

Please write clearly in block capitals.

Centre number

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Candidate number

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Surname

StemUp Model Solution

Forename(s)

Candidate signature

I declare this is my own work.

A-level CHEMISTRY

Paper 2 Organic and Physical Chemistry

Monday 19 June 2023

Afternoon

Time allowed: 2 hours

Materials

For this paper you must have:

- the Periodic Table/Data Booklet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a scientific calculator, which you are expected to use where appropriate.

Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do **not** write outside the box around each page or on blank pages.
- If you need extra space for your answer(s), use the lined pages at the end of this book. Write the question number against your answer(s).
- All working must be shown.
- Do **all** rough work in this book. Cross through any work you do not want to be marked.

Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 105.

For Examiner's Use	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
TOTAL	



J U N 2 3 7 4 0 5 2 0 1

Answer **all** questions in the spaces provided.

0 1

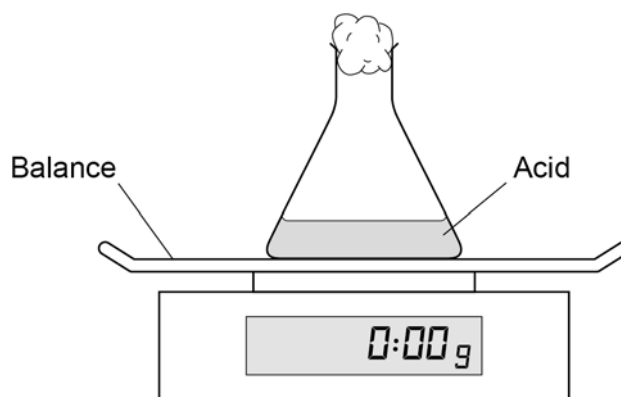
This question is about rates of reaction.

Figure 1 shows apparatus used to measure the rate of reaction when an acid reacts with an excess of solid sodium hydrogencarbonate, NaHCO_3

When different monoprotic organic acids are used, the rates at which gas escapes can be used to compare the strengths of the acids.

A timer is started when the NaHCO_3 is added to the acid and the mass of CO_2 gas lost is recorded at regular intervals.
(It is assumed that any change in mass is due to the loss of CO_2)

Figure 1



0 1 . 1

Suggest a reason why using a conical flask instead of a beaker would give more accurate results in this experiment.

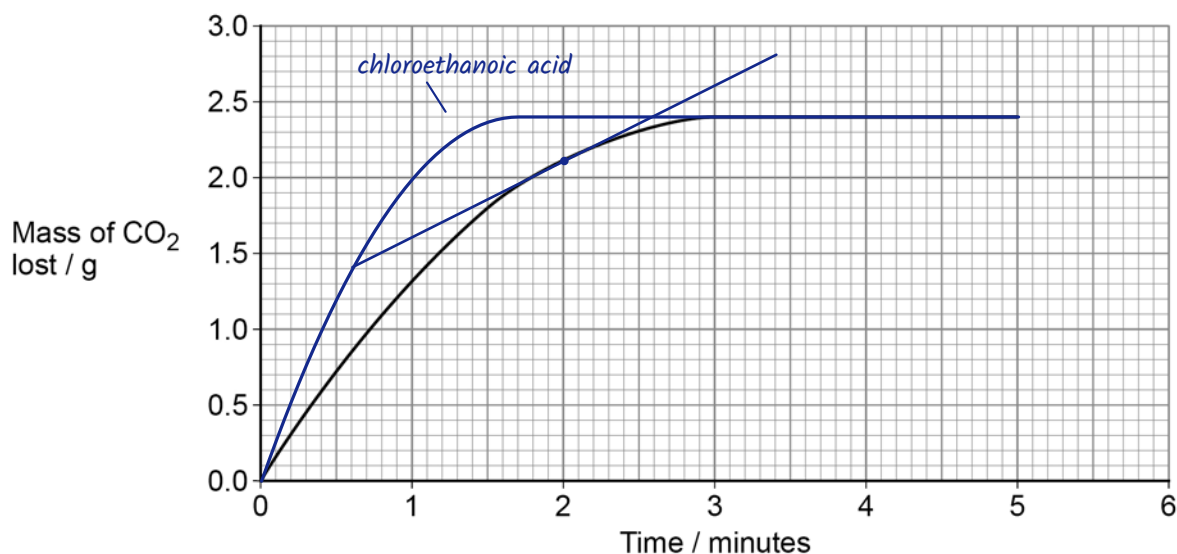
[1 mark]

The narrow neck reduces the loss of liquid droplets (acid spray) from the flask, so mass lost is only due to CO_2 .



Figure 2 shows the results of this experiment when 25.0 cm³ of a 2.23 mol dm⁻³ solution of ethanoic acid reacts with an excess of NaHCO₃

Figure 2



0 1 . 2 Use **Figure 2** to calculate the rate of reaction at 2 minutes.

Deduce the units of your calculated rate.

$$\begin{aligned} \text{gradient of tangent} &= (2.81 - 1.41) \div (3.40 - 0.60) \\ &= 1.40 \div 2.80 = 0.50 \end{aligned}$$

[3 marks]

Rate 0.50 Units g min⁻¹

0 1 . 3 Chloroethanoic acid is a stronger acid than ethanoic acid.

Sketch, on **Figure 2**, the curve you would expect when 25.0 cm³ of a 2.23 mol dm⁻³ solution of chloroethanoic acid reacts with an excess of NaHCO₃

Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

[3 marks]

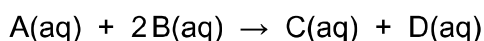
Cl is an electron-withdrawing group (negative inductive effect).

*This weakens the O-H bond (increases the polarity of the O-H bond),
so H⁺ ions are released more readily.*



0 2

A and B react together in the presence of an acid catalyst.



The rate equation for this reaction is

$$\text{rate} = k[B]^2[H^+]$$

Table 1 shows how the values of the relative initial rate vary with different concentrations of each reagent at the same temperature.

