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

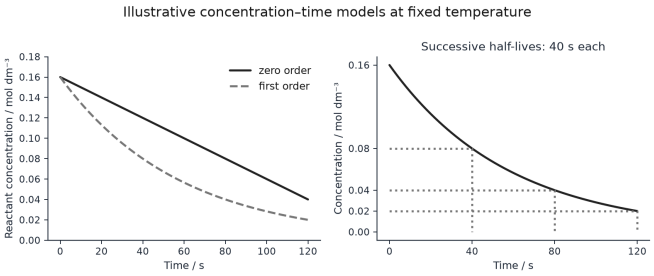
Orders come from controlled comparisons

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

Calculate k and derive its units

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

Read the curve, not one isolated point



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

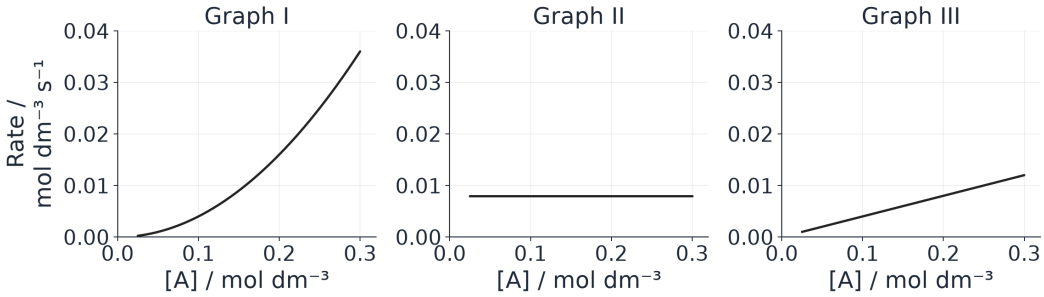
Mechanisms must satisfy two constraints

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

Temperature and surface catalysis

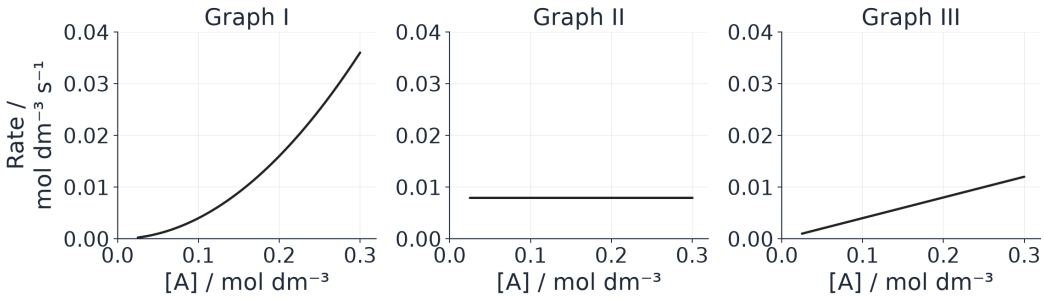
1. **1** For supplied $\ln k = \ln A - E_a/(RT)$, gradient against $1/\mathrm{T}$ is $-E_a/R$.
2. **2** Use kelvin and consistent J/kJ.
3. **3** Heterogeneous catalysts adsorb reactants; poisons can block active sites.

Attempt: read three rate graphs



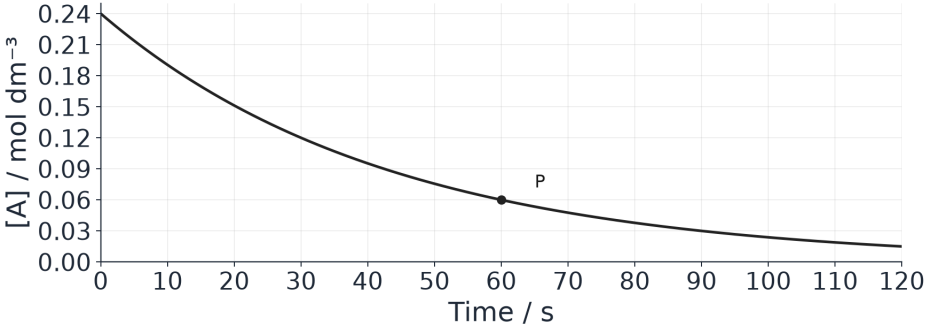
1. **1** Identify the **order** in A for graphs I, II and III.
2. **2** Use the change in rate when concentration doubles; restrict claims to the measured range.

