

2 · Energetics, Group Chemistry, Halogenoalkanes and Alcohols

Pearson Edexcel · International A-Level · Chemistry

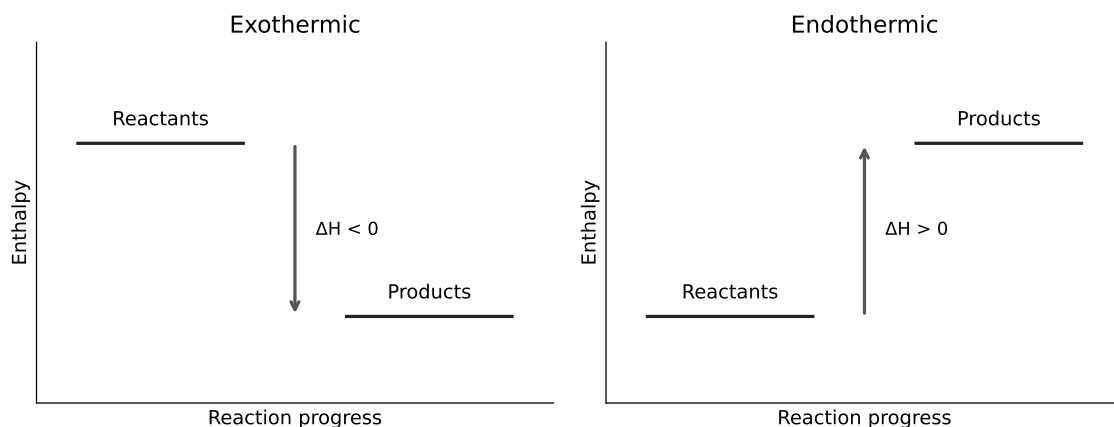
Choose a model before choosing an equation

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 .



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, $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ is an atomisation equation, whereas $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$ 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 $4.18 \text{ J g}^{-1}^\circ\text{C}^{-1}$ and negligible cup heat capacity.

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

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

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

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

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 $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$, use $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, $\Delta H = -394 \text{ kJ mol}^{-1}$, and the reverse of $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$, whose forward $\Delta H = -283 \text{ kJ mol}^{-1}$. The target is the sum, so $\Delta H = -394 - (-283) = -111 \text{ kJ mol}^{-1}$. 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.

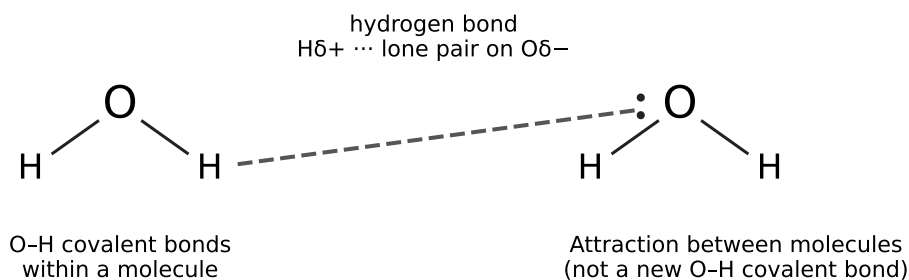
$$\Delta H \approx \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$$

For $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$, let $\text{H-H} = 436$, $\text{Cl-Cl} = 243$ and $\text{H-Cl} = 431 \text{ kJ mol}^{-1}$. Then $\Delta H \approx 436 + 243 - 2(431) = -183 \text{ kJ mol}^{-1}$. Conversely, if $\Delta H = -184 \text{ kJ mol}^{-1}$, $E(\text{H-Cl}) = [436 + 243 - (-184)]/2 = 431.5 \text{ kJ mol}^{-1}$. 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

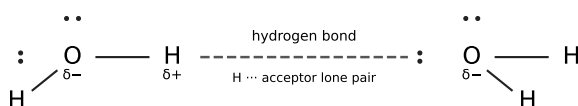
All atoms and molecules have London forces, caused by instantaneous dipoles inducing dipoles in neighbouring particles. More electrons and a more polarisable electron cloud usually strengthen these forces. Permanent dipole–dipole attractions also occur between polar molecules. A **hydrogen bond** is 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.

