Unit 2: Energetics, groups and organic reactions

Pearson acquired Topics 6–10, core practicals 2–8; practical experience and bank holds remain explicit.

Choose the chemical model

1. **1** Energy, attractions, electron transfer and collision models explain different observations.
2. **2** Use Unit 1 mole ratios, polarity and structural formulae; state conditions before predicting products.

The sign belongs to the reaction

1. **1** At constant pressure, ΔH is the reaction heat change.
2. **2 Exothermic**: surroundings warm and reaction ΔH is negative.
3. **3** Standard data specify 100 kPa, temperature and physical states.

Definitions fix the mole basis

1. **1** Formation: one mole of compound from standard-state elements.
2. **2** Combustion: complete burning of one mole of substance.
3. **3 Neutralisation**: one mole of water formed; **atomisation**: one mole of gaseous atoms.

Calorimetry: energy then amount

1. **1** $q = mc\Delta T = 100.0\,g \times 4.18\,J g^{-1}\,^\circ C^{-1} \times 6.8\,^\circ C = 2.842\,kJ$.
2. **2** $n(\mathrm{H_2O}) = cV = 1.00\,mol\,dm^{-3} \times 0.0500\,dm^3 = 0.0500\,mol$.
3. **3** $\Delta H = -q/n = -56.8\,kJ\,mol^{-1}$; use total heated mass and limiting amount.

Check the sign and denominator

Your turn

The solution gains 1.20 kJ while 0.0200 mol reacts. What is the molar reaction enthalpy?

A. $+60.0\ \text{kJ mol}^{-1}$

B. $-60.0\ \text{kJ mol}^{-1}$

C. $-0.0240\ \text{kJ mol}^{-1}$

D. $-1.20\ \text{kJ mol}^{-1}$

Energy conservation gives the answer

1. **1** $\Delta H = -q/n = -1.20\,kJ/0.0200\,mol = -60.0\,kJ\,mol^{-1}$.
2. **2** B is correct. A uses the solution sign; C multiplies by amount; D omits the mole basis.

Hess: cancel species first

1. **1** $\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$: -394 kJ mol^{-1}.
2. **2** Reverse $\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2}$: $+283$ kJ mol^{-1}.
3. **3** Sum: $\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO}$; $\Delta\mathrm{H} = -111$ kJ mol^{-1}.

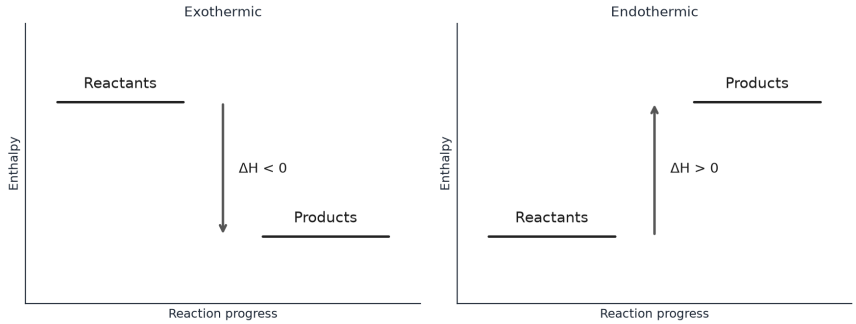
Bond estimates have assumptions

1. **1** Count bonds broken minus bonds formed, including coefficients.
2. **2** For $H_2 + Cl_2 \rightarrow 2HCl$: $436 + 243 - 2(431) = -183$ kJ mol^{-1}.
3. **3** Mean values describe gas-phase bonds in averaged environments; ΔH does not determine rate.

Your turn: the level fixes the sign

1. **Set up** Draw **exothermic** and **endothermic** enthalpy-level diagrams.
2. **Reason** Label both levels and the signed ΔH arrow; the horizontal axis is reaction progress.

Initial and final levels determine ΔH

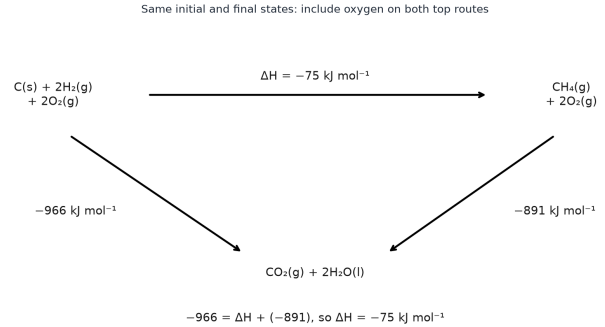


1. **Set up Exothermic** products lie lower: the reaction ΔH arrow points down.
2. **Reason Endothermic** products lie higher: the arrow points up.

