Questions

Q1.

The preparation of 2-chloro-2-methylpropane, $(CH_3)_3CCl$, involves the reaction of concentrated hydrochloric acid with 2-methylpropan-2-ol, $(CH_3)_3COH$, a tertiary alcohol.

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

In an experiment, 12.0 g of 2-methylpropan-2-ol was shaken with excess concentrated hydrochloric acid in a separating funnel.

After about 15 minutes, the product formed as a separate layer.

Data:

Substance	Boiling temperature / °C	Density / $g\,cm^{-3}$
2-methylpropan-2-ol	82	0.79
2-chloro-2-methylpropane	51	0.84
water	100	1.00

The dried 2-chloro-2-methylpropane was transferred to the distillation apparatus.

11.6 cm^3 of 2-chloro-2-methylpropane was collected from 12.0 g of 2-methylpropan-2-ol.

Infrared spectroscopy can be used to determine the purity of a substance.

(i) State how infrared spectroscopy could be used to show that no 2-methylpropan-2-ol was present in the distillate.

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(ii) Give one advantage and one disadvantage of using a chemical test rather than infrared spectroscopy to determine whether any of the 2-methylpropan-2-ol remained.

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(Total for question = 3 marks)

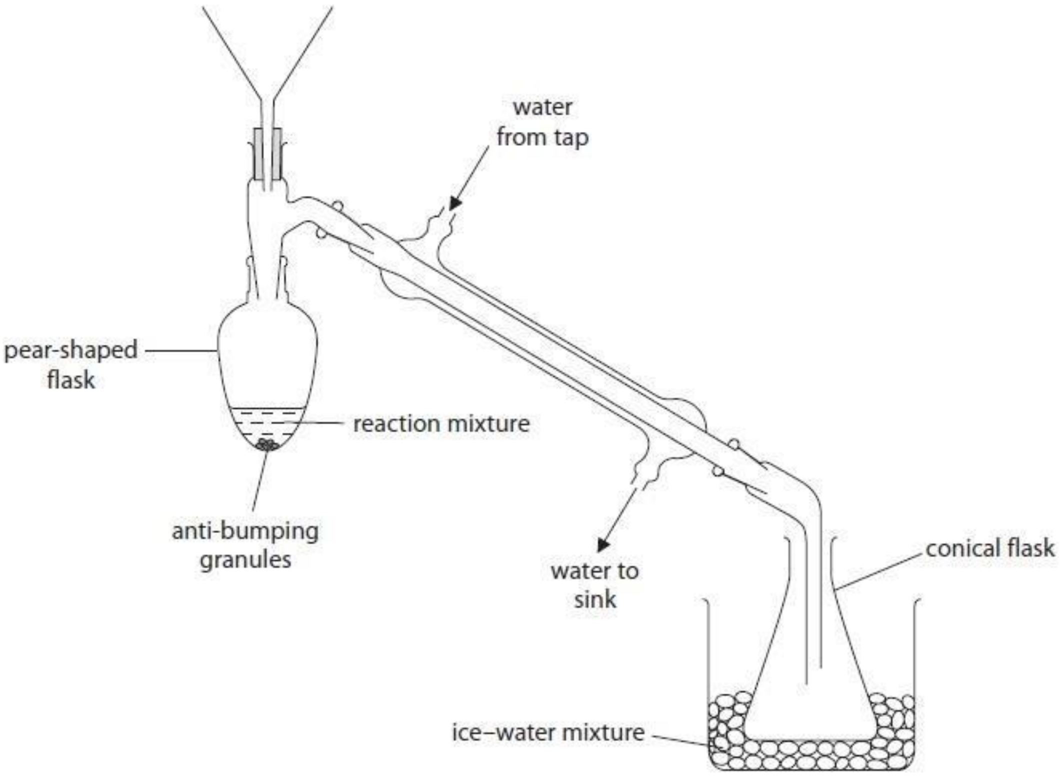
Q2.

This question is about the preparation of a sample of the ketone, 3-methylbutan-2-one.

A student's research suggested that 3-methylbutan-2-one may be prepared by oxidising 3-methylbutan-2-ol with acidified potassium dichromate(VI) solution.