Reveal: order follows the shape



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

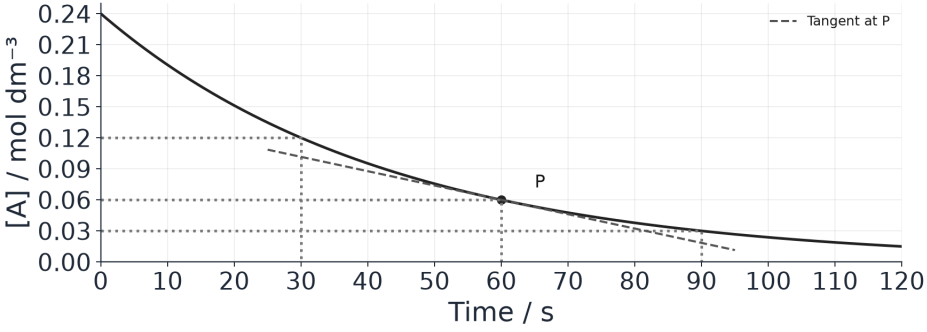
Attempt: half-lives and a tangent



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

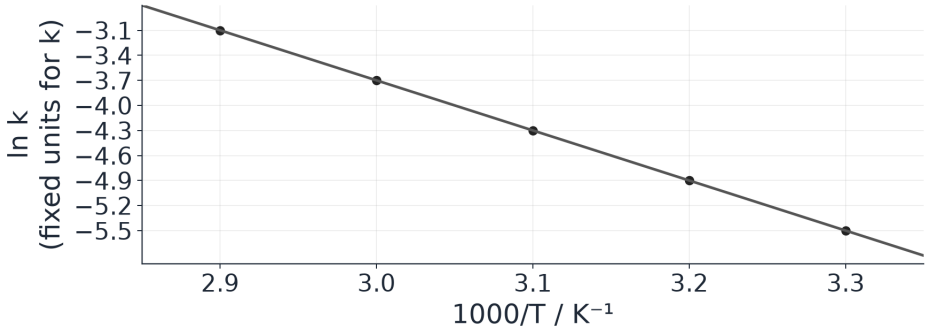
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Reveal: constant halves and local slope



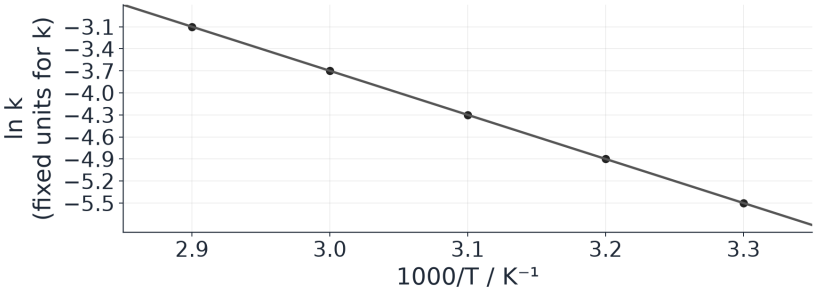
1. **1** 0.120→0.060→0.030 takes 30 s then 30 s: supports first **order**.
2. **2** Tangent gradient≈−0.00139mol dm^{-3} s^{-1}; disappearance rate≈+0.00139.

Attempt: check the Arrhenius axis



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

Reveal: include the scaling factor



1. **1** Plotted gradient=(−5.5+3.1)/(3.3−2.9)=−6.0.
2. **2** Ea=−1000R×gradient=49860J/mol=49.9kJ/mol.
3. **3** Omitting 1000 makes the answer one thousand times too small.

Attempt: propose a compatible mechanism

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

Reveal: a balanced possible sequence

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

Reveal: rate and overall equation agree

1. **1** $r = k_2[PH^+] = k_2K[P][H^+]$:first **order** in P and **acid**, zero in iodine.
2. **2** Overall: $P + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$; PH^+ and E cancel.
3. **3** The catalytic acid is regenerated; iodination also generates acid. Agreement is not unique proof.