Your turn: draw the whole Hess cycle

1. **Set up** Find C(graphite) + $2H_2(g) \rightarrow CH_4(g)$ using combustion data.
2. **Reason** C: -394; H_2: -286; CH_4: -891 kJ mol^{-1}. Draw a common final state with the correct oxygen amount.

Match both routes before subtracting

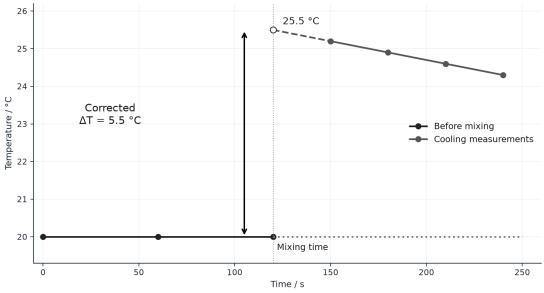


1. **Set up** Carbon + two hydrogen moles: $-394 + 2(-286) = -966$ kJ mol^{-1}.
2. **Reason** $-966 = \Delta H + (-891)$, so $\Delta H = -75$ kJ mol^{-1}.

Your turn: correct the mixing temperature

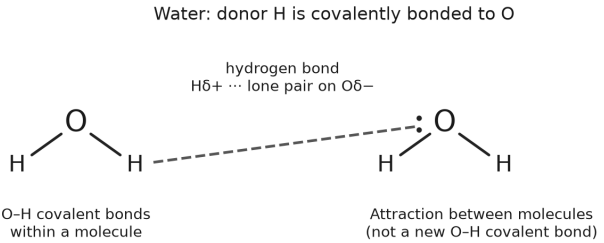
1. **Set up** Before mixing at 120 s: 20.0 °C. After: 25.2 °C at 150 s, then 24.9, 24.6, 24.3 °C at 180, 210, 240 s.
2. **Reason** Plot and extrapolate to mixing. Then use 80.0 g, c = 4.18 J g^{-1} $°C^{-1}$ and 0.0400 mol water to find ΔH.

Cooling correction restores the missing rise



1. **Set up** Extrapolate to 25.5 °C at 120 s: corrected $\Delta T = 5.5$ °C.
2. **Reason** $q = 80.0(4.18)(5.5) = 1839.2$ J; $\Delta H = -1.8392/0.0400 = -46.0$ kJ mol^{-1}.

Hydrogen bonding needs a donor



H bonded to N, O or F can attract a suitable lone pair on another molecule.

Boiling separates molecules

1. **1** More electrons usually strengthen **London forces**; alkane boiling temperatures rise with chain length.
2. **2** Branching reduces effective contact between isomers.
3. **3** Alcohols also hydrogen-bond; HF is unusually high compared with HCl/HBr/HI.

Water, ice and solvent evidence

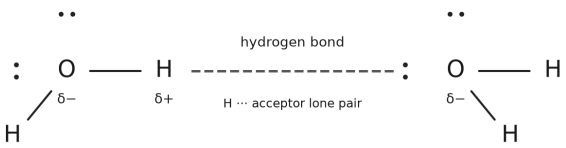
1. **1** An open hydrogen-bonded ice structure gives lower density than liquid water.
2. **2** Water hydrates ions and hydrogen-bonds with small alcohols.
3. **3** A polar C–X bond alone does not make a halogenoalkane water-soluble.

Your turn: three hydrogen-bonded liquids

1. **Attempt** Draw one hydrogen-bonded pair each for water, ammonia and HF.
2. **Label** Show all atoms, covalent bonds, acceptor lone pairs and the donor/acceptor partial charges.

