

Unit 4: Rates, equilibria and further organic chemistry

Topics 11–15, core practical knowledge retained; original questions and narration.

Full acceptance remains in progress.

Fast, feasible or product-rich?

- 1 Rate concerns speed; total entropy concerns feasibility; K concerns equilibrium composition.
- 2 Use Unit 1 mole ratios and Unit 2 energy, collision and equilibrium models.

Orders come from controlled comparisons

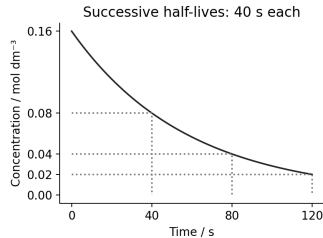
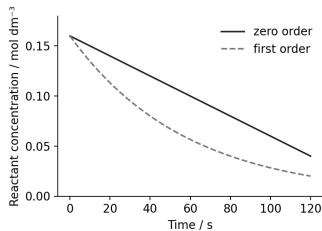
- 1 Doubling A doubles rate: first order in A.
- 2 Doubling B quadruples rate: second order in B.
- 3 $r = k[A][B]^2$; overall order is three, independent of overall coefficients.

Calculate k and derive its units

- 1 $k = 0.00800/[0.100(0.200)^2] = 2.00$.
- 2 For third order, units are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$.
- 3 Temperature must be held fixed for comparisons.

Read the curve, not one isolated point

Illustrative concentration-time models at fixed temperature



A straight concentration–time line supports zero order.

Infer an unfamiliar rate law

Your turn

Doubling A quadruples rate; tripling B triples rate. Which law fits?

A. $r = k[A][B]$

B. $r = k[A]^2[B]$

C. $r = k[A][B]^3$

D. $r = k[A]^2$

Reveal: keep the variables separate

- 1** B: $r = k[A]^2[B]$, overall order three.
- 2** A gives the wrong A order; C gives the wrong orders; D ignores the B dependence.

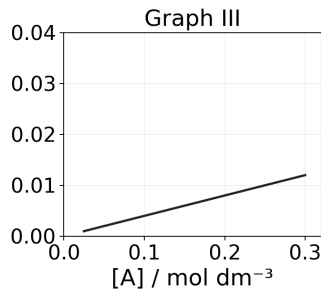
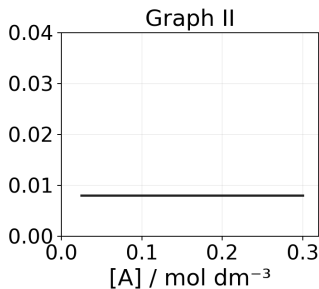
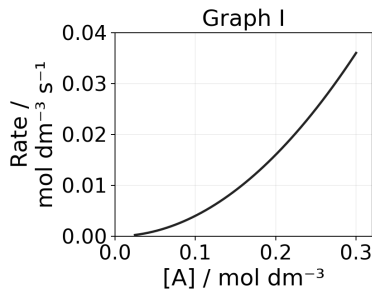
Mechanisms must satisfy two constraints

- 1 Steps must sum to the overall equation and agree with the measured rate law.
- 2 S_N1: slow ionisation; S_N2: concerted nucleophile attack and leaving-group departure.
- 3 Agreement supports a mechanism but does not uniquely prove it.

Temperature and surface catalysis

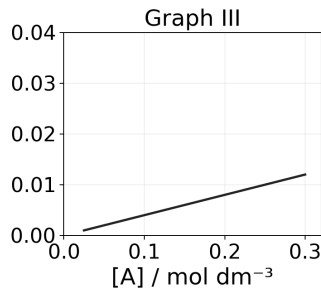
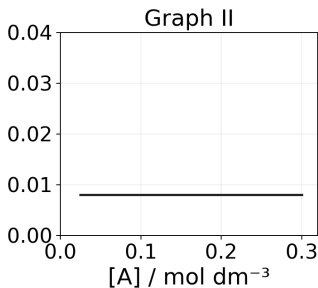
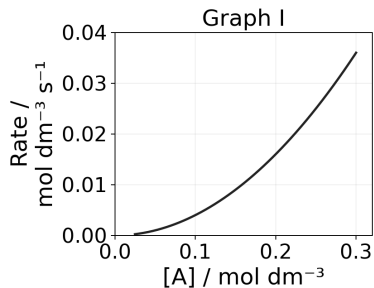
- 1 For supplied $\ln k = \ln A - E_a/(RT)$, gradient against $1/T$ is $-E_a/R$.
- 2 Use kelvin and consistent J/kJ.
- 3 Heterogeneous catalysts adsorb reactants; poisons can block active sites.