Water: donor H is covalently bonded to O

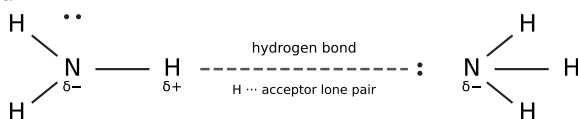


Solid line: covalent bond Dashed line: hydrogen bond

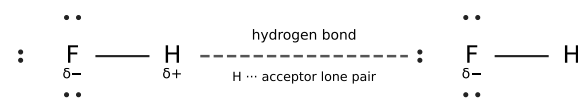
Water



Ammonia



Hydrogen fluoride



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 $\text{Cr}_2\text{O}_7^{2-}$, $2x + 7(-2) = -2$, 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, $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ and $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ give $\text{Mg} + \text{Cl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-$. 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	$\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$; $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Sulfate	Acidify with dilute HCl, then add $\text{BaCl}_2(\text{aq})$; white precipitate	$\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$; acid removes carbonate interference
Ammonium	Add $\text{NaOH}(\text{aq})$, warm gently; gas turns damp red litmus blue and gives white fumes with HCl	$\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$; $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
Halide	Acidify with dilute HNO_3 , then add $\text{AgNO}_3(\text{aq})$	$\text{Ag}^+ + \text{X}^- \rightarrow \text{AgX}(\text{s})$; 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 $0.0500\text{ mol dm}^{-3}\text{ Na}_2\text{CO}_3$ needs 24.60 cm^3 of HCl . The equation is $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$.

$$n(\text{Na}_2\text{CO}_3) = cV = 0.0500 \times 0.02500 = 0.001250\text{ mol}$$

$$n(\text{HCl}) = 2n(\text{Na}_2\text{CO}_3) = 0.002500\text{ mol}$$

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

Mass concentration is cM in g dm^{-3} . If each burette reading has uncertainty $\pm 0.05\text{ cm}^3$, the maximum uncertainty in a titre is $\pm 0.10\text{ cm}^3$; 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, $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$. 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 $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$: 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.

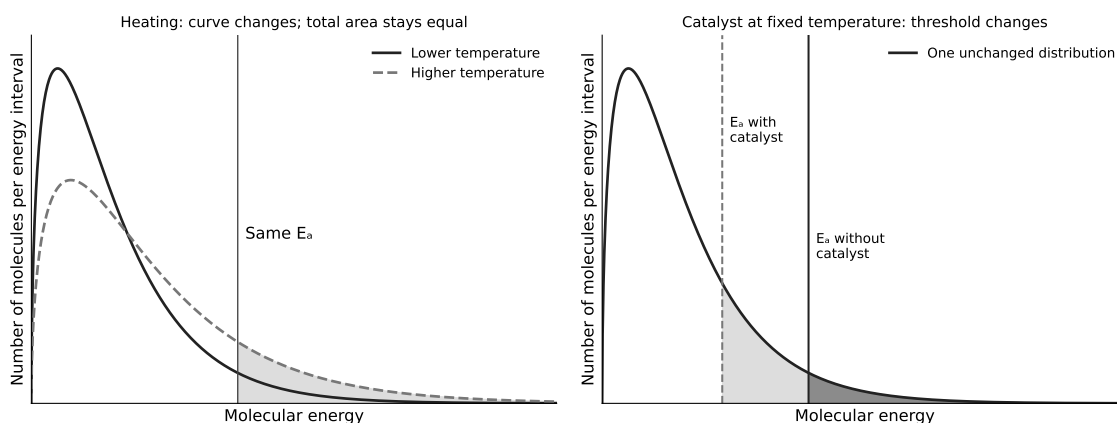
Cold dilute alkali gives $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$, the basis of hypochlorite bleach. Hot concentrated alkali gives $3\text{Cl}_2 + 6\text{OH}^- \rightarrow 5\text{Cl}^- + \text{ClO}_3^- + 3\text{H}_2\text{O}$; chlorine becomes -1 and $+5$. Analogous bromine and iodine equations follow the same atom/charge accounting under the specified conditions.

