cell potential predicts thermodynamic feasibility for the stated overall reaction under standard conditions. It does not predict a visible reaction rate. A high activation barrier can prevent an observable change. Non-standard concentrations can change the electrode potentials and even the predicted direction. Compare the same conditions; do not treat a standard table as a concentration-independent rule.

For a defined cell reaction, E°_{cell} is proportional to its standard total entropy change. It is also related to $\ln K$, with electron number and temperature included in the proportionality. Thus positive E° corresponds to positive total entropy and K > 1. Reversing the reaction changes the sign of E° and inverts K. Changing the balanced equation's scale changes the entropy change and electron number, but not the voltage.

A **reducing agent** donates electrons and is oxidised. The reduced form of a very negative-potential couple is usually a strong reducing agent. An **oxidising agent** accepts electrons and is reduced. The oxidised form of a very positive-potential couple is usually a strong oxidising agent. Name the actual species, not just "the half-cell".

A **disproportionation** reaction oxidises and reduces the same element from one starting oxidation state. To test it, use the reductions leading to the starting state and away from it. If the reduction of the starting species is more positive than reduction into that state, the proposed disproportionation has positive E°. For illustrative $A^{3+}/A^{2+} = +0.80$ V and $A^{2+}/A = -0.20$ V, disproportionation of A^{2+} to A^{3+} and A gives $-0.20 - 0.80 = -1.00$ V. It is not feasible under those standard conditions. This example concerns hypothetical A, not measured values for a named metal.



Electron flow and separate ion conduction in a zinc–copper cell.

Redox titrations: use the electrons before the volume

Acidified manganate(VII) is reduced from purple MnO_4^- to nearly colourless Mn^{2+}:

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

Iron(II) loses one electron: $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Therefore one mole MnO_4^- reacts with five moles Fe^{2+}. Use dilute sulfuric acid. Hydrochloric acid can be oxidised; nitric acid can oxidise Fe^{2+} before titration. Near the endpoint add manganate(VII) dropwise while swirling. The first persistent faint pink shows a slight excess. No separate indicator is needed.

A 25.00 cm^3 Fe^{2+} sample requires 20.00 cm^3 of 0.0200 mol dm^{-3} MnO_4^-:

$$n(MnO_4^-) = 0.0200\ \text{mol}\,\text{dm}^{-3} \times \frac{20.00}{1000}\ \text{dm}^3 = 4.00 \times 10^{-4}\ \text{mol}$$

$$n(Fe^{2+}) = 5(4.00 \times 10^{-4}) = 2.00 \times 10^{-3}\ \text{mol}$$

$$c(Fe^{2+}) = \frac{2.00 \times 10^{-3}\ \text{mol}}{0.02500\ \text{dm}^3} = 0.0800\ \text{mol}\,\text{dm}^{-3}$$

For iodine and thiosulfate:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Add starch when the iodine solution becomes pale yellow. Adding it to concentrated iodine can make a strongly bound complex and an indistinct endpoint. The final blue-black colour disappears. If another oxidant liberates iodine from excess iodide, first use its equation to connect oxidant to iodine, then use the 1:2 iodine/thiosulfate ratio. These are different stoichiometric steps.

Core practicals 13a and 13b use redox titration to determine concentrations. Rinse a burette with its titrant and a pipette with the sampled solution. Water remaining in a conical flask does not change the moles transferred by the pipette. A burette reading uncertainty of ± 0.05 cm^3 at each end gives a worst-case titre uncertainty of ± 0.10 cm^3. For 20.00 cm^3, percentage uncertainty is $(0.10/20.00)100 = 0.50\%$. Include dilution and other apparatus uncertainties when the question requires the final concentration uncertainty. Repeat concordant titres reduce random variation; they do not remove a systematic concentration error.

Fuel cells require a continuing supply

A **fuel cell** produces electricity while fuel and oxidant enter from outside. For hydrogen and oxygen, the overall reaction is $2H_2 + O_2 \rightarrow 2H_2O$.

Medium	Oxidation half-equation	Reduction half-equation
Acidic	$2H_2 \rightarrow 4H^+ + 4e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Alkaline	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Cancel H^+ or OH^- only after matching electrons. Both media give the same overall equation. Hydrogen-cell operation produces water, but hydrogen production, storage and transport have environmental costs. Methanol is easier to store as a liquid but produces CO_2. Its overall oxygen-cell equation is $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$. Compare total production pathways and energy efficiency, not just the cell's exhaust.

Transition metals: distinguish atoms, ions and complexes

A **transition element** forms at least one stable ion with an incomplete d subshell. Scandium forms Sc^{3+}, which is d^0, and zinc forms Zn^{2+}, which is d^{10}. They do not meet this definition. Copper qualifies because Cu^{2+} is d^9, even though Cu^+ is d^{10}.

For Sc to Zn, the neutral atom configurations after [Ar] are: Sc $3d^14s^2$; Ti $3d^24s^2$; V $3d^34s^2$; Cr $3d^54s^1$; Mn $3d^54s^2$; Fe $3d^64s^2$; Co $3d^74s^2$; Ni $3d^84s^2$; Cu $3d^{10}4s^1$; Zn $3d^{10}4s^2$. Chromium and copper are exceptions to the simple filling pattern. When these atoms form positive ions, remove 4s electrons before 3d electrons. Fe^{2+} is $[Ar]3d^6$, not $[Ar]3d^44s^2$. Similar 3d and 4s energies help explain variable oxidation states.

A **ligand** donates a lone pair to a metal ion, forming a coordinate bond. A **complex ion** contains a central metal ion surrounded by ligands. The **coordination number** counts donor atoms directly bonded to the metal, not the number of ligand molecules. Six water ligands give $[Cu(H_2O)_6]^{2+}$, coordination

number six. Three bidentate ethanedioate ligands also give coordination number six.