Attempt: read three rate graphs



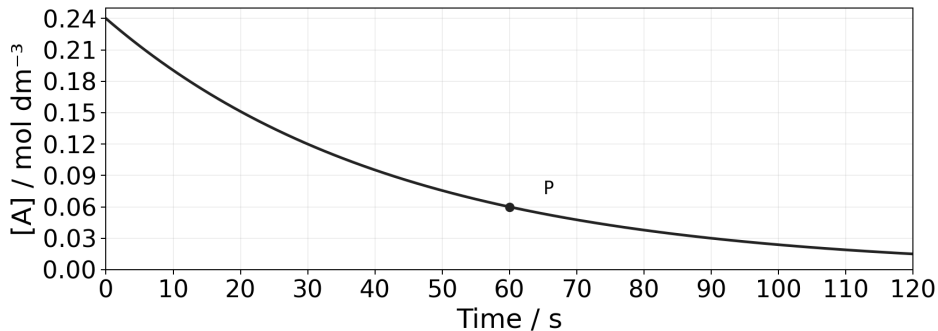
- 1 Identify the order in A for graphs I, II and III.
- 2 Use the change in rate when concentration doubles; restrict claims to the measured range.

Reveal: order follows the shape



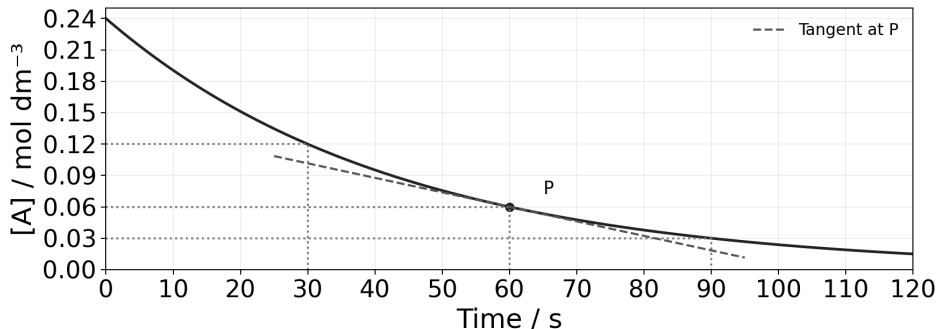
- 1 I: rate quadruples when A doubles, second order.
- 2 II: rate stays fixed, zero order over the measured range.
- 3 III: rate doubles, first order.

Attempt: half-lives and a tangent



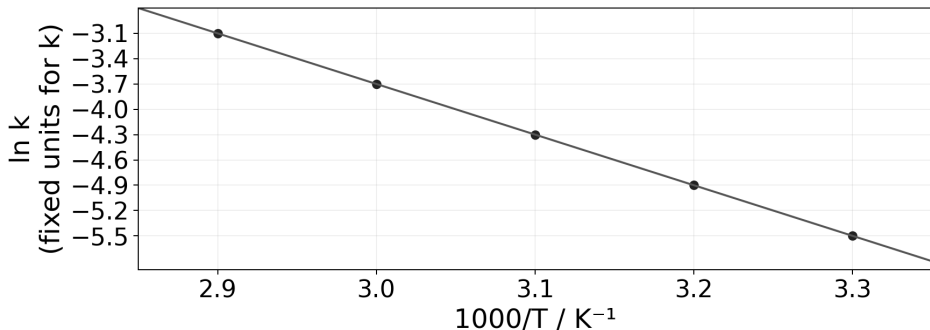
- 1 Read two successive half-lives from the curve.
- 2 Draw a tangent at P and estimate the positive disappearance rate.