Table 1

Experiment	[A] / mol dm ⁻³	[B] / mol dm ⁻³	[H ⁺] / mol dm ⁻³	Relative initial rate
1	0.40	0.20	0.10	1.00
2	0.50	0.20	0.10	1.00
3	0.40	0.16	0.10	0.64
4	0.50	0.30	0.06	1.35

0 2 . 1

Complete **Table 1** by calculating the missing values.

[3 marks]

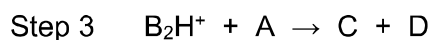
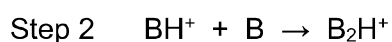
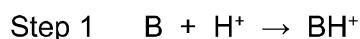
Exp 2: only [A] changes and rate is zero order in A, so rate = 1.00

Exp 3: $([B] \div 0.20)^2 = 0.64$, $[B] \div 0.20 = 0.80$, $[B] = 0.16$

Exp 4: rate = $1.00 \times (0.30 \div 0.20)^2 \times (0.06 \div 0.10) = 2.25 \times 0.60 = 1.35$

0 2 . 2

A suggested mechanism for the reaction is shown.



Deduce the rate-determining step for this reaction.

Give a reason for your answer.

[2 marks]

Rate-determining step Step 2

Reason By the end of step 2, one H^+ and two molecules of B have been used, matching the rate equation; A only reacts after step 2 (zero order).



Turn over for the next question

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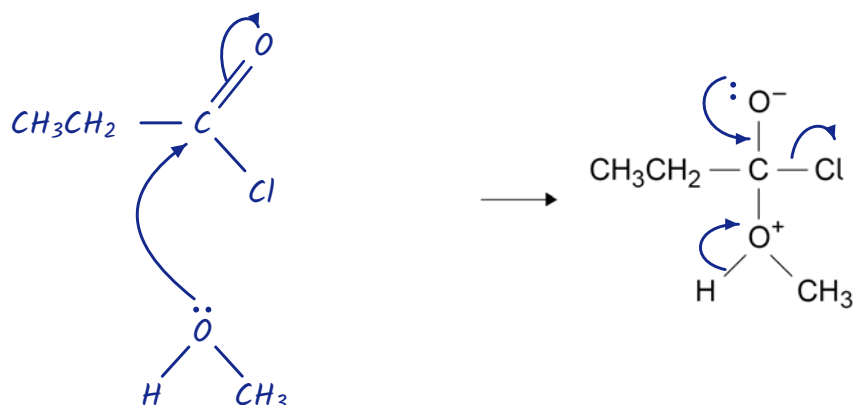
0 3

This question is about intermediates in reaction mechanisms.

0 3 . 1

Figure 3 shows an intermediate formed in the first step of a nucleophilic addition–elimination mechanism.

Figure 3



Complete **Figure 3** to show the structures of the two reactant species with curly arrows and relevant lone pairs of electrons involved in the formation of the intermediate.

Draw curly arrows and relevant lone pairs of electrons on the intermediate to show how the final products are formed.

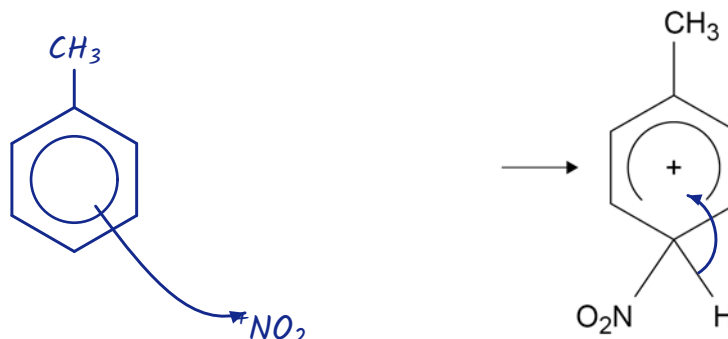
[4 marks]



0 3 . 2

Figure 4 shows an intermediate formed in the first step of a reaction mechanism of methylbenzene.

Figure 4



Complete **Figure 4** to show the reactant species and any curly arrows involved in the formation of the intermediate.

Draw a curly arrow on the intermediate to show how the product is formed.

Give the name of the reaction mechanism.

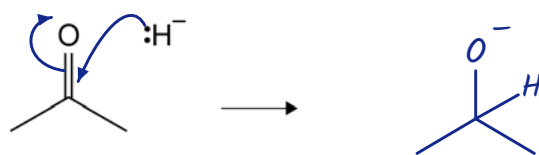
[4 marks]

Name of mechanism Electrophilic substitution

0 3 . 3

Figure 5 shows the reactant species involved in the first step of a mechanism.

Figure 5



Complete **Figure 5** to show the structure of the intermediate formed with curly arrows involved in its formation.

Give the name of the reaction mechanism.

[4 marks]

Name of mechanism Nucleophilic addition

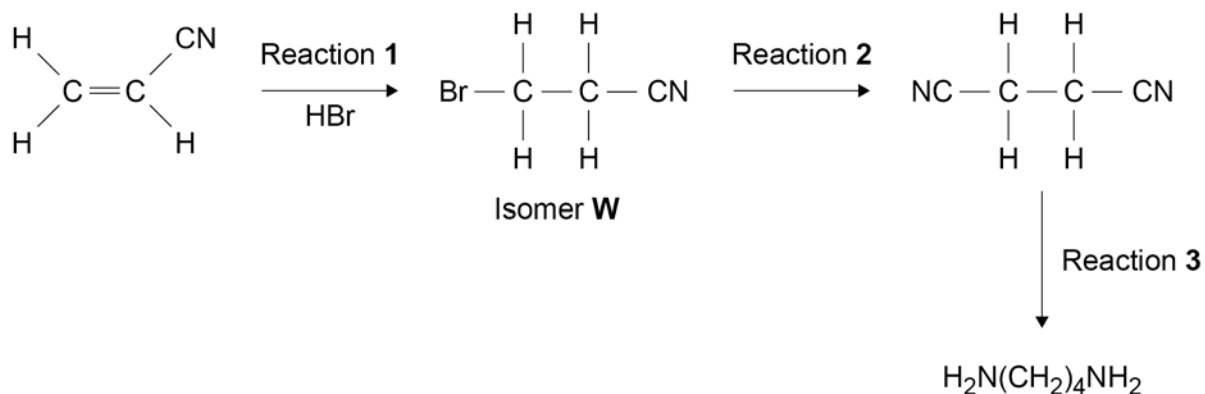
12

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0 4

Acrylonitrile, $\text{H}_2\text{C}=\text{CHCN}$, can be used as a starting material for the synthesis of butane-1,4-diamine, as shown in this reaction scheme.