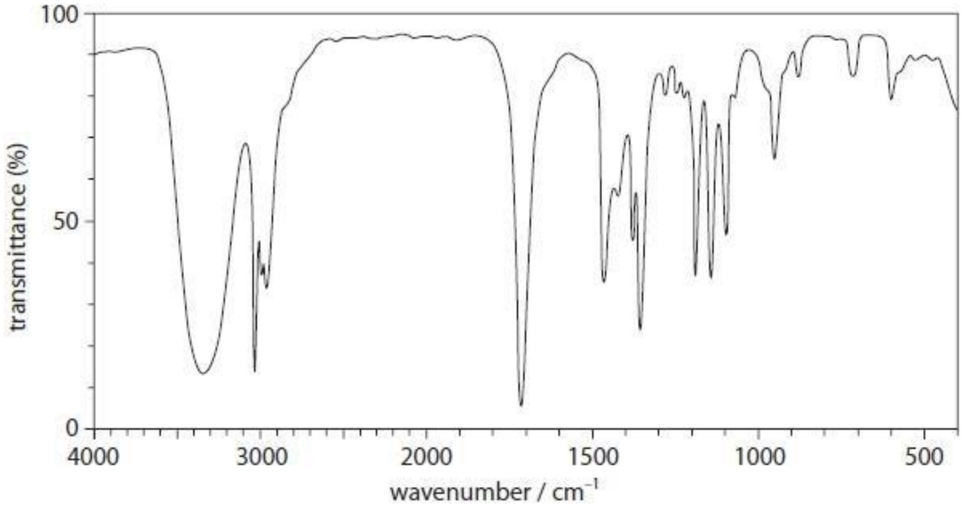
The student sets up the apparatus as shown in the diagram. You may assume that all the equipment is suitably clamped.

The student adds dilute sulfuric acid to the pear-shaped flask. A mixture of potassium dichromate(VI) and 3-methylbutan-2-ol is then added slowly to the dilute sulfuric acid in the flask.



The organic mixture was separated from the aqueous layer and dried.

The infrared spectrum of the organic mixture is shown.



(i) By reference to any relevant peak(s), deduce how the infrared spectrum shows that the mixture contains 3-methylbutan-2-one.

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(ii) From the infrared spectrum, the student concludes that the mixture contains another organic compound.

The mixture is redistilled and the fraction that boils in the range 93–95°C is collected. The boiling temperature of 3-methylbutan-2-one is 94°C.

Predict any change(s) you would see in the infrared spectrum after redistillation, justifying your answer.

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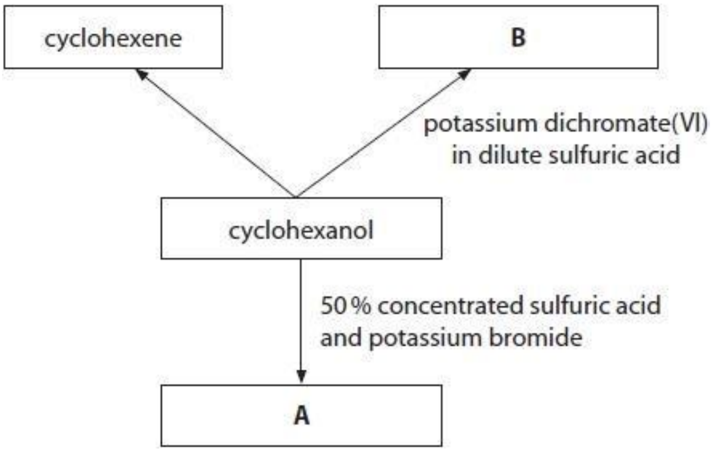
(Total for question = 4 marks)

Q3.

This question is about some reactions of cyclohexanol.



(i) Give the name **and** displayed formula of compound **B**.

