

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:

$$r = k[A]^m[B]^n$$

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 $r = k[A][B]^2$ and overall order is three.

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

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.

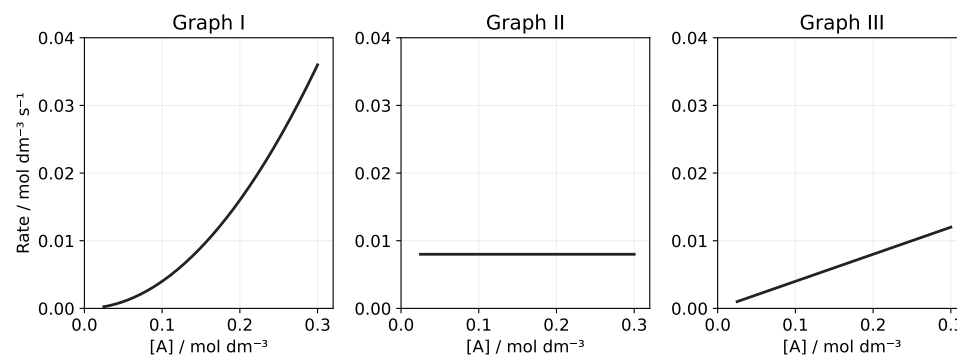
■ Graphs, half-life and method choice

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.



■ 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

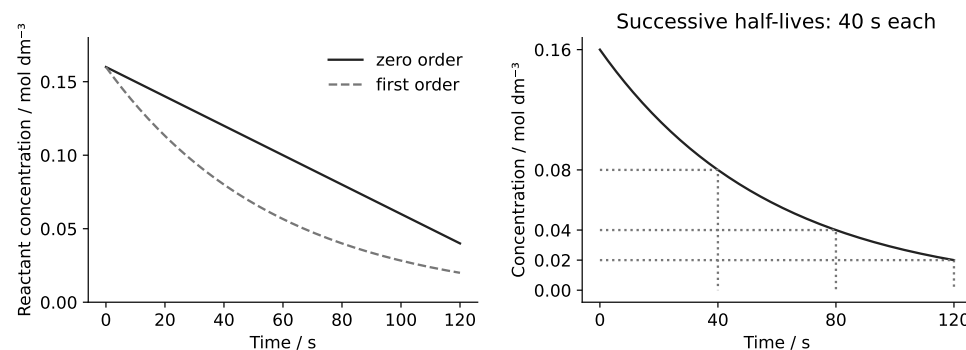
When supplied, use the Arrhenius relation $k = Ae^{-E_a/(RT)}$, or $\ln k = \ln A - E_a/(RT)$. On a graph of $\ln k$ against $1/T$, gradient = $-E_a/R$. Use kelvin and match energy units to $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$. A measured gradient of -6200 K gives:

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

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 concentration–time models at fixed temperature



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** :

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

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

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

$\Delta H/\Delta S_{\text{system}} = 30000/120 = 250 \text{ K}$; 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 $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$, 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: $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$. 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.

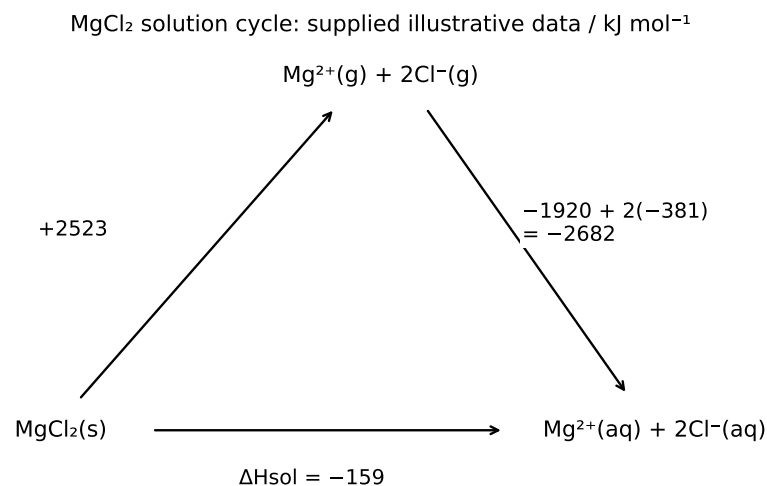
Hydration enthalpy forms one mole of aqueous ions from gaseous ions, normally exothermically. Solution enthalpy dissolves one mole of solute in sufficient water

that further dilution gives no enthalpy change, under the stated standard conditions. With the lattice **formation** convention:

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

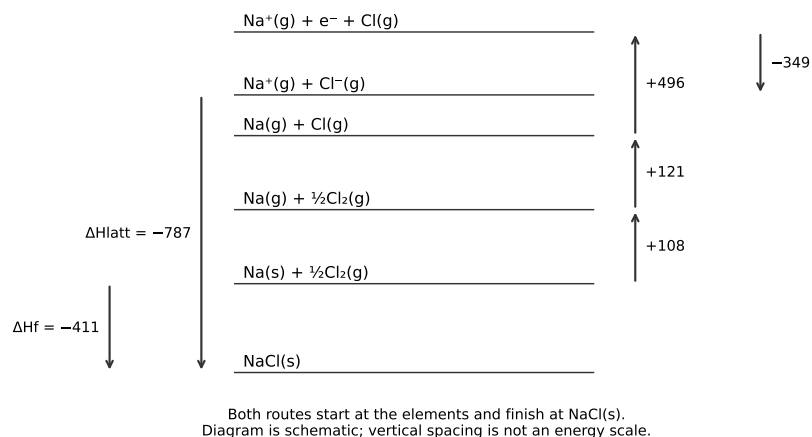
If lattice formation is -780 and the total hydration enthalpy is -760 kJ mol^{-1} , solution enthalpy is $+780 - 760 = +20 \text{ kJ mol}^{-1}$. Smaller ions and greater ionic charge usually make both lattice formation and hydration more negative. Because these effects compete, one trend alone cannot 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 $+2523 \text{ kJ mol}^{-1}$, 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.



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 Born-Haber cycle: illustrative values / kJ mol⁻¹



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 NH₃, N₂ and H₂ respectively, $K_c = (0.200)^2/[0.100(0.300)^3] = 14.8 \text{ dm}^6 \text{ mol}^{-2}$. 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 dm³. 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:

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

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 N₂O₄ and 2.00 mol NO₂, the partial pressures are 1.00 and 2.00 atm. Thus $K_p = 4.00 \text{ atm}$. 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 K_c/K_p 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 NH₄⁺/NH₃ and H₂O/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.

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

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 $[H^+] = 3.98 \times 10^{-4} \text{ mol dm}^{-3}$. 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 $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$, when given. A strong base giving $[OH^-] = 0.0100 \text{ mol dm}^{-3}$ gives $[H^+] = K_w/[OH^-] = 1.00 \times 10^{-12} \text{ mol dm}^{-3}$ and $\text{pH} = 12.00$. In general neutral means $[H^+] = [OH^-]$; pH 7 is neutral at this temperature, not a universal temperature-independent rule. $\text{p}K_a = -\log_{10} K_a$ and $\text{p}K_w = -\log_{10} K_w$ 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 $K_a = 1.80 \times 10^{-5} \text{ mol dm}^{-3}$ and $c = 0.100 \text{ mol dm}^{-3}$, $[\text{H}^+] \approx 1.34 \times 10^{-3} \text{ mol dm}^{-3}$, so $\text{pH} \approx 2.87$. 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 $\text{pH} = 2.90$ for $0.100 \text{ mol dm}^{-3}$ acid, $x = 10^{-2.90} = 1.26 \times 10^{-3} \text{ mol dm}^{-3}$. Then $K_a = x^2/(c-x) = 1.61 \times 10^{-5} \text{ mol dm}^{-3}$. 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, $[\text{H}^+]$ 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.

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

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

For a required **final** total $[\text{HA}] + [\text{A}^-]$, solve the ratio and total together. At target pH 5.00 with $K_a = 2.00 \times 10^{-5} \text{ mol dm}^{-3}$, the ratio is 2.00. If the total is $0.120 \text{ mol dm}^{-3}$, final $[\text{HA}]$ is 0.0400 and $[\text{A}^-]$ is $0.0800 \text{ mol dm}^{-3}$. 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 $0.0800(250.0/60.0) = 0.333 \text{ mol dm}^{-3}$. 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: $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$. Suppose 0.0100 mol HA initially meets 0.00400 mol OH^- . Afterwards $\text{HA} = 0.00600 \text{ mol}$ and $\text{A}^- = 0.00400 \text{ mol}$, so use their 2:3 ratio; common final volume

cancels in the ratio. Using the initial acid amount would be wrong. Beyond equivalence the excess strong base controls pH and the acid-buffer expression no longer applies.