0 4 . 1

Use IUPAC rules to name isomer **W**.

[1 mark]

3-bromopropanenitrile

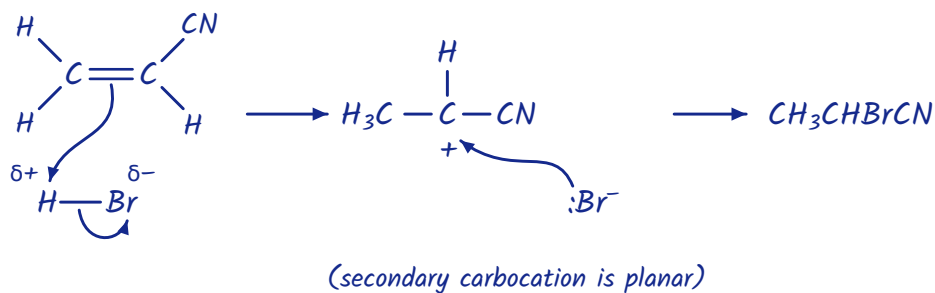
0 4 . 2

Reaction **1** produces a mixture of **W** and two other isomers.

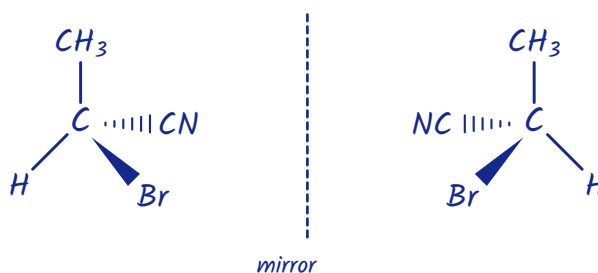
Draw the structures of the two other isomers.

Explain, by considering the mechanism of this reaction, why **all** three isomers are formed.

[6 marks]



The two other isomers (enantiomers of 2-bromopropanenitrile):



Reaction 1 is electrophilic addition. The $C=C$ π bond attacks the δ^+ H of HBr and the H-Br bond breaks heterolytically, forming Br^- and a carbocation (2 curly arrows, as drawn on page 8).

If the H adds to the CH carbon, a primary carbocation forms, $^+CH_2CH_2CN$ ($H_2C^+-CH_2-CN$). Br^- attacks this C^+ to give W, 3-bromopropanenitrile.

If the H adds to the CH_2 carbon, a secondary carbocation forms, CH_3-C^+H-CN . Br^- attacks this to give the other structural isomer, 2-bromopropanenitrile, $CH_3CHBrCN$.

2-bromopropanenitrile has a chiral carbon: the C is bonded to four different groups (H, CH_3 , Br and CN). So it exists as two optical isomers (enantiomers), which are non-superimposable mirror images of each other.

The secondary carbocation is planar (trigonal planar around the C^+), so Br^- can attack from above or below the plane with equal probability.

This gives equal amounts of the two enantiomers (a racemic mixture).

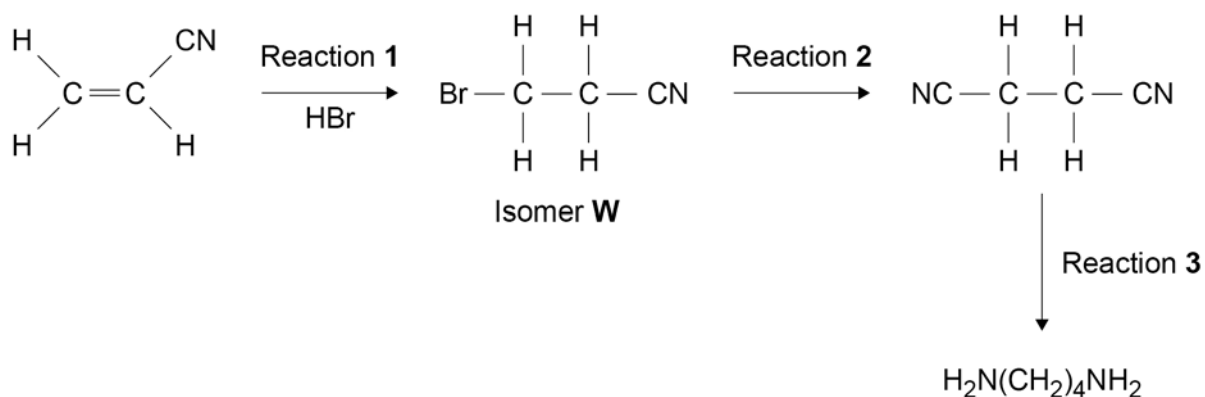
So three isomers form in total: W and the two enantiomers of 2-bromopropanenitrile.

Question 4 continues on the next page

Turn over ►



The reaction scheme is repeated here.



0 4 . 3 Identify the reagent that is warmed with isomer **W** in reaction 2.

State the other reaction condition needed.

[2 marks]

Reagent KCN (potassium cyanide)

Condition Aqueous ethanol as solvent (warm)

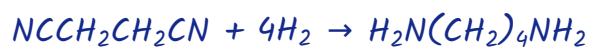
0 4 . 4 State the reagent and reaction conditions needed for reaction 3.