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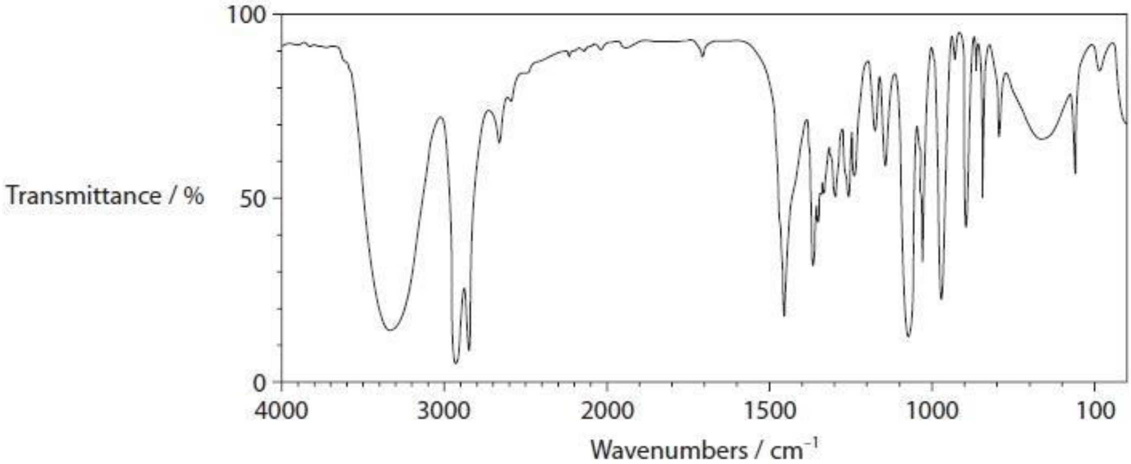
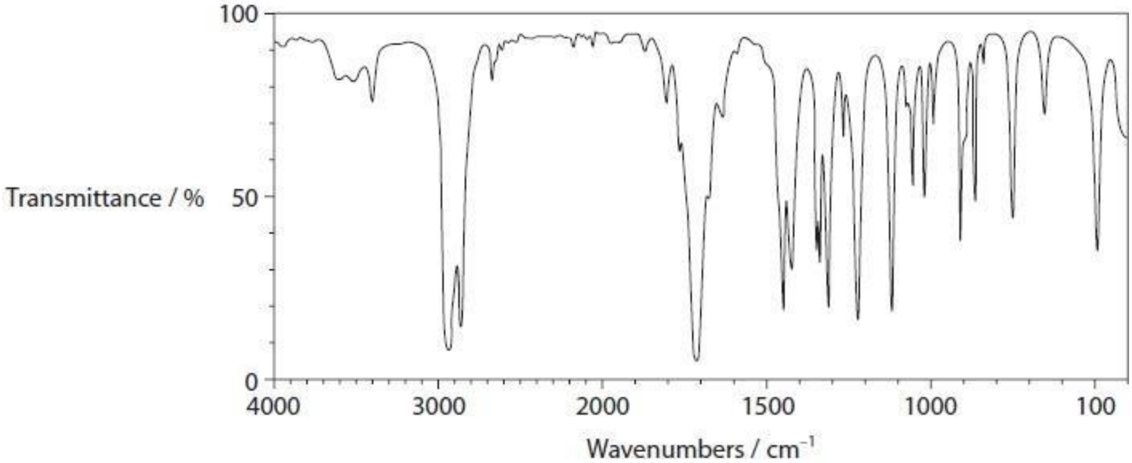
(ii) The infrared (IR) spectra of cyclohexanol and compound **B** are shown.

IR Spectrum of cyclohexanol



IR Spectrum of compound **B**



Identify the bonds, using **both** IR spectra, that help to confirm the reaction of cyclohexanol to produce compound **B**.
Your answer must include the wavenumber ranges of any relevant bonds.