Reveal: constant halves and local slope



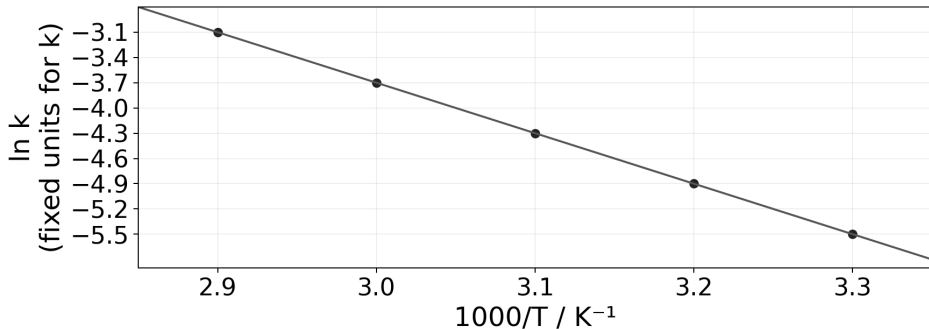
- 1 1 0.120 $\rightarrow$ 0.060 $\rightarrow$ 0.030 takes 30 s then 30 s: supports first order.
- 2 2 Tangent gradient $\approx -0.00139 \text{ mol dm}^{-3} \text{ s}^{-1}$; disappearance rate $\approx +0.00139$.

Attempt: check the Arrhenius axis



- 1 Find the plotted gradient using two points on the line.
- 2 The horizontal variable is $1000/T$: calculate E_a with $R=8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

Reveal: include the scaling factor



- 1 Plotted gradient = $(-5.5 + 3.1) / (3.3 - 2.9) = -6.0$.
- 2 $E_a = -1000R \times \text{gradient} = 49860 \text{ J/mol} = 49.9 \text{ kJ/mol}$.
- 3 Omitting 1000 makes the answer one thousand times too small.

Attempt: propose a compatible mechanism

- 1 Use propanone P, its O-protonated form PH^+ and enol E.
- 2 Propose rapid protonation, slow enol formation, then fast iodination.
- 3 Match $r=k[\text{P}][\text{H}^+]$ and zero iodine order; check atom/charge balances and net acid.

Reveal: a balanced possible sequence

- 1 Fast equilibrium: $P + H^+ \rightleftharpoons PH^+$.
- 2 Slow enol formation: $PH^+ \rightarrow E + H^+$.
- 3 Fast iodination: $E + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$.

Reveal: rate and overall equation agree

- 1** $r = k_2[\text{PH}^+] = k_2K[\text{P}][\text{H}^+]$: first order in P and acid, zero in iodine.
- 2** Overall: $\text{P} + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{H}^+ + \text{I}^-$; PH^+ and E cancel.
- 3** The catalytic acid is regenerated; iodination also generates acid. Agreement is not unique proof.

Choose a signal that actually changes

- 1 NaOH hydrolysis of an ester replaces mobile OH^- with less mobile ethanoate.
- 2 Calibrate conductivity against composition; control temperature, probe geometry, mixing and solvent background.
- 3 A closed reaction producing no gas cannot be followed by gas volume or mass loss.

Entropy: the system is only one part

- 1 $\Delta S(\text{system}) = \text{sum of product entropies minus reactant entropies, with coefficients.}$
- 2 $\Delta S(\text{surroundings}) = -\Delta H/T$, using joules with entropy in $\text{J mol}^{-1} \text{K}^{-1}$.
- 3 Add both terms before judging the sign.

Worked total entropy

- 1 At 298 K: $\Delta H = -40.0 \text{ kJ mol}^{-1}$, $\Delta S(\text{system}) = -100 \text{ J mol}^{-1} \text{ K}^{-1}$.
- 2 $\Delta S(\text{surroundings}) = 40000/298 = +134 \text{ J mol}^{-1} \text{ K}^{-1}$.
- 3 Total = $+34 \text{ J mol}^{-1} \text{ K}^{-1}$: forward direction favoured, not necessarily fast.

Find the temperature boundary

Your turn

$\Delta H = +36.0 \text{ kJ mol}^{-1}$; $\Delta S(\text{system}) = +120 \text{ J mol}^{-1} \text{ K}^{-1}$. Which condition gives positive total entropy?

- A. T below 300 K
- B. T above 300 K
- C. Every temperature
- D. No temperature

Reveal: boundary and assumption

- 1 B: $120 - 36000/T > 0$ when $T > 300$ K.
- 2 At 300 K total entropy is zero.
- 3 This boundary treats ΔH and system ΔS as approximately constant.