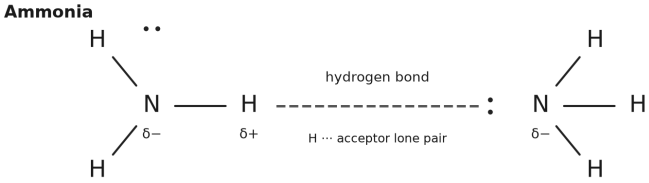
Water: donor H and acceptor lone pair

Water



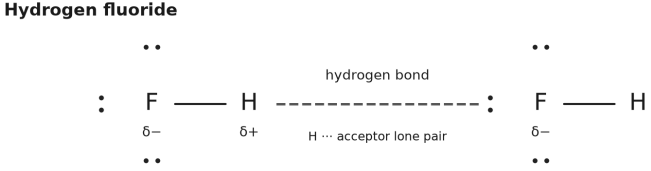
1. **Donor** The donor H is covalently bonded to O; the dashed line is between molecules.
2. **Acceptor** The neighbouring O lone pair attracts H$\delta+$; solid lines retain the covalent bonds.

Ammonia: donor H and acceptor lone pair



1. **Donor** The donor H is covalently bonded to N; the dashed line is between molecules.
2. **Acceptor** The neighbouring N lone pair attracts H$\delta+$; solid lines retain the covalent bonds.

Hydrogen fluoride: donor H and acceptor lone pair



1. **Donor** The donor H is covalently bonded to F; the dashed line is between molecules.
2. **Acceptor** The neighbouring F lone pair attracts H$\delta+$; solid lines retain the covalent bonds.

Oxidation numbers and agents

1. **1** Oxidation loses electrons and raises **oxidation number**; reduction does the reverse.
2. **2** The **oxidising agent** gains electrons and is reduced.
3. **3** O is -1 in peroxides; H is -1 in metal hydrides. Sum values to the species charge.

Balance electrons and charge

1. **1** $\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^{-}$ and $\mathrm{Cu}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu}$.
2. **2** Multiply by 2 and 3 so six electrons cancel.
3. **3** $2\mathrm{Al} + 3\mathrm{Cu}^{2+} \rightarrow 2\mathrm{Al}^{3+} + 3\mathrm{Cu}$; Cu^{2+} is the **oxidising agent**.

Group trends need two models

1. **1** Down Groups 1/2, radius and **shielding** increase; outer electrons are lost more easily.
2. **2** Small high-charge-density cations polarise anions strongly, lowering carbonate/nitrate thermal stability.
3. **3** Group 2 hydroxides become more soluble down the group; sulfates less soluble.

Observe without mixing up reactions

1. **1** Li_2CO_3 and Group 2 carbonates give oxide + CO_2 on heating.
2. **2** Most Group 1 nitrates give nitrite + O_2; lithium and Group 2 nitrates also give NO_2.
3. **3** Flame-test colours arise from electron transitions, not the ordinary colour of the solid.

Your turn: two Group 2 solubility trends

1. **Set up** Equal volumes of saturated $Mg(OH)_2$ and $Ba(OH)_2$ are titrated with the same acid. Which needs more?
2. **Reason** Equal Mg^{2+}/Ba^{2+} concentrations receive excess sulfate. Which gives more **precipitate**? Explain both.

Opposite solubility trends explain the evidence

1. **Set up** $Ba(OH)_2$ is more soluble: its equal saturated volume contains more OH^- and needs more acid.
2. **Reason** $BaSO_4$ is less soluble: equal initial cation amounts give more solid with excess sulfate.
3. **Conclude** Solubility controls dissolved amount; it is different from dissociation strength.

Controls distinguish chemical evidence from contamination

1. **Set up** Match measured amounts, particle size, apparatus and heating rate; compare sample temperature at a consistent decomposition criterion.
2. **Reason** CO_2: milky limewater; O_2: glowing splint relights; NO_2: brown and acidic.
3. **Conclude** Clean flame-test wire and keep the flame region/loading consistent. Na yellow, K lilac, Ca brick-red, Sr crimson-red; sodium carry-over can mask another colour.

Separate aliquots protect the evidence

1. **1** Carbonate + acid gives CO_2; confirm with limewater.
2. **2** Sulfate: dilute HCl then $BaCl_2$ gives white $BaSO_4$.
3. **3** Ammonium + warm NaOH gives NH_3; damp red litmus turns blue.

A titre is a difference

1. **1** Rinse burette/pipette with their own solutions; fill the jet and remove the funnel.
2. **2** Use **concordant** accurate titres, not the rough trial.
3. **3** Two ± 0.05 cm^3 readings give ± 0.10 cm^3 maximum titre uncertainty.