Water, OH^-, NH_3 and Cl^- are monodentate . Ethane-1,2-diamine, often written en, is bidentate . $EDTA^{4-}$ can be hexadentate . Neutral ligands do not change the ion's charge; each anionic ligand contributes its charge. In $[Fe(CN)_6]^{3-}$, six CN^- contribute -6, so iron is $+3$.

Six ligand electron-pair regions repel and arrange around the metal with the greatest available separation. This gives an octahedral arrangement for the six-coordinate complexes here. Larger chloride ligands favour four-coordinate complexes such as tetrahedral $[CoCl_4]^{2-}$. Some four-coordinate complexes are square planar . Cisplatin has two NH_3 and two Cl ligands around platinum in a square plane. The two chloride ligands are adjacent in the cis form; opposite positions define the trans form. Cisplatin is used in cancer treatment as the single cis isomer, not a mixture with the trans form. A four-coordinate formula alone does not prove tetrahedral geometry.

Colour and ligand exchange

Ligands split the d orbitals into different energy levels. Absorbing visible light can promote a d electron between these levels. The remaining transmitted/reflected light produces the observed colour. Changing the metal oxidation state, ligand or coordination number can change the energy gap and colour. A d^0 or d^{10} ion has no suitable d–d transition; this explains many colourless complexes, but does not claim every colour in chemistry is a d–d transition.

A **ligand exchange** replaces one ligand with another. Excess ammonia changes the pale blue copper(II) aqueous complex into a deep blue solution:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

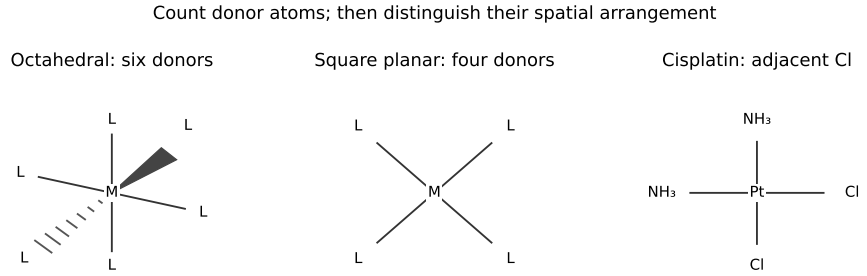
Initially, a small amount of NH_3 acts as a base and makes a pale blue hydroxide precipitate. In excess NH_3, that precipitate dissolves as the ammine complex forms. Do not describe both stages as one precipitate colour change. Excess concentrated chloride gives yellow $[CuCl_4]^{2-}$, often through an observed green mixture:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

For cobalt, pink $[Co(H_2O)_6]^{2+}$ exchanges with chloride to form blue $[CoCl_4]^{2-}$. Adding water shifts towards pink; increasing chloride concentration favours blue. State whether water or chloride concentration changed before explaining the equilibrium.

Replacing six water ligands with three bidentate ligands releases six free water molecules while using three free ligand molecules. The increase in freely moving particles often favours the chelate complex through entropy. It is not simply "more coordinate bonds": both complexes can have six metal–donor bonds. In haemoglobin, Fe^{2+} is held by a polydentate ligand and binds oxygen reversibly. Carbon

monoxide competes strongly for binding and prevents normal oxygen transport. The detailed haem structure is not required here.



Six-coordinate octahedral and four-coordinate square-planar arrangements.

Metal-ion tests and redox changes

Hydroxide removes protons from coordinated water, producing a hydrated hydroxide precipitate. A simplified equation is $Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3(s)$. A hydrated-complex equation is:

$$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3](s) + 3H_2O$$

Ammonia first accepts protons from coordinated water; write NH_4^+ as a product. For copper:

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+$$

The following table distinguishes initial precipitates from the solution in excess reagent. Observations refer to fresh aqueous tests. Air oxidation and slow ligand substitution can change colours during standing; record those conditions rather than silently combining stages.

Ion	Initial hydroxide precipitate	Excess NaOH	Excess NH_3
Cr^{3+}	Green/grey-green	Dissolves, green solution	Dissolves slowly in a large excess to a purple $[Cr(NH_3)_6]^{3+}$ solution
Mn^{2+}	Off-white, darkens in air	Remains	Remains
Fe^{2+}	Green, turns brown in air	Remains	Remains

Ion	Initial hydroxide precipitate	Excess NaOH	Excess NH_3
Fe^{3+}	Red-brown	Remains	Remains
Co^{2+}	Blue initially; may change on standing	Remains	Can dissolve to a straw-coloured ammine solution; air oxidation changes it
Ni^{2+}	Green	Remains	Dissolves to a blue/violet ammine solution
Cu^{2+}	Pale blue	Remains	Dissolves to deep blue solution
Zn^{2+}	White	Dissolves, colourless solution	Dissolves, colourless solution

The initial precipitate column applies to small additions of either hydroxide or ammonia in these tests. For a divalent metal M, the simplified equations are $M^{2+} + 2OH^- \rightarrow M(OH)_2(s)$ and $M^{2+} + 2NH_3 + 2H_2O \rightarrow M(OH)_2(s) + 2NH_4^+$. Here M can be Mn, Fe, Co, Ni, Cu or Zn. For Cr^{3+} and Fe^{3+}, replace the coefficients 2 with 3 and use $M(OH)_3$. These formulae describe the same proton-removal chemistry as the hydrated-complex equations.

