Oxford Cambridge and RSA

Friday 27 May 2022 – Afternoon

AS Level Chemistry A

H032/02 Depth in chemistry

Time allowed: 1 hour 30 minutes

You must have:
- the Data Sheet for Chemistry A

You can use:
- a scientific or graphical calculator
- an HB pencil

Please write clearly in black ink. **Do not write in the barcodes.**

Centre number | | | | | | Candidate number | | | | |

First name(s) _____

Last name StemUp Model Solution

INSTRUCTIONS
- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION
- The total mark for this paper is **70**.
- The marks for each question are shown in brackets **[ ]**.
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **16** pages.

ADVICE
- Read each question carefully before you start your answer.

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Answer **all** the questions.

1 Lime is a citrus fruit containing citric acid, $C_6H_8O_7$.

(a) Citric acid is a weak organic acid.

(i) What is meant by an **acid**?

An acid is a proton (H^+) donor; it releases H^+ ions in solution. **[1]**

(ii) What is meant by an acid that is **weak**?

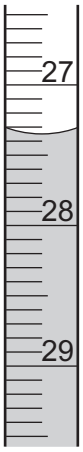
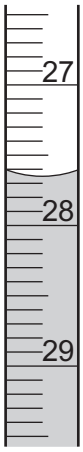
A weak acid only partially dissociates (ionises) in solution, so only some of its H^+ ions are released. **[1]**

(b) A student carries out a titration to determine the mass of citric acid in a lime.
The student follows the method below:

- Squeeze the juice out of two limes.
- Transfer the juice into a 250.0 cm^3 volumetric flask and make up to the mark with distilled water.
- Pipette 25.0 cm^3 of the diluted lime juice into a conical flask and add a few drops of phenolphthalein indicator.
- Titrate this solution with 0.800 mol dm^{-3} NaOH(aq).

The student carries out a trial titration, followed by three further titrations.

The diagram shows the burette readings for the three further titrations.
Each reading is measured to the nearest 0.05 cm^3.

Titration 1		Titration 2		Titration 3	
Initial reading	Final reading	Initial reading	Final reading	Initial reading	Final reading
					

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(i) Record the student's burette readings in the table below.

Calculate the mean titre, to the nearest 0.05 cm^3, that the student should use to analyse the results.

	Titration 1	Titration 2	Titration 3
Final reading / cm^3	27.35	27.65	27.85
Initial reading / cm^3	0.05	0.10	0.45
Titre / cm^3	27.30	27.55	27.40

Titrations 1 and 3 are concordant (within 0.10 cm^3):

mean titre = (27.30 + 27.40) ÷ 2 = 27.35 cm^3

mean titre .....27.35..... cm^3 **[4]**

(ii) Citric acid, $C_6H_8O_7$, is neutralised by NaOH as shown in the equation below.

$C_6H_8O_7 + 3NaOH \rightarrow Na_3C_6H_5O_7 + 3H_2O$

Calculate the mass, in g, of citric acid in **one** lime.

Assume that citric acid (M_r = 192.0) is the only acid in lime juice.

n(NaOH) = 27.35 × 0.800 ÷ 1000 = 0.02188 mol

n($C_6H_8O_7$) in 25.0 cm^3 = 0.02188 ÷ 3 = 7.293 × 10^{-3} mol

n($C_6H_8O_7$) in 250.0 cm^3 = 10 × 7.293 × 10^{-3} = 0.07293 mol

mass in two limes = 0.07293 × 192.0 = 14.00 g

mass in one lime = 14.00 ÷ 2 = 7.00 g

mass of citric acid in **one** lime = ...7.00..... g **[5]**

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(c) The student's teacher thinks that there is an unnecessary safety risk in using a sodium hydroxide concentration of 0.800 mol dm^{-3} for the titration.

Suggest how the student could modify the method using a sodium hydroxide concentration of 0.200 mol dm^{-3} instead of 0.800 mol dm^{-3}.