Give an equation for reaction 3.

[2 marks]

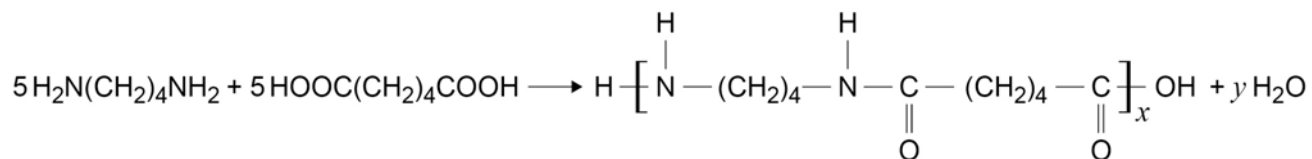
Reagent and conditions H₂ with a Ni catalyst

Equation



0 4 . 5

An incomplete equation for the formation of nylon 4,6 from five molecules of butane-1,4-diamine and five molecules of hexanedioic acid is shown.



Deduce the values of x and y in this equation.

[2 marks]

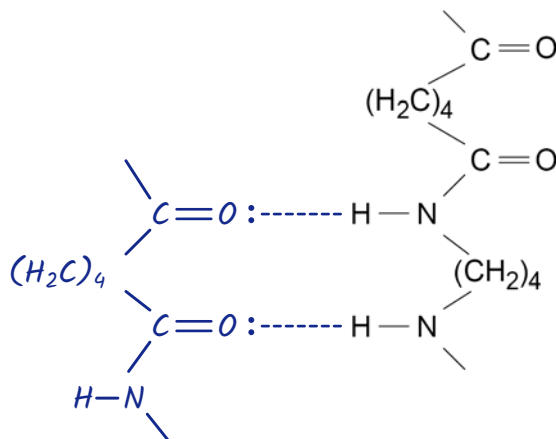
5 repeat units, so $x = 5$; 10 monomers join by $2 \times 5 - 1 = 9$ amide links, so $y = 9$

x 5 y 9

0 4 . 6

Figure 6 shows a section of the nylon 4,6 polymer molecule.

Figure 6



Draw, on **Figure 6**, another section of nylon 4,6 polymer showing two hydrogen bonds between the two sections.

[2 marks]

15

Turn over ►

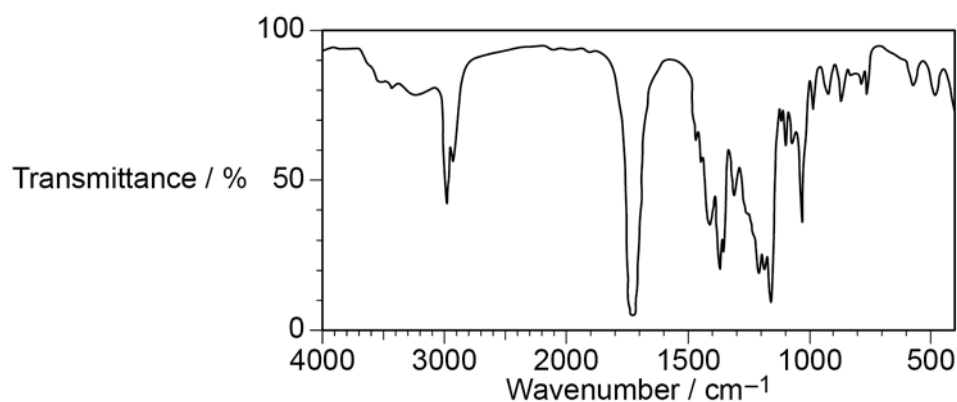


0 5

This question is about compound **Z**, with molecular formula $C_7H_{12}O_3$

Figure 7 shows the infrared spectrum of **Z**.

Figure 7



0 5 . 1

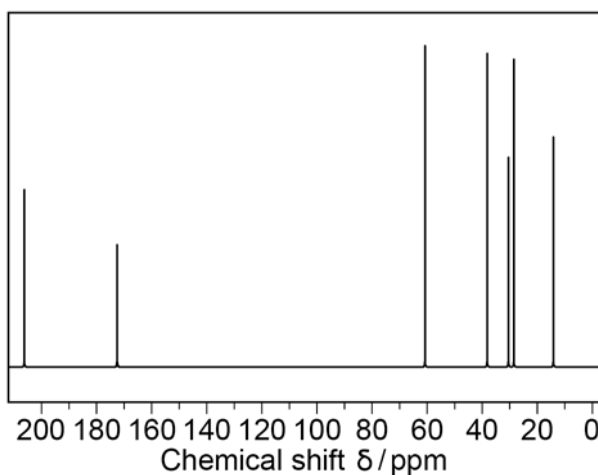
Identify the bond that causes the absorption at 1725 cm^{-1}

[1 mark]

C=O

Figure 8 shows the ^{13}C NMR spectrum of **Z**.

Figure 8



0 5 . 2

How many different carbon environments are there in a molecule of **Z**?

[1 mark]

	5	6	7	8
Tick (✓) one box			✓	

0 5 . 3

State the type of carbon environment that causes the peak at $\delta = 174\text{ ppm}$

Use **Table C** in the Data Booklet to help you answer this question.

[1 mark]

Ester: $R-C(=O)-O-$, the C of the $C=O$ in an ester



0 5 . 4

Table 2 shows data from the ^1H NMR spectrum for compound Z.

Table 2

Chemical shift δ / ppm	4.10	2.60	2.56	2.19	1.26
Integration ratio	2	2	2	3	3
Splitting pattern	quartet	triplet	triplet	singlet	triplet

Explain what can be deduced from the splitting patterns and chemical shift values for the peaks at $\delta = 4.10$ ppm and at $\delta = 1.26$ ppm

Deduce the part of the structure of Z that causes the peaks at $\delta = 4.10$ ppm and $\delta = 1.26$ ppm

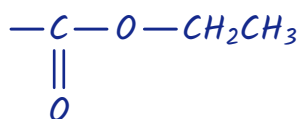
Use Table B in the Data Booklet to help you answer this question.