For the excess-ammonia stage, $Co(OH)_2$ or $Ni(OH)_2$ can form $[M(NH_3)_6]^{2+}$ with six NH_3, releasing two OH^-. Zinc forms $[Zn(NH_3)_4]^{2+}$ with four NH_3, releasing two OH^-. For copper, $Cu(OH)_2 + 4NH_3 + 2H_2O \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$. These equilibria account for dissolution in sufficient ammonia; the observed extent and subsequent cobalt oxidation depend on conditions. Manganese and iron precipitates do not dissolve in excess ammonia; $Cr(OH)_3$ dissolves only slowly in a large excess, by ligand exchange to $[Cr(NH_3)_6]^{3+}$. Do not use the deep-blue copper colour for every ammine complex.

The **amphoteric** $Cr(OH)_3$ and $Zn(OH)_2$ react with excess hydroxide. For example $Zn(OH)_2(s) + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$. Zinc also forms $[Zn(NH_3)_4]^{2+}$ in excess ammonia. "Dissolves in both" does not mean both ligands produce the same complex. Chromium(III) may be represented as $[Cr(OH)_6]^{3-}$ in excess hydroxide; follow the species convention supplied in the question.

Vanadium shows several oxidation states in acidic solution: V(V), yellow VO_2^+; V(IV), blue VO^{2+}; V(III), green V^{3+}; V(II), violet V^{2+}. Zinc in acid reduces through these stages. Yellow and blue mixed during a change can look green; this alone is not proof of pure V^{3+}. Combine colour with the reaction conditions and electrode data.

Acidified orange dichromate(VI) is reduced to green Cr^{3+}. Zinc in acid can reduce it further to blue Cr^{2+}; air readily oxidises Cr^{2+} back. In alkaline solution, hydrogen peroxide can oxidise Cr(III) to yellow chromate(VI). Subsequent acidification favours orange dichromate:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Chromium stays +6 in this equilibrium. It is an acid–base equilibrium, not a redox change. Check oxidation numbers before assuming every colour change transfers electrons.

■ Catalysts can change oxidation state

In the Contact process, V_2O_5 catalyses SO_2 oxidation. A useful cycle is $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$, then $2V_2O_4 + O_2 \rightarrow 2V_2O_5$. Add the steps to cancel the catalyst and recover $2SO_2 + O_2 \rightarrow 2SO_3$. On catalytic-converter surfaces, reactants adsorb, react through a lower-energy pathway and desorb. For example $2CO + 2NO \rightarrow 2CO_2 + N_2$. Surface blockage reduces the available sites.

For the aqueous iodide/peroxodisulfate reaction, Fe^{2+}/Fe^{3+} provides a homogeneous cycle:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

Adding cancels iron ions. For acidified manganate(VII) and ethanedioate, Mn^{2+} product acts as an autocatalyst . The reaction can start slowly, accelerate as Mn^{2+} builds up, then slow as reactants are used. Core practical 14 prepares a transition-metal complex: calculate limiting amount and theoretical yield, isolate and dry crystals, and distinguish product loss from impurities that falsely raise mass.

Arenes: substitution preserves the delocalised ring

Benzene is an **arene** . Its six p orbitals overlap into a delocalised electron system above and below the carbon plane. The carbon–carbon bonds have equal lengths, between typical single and double bonds. X-ray evidence supports equal bond lengths. Its infrared spectrum has aromatic ring vibrations and aromatic C–H absorption above 3000 cm^{-1}. Use supplied reference data to compare its bands with a localised-alkene prediction; IR alone does not count three ordinary isolated double bonds. Together with its lower-than-expected hydrogenation enthalpy, the evidence disagrees with the three-isolated-bond model.

If one isolated double bond gives hydrogenation enthalpy -120 kJ mol^{-1}, three would predict -360. An illustrative measured benzene value of -208 is 152 kJ mol^{-1} less exothermic. Benzene starts at lower enthalpy than that localised model. This comparison uses a hypothetical reference; benzene does not rapidly switch between three fixed double bonds.

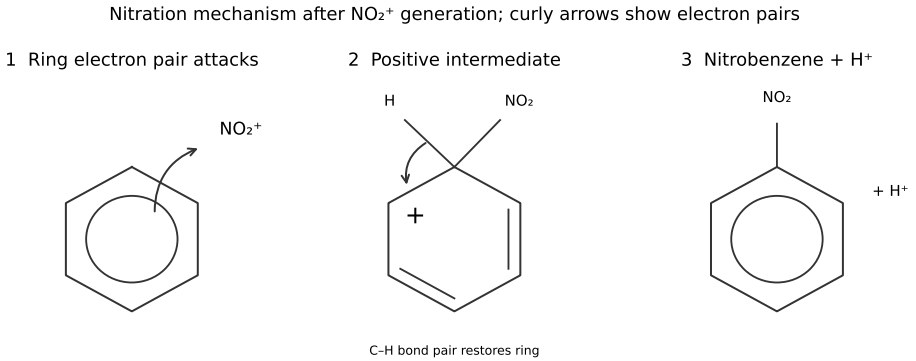
Benzene usually resists addition because it would destroy ring delocalisation. It does not decolourise bromine water like an alkene under the usual test conditions. It burns with a smoky flame when combustion is incomplete because of its high carbon proportion. Substitution replaces H while restoring the delocalised ring.

An **electrophilic substitution** reaction has three essential stages: generate the electrophile, use a ring electron pair to form a C–E bond, then lose H^+ to restore delocalisation. The intermediate has a positive charge and a ring carbon bonded to both H and E. Draw a curly arrow from the ring electron system to E^+, then from the C–H bond back into the ring. An arrow starting at H^+ is not electron flow.