Choose a signal that actually changes

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

Entropy: the system is only one part

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

Worked total entropy

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

Find the temperature boundary

Your turn

$\Delta H = +36.0$ kJ mol^{-1}; $\Delta S(\text{system}) = +120$ J mol^{-1} 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. **1** B: $120 - 36000/T > 0$ when $T > 300$ K.
2. **2** At 300 K total **entropy** is zero.
3. **3** This boundary treats ΔH and system ΔS as approximately constant.

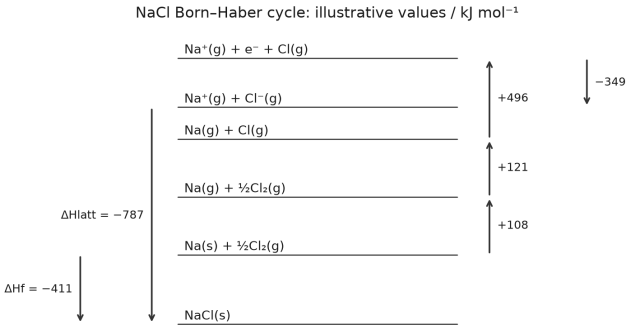
Attempt: explain entropy without a number

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

Reveal: compare accessible arrangements

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

Lattice signs and complete routes



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

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Solution and bonding interpretation

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

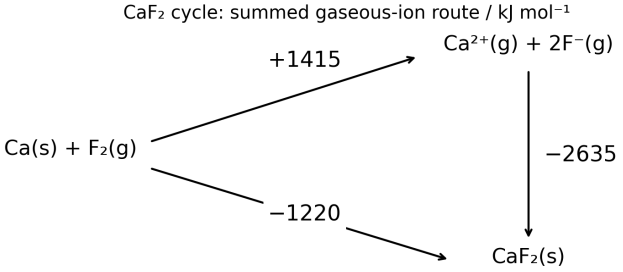
Attempt: construct the whole Born–Haber route

1. **1** Draw CaF_2 formation through gaseous atoms and gaseous ions, including electron counts.
2. **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. **1** Ca and two F atomisations:$178+2(79)=336\text{kJ/mol}$.
2. **2** Two Ca ionisations:$590+1145=1735\text{kJ/mol}$.
3. **3** Two F electron affinities:$2(-328)=-656\text{kJ/mol}$.
4. **4** Gaseous-ion route:$336+1735-656=1415\text{kJ/mol}$.

Reveal: join the matching endpoints

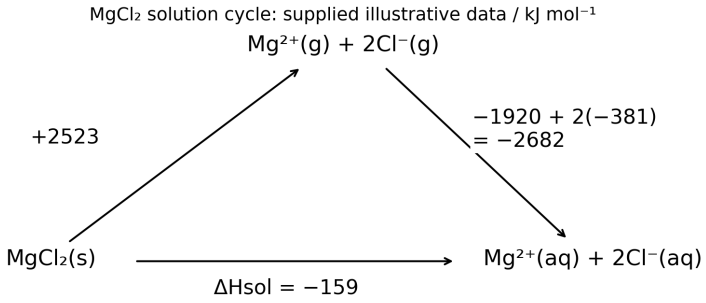


1. **1** $-1220 = 1415 + \Delta H\text{lattice}$, so lattice formation $= -2635\,\text{kJ/mol}$.
2. **2** Both routes form one mole $CaF_2(s)$; two first affinities are not one second affinity.

Attempt: separate lattice and hydration

1. **1** Construct $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ through gaseous ions.
2. **2** Use lattice formation-2523, Mg^{2+} hydration-1920, each Cl^- hydration$-381 kJ/mol$; define each molar process.

Reveal: reverse and multiply the right terms



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

Equilibrium amounts before constants

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

Partial pressures and temperature

1. **1 Partial pressure** = **mole fraction** $\times$ total pressure.
2. **2** For $N_2O_4 \rightleftharpoons 2NO_2$, $K_p = p(NO_2)^2/p(N_2O_4)$.
3. **3** Only temperature changes K; catalysts change approach speed.