The student should aim to have the same titre as in the original method.

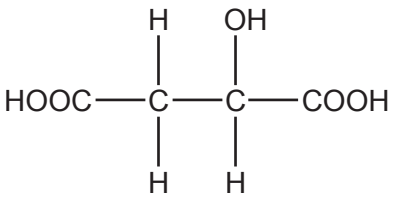
Justify your answer.

Use half a lime instead of two limes (or make up the juice to 1 dm^3 in a 1000 cm^3 volumetric flask).

NaOH is 4 times more dilute (0.800 ÷ 4), so each 25.0 cm^3 sample needs 4 times less citric acid for the same titre. **[2]**

(d) Other fruits contain different organic acids.

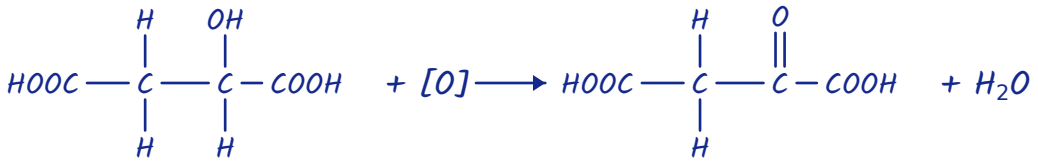
Apple juice contains malic acid which has the following structure.



Malic acid can be oxidised by heating with acidified potassium dichromate(VI).

Write a balanced equation for the reaction, showing the structure of the organic product.

Use [O] to represent the oxidising agent.



[2]

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2 This question is about some Group 2 elements and their compounds.

(a) Strontium and calcium both react with water.

(i) Write an equation for the reaction of strontium with water.

$Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2$ **[1]**

(ii) Using oxidation numbers, explain why the reaction of strontium with water is a redox reaction.

Sr is oxidised: its oxidation number increases from 0 to +2.

H is reduced: its oxidation number decreases from +1 (in H_2O) to 0 (in H_2).

Oxidation and reduction both take place, so it is a redox reaction. **[2]**

(iii) Explain why calcium reacts more slowly with water than strontium does.

Ca has a smaller atomic radius than Sr (fewer shells), so its outer electrons are closer to the nucleus, and Ca has less shielding.

So Ca has a greater nuclear attraction on its outer electrons; Ca has a higher ionisation energy, so more energy is needed to lose the outer electrons. **[3]**

(b) A student adds barium oxide, BaO, to water.

A reaction takes place forming a colourless solution.

(i) Predict the approximate pH of the colourless solution.

pH = 13 **[1]**

(ii) A student adds a few drops of dilute sulfuric acid to the colourless solution.

Describe what the student would observe, and give the formula of the barium compound produced.

Observation A white precipitate forms

Formula of barium compound $BaSO_4$

[2]

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3 A student investigates some reactions of zinc compounds and zinc metal.

(a) The student investigates the rate of reaction between zinc carbonate, $ZnCO_3(s)$, and dilute hydrochloric acid, $HCl(aq)$.

$$ZnCO_3(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$$

The student follows the method outlined below:

- Add 50 cm^3 of dilute $HCl(aq)$ into a conical flask at 20 °C.
- Place the flask on a top-pan balance.
- Add an excess of $ZnCO_3(s)$ to the flask.
- Record the mass of the flask and contents on the top-pan balance every 30 seconds.

The student plots a graph of mass against time, shown in **Fig. 3.1** below.