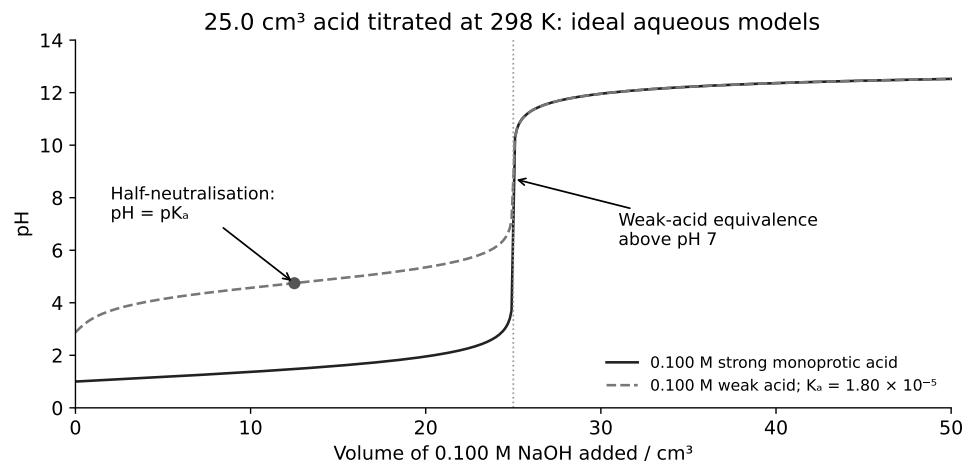
On a titration curve, distinguish initial pH, buffer region, steep change, equivalence and excess titrant. Strong acid–strong base has equivalence near pH 7 at 298 K. Weak acid–strong base has equivalence above 7; strong acid–weak base below 7. Weak acid–weak base usually lacks a sharp enough vertical 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, $[\text{HA}] = [\text{A}^-]$, so $\text{pH} = \text{p}K_a$. 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 $\text{B} + \text{H}^+ \rightarrow \text{BH}^+$. At half-equivalence equal B and BH^+ give $\text{pH} \approx \text{p}K_a$ of BH^+ . If this pH is 9.25, its $K_a = 10^{-9.25} = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$. 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, $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$ consumes added acid and $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ 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.



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 CH₃CH₂CHO and propanone CH₃COCH₃. 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 ₂ O 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, CH₃CHO + 2[H] → CH₃CH₂OH. 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'

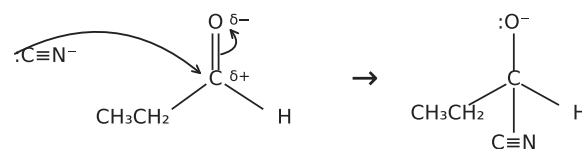
reagent and cyanide chemistry require controlled laboratory handling and disposal; do not store or improvise these reagents.

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 CH₃CH₂CH(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.

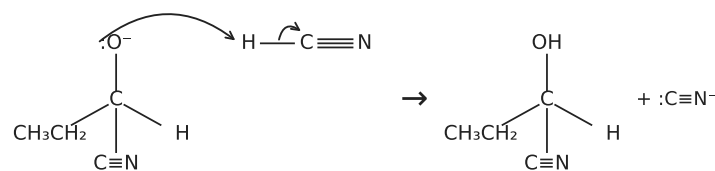
The full propanal mechanism includes the second electron-pair transfer: an O⁻ lone pair goes to the H of H-C≡N, and the H-C bond pair returns to cyanide carbon. The product CH₃CH₂CH(OH)CN retains all four carbons, and CN⁻ is regenerated.

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⁻

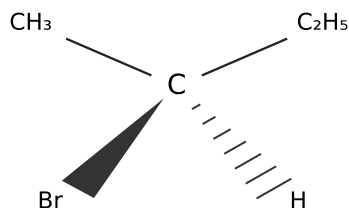


O lone pair → H; H-C bond pair → C. Product: CH₃CH₂CH(OH)CN.

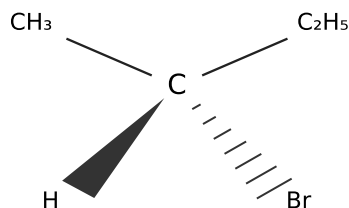
The iodoform test uses iodine in alkali: compounds with CH₃CO- give a yellow CHI₃ precipitate. Ethanal also fits this pattern with H as its other carbonyl substituent. Ethanol and secondary alcohols of type CH₃CH(OH)R can first oxidise to a suitable carbonyl and also give a positive result. A positive test does not prove every unknown is propanone.

Swap two groups to obtain the other enantiomer

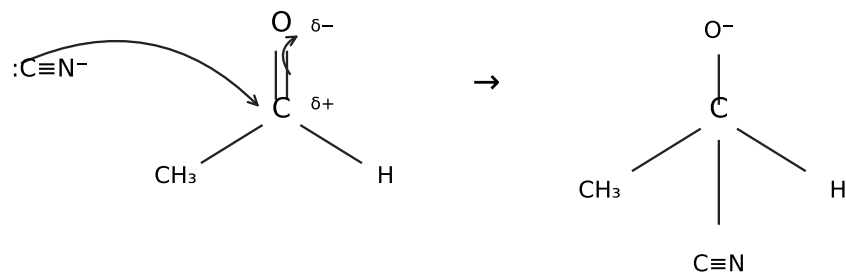
One enantiomer of 2-bromobutane



Opposite configuration



Nucleophilic addition to ethanal: first step



Then O⁻ takes H⁺ from HCN: CH₃CH(OH)CN + CN⁻.
Arrows start at an electron pair; CN⁻ attacks through carbon.