Attempt: explain entropy without a number

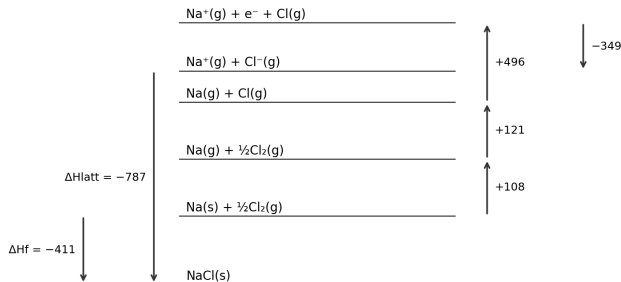
- 1 Describe warming, melting and boiling from a perfect crystal at 0 K.
- 2 Why can ionic dissolution have either system-entropy sign? Why does gas spread?

Reveal: compare accessible arrangements

- 1 Perfect-crystal entropy is zero at 0 K; warming and melting/boiling increase it.
- 2 Ions disperse on dissolution, but hydration can order water.
- 3 Gas spreading increases accessible arrangements; the spontaneous direction increases total entropy.

Lattice signs and complete routes

NaCl Born-Haber cycle: illustrative values / kJ mol^{-1}



Both routes start at the elements and finish at NaCl(s).
Diagram is schematic; vertical spacing is not an energy scale.

Lattice formation: gaseous ions $\rightarrow$ one mole of solid; negative.

Solution and bonding interpretation

- 1 $\Delta H(\text{solution}) = -\Delta H(\text{lattice formation}) + \text{total hydration enthalpy}.$
- 2 -850 and -820 give $+30 \text{ kJ mol}^{-1}.$
- 3 Extra stabilisation relative to a purely ionic model supports covalent character; solubility also needs entropy.

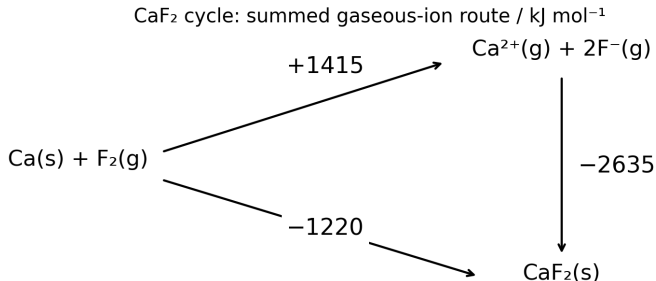
Attempt: construct the whole Born–Haber route

- 1 Draw CaF_2 formation through gaseous atoms and gaseous ions, including electron counts.
- 2 Supplied kJ/mol : formation -1220 ; Ca atomisation 178 ; F atomisation 79 ; Ca ionisations $590/1145$; F affinity -328 .

Reveal: count the two fluorine atoms

- 1 Ca and two F atomisations: $178 + 2(79) = 336 \text{ kJ/mol}$.
- 2 Two Ca ionisations: $590 + 1145 = 1735 \text{ kJ/mol}$.
- 3 Two F electron affinities: $2(-328) = -656 \text{ kJ/mol}$.
- 4 Gaseous-ion route: $336 + 1735 - 656 = 1415 \text{ kJ/mol}$.

Reveal: join the matching endpoints

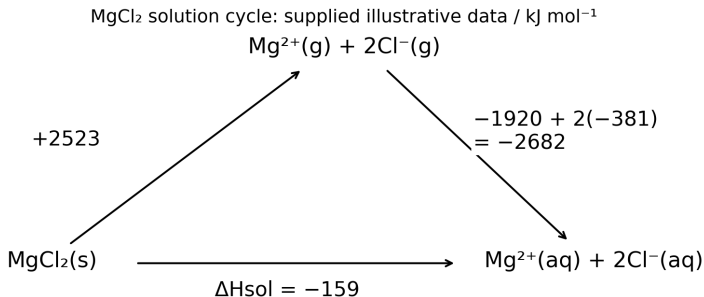


- 1 $-1220 = 1415 + \Delta H_{\text{lattice}}$, so lattice formation = -2635 kJ/mol .
- 2 Both routes form one mole CaF₂(s); two first affinities are not one second affinity.

Attempt: separate lattice and hydration

- 1 Construct $\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ through gaseous ions.
- 2 Use lattice formation -2523 , Mg^{2+} hydration -1920 , each Cl^{-} hydration -381kJ/mol ; define each molar process.

Reveal: reverse and multiply the right terms



- 1 Reverse lattice formation: +2523 kJ/mol; hydrate both chlorides.
- 2 Total hydration = $-1920 + 2(-381) = -2682$; solution enthalpy = -159 kJ/mol.