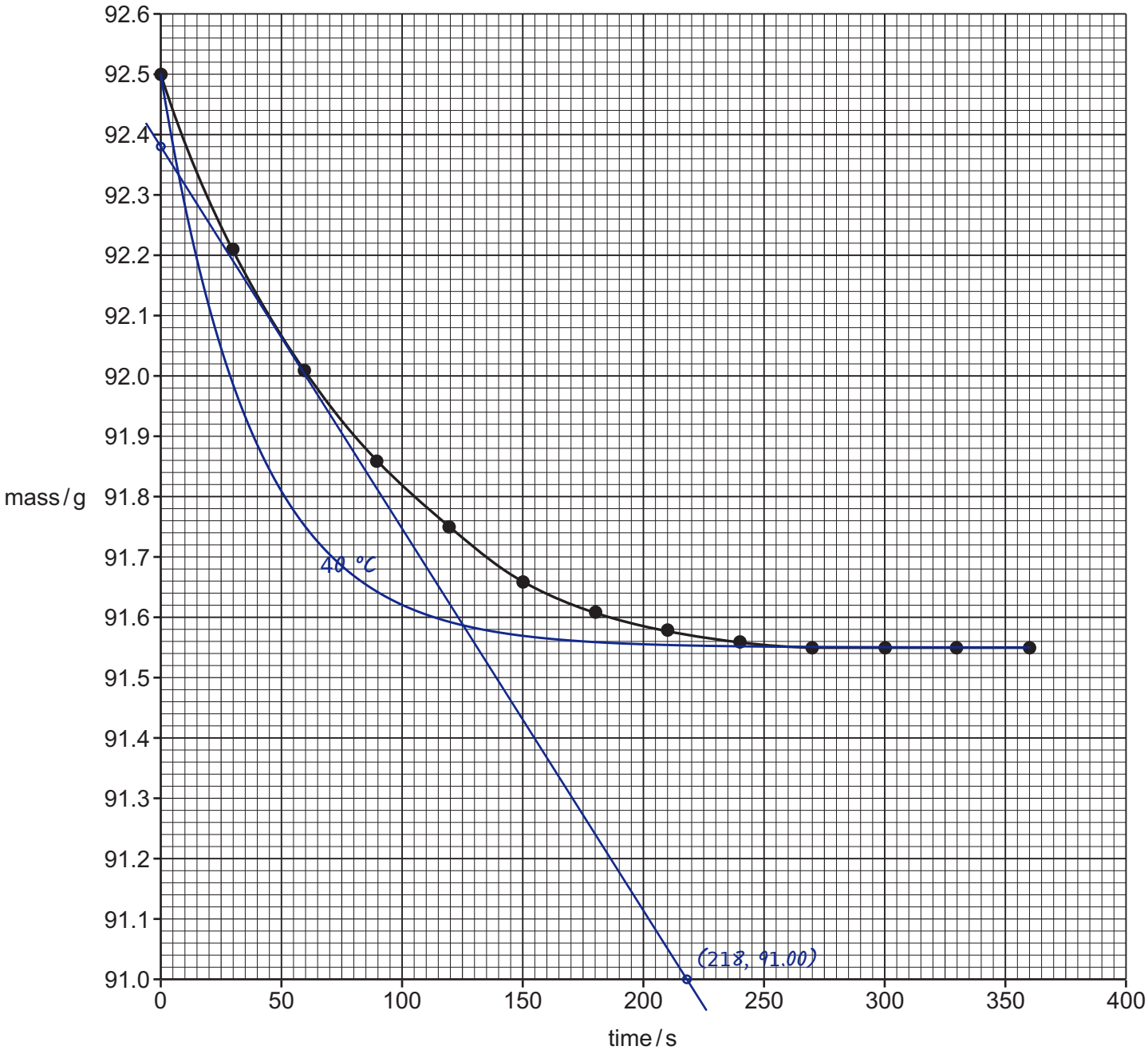

Fig. 3.1

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(i) The graph shows that the reaction gets slower over time, and eventually stops.

Explain why, in terms of collision theory.

As the reaction proceeds, HCl is used up so the concentration of acid decreases; there are fewer H^+ ions in the same volume.
So there are fewer collisions per second (less frequent collisions) between acid particles and $ZnCO_3$, so the rate decreases.
The reaction stops when all of the HCl (the limiting reagent) has reacted, as $ZnCO_3$ is in excess.