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 $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$. Aqueous alkali under reflux gives $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + \text{NH}_3$; acidify afterwards for the free acid. Both routes retain the nitrile carbon. Reducing propanoic acid uses $\text{CH}_3\text{CH}_2\text{COOH} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$, 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

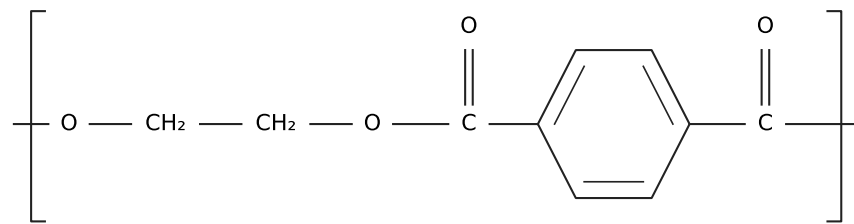
converts RCOOH to the **acyl chloride** RCOCl , with POCl_3 and HCl also formed. Heating an acid with an alcohol and an acid catalyst establishes an esterification equilibrium: $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$. The product is ethyl ethanoate; the alcohol supplies the alkyl name and the acid supplies the carboxylate name.

Acyl chlorides react readily with nucleophiles. $\text{RCOCl} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{HCl}$; with $\text{R}'\text{OH}$ they give $\text{RCOOR}' + \text{HCl}$. With excess NH_3 they give RCONH_2 and NH_4Cl overall: $\text{RCOCl} + 2\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{NH}_4\text{Cl}$. With a primary amine $\text{R}'\text{NH}_2$ 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 + $\text{NaOH} \rightarrow$ 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 $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$ 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.

Terylene: completed repeat unit with para benzene links



From ethane-1,2-diol and benzene-1,4-dicarboxylic acid; ester links form by condensation.

Spectroscopy and chromatography: combine independent constraints

Accurate mass can distinguish formulae with the same nominal integer mass. With $\text{C} = 12.0000$, $\text{H} = 1.0078$ and $\text{O} = 15.9949$, $\text{C}_2\text{H}_6\text{O}$ 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, $\text{C}_3\text{H}_8\text{O}$ gives accurate relative mass 60.0573 and $\text{C}_2\text{H}_4\text{O}_2$ 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.

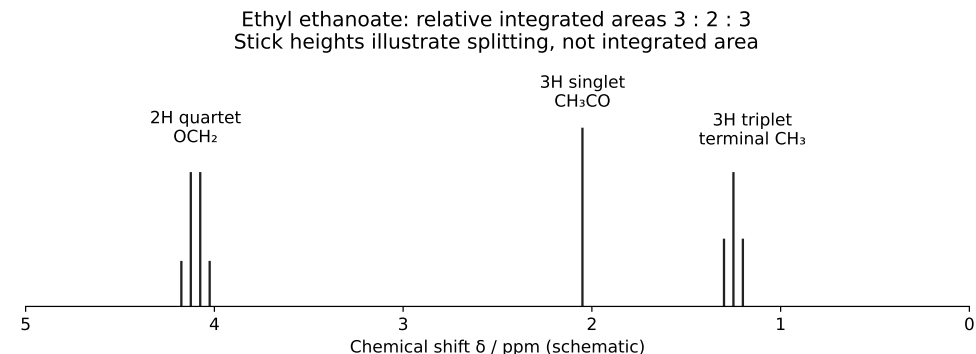
Carbon-13 NMR gives one signal per distinct carbon environment in the simple spectra considered here. Symmetry can make different carbon atoms equivalent: propanone has two carbon environments, not three; propanal has three. Use supplied chemical-shift data to distinguish carbonyl, C–O and hydrocarbon 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, $\text{CH}_3\text{COCH}_2\text{CH}_3$, 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 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 R_f 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.



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 $\Delta H = +24.0 \text{ kJ mol}^{-1}$ and $\Delta S(\text{system}) = +80.0 \text{ J mol}^{-1} \text{ K}^{-1}$. 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 $\text{A}^-:\text{HA}$ ratio and explain why initial acid amount is unsuitable in the buffer expression.
5. A $\text{C}_3\text{H}_6\text{O}$ 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) $r = k[\text{A}]$ 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) $+900 - 930 = -30 \text{ kJ mol}^{-1}$; 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.