Acid strength and concentration differ

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

Weak acid: calculate and check

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

Buffers consume added reagent

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

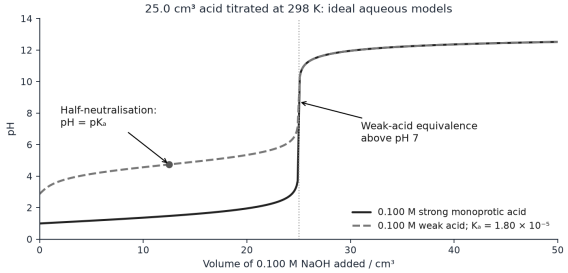
Buffer after neutralisation

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

Reveal: measure the fraction before using the model

1. **1** Final c$=1.00\times10^{-4}$M; [H$^+$]$=10^{-4.57}=2.69\times10^{-5}$M.
2. **2 Dissociation**$\approx$26.9%: equilibrium HA is appreciably below initial c.
3. **3** Repeated half-log predictions are not reliable at this dilution.

Attempt: design both stock concentrations

1. **1** Target pH 5.00, Ka 2.00×10^{-5}M; final [HA]+[A^-]=0.120 M.
2. **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. **1** Ratio A^-:HA=2:1; final concentrations 0.0800 and 0.0400 M.
2. **2** **Acid** stock=0.0400×250/40=0.250 M.
3. **3** Salt stock=0.0800×250/60=0.333 M; dilute mixed aliquots to 250.0 cm^3.

Attempt: reverse the titration direction

1. **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. **2** Identify the **acid** whose Ka is measured; find pH at 20.0 cm^3.

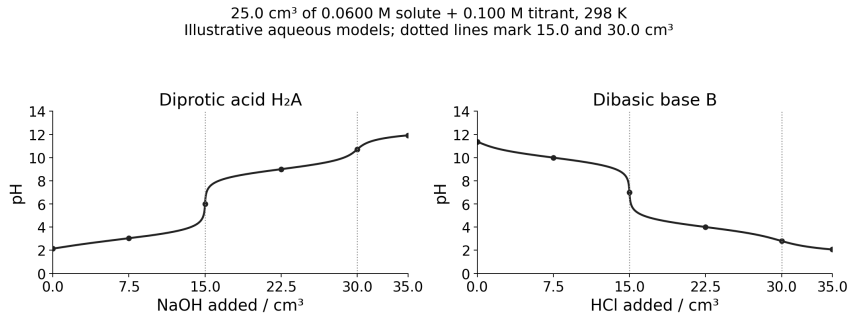
Reveal: track B and its conjugate acid

1. **1** At half-equivalence B=BH^+, so pKa(BH^+)=9.25; Ka=5.62×10^{-10}M.
2. **2** At 20.0 cm^3, B=0.000500 mol and BH^+=0.00200 mol.
3. **3** pH=9.25+log(0.000500/0.00200)=8.65; B consumes added H^+.

Attempt: draw two stages in opposite directions

1. **1** 25.0 cm^3 of 0.0600 M H_2A or dibasic B receives 0.100 M **titrant**.
2. **2** Calculate both equivalence volumes; sketch rising **acid** and falling **base** curves. Use worksheet 4.4.4 data.

Reveal: one and two titrant equivalents



1. **1** n(solute)=0.00150 mol: equivalence amounts at 15.0 and 30.0 cm^3.
2. **2** Plot the supplied points smoothly; the stages need not have identical jump sizes.

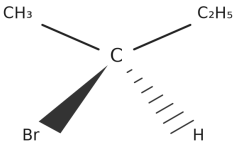
Buffers support living systems with finite capacity

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

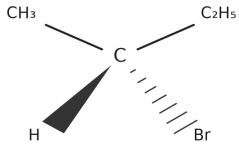
Chirality needs four different groups

Swap two groups to obtain the other enantiomer

One enantiomer of 2-bromobutane



Opposite configuration

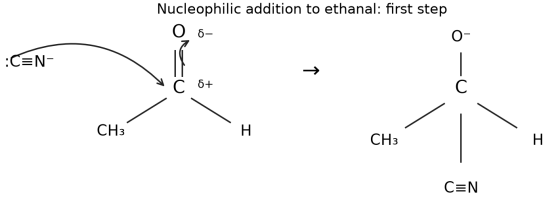


2-bromobutane has Br, H, CH_3 and C_2H_5 at carbon 2.