Reaction	Reagents and conditions	Product/change
Bromination	Br_2 with $FeBr_3$ or $AlBr_3$ catalyst	Bromobenzene + HBr
Nitration	Concentrated HNO_3/H_2SO_4, warm controlled conditions	Nitrobenzene + H_2O
Sulfonation	Fuming sulfuric acid	Benzenesulfonic acid
Friedel–Crafts alkylation	Halogenoalkane with anhydrous $AlCl_3$	Alkylbenzene
Friedel–Crafts acylation	Acyl chloride with anhydrous $AlCl_3$	Aryl ketone

For nitration, $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ generates the nitronium ion. Ring substitution gives nitrobenzene and releases H^+, regenerating the acid catalyst. For Friedel–Crafts acylation, $RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$; substitution then forms HCl and regenerates $AlCl_3$. For bromination, the simple electrophile model is $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$. $FeBr_4^-$ accepts the released H^+ to form HBr and regenerate $FeBr_3$. For alkylation, $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$; $AlCl_4^-$ accepts H^+ to form HCl and regenerate $AlCl_3$. In each case the ring-attack and ring-restoration electron-pair arrows follow the nitration pattern. These are simplified mechanism models of catalyst-assisted electrophile generation; free ions are not assumed to exist in the original reagent bottle. Sulfonation conditions and products are required here; its detailed mechanism is outside this specification statement.

Phenol reacts much more easily with bromine water, giving a white precipitate of 2,4,6-tribromophenol and decolourisation without a halogen carrier. Oxygen's lone pair increases ring electron density by interaction with the ring. This makes attack by an electrophile easier. Do not transfer benzene's catalyst requirement to phenol.



Electron-pair arrows for benzene nitration after electrophile generation.

Amines and amides: the nitrogen lone pair matters

An **amine** derives from ammonia by replacing H with carbon groups. Butan-1-amine is $CH_3CH_2CH_2CH_2NH_2$; phenylamine is $C_6H_5NH_2$. Nitrogen's lone pair accepts H^+, making amines bases and nucleophiles. $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$, and $RNH_2 + HCl \rightarrow RNH_3^+Cl^-$. Small amines dissolve in water through hydrogen bonding. Solubility generally falls as the non-polar carbon group grows.

Aliphatic amines are generally stronger bases than ammonia in the comparisons required here. Alkyl groups increase electron density at nitrogen. Phenylamine is a weaker base because its lone pair interacts with the aromatic ring and is less available to bind H^+. Basicity is not decided by counting N–H bonds. Hydrogen bonding also raises boiling points compared with similar-sized hydrocarbons.

Excess ethanolic ammonia with a halogenoalkane, heated in a sealed apparatus under the approved procedure, forms a primary amine. Excess ammonia reduces further substitution but does not make it impossible. The amine product can attack more halogenoalkane, giving secondary/tertiary amines and eventually a quaternary ammonium salt. Butylamine can also act as a ligand towards Cu^{2+} through its lone pair.

Reducing a nitrile with $LiAlH_4$ in dry ether followed by suitable aqueous work-up gives a primary amine. R–C≡N becomes R–CH_2NH_2. The nitrile carbon remains in the chain. Making a nitrile from a halogenoalkane using ethanolic cyanide then reducing it increases the carbon chain by one overall.

Reduce nitrobenzene using tin and concentrated HCl under reflux. The acidic mixture initially contains the phenylammonium salt. Add alkali during work-up to liberate phenylamine. Writing free phenylamine as the only species in the strongly acidic reaction mixture misses this stage.

An **amide** has nitrogen bonded to a carbonyl carbon. Ethanoyl chloride re-

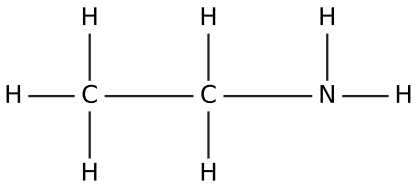
acts with a primary amine to form a substituted amide. $CH_3COCl + 2C_4H_9NH_2 \rightarrow CH_3CONHC_4H_9 + C_4H_9NH_3^+Cl^-$. One amine molecule forms the amide; another neutralises HCl. The amide lone pair interacts with the carbonyl system, so amides are much less basic than amines. Do not name CH_3CONH_2 as an amine or confuse its C=O with a ketone.

Names and complete structures

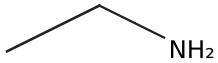
Use –amine for the amine, –amide for the amide and an amino– prefix with the carboxylic-acid parent for an amino acid. Ethanamine is $CH_3CH_2NH_2$; ethanamide is CH_3CONH_2; alanine is 2-aminopropanoic acid. A displayed formula includes every atom and bond. A skeletal formula omits carbon labels and their attached hydrogens, but retains nitrogen, oxygen and their attached hydrogens.

Ethanamine (ethylamine)

Displayed formula



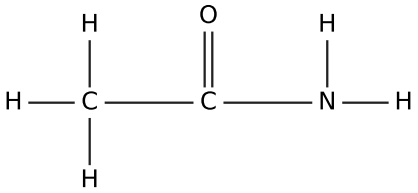
Skeletal formula



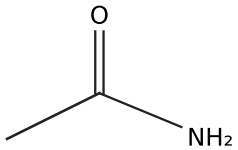
Completed displayed and skeletal formulae: ethylamine.

Ethanamide

Displayed formula



Skeletal formula



Completed displayed and skeletal formulae: ethanamide.

Diazotisation and colour

Cold nitrous acid, made from $NaNO_2$ and dilute acid, reacts with phenylamine below about 10 °C to form a diazonium salt. Keep the mixture cold because these salts are unstable when warmed. Coupling with phenol in alkaline solution produces an azo compound containing –N=N– between aromatic systems. The extended delocalised system absorbs visible light, producing colour. Distinguish making the diazonium ion from the separate coupling step.