Equilibrium amounts before constants

- 1 For $A + B \rightleftharpoons C$, initially 0.500 mol each A/B produces 0.200 mol C.
- 2 Equilibrium amounts are 0.300, 0.300 and 0.200 mol.
- 3 In 2.00 dm^3 : $K_c = 0.100/(0.150^2) = 4.44 \text{ dm}^3 \text{ mol}^{-1}$.

Partial pressures and temperature

- 1 Partial pressure = mole fraction $\times$ total pressure.
- 2 For $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, $K_p = p(\text{NO}_2)^2/p(\text{N}_2\text{O}_4)$.
- 3 Only temperature changes K ; catalysts change approach speed.

Acid strength and concentration differ

- 1 Conjugate pairs differ by one H^+ .
- 2 Strong/weak describes dissociation; concentrated/dilute describes amount per volume.
- 3 $\text{pH} = -\log_{10}[\text{H}^+]$; $K_w = [\text{H}^+][\text{OH}^-]$ at the specified temperature.

Weak acid: calculate and check

- 1 $[H^+] \approx \sqrt{K_a c} = \sqrt{1.80 \times 10^{-5} \times 0.100} = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$.
- 2 $\text{pH} \approx 2.87$; dissociation fraction is 1.34%.
- 3 Core practical 11: calibrate pH meter, know concentration and control temperature.

Buffers consume added reagent

- 1 Added H^+ reacts with A^- ; added OH^- reacts with HA .
- 2 React the moles first, then use $[\text{H}^+] \approx K_a[\text{HA}]/[\text{A}^-]$.
- 3 Both components must remain; buffer capacity is finite.

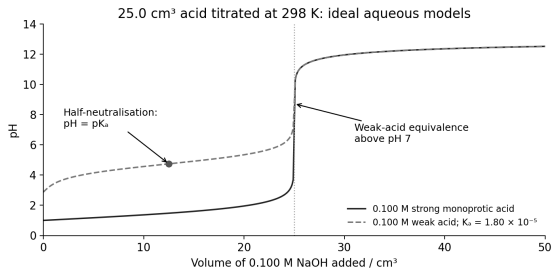
Buffer after neutralisation

Your turn

0.0100 mol HA receives 0.00400 mol OH^- . Which HA:A⁻ ratio enters the buffer expression?

- A. 10:4
- B. 6:4
- C. 4:6
- D. 10:6

Reveal and indicator choice



B: HA remaining = 0.00600 mol; A⁻ formed = 0.00400 mol.

Attempt: test the dilution approximation

- 1 HA starts at 0.100 M, pH 3.00; after 1000-fold dilution, pH 4.57.
- 2 Find $[H^+]$ and percentage dissociation. Is $c-x \approx c$ valid?

Reveal: measure the fraction before using the model

- 1 Final $c=1.00\times 10^{-4}\text{M}$; $[\text{H}^+]=10^{-4.57}=2.69\times 10^{-5}\text{M}$.
- 2 Dissociation $\approx 26.9\%$: equilibrium HA is appreciably below initial c .
- 3 Repeated half-log predictions are not reliable at this dilution.

Attempt: design both stock concentrations

- 1 Target pH 5.00, K_a $2.00 \times 10^{-5} \text{ M}$; final $[\text{HA}] + [\text{A}^-] = 0.120 \text{ M}$.
- 2 Make 250.0 cm^3 from 40.0 cm^3 acid stock and 60.0 cm^3 salt stock. Find both stock concentrations.

Reveal: final concentrations differ from stocks

- 1 Ratio $A^-:HA=2:1$; final concentrations 0.0800 and 0.0400 M.
- 2 Acid stock $=0.0400 \times 250/40=0.250$ M.
- 3 Salt stock $=0.0800 \times 250/60=0.333$ M; dilute mixed aliquots to 250.0 cm³.

Attempt: reverse the titration direction

- 1 25.0 cm^3 of 0.100 M B receives 0.100 M HCl ; pH at 12.5 cm^3 is 9.25.
- 2 Identify the acid whose K_a is measured; find pH at 20.0 cm^3 .