Titration: ratio before concentration

1. **1** 25.00 cm^3 of 0.0500 mol dm^{-3} Na_2CO_3 uses 24.60 cm^3 HCl; ratio is 1:2.
2. **2** $n(\text{carbonate}) = cV = 0.001250\ mol$; $n(\text{HCl}) = 0.002500\ mol$.
3. **3** $c(\text{HCl}) = n/V = 0.002500\ mol/0.02460\ dm^3 = 0.1016\ mol\,dm^{-3}$.

Your turn: retain both possible anions

1. **Set up** A salt releases gas turning limewater milky with acid. A fresh aliquot gives ammonia with warm NaOH.
2. **Reason** Identify the supported ions and write both NH_3 production and HCl-fume equations. Can you distinguish carbonate from hydrogencarbonate?

A positive gas test has a limited conclusion

1. **Set up** $\mathrm{NH_4^+ + OH^- \rightarrow NH_3 + H_2O}$ supports ammonium.
2. **Reason** $\mathrm{NH_3 + HCl \rightarrow NH_4Cl}$ explains the white fumes.
3. **Conclude** Both carbonate and hydrogencarbonate release $\mathrm{CO_2}$ with acid; the evidence does not select just one.

Your turn: a solid acid measures NaOH

1. **Set up** H_2A has M = 126.0 g mol^{-1}; dissolve 1.575 g and make to 250.0 cm^3.
2. **Reason** 25.00 cm^3 acid requires 23.80 cm^3 NaOH. Use $H_2A + 2NaOH \rightarrow Na_2A + 2H_2O$ to find NaOH concentration.

The acid aliquot determines twice the alkali amount

1. **Set up** $n(\text{acid, total}) = 1.575\,g/(126.0\,g\,mol^{-1}) = 0.01250\,mol$.
2. **Reason** One tenth is pipetted: $n(\text{NaOH}) = 2(0.001250\,mol) = 0.002500\,mol$.
3. **Conclude** $c(\text{NaOH}) = 0.002500\,mol/0.02380\,dm^3 = 0.1050\,mol\,dm^{-3}$.

Your turn: determine HCl concentration

1. **Set up** 25.00 cm^3 HCl uses 24.60 cm^3 of 0.1000 mol dm^{-3} NaOH.
2. **Reason** Calculate concentration, then explain rinsing, meniscus readings and the phenolphthalein endpoint.

The ratio precedes the concentration

1. **Set up** n(NaOH) $= 0.1000 \times 0.02460 = 0.002460$ mol; c(HCl) $= 0.002460/0.02500 = 0.09840$ mol dm^{-3}.
2. **Reason** Rinse pipette with HCl, burette with NaOH, flask with deionised water; fill the jet and read at eye level.
3. **Conclude** Swirl and add dropwise near the first persistent pale-pink endpoint; repeat to concordance and exclude the rough titre.

Halogen oxidising power decreases

1. **1** Cl_2 displaces Br^- and I^-; Br_2 displaces I^-; I_2 displaces neither.
2. **2** Increasing radius/**shielding** weakens attraction for an incoming electron.
3. **3** Iodine is brown in water but violet in a suitable non-polar organic solvent.

Conditions change the chlorine product

Your turn

Hot concentrated alkali reacts with chlorine. Which oxyanion forms?

A. ClO^-
B. ClO_3^-
C. Cl^- only
D. No reaction

Disproportionation balances electron changes

1. **1** $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$.
2. **2** Answer B. Chlorine goes $0 \rightarrow -1$ and $0 \rightarrow +5$.
3. **3** Cold dilute alkali instead forms ClO^-. Conditions belong in the answer.

Halide tests and reducing power

1. **1** Acidify with HNO_3 before $AgNO_3$: AgCl white, AgBr cream, AgI yellow.
2. **2** AgCl dissolves in dilute NH_3; AgBr needs concentrated NH_3; AgI remains.
3. **3** With concentrated H_2SO_4, bromide and especially iodide can reduce sulfur; chloride normally only gives HCl.

Name the attracted electron pair

1. **Set up Electronegativity** concerns a shared bonding pair; oxidising power concerns electron gain in redox.
2. **Reason** Both decrease from Cl to Br to I as radius and **shielding** weaken attraction despite greater nuclear charge.