..... **[3]**

(ii) Using the graph in **Fig. 3.1**, find the rate of reaction, in $g\,s^{-1}$, at 50 seconds.

Show your working on the graph and in the space below.

Tangent drawn at t = 50 s on Fig. 3.1, through (0, 92.38) and (218, 91.00):
gradient = (92.38 − 91.00) ÷ (218 − 0) = 1.38 ÷ 218
= 6.33×10^{-3} g s^{-1}

rate of reaction = ...6.33×10^{-3}.... $g\,s^{-1}$ **[2]**

(iii) The student repeats the experiment but heats 50 cm^3 of dilute hydrochloric acid up to 40 °C before adding the $ZnCO_3$(s).

On **Fig. 3.1**, sketch the curve the student would obtain. **[2]**

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(b) The student investigates the reaction between zinc and dilute sulfuric acid.

$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$ $\Delta H = -140\,kJ\,mol^{-1}$

Copper(II) sulfate is a catalyst for this reaction.

- The student adds a piece of zinc to each of two test tubes.
- The student adds a few drops of aqueous copper(II) sulfate to one of the test tubes, forming a pale blue solution.
- The student adds an excess of dilute sulfuric acid to each test tube.

(i) Describe **two** differences the student would observe between the test tubes.

1 Bubbles of gas (H_2) are given off more quickly (more vigorous fizzing) in the tube with $CuSO_4$.

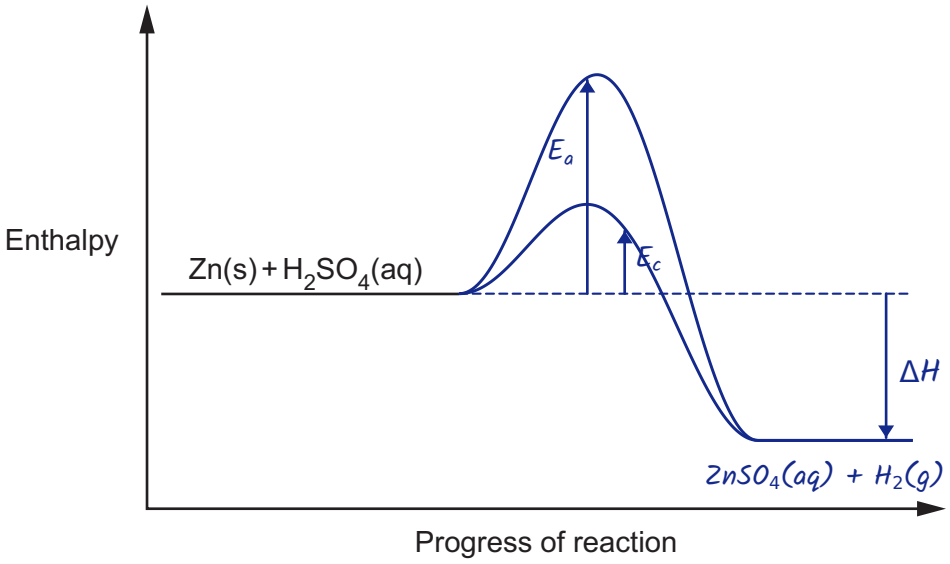
2 The zinc dissolves (disappears) more quickly in the tube with $CuSO_4$.

[2]

(ii) Using the axes below, sketch an enthalpy profile diagram for the reaction with and without the catalyst.

On your diagram, include the following labels:

- ΔH, the enthalpy change
- E_a, the activation energy **without** a catalyst
- E_c, the activation energy **with** a catalyst.



[3]

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4 This question is about the manufacture of hydrogen, H_2.

(a) In industry, hydrogen is manufactured from methane, as shown in **Equilibrium 4.1**.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +206\,kJ\,mol^{-1}$ **Equilibrium 4.1**

The industrial process is carried out at 15 atmospheres pressure and at a temperature of 800 °C using an excess of steam. A nickel catalyst is used.