Amino acids, proteins and polymers

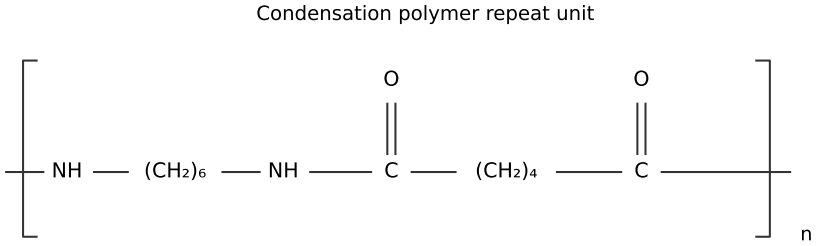
An **amino acid** contains both amine and carboxylic acid groups. A typical α-amino acid is $H_2N–CH(R)–COOH$. Most have a chiral central carbon, but glycine has two H atoms and is achiral. In the solid and much aqueous solution, proton transfer gives a **zwitterion** , $^+H_3N–CH(R)–COO^-$. Its net charge is zero, but it contains two charged groups. It is not an uncharged $H_2N/COOH$ molecule.

In acid the principal form is $^+H_3N–CH(R)–COOH$. In alkali it is $H_2N–CH(R)–COO^-$. Explain changes by adding/removing protons at the correct group. To investigate acid/base behaviour, add acid and alkali separately to measured amino-acid samples and follow pH with a calibrated meter. To investigate optical activity, zero a polarimeter with the solvent, then measure a clear solution with plane-polarised monochromatic light. Control concentration, path length, temperature and wavelength when comparing rotations. Pure opposite enantiomers rotate equally in opposite directions under matched conditions. A racemic mixture has zero net rotation; glycine is also inactive, so zero alone does not prove a racemate.

Linking an amino group and carboxyl group produces an amide or **peptide bond** , –C(=O)–NH–, with loss of water. Two different amino acids can give two ordered dipeptides; reversing their order changes the molecule.

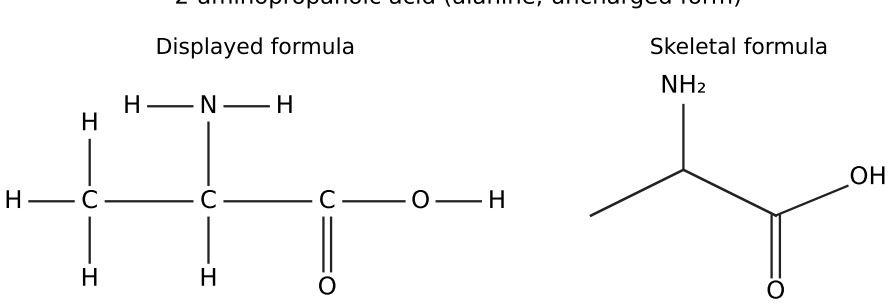
A **polyamide** forms by condensation between suitable diamines and dicarboxylic acids or their acyl chlorides. Nylon-6,6 uses $H_2N(CH_2)_6NH_2$ and $HOOC(CH_2)_4COOH$. Its repeat is $[–NH(CH_2)_6NHCO(CH_2)_4CO–]$ with continuing bonds at both ends. Protein chains are polyamides formed from amino acids. Their N–H and C=O groups form hydrogen bonds between chains, affecting strength and melting behaviour.

Poly(propenamide), $[–CH_2–CH(CONH_2)–]$, is an addition polymer. The side group contains an amide, but the backbone forms by opening the C=C bond without elimination of a small molecule. Poly(ethenol), $[–CH_2–CH(OH)–]$, has many hydroxyl groups that hydrogen-bond to water. Its water solubility allows suitable laundry bags or liquid-detergent capsules to dissolve during washing. Distinguish water-soluble polymers from polymers that merely absorb water; formulation and conditions matter.



Nylon-6,6: open bonds continue through the brackets; amide links lie in the backbone.

Completed nylon-6,6 repeat with backbone amide links and open bonds.



Completed displayed and skeletal formulae: alanine.

Plan a synthesis, then choose the purification

A **Grignard reagent** is made by reacting a halogenoalkane with magnesium in dry ether: RX + Mg → RMgX. Water destroys it, forming RH. Dry glassware and solvent matter because this reaction consumes the intended reagent before it can build the carbon chain.

With CO_2 followed by acidic work-up, RMgX forms RCOOH, adding one carbon. With methanal, it forms a primary alcohol; with another aldehyde, a secondary alcohol; with a ketone, a tertiary alcohol. The carbon group R bonds to the former carbonyl carbon. Oxygen becomes OH during the separate acidic work-up. Count every carbon from both starting fragments.

For example ethylmagnesium bromide plus ethanal gives $CH_3CH(OH)CH_2CH_3$ after work-up: butan-2-ol. Using methanal instead gives propan-1-ol. Adding acid before the carbonyl consumes the Grignard reagent, so the order cannot be reversed.

When a task specifies four synthetic conversions, one valid route is bromoethane → ethanol (aqueous OH^-, heat) → ethanal (controlled oxidation and distillation) →

butan-2-ol (ethylmagnesium bromide, dry ether, then acidic work-up) → butan-2-one (oxidation). Each arrow changes the main organic compound. The Grignard reagent is prepared separately. Check functional group, carbon count and conditions at every arrow.

Evidence can constrain an unfamiliar product

Use combustion data to determine the empirical formula; combine it with molar mass for the molecular formula. Element tests identify elements, not a unique structure. IR constrains functional groups; mass spectra constrain molecular mass and fragments. Carbon-13 NMR counts distinct carbon environments; proton NMR adds chemical shifts, integration and splitting. Several structures may fit one spectrum. Seek one structure fitting **all** the observations.