[5 marks]

Peak at $\delta = 4.10$ ppm *Quartet, so the neighbouring C has 3 H (a CH_3); δ 4.10 means the CH_2 is attached to the single-bonded O of an ester.*

Peak at $\delta = 1.26$ ppm *Triplet, so the neighbouring C has 2 H (a CH_2); δ 1.26 means it is an R-CH_3 (alkyl) group.*

Part of structure

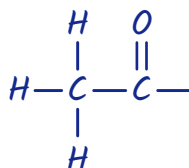


0 5 . 5

Deduce the part of the structure of Z that causes the peak at $\delta = 2.19$ ppm

[1 mark]

Part of structure

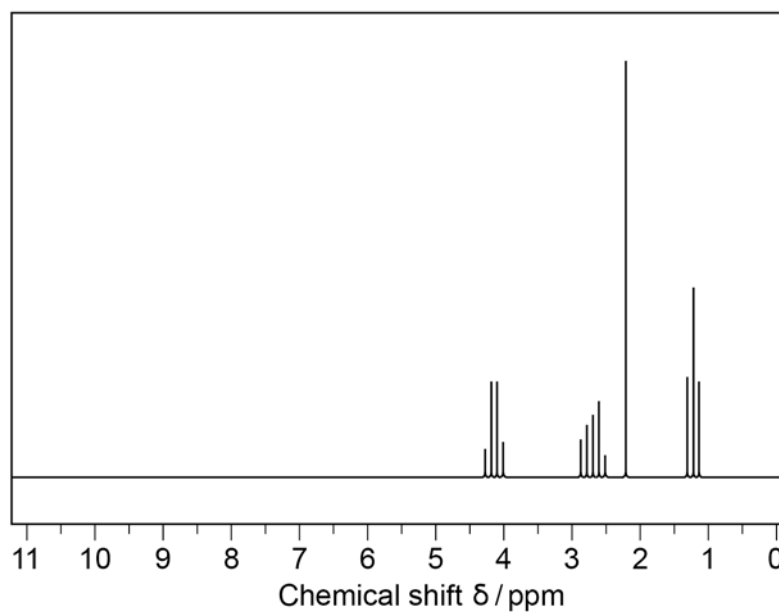


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Figure 9 shows the ^1H NMR spectrum of compound **Z**.

Figure 9



0 5 . 6

Suggest why it would be difficult to determine the structure of **Z** using the spectrum in **Figure 9**, without the information in **Table 2** on page 13.

[1 mark]

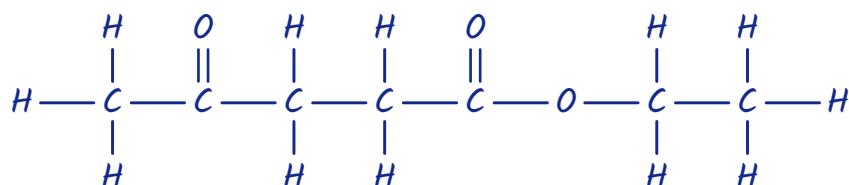
The peaks at $\delta = 2.60$ and 2.56 ppm overlap, so their splitting patterns cannot be deduced, and the spectrum gives no integration values.



0 5 7

Deduce the structure of **Z**.

[1 mark]



Turn over for the next question

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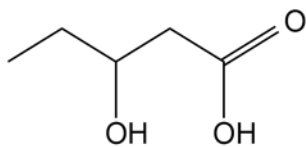
11

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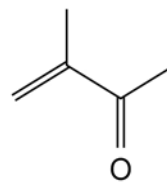


0 6

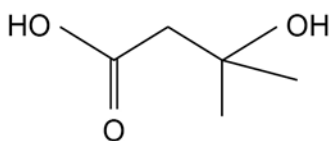
A student plans a series of chemical tests to confirm the identities of four organic liquids.



Liquid J



Liquid K



Liquid L



Liquid M

This is the student's method.

To separate test tubes containing samples of each liquid:

Test 1 add potassium dichromate(VI) solution and warm gently

Test 2 add Fehling's solution and cool in iced water

Test 3 add sodium hydrogencarbonate solution and test any gas produced with a lighted splint

Test 4 add bromine water and shake at room temperature.

0 6 . 1

Identify the missing reagent needed in **Test 1**.

[1 mark]

(Dilute) sulfuric acid, H₂SO₄



0 6 . 2

In addition to the missing reagent in **Test 1**, there is a mistake in the method for **two** of the other tests.

State the **two** mistakes.

Suggest how each of the mistakes should be corrected.

[2 marks]

Mistake 1 *Test 2: cooling with Fehling's solution in iced water*

Suggestion *Warm the mixture in a hot water bath instead.*

Mistake 2 *Test 3: testing the gas with a lighted splint*

Suggestion *Bubble the gas into limewater instead.*

0 6 . 3

The missing reagent is added and the mistakes are corrected.

Identify the liquid(s), **J**, **K**, **L** and **M**, that would react in each test.

State the expected observation for each reaction.