(i)* Explain why these conditions are used industrially. **[6]**

Temperature: the forward reaction is endothermic ($\Delta H = +206\ kJ\ mol^{-1}$), so a high temperature shifts the equilibrium position to the right, increasing the yield of H_2. A high temperature also increases the rate, as more particles have energy above E_a, so there are more successful collisions per second. However, high temperatures have a high energy demand and cost, so 800 °C is a compromise.

Pressure: the left-hand side has fewer gaseous moles (2 mol of gas form 4 mol of gas), so a low pressure shifts the equilibrium to the right, giving more H_2. But a low pressure reduces the rate, as gas molecules collide less often. So 15 atm is a compromise: slightly higher than optimum for yield to give a good rate, while high pressures would be expensive and unsafe.

Excess steam: increasing $[H_2O]$ shifts the equilibrium to the right, converting more of the methane to H_2.

Nickel catalyst: it provides an alternative route with a lower activation energy, so it increases the rate without needing an even higher temperature (saving energy). It does not affect the position of equilibrium, but equilibrium is reached faster.

Additional answer space if required.

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(ii) A chemist mixes $CH_4(g)$ and $H_2O(g)$ and leaves the mixture to reach equilibrium.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +206\,kJ\,mol^{-1}$ **Equilibrium 4.1**

The equilibrium mixture contains the following concentrations.

Substance	Concentration / mol dm^{-3}
$CH_4(g)$	0.111
$H_2O(g)$	0.682
$CO(g)$	0.510
$H_2(g)$	1.530

Write an expression for the equilibrium constant, K_c, for **Equilibrium 4.1** and calculate the numerical value of K_c.

Give your answer to **3** significant figures.

$$K_c = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]} = \frac{0.510 \times 1.530^3}{0.111 \times 0.682} = 24.129$$

K_c = ...24.1..... mol^2 dm^{-6} **[2]**

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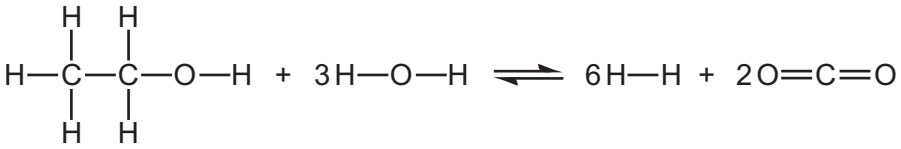
(b) Hydrogen can also be manufactured by reacting ethanol with steam, as shown in **Equilibrium 4.2**.



Equilibrium 4.2

Average bond enthalpies are shown in the table below.

Bond	C–H	C–C	C–O	O–H	H–H	C=O
Average bond enthalpy / kJ mol^{-1}	+415	+347	+358	+464	+435	+805

Calculate ΔH, in kJ mol^{-1}, for the forward reaction in **Equilibrium 4.2**.

Bonds broken: 5(C–H) + (C–C) + (C–O) + 7(O–H)

= 5(415) + 347 + 358 + 7(464) = 6028 kJ

Bonds made: 6(H–H) + 4(C=O) = 6(435) + 4(805) = 5830 kJ

ΔH = bonds broken − bonds made = 6028 − 5830 = +198 kJ mol^{-1}

ΔH = ...+198..... kJ mol^{-1} **[3]**

(c) CO_2 and H_2O molecules have different shapes.

State the bond angles in CO_2 and H_2O molecules and explain, in terms of electron pair repulsion, why the bond angles are different.

Bond angles: CO_2 = 180°; H_2O = 104.5°.

In CO_2 the C atom has 2 double bonds (2 bonding regions) and no lone pairs, which repel equally and get as far apart as possible, so CO_2 is linear.