Reveal: track B and its conjugate acid

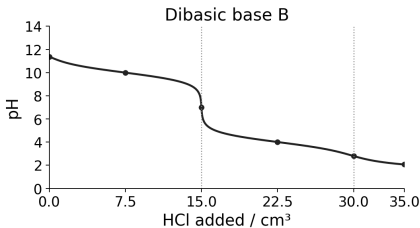
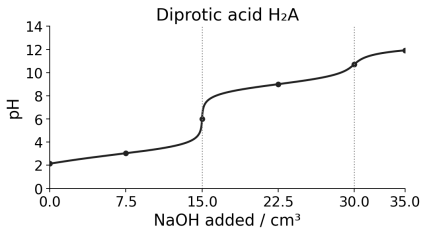
- 1 At half-equivalence $B=BH^+$, so $pK_a(BH^+)=9.25$; $K_a=5.62\times 10^{-10}M$.
- 2 At 20.0 cm^3 , $B=0.000500\text{ mol}$ and $BH^+=0.00200\text{ mol}$.
- 3 $pH=9.25+\log(0.000500/0.00200)=8.65$; B consumes added H^+ .

Attempt: draw two stages in opposite directions

- 1 25.0 cm³ of 0.0600 M H₂A or dibasic B receives 0.100 M titrant.
- 2 Calculate both equivalence volumes; sketch rising acid and falling base curves.
Use worksheet 4.4.4 data.

Reveal: one and two titrant equivalents

25.0 cm³ of 0.0600 M solute + 0.100 M titrant, 298 K
Illustrative aqueous models; dotted lines mark 15.0 and 30.0 cm³



- 1 **1** $n(\text{solute}) = 0.00150 \text{ mol}$: equivalence amounts at 15.0 and 30.0 cm³.
- 2 **2** Plot the supplied points smoothly; the stages need not have identical jump sizes.

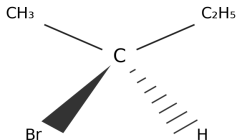
Buffers support living systems with finite capacity

- 1 HCO_3^- consumes H^+ ; H_2CO_3 consumes OH^- . Stable pH supports enzyme conditions.
- 2 Buffers are consumed; blood also needs respiratory and renal regulation.
- 3 Food buffering limits pH changes from microbial activity; it does not sterilise food.

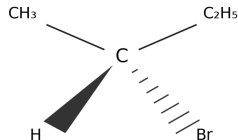
Chirality needs four different groups

Swap two groups to obtain the other enantiomer

One enantiomer of 2-bromobutane



Opposite configuration

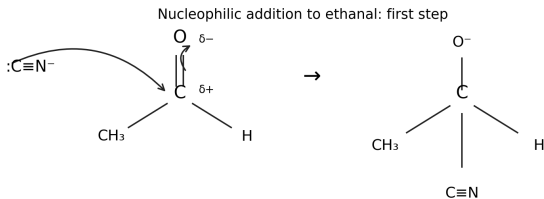


2-bromobutane has Br, H, CH₃ and C₂H₅ at carbon 2.

Carbonyl tests constrain identity

- 1 Both aldehydes and ketones give 2,4-DNPH precipitates.
- 2 Aldehydes give Tollens' silver or warm Fehling's brick-red precipitate; ordinary ketones do not.
- 3 LiAlH_4 in dry ether reduces aldehydes to primary and ketones to secondary alcohols, after work-up.

Show electron pairs, then protonate



CN^- attacks through carbon; the $\text{C}=\text{O}$ π pair moves to oxygen.

Attempt: use optical and structural evidence together

- 1 Enantiopure chiral halogenoalkane gives a structurally chiral alcohol with zero rotation.
- 2 Which simple substitution model is supported? Contrast with inversion and explain the structural control.

Reveal: a chiral racemate supports the planar model

- 1** A chiral product with zero rotation supports equal enantiomers; ideal SN1 allows two-face attack.
- 2** Simple SN2 gives inversion and an enantiopure product; zero rotation alone could also mean achiral structure.

Hydrogen bonds require a donor and acceptor

- 1** Carbonyl O accepts a hydrogen bond from water. Simple aldehydes/ketones lack an O-H donor.
- 2** Acids form hydrogen-bonded associations; compare similar-sized molecules for boiling points.
- 3** A longer non-polar chain can reduce water solubility without removing the polar group.

Attempt: identify the purified derivative

- 1** U gives DNPH, no Tollens' silver and positive iodoform; derivative melts at 125–127°C.
- 2** Illustrative reference values: propanal 146°C, propanone 126°C, butan-2-one 116°C. Select and justify.