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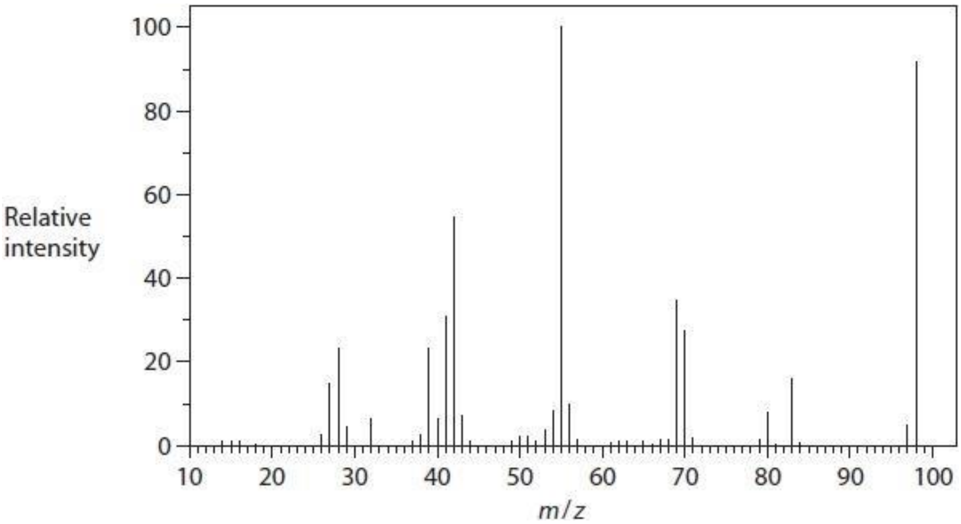
(iii) The mass spectrum of compound **B** is shown.



Deduce the relative molecular mass of compound **B** using the mass spectrum. Justify your answer.

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(iv) In the mass spectrum of cyclohexanol, there is a peak at *m/z* = 83.

Give the formula of a fragment that could be responsible for this peak.

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(Total for question = 7 marks)

Q4.

Analysis shows that a compound has the molecular formula $C_4H_8O_2$.

A student suggests that the compound could be either **A** or **B**.

$CH_3CH_2CH_2COOH$ or $HOCH_2CH{=}CHCH_2OH$

A **B**

Another student suggests that the compound could contain an aldehyde and an alcohol functional group, with structure **C**.

$HOCH_2CH_2CH_2CHO$

C

Complete the table to show how the infrared spectra of **A**, **B** and **C** would be expected to differ in the wavenumber range **1800-1600 cm**$^{-1}$.
Use information from the Data Booklet.

(3)

Absorbance	Wavenumber range / cm^{-1}
Absorbance expected in infrared spectrum of **A** but **not** in **B** or **C**	
Absorbance expected in infrared spectrum of **B** but **not** in **A** or **C**	
Absorbance expected in infrared spectrum of **C** but **not** in **A** or **B**	

(Total for question = 3 marks)

Q5.

* This question is about compounds with the molecular formula C_4H_8O.

Three different compounds, **A**, **B** and **C**, have the molecular formula C_4H_8O.

Information about these three compounds includes:

- all three compounds have infrared absorptions at about 3500 cm^{-1}
- the infrared spectra of **A** and **B** each contain a peak at about 1650 cm^{-1}, while that of **C** does not
- only **A** has a branched carbon chain
- **B** is the *E*-isomer of a pair of stereoisomers.

Deduce a possible **displayed** formula for each of the compounds **A**, **B** and **C**.

You must use **all** the information and the Data Booklet to fully justify each of your structures.

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(Total for question = 6 marks)

Q6.

Organic compounds containing nitrogen include amides, amines, amino acids and nitriles.

A compound produced a peak due to an N—H stretching vibration in its infrared spectrum with
a wavenumber of 3220 cm^{-1}.

This compound could be

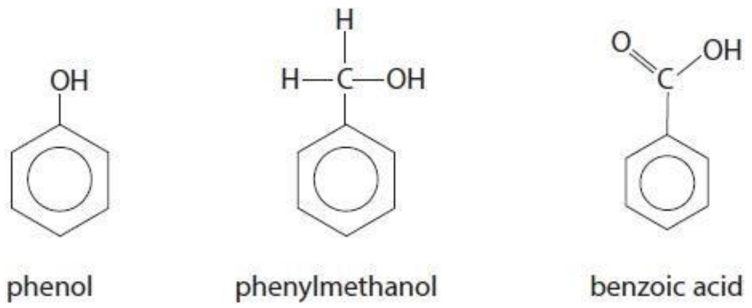
(1)

- ☐ **A** an amide
- ☐ **B** an amine
- ☐ **C** either an amide or an amine
- ☐ **D** neither an amide nor an amine

(Total for question = 1 mark)

Q7.

This is a question about the analysis of three aromatic substances with —OH groups.