Your turn: name the solvent before the colour

1. **Set up** Add a small amount of Br_2 to excess KI or KCl, then extract into cyclohexane.
2. **Reason** Bromine is orange and iodine purple in this solvent. Predict both layers and write the reaction.

Displacement changes the halogen species

1. **Set up** KI gives purple I_2: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$.
2. **Reason** KCl retains orange Br_2 because bromine cannot oxidise chloride under these conditions.

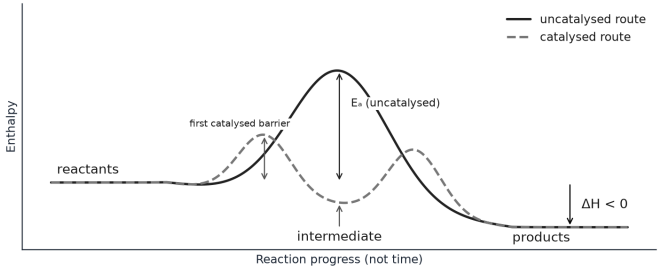
Your turn: three sulfur reduction products

1. **Set up** HI reduces H_2SO_4 to SO_2, S or H_2S while forming I_2.
2. **Reason** Balance each route and state all three final sulfur oxidation numbers.

Balance atoms and track sulfur

1. **Set up** $2\mathrm{HI} + \mathrm{H_2SO_4} \rightarrow \mathrm{I_2} + \mathrm{SO_2} + 2\mathrm{H_2O}$; S: $+6 \rightarrow +4$.
2. **Reason** $6\mathrm{HI} + \mathrm{H_2SO_4} \rightarrow 3\mathrm{I_2} + \mathrm{S} + 4\mathrm{H_2O}$; S: $+6 \rightarrow 0$.
3. **Conclude** $8\mathrm{HI} + \mathrm{H_2SO_4} \rightarrow 4\mathrm{I_2} + \mathrm{H_2S} + 4\mathrm{H_2O}$; S: $+6 \rightarrow -2$.
4. **Check** Iodide is oxidised from -1 to 0; oxidising sulfuric acid consumes the desired HI.

The catalyst changes the pathway



The catalysed route has an intermediate and lower activation barriers.

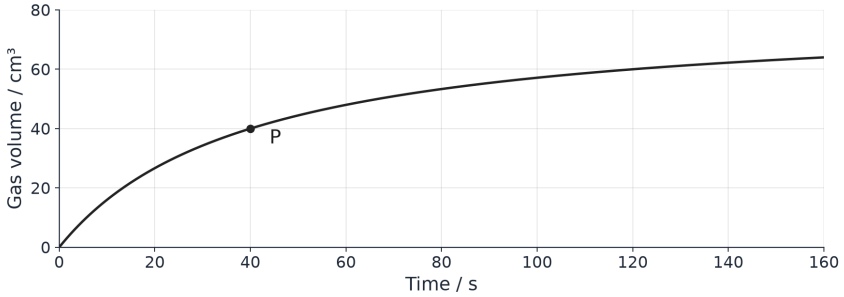
Rate measurements answer different questions

1. **1** For a fixed endpoint, comparative rate is $1/t$ in s^{-1}.
2. **2** Instantaneous gas rate is a tangent gradient, not final volume / total time.
3. **3** Higher temperature increases the fraction beyond Ea; a **catalyst** lowers Ea without changing the distribution.

Equilibrium is dynamic

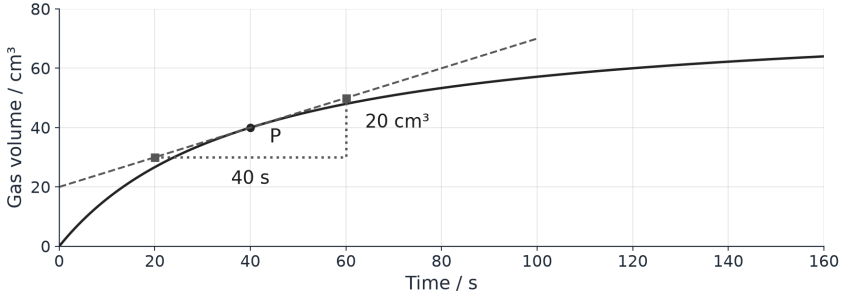
1. **1** Forward and reverse rates are equal in a closed system; concentrations need not be equal.
2. **2** Higher pressure favours fewer gas moles; higher temperature favours the **endothermic** direction.
3. **3** A **catalyst** reaches the same equilibrium sooner. Industrial operation balances rate, yield and cost.