An unknown has formula C_3H_6O, a strong C=O absorption, a proton signal near 9–10 ppm, and a positive Tollens' test. Propanal fits the aldehyde proton and oxidation test. Propanone fits the formula and C=O but lacks an aldehyde H and normally gives a negative Tollens' test. Predict propanal's three carbon environments and its aldehyde/CH_2/CH_3 proton environments as a further check. Core practical 15 identifies both inorganic and organic unknowns through a planned sequence of small-scale tests, with positive controls and separate samples. Use metal-ion precipitation/excess-reagent tests for appropriate inorganic samples. Avoid adding every reagent to one tube: later changes may come from previous reagents rather than the original unknown.

Isolation is not the same as reaction

Reflux heats a mixture without losing volatile reactants: vapour condenses and returns. Distillation collects a volatile component separately. Never seal a heated reflux apparatus. During extraction , a separating funnel divides immiscible layers. Identify which layer contains the product from solvent density and solubility; the organic layer is not always uppermost. Vent the funnel away from people.

Water washes remove water-soluble impurities. Sodium carbonate washes remove acidic impurities but release CO_2, so vent carefully. A suitable anhydrous drying agent removes residual water from an organic liquid; filter or decant before distillation. Steam distillation carries a suitable water-insoluble volatile compound over with steam at a lower temperature than its normal boiling point.

Recrystallisation dissolves an impure solid in a minimum amount of hot solvent. Cool to crystallise; filter, wash with a little cold solvent and dry. Too much solvent lowers recovery. Insoluble impurities can be removed by hot filtration, while soluble impurities remain mainly in the mother liquor. A narrow melting range near the expected value supports purity; a lower, broader range suggests impurities. For melting temperature, use a dry finely powdered sample in a capillary and heat slowly near the expected range. Record the first melting and completion temperatures. For a liquid boiling temperature, place the thermometer bulb at the side-arm entrance so

vapour reaching the condenser passes it. Record the pressure and a steady boiling temperature; compare reference values at matching pressure. Mixtures can boil over a range. Neither melting point nor percentage yield alone proves identity.

Core practical 16 prepares aspirin by acylating salicylic acid with ethanoic anhydride under the approved method, then purifying the solid. Calculate theoretical yield from the limiting reagent using the 1:1 salicylic acid/aspirin ratio. If 1.38 g salicylic acid ($M = 138$ g mol^{-1}) is limiting, $n = 1.38/138 = 0.0100$ mol and theoretical aspirin mass is $0.0100 \times 180 = 1.80$ g. A dry yield of 1.26 g gives $(1.26/1.80)100 = 70.0\%$. Wet crystals can give an artificially high yield and a misleading melting range.

Independent transfer checks

1. A cell uses reduction couples +0.54 V and −0.25 V. Give the positive electrode, E°cell, and one reason a predicted reaction may not be seen.
2. A 25.00 cm^3 aliquot liberates iodine requiring 18.00 cm^3 of 0.100 mol dm^{-3} thiosulfate. Calculate iodine moles. State what extra equation is needed to find the original oxidant concentration.
3. A four-coordinate complex is blue. Explain why these facts alone do not establish its geometry or the metal oxidation state.
4. Methanal reacts with propylmagnesium bromide, then acid. Identify the alcohol and explain the effect of adding water too early.
5. A polymer has –CONH$_2$ side groups and a carbon-only backbone. Decide whether the presence of amide groups proves condensation polymerisation.

Answers: 1. The +0.54 V reduction is at the positive electrode; E°cell = 0.79 V. A high activation barrier can make the reaction too slow. Non-standard conditions also limit the standard prediction. 2. Thiosulfate amount = $0.100 \times 0.01800 = 0.00180$ mol; iodine = 0.000900 mol. The oxidant/iodide equation gives the separate mole ratio. 3. Four-coordinate complexes may be tetrahedral or square planar; colour also depends on ligand and coordination, so further evidence is needed. 4. Butan-1-ol; water consumes the Grignard reagent and forms propane. 5. No: poly(propenamide) forms by addition across C=C while retaining amide side groups.

6 · Practical Skills in Chemistry II

Pearson Edexcel · International A-Level · Chemistry

Analysis, synthesis and the judgement between

WCH16 takes the bench work of Units 4 and 5 and asks you to defend it: which **cation** is this when two **precipitates** look alike, why the volume of one **reagent** need not be exact, which **titres** enter the mean, and what a straight line's **gradient** is worth in kJ mol^{-1}. The paper rewards the chemist who knows *why* each step happened – and it will happily test the scheme word-for-word.

WCH16/01 Practical Skills in Chemistry II is 1 hour 20 minutes, 50 marks, all compulsory, mostly on Units 4–5 but free to draw on Units 1–2. The assessed abilities match Unit 3's – practical problem-solving, methods, numeracy, apparatus – now applied to equilibria, kinetics, transition metals and organic synthesis.

The IA2 core practicals

Core practical	What it does	Key skill
9a Iodine–propanone rate	**Quench** samples in ice, **titrate** remaining iodine with thiosulfate	Quenching and titrimetric rate-following
9b Clock reaction	Harcourt–Esson: time to the **starch endpoint**; $1/t \propto$ initial rate	Timing, temperature control
10 Activation energy	Clock reaction across temperatures; plot ln(1/t) against 1/T	Arrhenius graph: gradient $= -E_a/R$
11 Ka of a weak acid	pH measurements (or titration curve) of a weak acid	pH meter use, Ka from data
12 Electrochemical cells	Measure emf of metal/metal-ion **half-cells** joined by a **salt bridge**	Cell diagrams, conditions affecting emf
13a Redox titration: Fe^{2+}	Titrate iron(II) against potassium manganate(VII), acidified	Self-indicating endpoint (purple persists)
13b Redox titration: iodine	Iodine against sodium thiosulfate with starch	Accurate endpoint management
14 Transition metal complex	Prepare a complex salt from solution, crystallise, dry	Quantitative preparation and **purity**
15 Inorganic/organic unknowns	The full A2 qualitative scheme	Complex-ion equations and deductions
16 Aspirin preparation	Salicylic acid + ethanoic anhydride; recrystallise; melting temperature	**Yield**, **purification**, purity checks

Cations at A2: precipitates, complexes, air

add aqueous NaOH dropwise, then in excess:

Cu^{2+}	pale blue ppt	in excess NH3: deep blue solution
Fe^{2+}	green ppt, browns in air	insoluble in excess
Fe^{3+}	rust-brown ppt	insoluble in excess
Mn^{2+}	pale brown ppt, darkens in air	insoluble in excess
NH_4^+	no ppt; NH3 turns red litmus blue	on warming

Observation table for adding aqueous sodium hydroxide dropwise and in excess to five cations.