Spectroscopy is an effective means of distinguishing between molecules.

(i) Compare and contrast the infrared spectra of phenol, phenylmethanol and benzoic acid. Include relevant bonds and their wavenumber ranges using the Data Booklet.

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(ii) Predict the number of peaks present, and their chemical shifts, in the ^{13}C nuclear magnetic resonance (NMR) spectrum of
phenylmethanol.
Use the information in the Data Booklet to help you.

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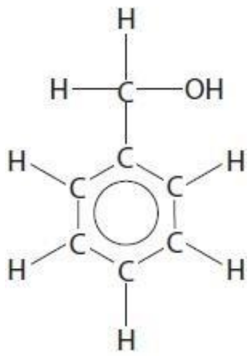

phenylmethanol

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(iii) Give the formula of a fragment ion, with its *m*/*z* value, that you would expect to be present in the mass spectrum of
benzoic acid but **not** in the mass spectrum of phenol or the mass spectrum of phenylmethanol.

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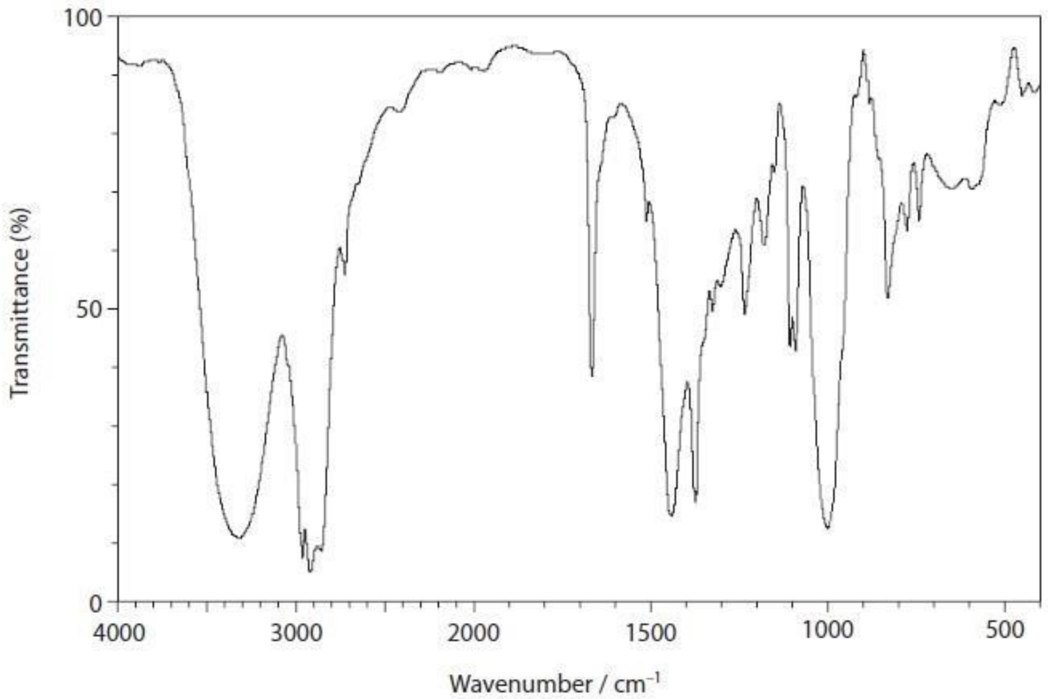
(Total for question = 10 marks)

Q8.

(a) The infrared spectrum of geraniol is shown.



Using the table of absorptions from the Data Booklet and the infrared spectrum, give the **names** of the two functional groups present in geraniol.To confirm these functional groups, give the wavenumber ranges and their corresponding bonds.

(2)

First functional group

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Second functional group

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(b) Give **one** chemical test that you could use to confirm the presence of each of the two functional groups suggested in part (a). Predict a result for each test.

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Test and result for first functional group

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Test and result for second functional group

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(Total for question = 6 marks)

Q9.

(a) This question is about the analysis of an unknown carboxylic acid **X** by three students.

The students analyse the mass spectrum of **X** and find that it has a molecular ion peak at *m* / *z* = 116.

The three students each propose a different structural formula for compound **X**.