Your turn: draw a tangent at P



1. **Set up** Draw the tangent at P, then choose two separated points on that straight line.
2. **Reason** Find the instantaneous gas-production rate with units.

A tangent gives the local rate

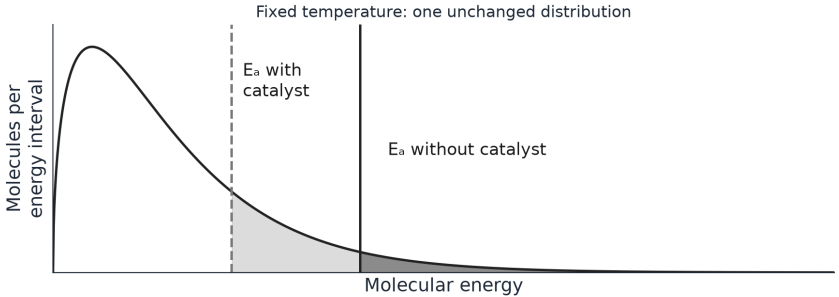


1. **Set up** Use tangent points (20 s, 30 cm^3) and (60 s, 50 cm^3).
2. **Reason** Rate $= (50 - 30)/(60 - 20) = 0.50$ cm^3 s^{-1}. Origin to P gives the earlier average, 1.0 cm^3 s^{-1}.

Your turn: a catalyst changes which feature?

1. **Set up** At fixed temperature, draw the energy distribution and two activation thresholds.
2. **Reason** Shade the sufficiently energetic fraction for each pathway. State what remains unchanged.

Lower threshold, unchanged molecular energies



1. **Set up** Catalysed E_a lies to the left; more collisions have enough energy.
2. **Reason** The same curve, total population and mean energy remain. Equilibrium yield at this temperature is unchanged.

Your turn: test both plant requirements

1. **Set up** 450 / 550 / 650 K: yields 92 / 76 / 46%; rates 0.040 / 0.60 / 2.5 mol min^{-1}.
2. **Reason** Require yield $\geq$70% and rate $\geq$0.50 mol min^{-1}. Choose the temperature and reject the others using the data.

Both limits define the compromise

1. **Set up** 550 K passes: 76% $\geq$70% and 0.60 $\geq$0.50 mol min^{-1}.
2. **Reason** 450 K is too slow; 650 K gives too little equilibrium product.
3. **Conclude** For an **exothermic** forward reaction, heating favours reverse reaction but raises the energetic collision fraction.

Solvent chooses the reaction emphasis

1. **1** Warm aqueous KOH: bromoethane $\rightarrow$ ethanol by substitution.
2. **2** Hot ethanolic KOH: bromoethane $\rightarrow$ ethene by elimination.
3. **3** Alcoholic KCN gives propanenitrile; alcoholic excess NH_3 under pressure gives ethylamine.

Electron arrows show the mechanism

1. **1** OH^- lone pair $\rightarrow$ carbon bearing Br; C–Br bond $\rightarrow$ Br.
2. **2** With NH_3, an alkylammonium ion forms first; a second NH_3 removes a proton.
3. **3** For matched **hydrolysis**, weaker C–I reacts faster than C–Br then C–Cl; control temperature and concentrations.

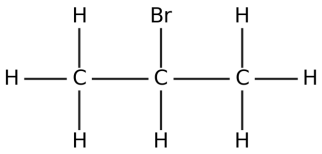
Your turn: names and two drawing conventions

1. **Set up** Name $CH_3CHBrCH_3$ and $CH_3CH(OH)CH_2CH_3$.
2. **Reason** Draw each displayed and skeletal formula. Check every carbon valence and the O–H hydrogen.