With aqueous sodium hydroxide: Cu^{2+} gives a pale blue precipitate (deep blue solution in excess ammonia); Fe^{2+} a **green** precipitate that browns in air; Fe^{3+} a rust-brown precipitate; Mn^{2+} a **pale brown precipitate that darkens on standing** – the 2025 paper's cation; NH_4^+ no precipitate, but warming releases ammonia that turns damp red **litmus** blue. **Ionic equations** may use either form:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

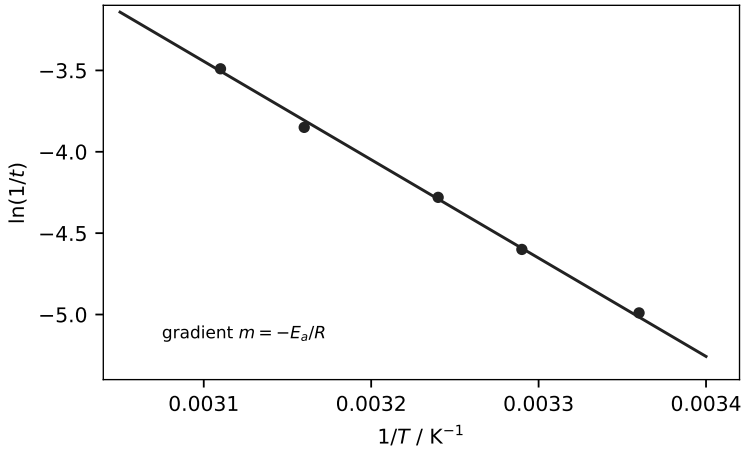
$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2(H_2O)_4 + 2H_2O$$

Dissolving iron(III) hydroxide in sulfuric acid gives the yellow-brown $[Fe(H_2O)_6]^{3+}$ complex. An unknown with M_r 197.9 and a Mn^{2+}/Cl^- analysis is $MnCl_2 \cdot 4H_2O$: $197.9 - (54.9 + 71.0) = 72.0 = 4 \times 18.0$. A salt holding two cations (green ppt + ammonia on warming + white ppt with acidified barium chloride) is Mohr's salt, $(NH_4)_2Fe(SO_4)_2$.

The clock reaction and activation energy

Thiosulfate is added in a **small known amount** to the peroxodisulfate–iodide mixture: it reacts with the iodine as it forms ($2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$), so the **colour change is delayed** until the thiosulfate is used up (a **clock reaction**) – then the next iodine turns the starch **blue-black** (from colourless). Because the same small amount of iodine is waiting at every endpoint, $1/t$ is proportional to the initial rate. Two technique marks hide in the 2025 scheme: a **burette** (not

a **measuring cylinder**) adds even the starch, because keeping the **total volume identical keeps the reactant concentrations constant** between runs – not because burettes are more precise; and both tubes equilibrate in the **water bath** before mixing, with the temperature recorded *in the reaction mixture*.



The Arrhenius plot from clock-reaction data: a straight line of ln(1/t) against 1/T with gradient -Ea/R.

Completing the table is arithmetic discipline: $T(\mathrm{K}) = T(^\circ\mathrm{C}) + 273$, $1/t$ to 3 significant figures, $\ln(1/t)$ to 2 decimal places. The straight line of $\ln(1/t)$ against $1/T$ has gradient $m = -E_a/R$ with E_a the **activation energy** :

$$E_a = -mR = 6045 \times 8.31 = 50\,234 \text{ J mol}^{-1} = 50.2 \text{ kJ mol}^{-1}$$

Positive value, kJ mol^{-1}, no negative sign – the sign is already in the gradient.

Titrations that build an answer

The calcium hydroxide experiment shows the full chain. Why stand for a day? To reach **equilibrium** – a **saturated solution** . **Indicator** : **methyl orange** (yellow → orange) or **phenolphthalein** (pink → colourless). Titres 9.95, 9.55 and 9.45 cm^3: the first is not **concordant** and is excluded – mean $= (9.55 + 9.45)/2 = 9.50$ cm^3. The expected titre of 0.100 mol dm^{-3} HCl from the data-book **solubility** (1.56 g dm^{-3}):

$$c = 1.56/74.1 = 0.0211 \text{ mol dm}^{-3}; \quad n = 0.0211 \times 0.0250 = 5.26 \times 10^{-4} \text{ mol}$$

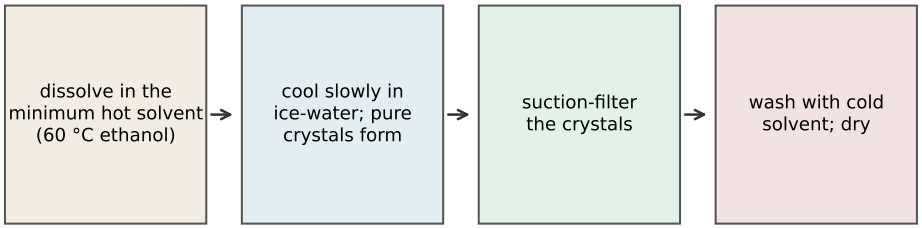
$$n(\mathrm{HCl}) = 2 \times 5.26 \times 10^{-4} = 1.05 \times 10^{-3} \text{ mol}; \quad V = \frac{1.05 \times 10^{-3}}{0.100} \text{ dm}^3 = 10.5 \text{ cm}^3$$

A mean titre *lower* than expected, given that solubility falls as temperature rises, means the experiment ran **warmer than 20 °C**. Finally $K_c = [\mathrm{Ca}^{2+}][\mathrm{OH}^-]^2 = 0.0190 \times (0.0380)^2 = 2.74 \times 10^{-5}$ $\mathrm{mol}^3\,\mathrm{dm}^{-9}$ – units derived, not remembered.