Reveal: combine tests with derivative data

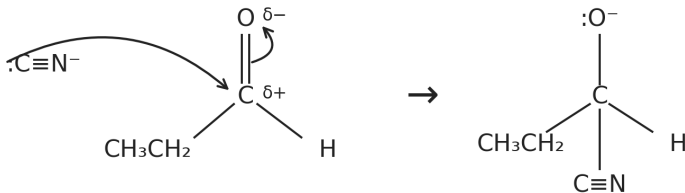
- 1** Propanone fits the supplied 126°C derivative reference and ketone test behaviour.
- 2** Butan-2-one also gives iodoform; that test alone cannot distinguish the two.
- 3** A sharp range supports purity; coincident reference ranges still limit identification.

Attempt: draw both cyanide-addition stages

- 1 Draw propanal + HCN with CN^- catalyst, including all four electron-pair arrows.
- 2 Show O^- , proton transfer from HCN, regenerated CN^- and the optical result.

Reveal: carbon attack gives the oxygen anion

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

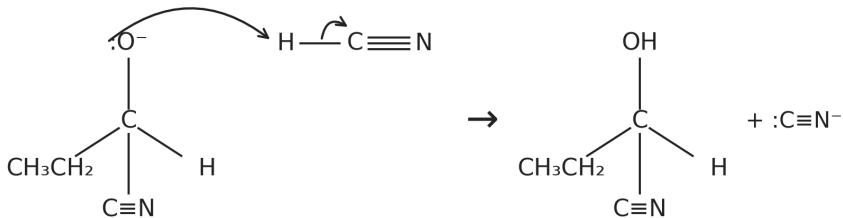


The negative charge is on oxygen; the new C-C bond retains the nitrile carbon.

- 1** CN^- attacks through its carbon lone pair; the C=O π pair moves to O.
- 2** The intermediate keeps the ethyl group, H and new nitrile carbon.

Reveal: HCN donates H and regenerates CN^-

2 Proton transfer from HCN regenerates CN^-



O lone pair $\rightarrow$ H; H-C bond pair $\rightarrow$ C. Product: $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

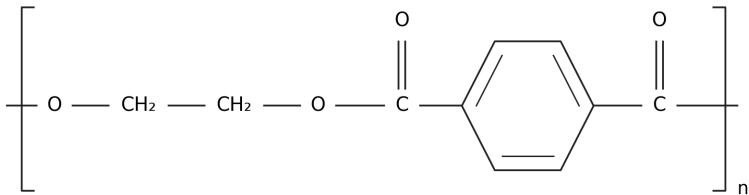
- 1 O^- lone pair $\rightarrow$ H of HCN; H-C bond pair $\rightarrow$ cyanide carbon.
- 2 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$ has a chiral centre; equal attack on two planar faces gives a racemate.

Carboxylic derivatives keep the acyl carbon

- 1 Acid + alcohol $\rightleftharpoons$ ester + water, with acid catalyst and heat.
- 2 Acyl chloride + $2\text{NH}_3 \rightarrow$ amide + NH_4Cl .
- 3 Alkaline ester hydrolysis produces carboxylate salt and alcohol.

Condensation and test limits

Terylene: completed repeat unit with para benzene links



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

A diacid and diol form a polyester with ester links and water.

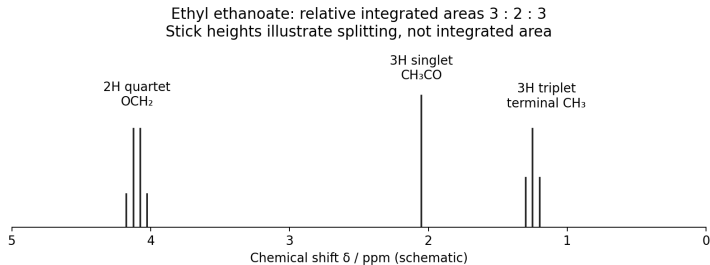
Attempt: retain the nitrile carbon

- 1 Write acid and alkaline hydrolysis equations for $\text{CH}_3\text{CH}_2\text{CN}$.
- 2 Give conditions, then obtain free acid from the alkaline product.

Reveal: acid and alkali have different final ions

- 1 Acid: $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$.
- 2 Alkali: $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + \text{NH}_3$.
- 3 Heat under reflux with aqueous reagent; acidify carboxylate afterwards.

Combine NMR features



Carbon-13 counts environments, not atoms.