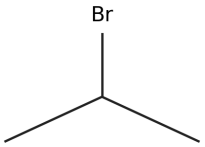
2-Bromopropane has a secondary functional carbon

2-Bromopropane: $CH_3CHBrCH_3$

Displayed formula



Skeletal formula

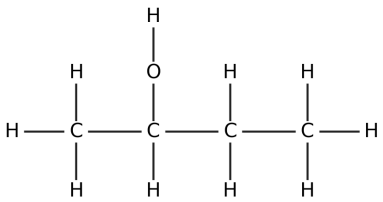


1. **Set up** The central carbon has two carbon neighbours, one Br and one H.
2. **Reason** The skeletal corner and both ends represent three carbons.

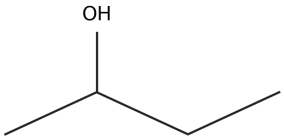
Butan-2-ol retains the O–H hydrogen

Butan-2-ol: $CH_3CH(OH)CH_2CH_3$

Displayed formula



Skeletal formula



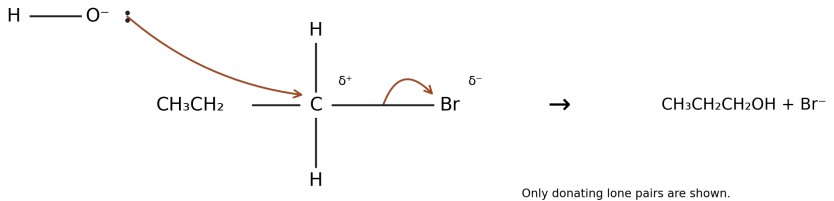
1. **Set up** Four carbons form the main chain; OH is on carbon 2.
2. **Reason** The OH-bearing carbon has two carbon neighbours, so the alcohol is secondary.

Your turn: draw hydroxide substitution

1. **Set up** Use 1-bromopropane and aqueous OH^-.
2. **Reason** Show the donating pair, two curly arrows, C–Br polarity and products.

Two arrows preserve electron pairs

Hydroxide substitutes for bromide

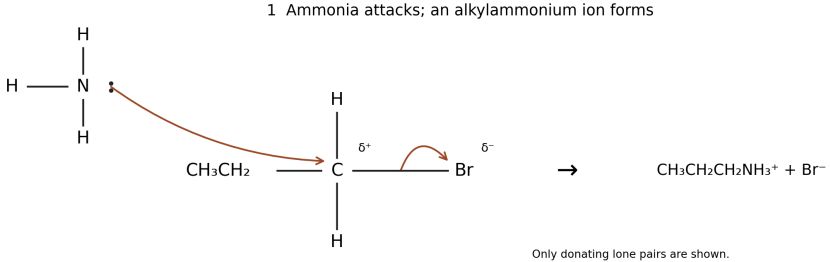


1. **Set up** O lone pair → the carbon bearing Br; C–Br bond pair → Br.
2. **Reason** Propan-1-ol and Br^- form; total charge remains -1.

Your turn: ammonia needs two stages

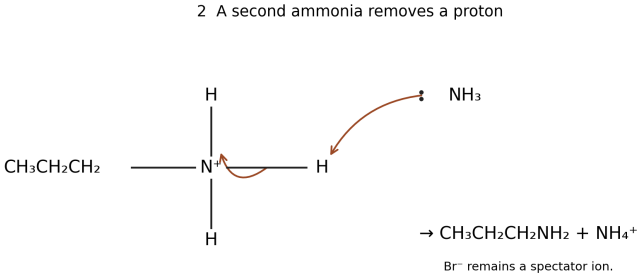
1. **Set up** Use excess alcoholic NH_3 under pressure with 1-bromopropane.
2. **Reason** Draw attack and proton transfer; retain every charge and show the second ammonia.

Attack forms the positively charged intermediate



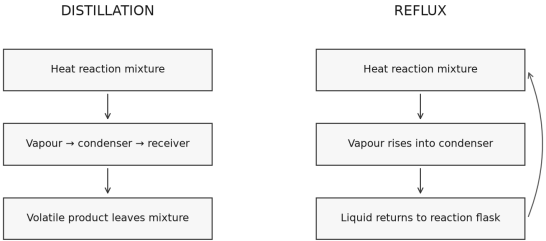
1. **Set up** NH_3 donates its lone pair to carbon while the C–Br pair goes to Br.
2. **Reason** The nitrogen has four bonds in $CH_3CH_2CH_2NH_3^+$; bromide balances its charge.