Structure 1 HOOCCH==CHCOOH

Structure 2 $HOCH_2CH{=}{=}CHCH_2COOH$

Structure 3 $CH_3CH_2CH_2CH_2CH_2COOH$

The students are given the infrared spectrum of **X**.

(i) State **two** wavenumber ranges of the infrared absorptions providing evidence that compound **X** is a carboxylic acid. Include the bonds responsible.

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(ii) One of the students suggests that this infrared spectrum and the data in the Data Booklet **alone** could be used to identify which of the three proposed structures is **X**.

Show that this student's suggestion is correct. Include relevant infrared data in your answer.

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(b) The students decide to carry out an acid-base titration to obtain further information about compound **X**.

Each student uses solid sodium hydroxide, NaOH, to prepare a solution of concentration 0.140 mol dm^{-3}.
Calculate the mass, in grams, of solid sodium hydroxide that each student should weigh out to prepare 250.0 cm^3 of a 0.140 mol dm^{-3} solution.

(2)

(c) Each of the students makes up 250.0 cm^3 of 0.140 mol dm^{-3} sodium hydroxide solution in a volumetric flask and titrates this solution with the same solution of **X** of known concentration.

Student A

- correctly prepares the 0.140 mol dm^{-3} sodium hydroxide solution and pipettes a volume of 10.0 cm^3 of the solution into a conical flask
- fills a burette with the solution of **X** and carries out a titration
- repeats the procedure until obtaining concordant results
- obtains a mean titre of 10.20 cm^3.

Student B

- dissolves the sodium hydroxide in distilled water and transfers the solution to a volumetric flask
- adds more distilled water to the volumetric flask and mixes the solution
- notices that the volumetric flask has been filled with distilled water several cm^3 beyond the graduation mark
- realises the mistake, removes the extra solution and discards it
- pipettes 10.0 cm^3 of the sodium hydroxide solution into a conical flask and titrates this with the solution of **X**.

Student C

- correctly prepares the 0.140 mol dm^{-3} sodium hydroxide solution
- washes a conical flask thoroughly with distilled water and pipettes 10.0 cm^3 of the sodium hydroxide solution into the wet conical flask
- titrates the contents of the conical flask with the solution of **X**.

(i) Explain how, if at all, Student **B**'s mistake affects the value of the titre.

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(ii) Explain how, if at all, Student **C**'s use of a wet conical flask affects the value of the titre.

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(iii) Student **A** uses three pieces of apparatus to measure volumes in this experiment.

- The burette has an uncertainty of ±0.05 cm^3 for each volume reading
- The volumetric flask has an uncertainty of ±0.30 cm^3 for the volume
- The pipette has an uncertainty of ±0.04 cm^3 for the volume

Show by calculation which volume measurement has the lowest percentage uncertainty.

(3)

(d) Student **A** calculates the correct value for the molar mass of compound **X**, using the mean titre of 10.20 cm^3. The results indicate that **X** has **structure 1**.

Structure 1 HOOCCH==CHCOOH
Structure 2 $HOCH_2CH{=}{=}CHCH_2COOH$
Structure 3 $CH_3CH_2CH_2CH_2CH_2COOH$

(i) Write the equation for the reaction between **structure 1** and sodium hydroxide solution. State symbols are not required.

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(ii) Deduce the value that would have been obtained for the mean titre if the structural formula of **X** had been **structure 2**.
Justify your answer.

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(e) The students could have identified the three structures using chemical tests.

Complete the table to show whether or not the suggested structures react with bromine water and when heated with acidified potassium dichromate(VI).
Use a tick (✓) if a reaction occurs.
Use a cross (✗) if no reaction occurs.

(2)

Structure	Test with bromine water	Test with acidified potassium dichromate(VI)
HOOCCH═CHCOOH		
$HOCH_2CH{=}CHCH_2COOH$		
$CH_3CH_2CH_2CH_2CH_2COOH$		

(f) The structure HOOCCH==CHCOOH has two stereoisomers.

(i) Draw the structures of these stereoisomers.

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***E*-isomer**

***Z*-isomer**

(ii) State why HOOCCH==CHCOOH has *E*/*Z* isomers.

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(Total for question = 24 marks)