In H_2O the O atom has 2 bonding pairs and 2 lone pairs. Lone pairs repel more than bonding pairs, so the H–O–H angle is reduced to 104.5°.

..... **[4]**

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5 2-Bromobutane, $CH_3CH_2CHBrCH_3$, can be prepared by three different methods.

The relative molecular mass, M_r, of 2-bromobutane is 136.9.

(a) 2-Bromobutane can be prepared by reacting butane with bromine (**Reaction 5.1**).

$CH_3CH_2CH_2CH_3 + Br_2 \longrightarrow CH_3CH_2CHBrCH_3 + HBr$ **Reaction 5.1**

The reaction is initiated by the formation of bromine radicals from bromine.

(i) State the conditions for the formation of bromine radicals from bromine.

UV light (ultraviolet radiation) **[1]**

(ii) Write **two** equations for the propagation steps in the mechanism for **Reaction 5.1**.

Use structural formulae for organic species and dots (•) for unpaired electrons on radicals.

$CH_3CH_2CH_2CH_3$ + $Br\bullet$ → $CH_3CH_2\dot{C}HCH_3$ + HBr

$CH_3CH_2\dot{C}HCH_3$ + Br_2 → $CH_3CH_2CHBrCH_3$ + $Br\bullet$

[2]

(iii) The yield of $CH_3CH_2CHBrCH_3$ is only 30%.

Suggest **two** reasons why the yield of $CH_3CH_2CHBrCH_3$ is so low.

1 Further substitution: more H atoms are replaced, forming di- and tri-bromobutanes (e.g. $CH_3CH_2CBr_2CH_3$).

2 Substitution also occurs at a different position (an end carbon), forming 1-bromobutane, $CH_3CH_2CH_2CH_2Br$.

[2]

(b) 2-Bromobutane can also be prepared by reacting but-2-ene, $CH_3CH{=}CHCH_3$, with hydrogen bromide, HBr (**Reaction 5.2**).

$CH_3CH{=}CHCH_3 + HBr \longrightarrow CH_3CH_2CHBrCH_3$ **Reaction 5.2**

Explain, in terms of atom economy, why **Reaction 5.2** is more sustainable than **Reaction 5.1**.

Include calculations to justify your answer.

Reaction 5.1: atom economy = 136.9 ÷ (58.0 + 159.8) × 100 = 62.9%

Reaction 5.2: atom economy = 136.9 ÷ (56.0 + 80.9) × 100 = 100%

5.2 has the higher atom economy: 2-bromobutane is the only product, with no waste HBr. **[2]**

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(c) 2-Bromobutane can also be prepared by reacting butan-2-ol, $CH_3CH_2CHOHCH_3$, with sodium bromide and sulfuric acid (**Reaction 5.3**).

$CH_3CH_2CHOHCH_3 + H^+ + Br^- \longrightarrow CH_3CH_2CHBrCH_3 + H_2O$ **Reaction 5.3**

2-Bromobutane is a liquid with a boiling point of 91 °C and does not mix with water.

(i) A student plans to prepare 10.0 g of 2-bromobutane using **Reaction 5.3**.

The percentage yield is 67.0%.

Calculate the mass of $CH_3CH_2CHOHCH_3$ needed for this preparation.

Give your answer to **3** significant figures.

n(2-bromobutane) = 10.0 ÷ 136.9 = 0.07305 mol

yield is 67.0%, so n(butan-2-ol) = 0.07305 × 100 ÷ 67.0 = 0.1090 mol

$M_r(CH_3CH_2CHOHCH_3)$ = 74.0

mass = 0.1090 × 74.0 = 8.07 g

mass = ...8.07..... g **[3]**

(ii) The student mixes butan-2-ol, sodium bromide and sulfuric acid in a pear-shaped flask, and refluxes the mixture.

After 1 hour, the mixture in the flask has separated into two layers: an aqueous layer and an organic layer.