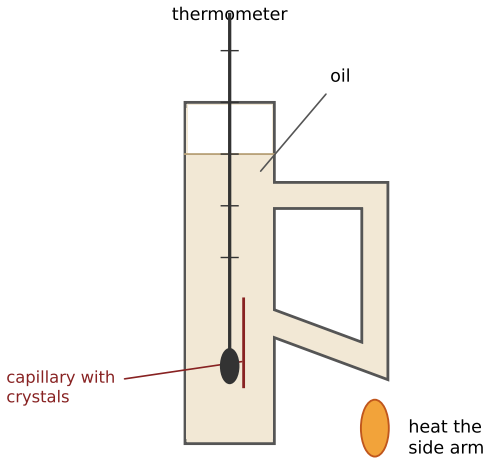
Preparing and purifying an organic solid

The phenyl benzoate preparation (benzoyl chloride + phenol in sodium hydroxide) is the template.

- **Safety**: gloves for weighing phenol (toxic by skin absorption); **fume cupboard** because **benzoyl chloride is toxic by inhalation**.
- **Why a volume may be inexact**: show by calculation which reagent limits. 9 $\mathrm{cm}^3 \times 1.21 = 10.89$ g $= 0.0775$ mol benzoyl chloride, against $5.00/94.0 = 0.0532$ mol phenol – benzoyl chloride is in **excess** , so its exact volume does not affect the yield.
- **Washing with water** removes the **soluble impurities** : excess benzoyl chloride (hydrolysed), HCl, NaOH, NaCl. Never say "insoluble impurities" – the scheme rejects it.
- **Recrystallisation** : dissolve in the minimum hot **solvent** – at 60 °C, below ethanol's boiling point and, crucially, below the product's melting temperature (71 °C), **so the crystals do not melt**; cool in ice-water; filter; wash with **cold** solvent, which removes soluble impurities while the crystals barely dissolve. A sharp **melting temperature** at the data-book value certifies purity.



Recrystallisation steps: dissolve hot, cool slowly, suction-filter, wash cold and dry.



A Thiele tube melting-temperature apparatus: oil bath, labelled thermometer, capillary of crystals, flame heat source.

Worked check (yield). n(phenol) = 5.00/94.0 = 0.0532 mol; 1:1 **stoichiometry** ; theoretical mass = 0.0532 × 198.0 = 10.5 g; at 65.0 % yield, mass = 6.85 g.

What written practice cannot do

As throughout this qualification, the written paper samples your *understanding* of practical work: the observations, the reasons, the arithmetic and the judgement. The manipulative craft – a clean titration endpoint, a working **Thiele tube** , a quantitative transfer – is built in class through the core practicals themselves.

Check yourself

1. A pale brown precipitate that darkens on standing in air: which cation, and what darkens it?
2. Write two acceptable ionic equations for the green precipitate when NaOH(aq) meets an Fe^{2+} solution.
3. Salt B gives a green precipitate with NaOH, ammonia on warming, and a white precipitate with acidified barium chloride. Deduce the salt.
4. Why is thiosulfate added to a clock reaction, and what ends the timing?
5. Titres 9.95, 9.55, 9.45 cm^3 – which enter the mean, and what is it?
6. From a ln(1/t)–1/T gradient of −6045 K, calculate E_a with unit.
7. Why dissolve the crude solid at 60 °C rather than at ethanol's boiling point?

8. Give two things a water wash removes from crude phenyl benzoate, and one phrase the scheme rejects.
9. Sketch or describe the melting-temperature apparatus, naming three labelled parts.
10. 5.00 g phenol (Mr 94.0) at 65.0 % yield gives what mass of phenyl benzoate (Mr 198.0)?

Answers: 1 Mn^{2+}; air oxidises the pale brown $Mn(OH)_2$ to a darker manganese(III/IV) oxide/hydroxide; 2 $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$, or $[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2(H_2O)_4 + 2H_2O$; 3 $(NH_4)_2Fe(SO_4)_2$ – NH_4^+, Fe^{2+} and SO_4^{2-}; 4 it reacts with iodine as it forms, delaying the starch colour until a fixed small amount of iodine has been produced; the blue-black colour; 5 9.55 and 9.45 (concordant within 0.2 cm^3); mean 9.50 cm^3; 6 $E_a = 6045 \times 8.31 = 50.2$ kJ mol^{-1}; 7 ethanol's boiling point (78 °C) is above the product's melting temperature (71 °C) – at the boil the crystals would melt; 60 °C dissolves without melting; 8 removes excess benzoyl chloride, HCl, NaOH or NaCl (soluble) – "insoluble impurities" is rejected; 9 Thiele tube (or boiling tube/beaker) filled with oil, labelled thermometer in the liquid, **capillary tube** of crystals attached, heated with a flame (not electrical); 10 $n = 5.00/94.0 = 0.0532$ mol; $0.0532 \times 198.0 \times 0.650 = 6.85$ g.