[8 marks]

Liquid(s) that react in **Test 1** *J and M*

Expected observation *Orange solution turns green*

Liquid(s) that react in **Test 2** *M*

Expected observation *Blue solution forms a brick-red precipitate*

Liquid(s) that react in **Test 3** *J and L*

Expected observation *Effervescence; the colourless gas turns limewater cloudy*

Liquid(s) that react in **Test 4** *K*

Expected observation *Orange bromine water turns colourless (decolourised)*

Turn over ►



0 6 . 4

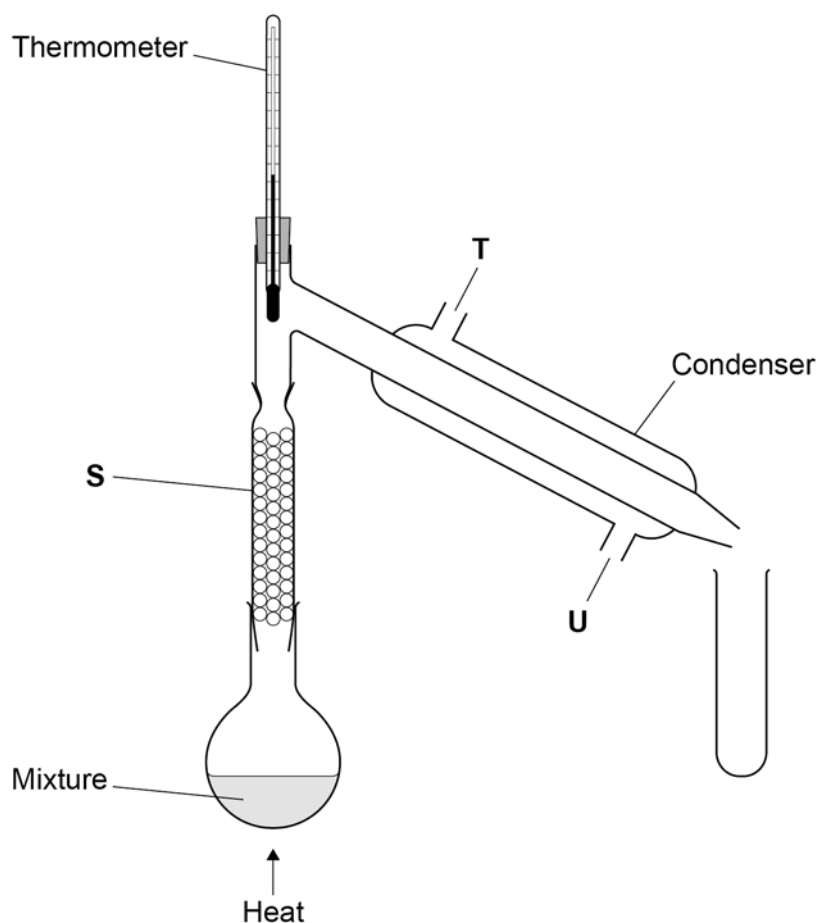
Figure 10 shows the apparatus that is used to separate a mixture of liquids **K** and **M** using fractional distillation.

Suggest labels that should be added to positions **S**, **T** and **U** in **Figure 10**.

Explain why fractional distillation is preferred to simple distillation to separate liquids **K** and **M**.

[3 marks]

Figure 10



Label **S** *Fractionating column (packed with glass beads)*

Label **T** *Water out*

Label **U** *Water in*

Explanation *Liquids K and M are likely to have similar boiling points, so fractional distillation separates them better.*



Turn over for the next question

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ANSWER IN THE SPACES PROVIDED**

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07

A gas syringe that does not have any graduations is calibrated using a known mass of propanone (boiling point = 56.2 °C).

The sealed gas syringe contains 0.146 g of propanone ($M_r = 58.0$) at a temperature of 95 °C and a pressure of 103 kPa

07.1

Calculate the volume, in cm^3 , of propanone in the gas syringe.

The gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

[4 marks]

$$n(\text{propanone}) = 0.146 \div 58.0 = 2.52 \times 10^{-3} \text{ mol}$$

$$T = 95 + 273 = 368 \text{ K}, \quad p = 103 \text{ kPa} = 103\,000 \text{ Pa}$$

$$pV = nRT, \text{ so } V = nRT \div p$$

$$V = (2.52 \times 10^{-3} \times 8.31 \times 368) \div 103\,000 = 7.47 \times 10^{-5} \text{ m}^3$$

$$V = 7.47 \times 10^{-5} \times 10^6 = 74.7 \text{ cm}^3 = 75 \text{ cm}^3$$

Volume of propanone 75 cm^3

07.2

The gas syringe is then cooled to 75 °C, without changing the pressure.

Calculate the decrease in volume.

(If you were unable to calculate the volume in Question **07.1**, you should use the volume 89 cm^3 . This is not the correct answer.)

[2 marks]

At constant pressure, V is proportional to T (in K):

$$\text{new } V = 75 \times (348 \div 368) = 71 \text{ cm}^3$$

$$\text{decrease} = 75 - 71 = 4 \text{ cm}^3$$

Decrease in volume 4 cm^3



0 7 . 3

The total uncertainty in using the balance to measure the mass of propanone in Question 07.1 is ± 0.001 g

Calculate the uncertainty that this causes in the volume, in cm^3 , of propanone calculated in Question 07.1.

(If you were unable to calculate the volume in Question 07.1, you should use the volume 89 cm^3 . This is not the correct answer.)

[2 marks]

$$\% \text{ uncertainty in mass} = (0.001 \div 0.146) \times 100 = 0.685 \%$$

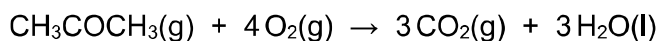
$$\text{uncertainty in volume} = (0.685 \div 100) \times 75 = 0.51 \text{ cm}^3$$

Uncertainty ± 0.5 cm^3

0 7 . 4

A 600 cm^3 sample of propanone is mixed with 2800 cm^3 of oxygen in a container at 60°C and 100 kPa . The mixture is ignited.

When the reaction is complete, the remaining mixture of gases is cooled to 60°C at 100 kPa



Calculate the total volume of the remaining gas mixture.

[2 marks]

$$\text{O}_2 \text{ used} = 4 \times 600 = 2400 \text{ cm}^3, \text{ so } \text{O}_2 \text{ left} = 2800 - 2400 = 400 \text{ cm}^3$$

$$\text{CO}_2 \text{ formed} = 3 \times 600 = 1800 \text{ cm}^3 \text{ (H}_2\text{O is a liquid)}$$

$$\text{total gas volume} = 1800 + 400 = 2200 \text{ cm}^3$$

Volume 2200 cm^3

10

Turn over ►



0 8

This question is about biofuels.

Palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$, can be made by hydrolysis of the triester in palm oil under acidic conditions.

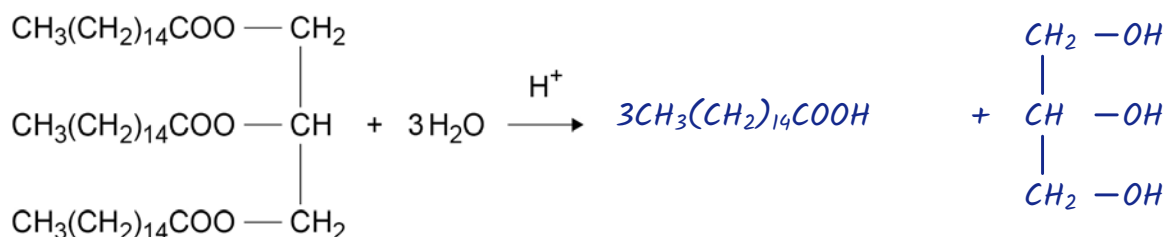
Palmitic acid can be used as a biofuel.

0 8

1

Complete the equation for the hydrolysis of the triester in palm oil under acidic conditions.

[2 marks]



0 8

2

Palmitic acid burns in air.

In a calorimetry experiment, combustion of 387 mg of palmitic acid increases the temperature of 0.150 kg of water from 23.9 °C to 37.5 °C

Calculate a value, in kJ mol^{-1} , for the enthalpy of combustion of palmitic acid in this experiment.

Give your answer to the appropriate number of significant figures.

The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$

[5 marks]

$$M_r \text{ of } \text{CH}_3(\text{CH}_2)_{14}\text{COOH} (\text{C}_{16}\text{H}_{32}\text{O}_2) = 256.0$$

$$n = 0.387 \div 256.0 = 1.51 \times 10^{-3} \text{ mol}$$

$$\Delta T = 37.5 - 23.9 = 13.6 \text{ K}$$

$$q = mc\Delta T = 150 \times 4.18 \times 13.6 = 8527.2 \text{ J} = 8.527 \text{ kJ}$$

$$\Delta H = -8.527 \div 1.51 \times 10^{-3} = -5641 \text{ kJ mol}^{-1}$$

$$\Delta H = -5640 \text{ kJ mol}^{-1} (3 \text{ s.f.})$$

Enthalpy of combustion -5640 kJ mol^{-1}



08.3

State how the value calculated in Question 08.2 is likely to differ from data book values.

Give one reason, other than heat loss, for this difference.

[2 marks]

Difference Less exothermic (less negative) than the data book value

Reason Incomplete combustion of the palmitic acid

08.4

A sample of a different biofuel, made from sewage sludge, is found to contain 37.08% carbon, 5.15% hydrogen and 24.72% oxygen by mass. The rest of the sample is sulfur.

Calculate the empirical formula of this biofuel.

[3 marks]

	C	H	O	S
%	37.08	5.15	24.72	$100 - 67.0 = 33.05$
$\div A_r$	$37.08 \div 12.0$	$5.15 \div 1.0$	$24.72 \div 16.0$	$33.05 \div 32.1$
moles	$= 3.09$	$= 5.15$	$= 1.545$	$= 1.030$
$\div 1.030$	3.00	5.00	1.50	1
$\times 2$	6	10	3	2

Empirical formula $C_6H_{10}O_3S_2$

08.5

Complete combustion of the biofuel made from sewage sludge produces the greenhouse gas carbon dioxide.

Suggest **one** other possible environmental problem with the complete combustion of this biofuel.

State the formula of the pollutant responsible for this problem.

[2 marks]

Environmental problem Acid rain, because the sulfur in the fuel burns to form sulfur dioxide.

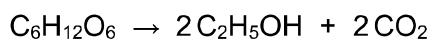
Formula SO_2

Turn over ►



0 8 . 6

Ethanol is a biofuel that can be produced by the fermentation of glucose.



Glucose has the structural formula shown.

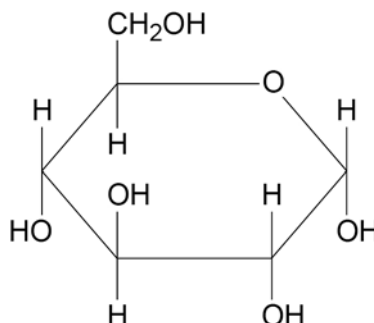


Table 3 shows some mean bond enthalpy values.

Table 3

	C-H	C-C	C-O	C=O	O-H
Mean bond enthalpy / kJ mol ⁻¹	412	348	360	805	463

Use the equation and the data in Table 3 to calculate an approximate value of ΔH for the fermentation of glucose. For this calculation you should assume that all the substances are in the gaseous state.

[3 marks]

Bonds broken in glucose: 5 C-C, 7 C-O, 7 C-H, 5 O-H

$$= (5 \times 348) + (7 \times 360) + (7 \times 412) + (5 \times 463) = 9459 \text{ kJ mol}^{-1}$$

Bonds made in $2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$: 2 C-C, 10 C-H, 2 C-O, 2 O-H, 4 C=O

$$= (2 \times 348) + (10 \times 412) + (2 \times 360) + (2 \times 463) + (4 \times 805)$$

$$= 9682 \text{ kJ mol}^{-1}$$

$$\Delta H = \text{bonds broken} - \text{bonds made} = 9459 - 9682 = -223 \text{ kJ mol}^{-1}$$

$$\Delta H \underline{\hspace{2cm} -223 \hspace{2cm}} \text{ kJ mol}^{-1}$$



0 8 7

The carbon dioxide produced from fermentation can be reacted with steam to make more ethanol.