Proton transfer restores the neutral amine



1. **Set up** A second NH_3 lone pair $\rightarrow$ N-bound H; the N–H pair returns to N.
2. **Reason** Propan-1-amine and NH_4^+ form; Br^- remains. The amine lone pair allows further substitution.

Product removal controls oxidation



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

Distillation removes volatile **aldehyde** before further oxidation.

Combine tests rather than guessing

1. **1** Primary alcohol $\rightarrow$ **aldehyde** or acid; secondary $\rightarrow$ ketone; tertiary resists the stated oxidant.
2. **2** Aldehyde reduces warm Fehling's solution; acid gives CO_2 with carbonate.
3. **3** Use molecular-ion mass, IR absorptions and chemical tests together; a carbonyl peak alone is ambiguous.

Your turn: separate three purification purposes

1. **Set up** The organic product has density 0.87 g cm^{-3}; the aqueous phase has density 1.00 g cm^{-3}.
2. **Reason** Identify the layer, then explain separation, drying, salt removal and boiling-temperature evidence.

Bulk water and residual water need different actions

1. **Set up** The stated product is the upper layer; separation removes the bulk aqueous phase.
2. **Reason** A suitable **anhydrous** salt removes residual water; filter or decant before **distillation**.
3. **Conclude** Measure vapour temperature at the condenser entrance and compare at the same pressure. A narrow range supports purity, not unique identity.

Your turn: a fragment is not a full structure

1. **Set up** C_3H_6O has molecular ion 58, fragment 29, carbonyl absorption and positive warm Fehling's test.
2. **Reason** Check the mass, propose two ion formulae of mass 29 and choose propanal or propanone from all evidence.

Combined evidence selects the aldehyde

1. **Set up** Both isomers have $M_r = 3(12)+6+16 = 58$. $C_2H_5^+$ and CHO^+ both have mass 29.
2. **Reason** Positive Fehling's evidence supports propanal. One fragment or carbonyl alone cannot uniquely establish the isomer.

Supplied IR data: carbon environments

Bond / environment	**Supplied region / cm^{-1}**
Alkane C–H	2850–3000
Alkene C–H	3000–3100
Aldehyde C–H	2700–2900
C=C	1620–1680
C=O	1680–1750

Supplied IR data: heteroatom environments

Bond / environment	**Supplied region / cm^{-1}**
Alcohol O–H	3200–3600, broad
Acid O–H	2500–3300, very broad
C–Cl	500–800
Amine N–H	3300–3500

Your turn: predict bonds before peaks

1. **Set up** Use the supplied tables for $CH_2{=}CHCH_2NH_2$ and $HOCH_2CHO$.
2. **Reason** List all relevant C–H environments and each additional functional-group absorption.

Each structural environment contributes evidence

1. **Set up** $CH_2{=}CHCH_2NH_2$: alkene/alkane C–H, C=C and N–H.
2. **Reason** $HOCH_2CHO$: alkane/**aldehyde** C–H, broad alcohol O–H and C=O.
3. **Conclude** Use the given ranges; alcohol O–H differs from the very broad acid O–H of CH_3COOH.

Your turn: combine inorganic and organic evidence

1. **Set up** A/B: white $BaSO_4$. Only A releases NH_3 with warm NaOH. C/D: M^+ 58 and carbonyl; only C gives positive Fehling's.
2. **Reason** Candidates: sodium sulfate, ammonium sulfate, propanal and propanone. Assign each and write the two ionic equations.

Independent tests separate the four candidates

1. **Set up** A: ammonium sulfate; B: sodium sulfate; C: propanal; D: propanone.
2. **Reason** $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(s)$.
3. **Conclude** Use fresh **aliquots**. Shared mass and carbonyl evidence do not distinguish C/D; the **aldehyde** reducing test does.

Independent identification

Your turn

C_3H_6O has a carbonyl IR absorption and gives a positive Fehling's test. Which structure fits all evidence?

A. CH_3COCH_3
B. CH_3CH_2CHO
C. $CH_3CH_2CH_2OH$
D. CH_3COOH

Check yourself

1. **1** B: propanal has formula C_3H_6O, a carbonyl and a reducing **aldehyde** group.
2. **2** A is propanone: formula and carbonyl fit, but Fehling's result does not.
3. **3** C and D have different formulae. No one test is a whole structural proof.