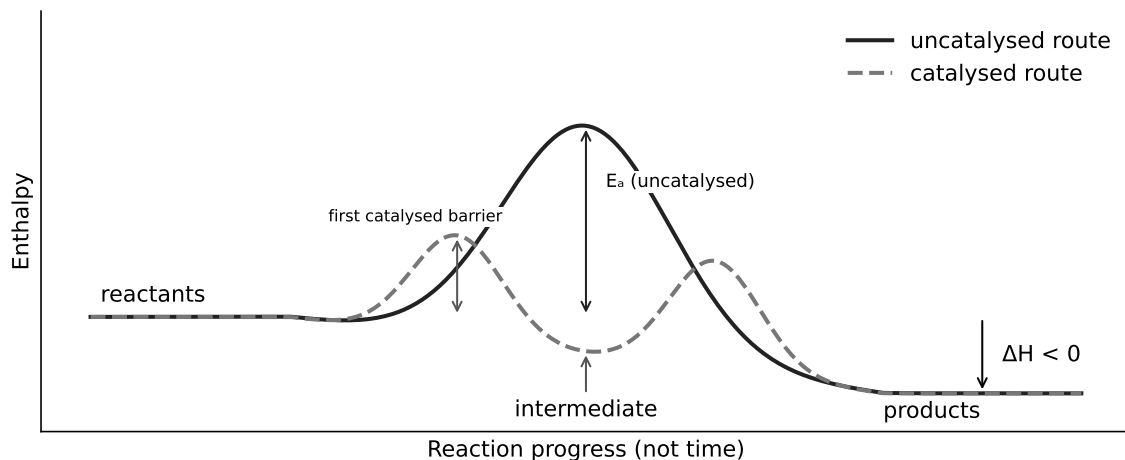
With concentrated H_2SO_4 , solid chloride salts undergo acid–base reaction to release HCl ; chloride is not a sufficiently strong reducing agent to reduce the acid under these conditions. Bromide first gives HBr , which can reduce sulfur from $+6$ to $+4$ in SO_2 while forming Br_2 : $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$. 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 $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$ and $6\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + \text{S} + 4\text{H}_2\text{O}$. For H_2S : $8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$. 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: $\text{HX} + \text{NH}_3 \rightarrow \text{NH}_4\text{X}$.

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.





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 $\text{mol dm}^{-3} \text{s}^{-1}$. 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 $(36 - 12)/(50 - 10) = 0.60 \text{ cm}^3 \text{s}^{-1}$. 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 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, 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

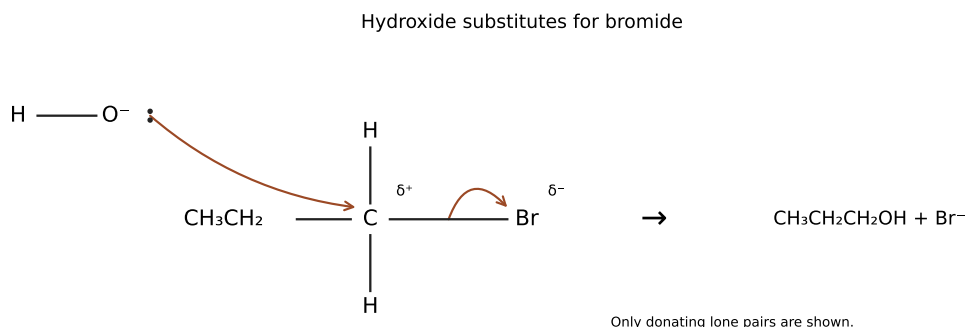
bearing X: one primary, two secondary, three tertiary. This is not the position number in its name. 1-bromobutane is primary; 2-bromobutane is secondary; 2-bromo-2-methylpropane is tertiary.

Reagent and conditions	Main change	Example carbon-count check
Aqueous KOH, warm/reflux	Substitution; OH ⁻ is a nucleophile	CH ₃ CH ₂ Br → CH ₃ CH ₂ OH; 2 C remain 2 C
Ethanolic KOH, heat	Elimination; OH ⁻ acts as a base	CH ₃ CH ₂ Br → CH ₂ =CH ₂ + HBr removed overall
Excess alcoholic NH ₃ , heat under pressure	Substitution to an amine	CH ₃ CH ₂ Br + 2NH ₃ → CH ₃ CH ₂ NH ₂ + NH ₄ Br
Alcoholic KCN, heat/reflux	Substitution to a nitrile	CH ₃ CH ₂ Br → CH ₃ CH ₂ CN; 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