The equation for this reaction is

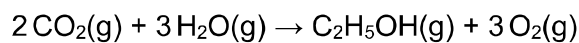


Table 4 shows some standard enthalpies of formation.

Table 4

	$\text{CO}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-394	0	-235	-242

Use the data in **Table 4** to calculate a standard enthalpy change value for this reaction.

[2 marks]

$$\Delta H = \Sigma \Delta_f H(\text{products}) - \Sigma \Delta_f H(\text{reactants})$$

$$\Delta H = (-235 + 0) - ((2 \times -394) + (3 \times -242))$$

$$\Delta H = -235 + 1514 = +1279 \text{ kJ mol}^{-1}$$

Standard enthalpy change +1279 kJ mol⁻¹

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Turn over for the next question

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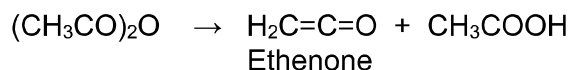


0 9

This question is about ethanoic anhydride.

In the gas phase, ethanoic anhydride $(\text{CH}_3\text{CO})_2\text{O}$ decomposes to form ethenone.

The equation is



0 9 . 1

Ethenone is the simplest member of the ketene homologous series. Ketenes **all** contain one $\text{C}=\text{C}$ double bond and one $\text{C}=\text{O}$ double bond.

Deduce the general formula for the ketene homologous series.

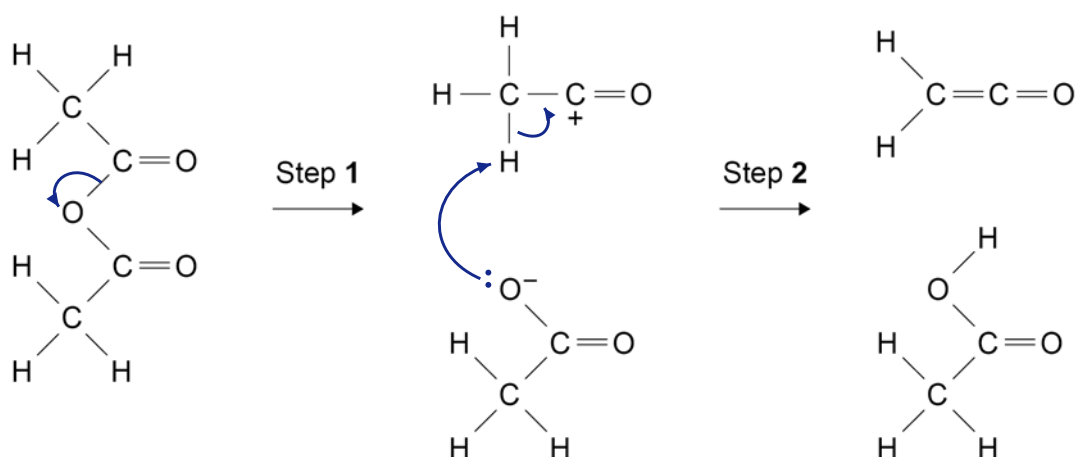
[1 mark]



0 9 . 2

Figure 11 shows an incomplete suggested mechanism for the decomposition of ethanoic anhydride.

Figure 11



Complete the mechanism in **Figure 11** by adding three curly arrows and any relevant lone pairs of electrons.

[3 marks]



0 9 . 3

For a chemical reaction the relationship between the rate constant, k , and the temperature, T , is shown by the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

For the decomposition of gaseous ethanoic anhydride

the activation energy, $E_a = 34.5 \text{ kJ mol}^{-1}$

the Arrhenius constant, $A = 1.00 \times 10^{12} \text{ s}^{-1}$

At temperature T_1 the rate constant, $k = 2.48 \times 10^8 \text{ s}^{-1}$

Calculate T_1

The gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

[3 marks]

$$\ln k = \ln A - E_a \div RT, \text{ so } \ln(k \div A) = -E_a \div RT$$

$$\ln(2.48 \times 10^8 \div 1.00 \times 10^{12}) = \ln(2.48 \times 10^{-4}) = -8.302$$

$$8.302 = 34\,500 \div (8.31 \times T)$$

$$T = 34\,500 \div (8.31 \times 8.302) = 500 \text{ K}$$

T_1 500 K

Question 9 continues on the next page

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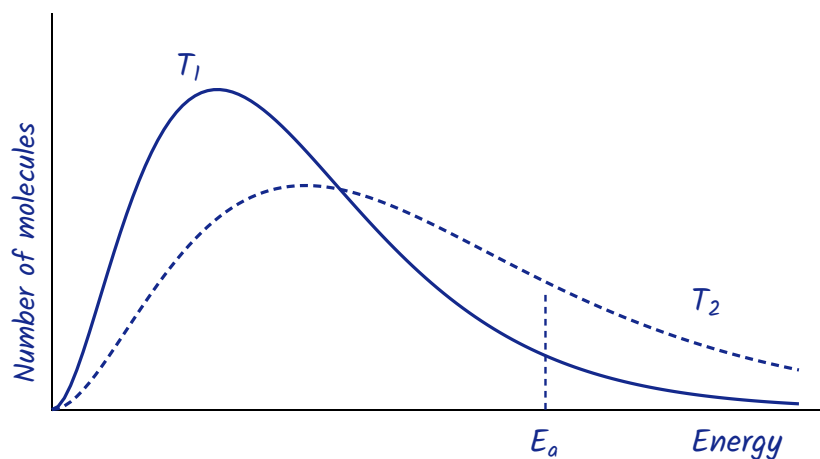
0 9 . 4

Sketch the Maxwell–Boltzmann distribution of molecular energies for gaseous ethanoic anhydride at temperature T_1 and at a higher temperature T_2

Include a label for each axis, and mark on the appropriate axis a typical position for the activation energy.

Explain why the rate of reaction is faster at T_2

[5 marks]



Explanation

At T_2 many more molecules have energy greater than or equal to E_a , so there are more frequent successful collisions.

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END OF QUESTIONS



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