Describe the procedures the student would need to carry out to obtain a pure, dry sample of 2-bromobutane from this mixture.

Pour the mixture into a separating funnel, let the layers separate and run off the aqueous layer, keeping the organic layer (2-bromobutane). Dry the organic layer with an anhydrous salt (e.g. anhydrous $MgSO_4$ or $CaCl_2$), then decant or filter off the drying agent. Distil the dried liquid and collect the fraction boiling at 91 °C.

..... **[3]**

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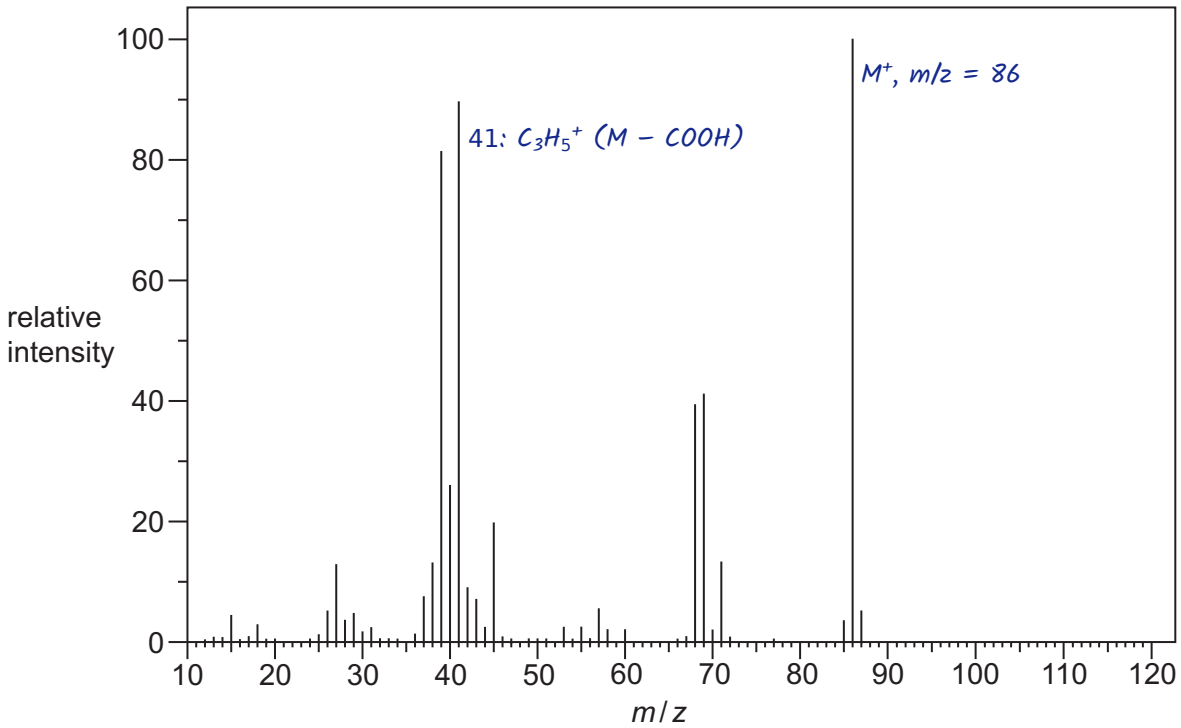
6* The organic compound **A** is unsaturated and is a *trans* stereoisomer.