Carbonyl tests constrain identity

1. **1** Both aldehydes and ketones give 2,4-DNPH precipitates.
2. **2** Aldehydes give Tollens' silver or warm Fehling's brick-red precipitate; ordinary ketones do not.
3. **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 C=O π pair moves to oxygen.

Attempt: use optical and structural evidence together

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

Reveal: a chiral racemate supports the planar model

1. **1** A chiral product with zero rotation supports equal **enantiomers**; ideal SN1 allows two-face attack.
2. **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. **1 Carbonyl** O accepts a hydrogen bond from water. Simple aldehydes/ketones lack an O–H donor.
2. **2** Acids form hydrogen-bonded associations; compare similar-sized molecules for boiling points.
3. **3** A longer non-polar chain can reduce water solubility without removing the polar group.

Attempt: identify the purified derivative

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

Reveal: combine tests with derivative data

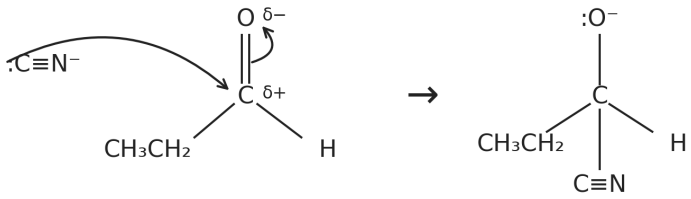
1. **1** Propanone fits the supplied 126°C derivative reference and **ketone** test behaviour.
2. **2** Butan-2-one also gives iodoform; that test alone cannot distinguish the two.
3. **3** A sharp range supports purity; coincident reference ranges still limit identification.

Attempt: draw both cyanide-addition stages

1. **1** Draw propanal + HCN with CN^- **catalyst**, including all four electron-pair arrows.
2. **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

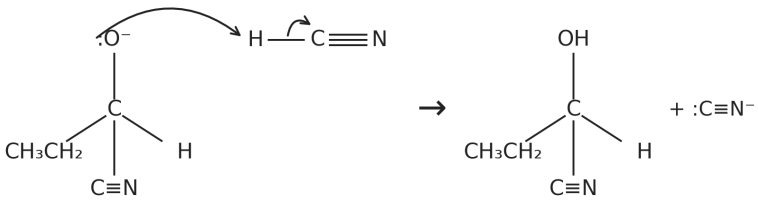


The negative charge is on oxygen; the new C–C bond retains the nitrile carbon.

1. **1** CN^- attacks through its carbon lone pair; the C=O π pair moves to O.
2. **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 → H; H–C bond pair → C. Product: $CH_3CH_2CH(OH)CN$.

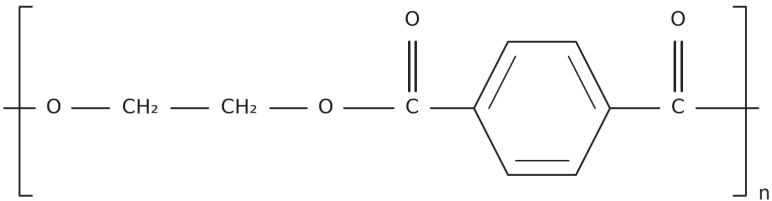
1. **1** O^- lone pair → H of HCN; H–C bond pair → cyanide carbon.
2. **2** $CH_3CH_2CH(OH)CN$ has a **chiral centre**; equal attack on two planar faces gives a racemate.

Carboxylic derivatives keep the acyl carbon

1. **1 Acid** + alcohol $\rightleftharpoons$ ester + water, with acid **catalyst** and heat.
2. **2 Acyl chloride** + $2NH_3 \rightarrow$ amide + NH_4Cl.
3. **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.

