

Exercise walk-through

2.5.4

Preparation, tests and spectral evidence

Pearson Edexcel · International A-Level · Chemistry

Opposite solubility trends explain the evidence

- 1 **Set up** $\text{Ba}(\text{OH})_2$ 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.

Independent identification

Your turn

$\text{C}_3\text{H}_6\text{O}$ has a carbonyl IR absorption and gives a positive Fehling's test. Which structure fits all evidence?

- A. CH_3COCH_3
- B. $\text{CH}_3\text{CH}_2\text{CHO}$
- C. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- D. CH_3COOH

Exercises 2.1·2.2

2.1 Write an equation with integer coefficients for complete combustion of propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$. Write its equation with PCl_5 and explain why HCl fumes alone do not uniquely identify an alcohol. [4]

2.2 Butan-1-ol is oxidised with potassium dichromate(VI) in dilute sulfuric acid. Route A distils the product as it forms; route B uses reflux with excess oxidant. The same oxidant reacts with butan-2-ol in route C. Name all three organic products and write [O] equations for A and B. State the dichromate colour change, the positive observation with warm Fehling's or Benedict's solution for A's product, and the observation when B's product meets sodium carbonate. [8]

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2.1 $2\text{C}_3\text{H}_7\text{OH} + 9\text{O}_2 \rightarrow 6\text{CO}_2 + 8\text{H}_2\text{O}$. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl}$. Water or a carboxylic acid can also produce HCl with PCl_5 , so fumes alone do not uniquely establish an alcohol.

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2.2 A butanal, B butanoic acid, C butanone. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O}$; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$. Dichromate changes orange to green. A gives a brick-red precipitate with warm Fehling's/Benedict's solution; B gives effervescence of CO_2 with sodium carbonate. Ketone C does not give the ordinary positive aldehyde test.

Exercises 2.3·3.1

2.3 A liquid organic product has density 0.87 g cm^{-3} and is extracted with an aqueous

3.1 An unknown has formula $\text{C}_3\text{H}_6\text{O}$, a singly charged molecular ion at m/z 58, a fragment at m/z 29, a carbonyl IR absorption and a positive warm Fehling's test. Consider propanal and propanone. Check the molecular mass; give two different ionic formulae of mass 29 using $\text{C} = 12$, $\text{H} = 1$, $\text{O} = 16$; then choose the supported isomer and explain why the single fragment cannot establish it alone.

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2.3 The stated organic product is the upper layer because $0.87 < 1.00 \text{ g cm}^{-3}$; do not generalise to every organic liquid. Layer separation removes the bulk aqueous phase, whereas an anhydrous salt removes residual water. Decant/filter the salt before distilling to leave the dried liquid product. Reflux returns condensate to the reaction vessel; distillation collects a volatile fraction separately. Place the bulb in the vapour path at the condenser entrance and compare at the same pressure. A narrow range supports purity, but another substance or mixture may have a similar range, so further identity evidence is needed.

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3.1 $M_r = 3(12) + 6(1) + 16 = 58$ for both isomers. C_2H_5^+ : $2(12) + 5 = 29$; CHO^+ : $12 + 1 + 16 = 29$. Positive Fehling's evidence supports propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, over propanone. A fragment mass permits different ionic formulae/pathways and does not uniquely locate the carbonyl; use the combined evidence.

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3.2 Use the supplied approximate absorption data to predict the relevant listed regions for each structure: $\text{CH}_2=\text{CHCH}_2\text{NH}_2$; $\text{CH}_3\text{CH}_2\text{Cl}$; HOCH_2CHO ; CH_3COOH . Include C–H regions and distinguish alcohol from acid OH. State functional groups and ranges, rather than claiming that one peak proves a whole structure. [11]

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
Alcohol O–H	3200–3600, broad
Carboxylic-acid O–H	2500–3300, very broad
C=O	1680–1750
C–Cl	500–800
Amine N–H	3300–3500

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3.2 Original marking guidance by structure:

- $\text{CH}_2=\text{CHCH}_2\text{NH}_2$: alkene C–H 3000–3100 and alkane C–H 2850–3000; C=C 1620–

Full solution 3.2

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- $\text{CH}_3\text{CH}_2\text{Cl}$: alkane C–H 2850–3000; C–Cl 500–800.
- HOCH_2CHO : alkane C–H 2850–3000 and aldehyde C–H 2700–2900; broad alcohol O–H 3200–3600; C=O 1680–1750.
- CH_3COOH : alkane C–H 2850–3000; very broad acid O–H 2500–3300; C=O 1680–1750.

The supplied regions overlap; intensities, shapes and other evidence matter. The alcohol and acid answers must distinguish their OH environments rather than merely state “OH present”.

Exercise 3.3

3.3 Four unknowns are, in some order, sodium sulfate, ammonium sulfate, propanal and propanone. Each test uses a fresh aliquot. Only A releases a gas on warming with NaOH; the gas turns damp red litmus blue. A and B give a white precipitate with acidified barium chloride. C gives a brick-red precipitate with warm Fehling's solution; D does not. Both C and D have a carbonyl absorption and molecular ion 58. Identify A–D, write ionic equations for the ammonium and sulfate tests, and explain why the separate aliquots matter and why the shared carbonyl/mass results cannot distinguish C from D.

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3.3 A ammonium sulfate; B sodium sulfate; C propanal; D propanone. $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$; $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$. Fresh aliquots prevent reagent carry-over from introducing ions or altering later test conditions. Both isomers contain C=O and have M_r 58, so those shared results cannot distinguish them; the aldehyde's reducing test does. This closed candidate list supports these assignments; it does not make the tests unique among all possible chemicals.