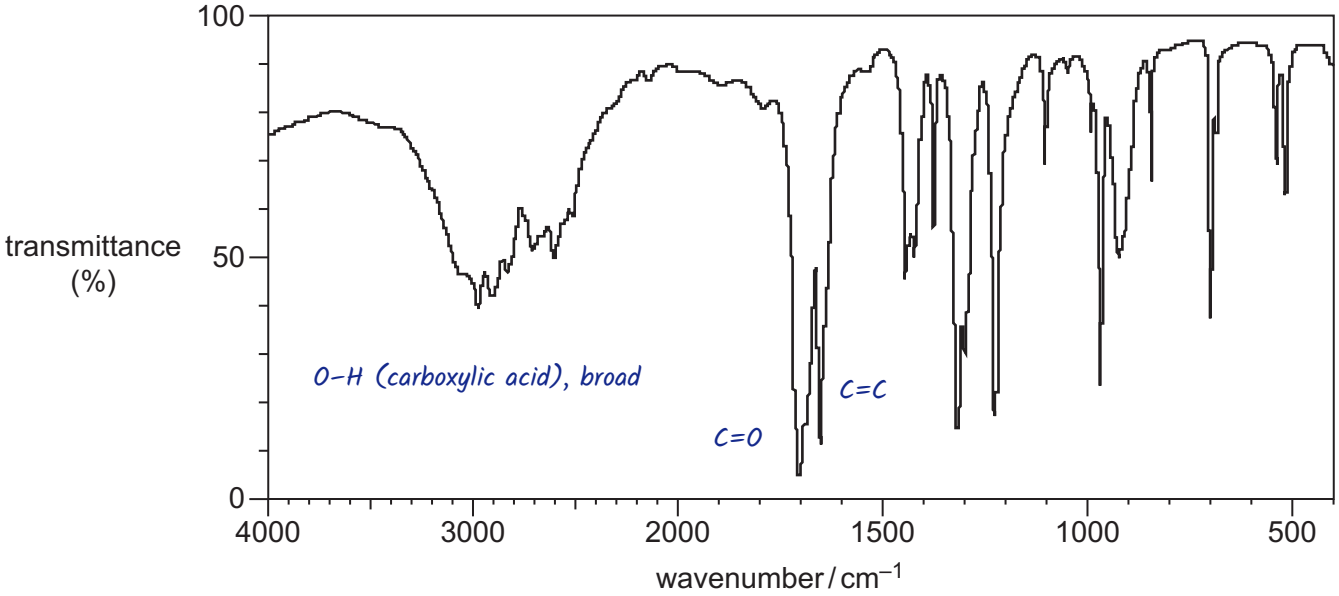
Compound **A** has the following composition by mass: C, 55.8%; H, 7.0%; O, 37.2%.

The mass spectrum and the infrared spectrum of compound **A** are shown below.

Mass spectrum



Infrared spectrum



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Use the information to determine the structure of compound **A**.

Explain your reasoning and show your working. **[6]**

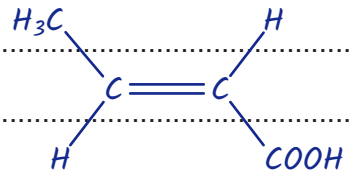
Empirical formula: C 55.8 ÷ 12.0 = 4.65; H 7.0 ÷ 1.0 = 7.0; O 37.2 ÷ 16.0 = 2.325. Ratio 4.65 : 7.0 : 2.325 = 2 : 3 : 1, so the empirical formula is C_2H_3O (43.0).

Mass spectrum: the molecular ion peak is at m/z = 86, so M_r = 86.0 = 2 × 43.0 and the molecular formula is $C_4H_6O_2$.

IR: the broad absorption at 2500 to 3300 cm^{-1} is O–H in a carboxylic acid; the strong peak at about 1700 cm^{-1} is C=O; the peak at about 1650 cm^{-1} is C=C.

So A is a carboxylic acid, –COOH, with a C=C (unsaturated). The peak at m/z = 41 is $C_3H_5^+$, from loss of COOH (86 – 45 = 41).

A is but-2-enoic acid, $CH_3CH{=}CHCOOH$. It has E/Z (cis-trans) isomers because each carbon of the C=C has two different groups attached (CH_3 and H; COOH and H). In the trans isomer the H atoms are on opposite sides of the double bond, as are CH_3 and COOH:



trans-but-2-enoic acid

Additional answer space if required.

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

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