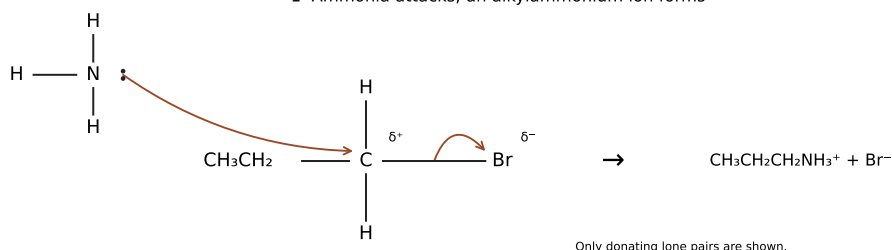
For primary bromoethane and OH⁻, draw one arrow from an oxygen lone pair to the carbon bearing Br and another from the C–Br bond to Br. Products are ethanol and Br⁻. For ammonia, the same electron-pair attack gives CH₃CH₂NH₃⁺ and Br⁻; a second ammonia removes H⁺ to give CH₃CH₂NH₂ and NH₄⁺. Include this proton-transfer step and charges. Detailed S_N1/S_N2 kinetics are Unit 4 material.

■ Complete primary substitution drawings

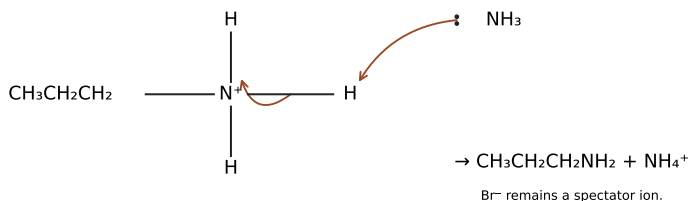
The following original example uses **1-bromopropane**, so count three carbons throughout. The hydroxide mechanism gives propan-1-ol; the ammonia route gives propan-1-amine after proton transfer. Only the donating lone pairs are drawn. The first ammonia stage produces a positively charged nitrogen with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



1 Ammonia attacks; an alkylammonium ion forms



2 A second ammonia removes a proton



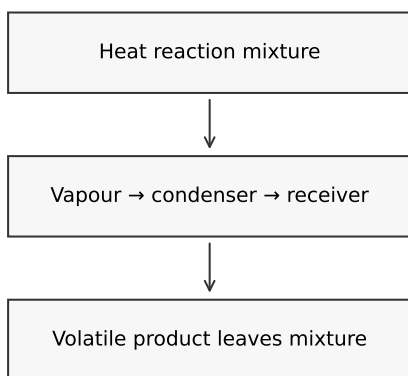
In core practical 5, compare equal concentrations/volumes of halogenoalkanes with the same silver nitrate/ethanol mixture at controlled temperature. Time formation of a comparable precipitate. Iodoalkanes hydrolyse faster than bromoalkanes, which hydrolyse faster than chloroalkanes, because C–I is weaker 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.

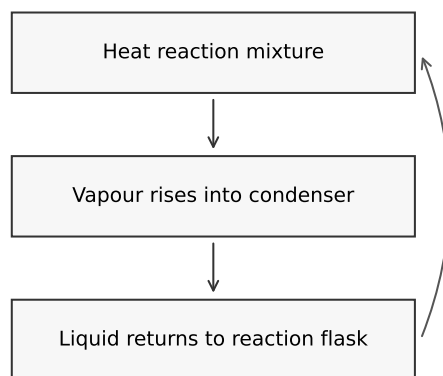
Alcohols, purification and spectral evidence

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: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$. Heat under reflux with excess oxidant to make the acid: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O}$. Secondary propan-2-ol gives propanone: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$. Tertiary alcohols resist oxidation under these conditions because the OH-bearing carbon lacks H. Orange dichromate turns green on reduction.

DISTILLATION



REFLUX



Process comparison only; use the approved apparatus and risk assessment.

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: $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$. 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: $\text{C}=\text{O}$, $\text{O}-\text{H}$, $\text{N}-\text{H}$, $\text{C}=\text{C}$, $\text{C}-\text{H}$ and $\text{C}-\text{X}$ can identify possible functional groups. Alcohol $\text{O}-\text{H}$ is broad; acid $\text{O}-\text{H}$ is very broad and appears with $\text{C}=\text{O}$. Both aldehydes and ketones have $\text{C}=\text{O}$, 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 com-

bines 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 $\text{C}_3\text{H}_6\text{O}$ has a $\text{C}=\text{O}$ 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; $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$, $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$. (4) Forward reaction is exothermic; a catalyst changes rates, not equilibrium composition at a fixed temperature. (5) Bromoethane; alcoholic KCN with heat gives $\text{CH}_3\text{CH}_2\text{CN}$; aqueous KOH gives ethanol. (6) Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$; propanone has the formula and carbonyl but does not reduce Fehling's solution under the stated test.