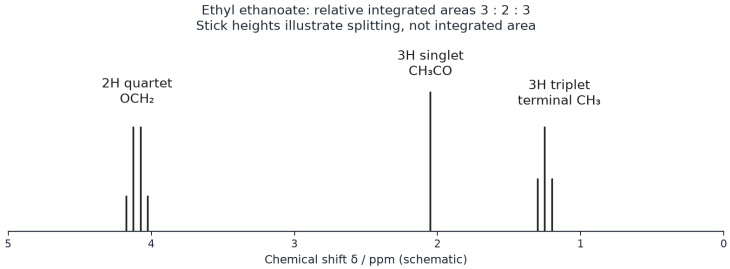
Attempt: retain the nitrile carbon

1. **1** Write **acid** and alkaline **hydrolysis** equations for CH_3CH_2CN.
2. **2** Give conditions, then obtain free acid from the alkaline product.

Reveal: acid and alkali have different final ions

1. **1 Acid**: $CH_3CH_2CN + 2H_2O + H^+ \rightarrow CH_3CH_2COOH + NH_4^+$.
2. **2** Alkali: $CH_3CH_2CN + H_2O + OH^- \rightarrow CH_3CH_2COO^- + NH_3$.
3. **3** Heat under **reflux** with aqueous reagent; acidify carboxylate afterwards.

Combine NMR features



Carbon-13 counts environments, not atoms.

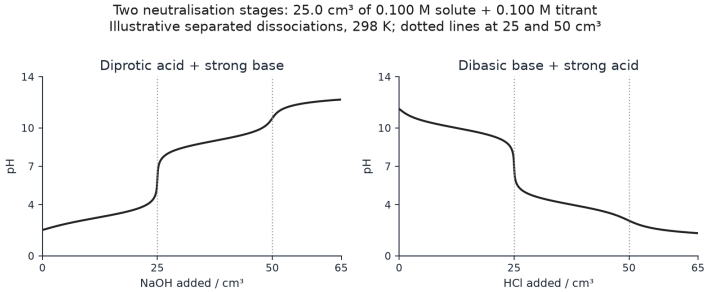
Chromatography is evidence with limits

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

Draw the curve from the species

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

Two stages require two mole calculations

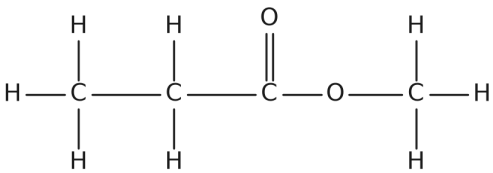


25.0 cm^3 of 0.100 M H_2A uses 25.0 cm^3 then 50.0 cm^3 total of 0.100 M NaOH.

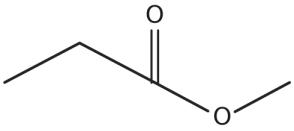
Names specify both sides of an ester

Methyl propanoate

Displayed formula



Skeletal formula



Methyl propanoate is $CH_3CH_2COOCH_3$: three acid-side carbons and one alcohol-side carbon.

Attempt: resolve nominal mass 60

1. **1** Calculate accurate masses of C_3H_8O and $C_2H_4O_2$ with C 12.0000, H 1.0078, O 15.9949.
2. **2** Measured 60.0210; **acid** O–H/C=O and two carbon-13 signals. Suggest a structure.

Reveal: formula before connectivity

1. **1** C_3H_8O:60.0573; $C_2H_4O_2$:60.0210. Difference 0.0363 resolves the formula.
2. **2** CH_3COOH fits the **acid** IR and two distinct carbon environments.
3. **3** Accurate mass selects a formula; the other evidence constrains its structure.

Attempt: predict both resolutions for butan-2-one

1. **1** For $CH_3COCH_2CH_3$, give proton sets, areas and simple n+1 **splitting**.
2. **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. **1** 3H acyl singlet; 2H quartet; 3H terminal triplet. Equivalent methyl H do not split each other.
2. **2** Acyl CH_3/CH_2 lie at 2.0–2.7ppm; terminal CH_3 at 0.8–1.5ppm in supplied data.
3. **3** Four carbon environments: three alkyl signals and one **ketone carbonyl** at 190–220ppm.

Migration depends on two phases

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

Independent structural identification

Your turn

C_3H_6O 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. **1** B: propanone has equivalent methyl carbons, a CH_3CO– group and **ketone** behaviour.
2. **2** Its HCN product has two identical methyl groups and is achiral.
3. **3** Reject alternatives using all observations, not one familiar test.