Chromatography is evidence with limits

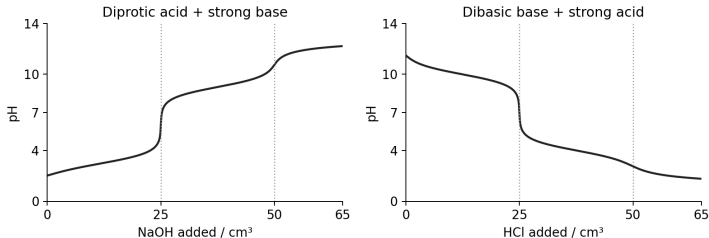
- 1 Rf uses distances from the same baseline and has no units.
- 2 Retention-time matches need matched conditions; one peak can conceal co-elution.
- 3 GC-MS adds mass/fragment evidence; standards, blanks and provenance remain essential.

Draw the curve from the species

- 1** At 298 K: strong/strong equivalence near 7; weak acid/strong base above 7; strong acid/weak base below 7.
- 2** Weak/weak usually has no sharp ordinary-indicator endpoint.
- 3** Label initial pH, added-volume axis, equivalence amount and excess-titrant region.

Two stages require two mole calculations

Two neutralisation stages: 25.0 cm^3 of 0.100 M solute + 0.100 M titrant
Illustrative separated dissociations, 298 K ; dotted lines at 25 and 50 cm^3

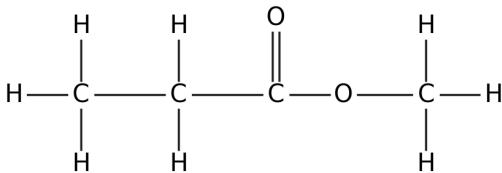


25.0 cm^3 of $0.100 \text{ M H}_2\text{A}$ uses 25.0 cm^3 then 50.0 cm^3 total of 0.100 M NaOH .

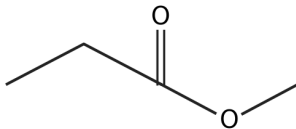
Names specify both sides of an ester

Methyl propanoate

Displayed formula



Skeletal formula



Methyl propanoate is $\text{CH}_3\text{CH}_2\text{COOCH}_3$: three acid-side carbons and one alcohol-side carbon.

Attempt: resolve nominal mass 60

- 1 Calculate accurate masses of $\text{C}_3\text{H}_8\text{O}$ and $\text{C}_2\text{H}_4\text{O}_2$ with C 12.0000, H 1.0078, O 15.9949.
- 2 Measured 60.0210; acid O-H/C=O and two carbon-13 signals. Suggest a structure.

Reveal: formula before connectivity

- 1 $\text{C}_3\text{H}_8\text{O}$:60.0573; $\text{C}_2\text{H}_4\text{O}_2$:60.0210. Difference 0.0363 resolves the formula.
- 2 CH_3COOH fits the acid IR and two distinct carbon environments.
- 3 Accurate mass selects a formula; the other evidence constrains its structure.

Attempt: predict both resolutions for butan-2-one

- 1 For $\text{CH}_3\text{COCH}_2\text{CH}_3$, give proton sets, areas and simple $n+1$ splitting.
- 2 Use supplied H regions 0.8–1.5/2.0–2.7ppm and C regions 8–50/190–220ppm.

Reveal: distinguish environments from atom totals

- 1** 3H acyl singlet; 2H quartet; 3H terminal triplet. Equivalent methyl H do not split each other.
- 2** Acyl CH_3/CH_2 lie at 2.0–2.7ppm; terminal CH_3 at 0.8–1.5ppm in supplied data.
- 3** Four carbon environments: three alkyl signals and one ketone carbonyl at 190–220ppm.

Migration depends on two phases

- 1 TLC distances 1.8/4.2cm with front 6.0cm give R_f 0.30/0.70.
- 2 Lower R_f means greater relative stationary-phase retention under the same conditions.
- 3 One GC peak/reference match can hide co-elution; add MS evidence and matched standards/blanks.

Independent structural identification

Your turn

$\text{C}_3\text{H}_6\text{O}$ has two carbon-13 signals, gives iodoform and no Tollens' silver. Which structure fits?

- ☐ A. Propanal
- ☐ B. Propanone
- ☐ C. Propan-1-ol
- ☐ D. Ethanoic acid

Check yourself

- 1** B: propanone has equivalent methyl carbons, a $\text{CH}_3\text{CO}-$ group and ketone behaviour.
- 2** Its HCN product has two identical methyl groups and is achiral.
- 3** Reject alternatives using all observations, not one familiar test.