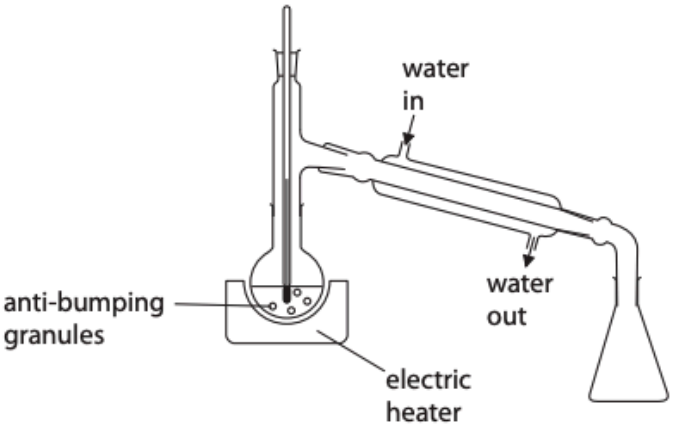
*(ii) Devise an experiment to compare the rates of hydrolysis of 2-chlorobutane, 2-bromobutane and 2-iodobutane.

State the trend in the rates of reaction. Justify your answer.

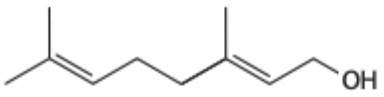
(6)



(i) Describe **three** ways in which this apparatus must be modified for safe and efficient use. Assume the apparatus is suitably clamped.

(3)

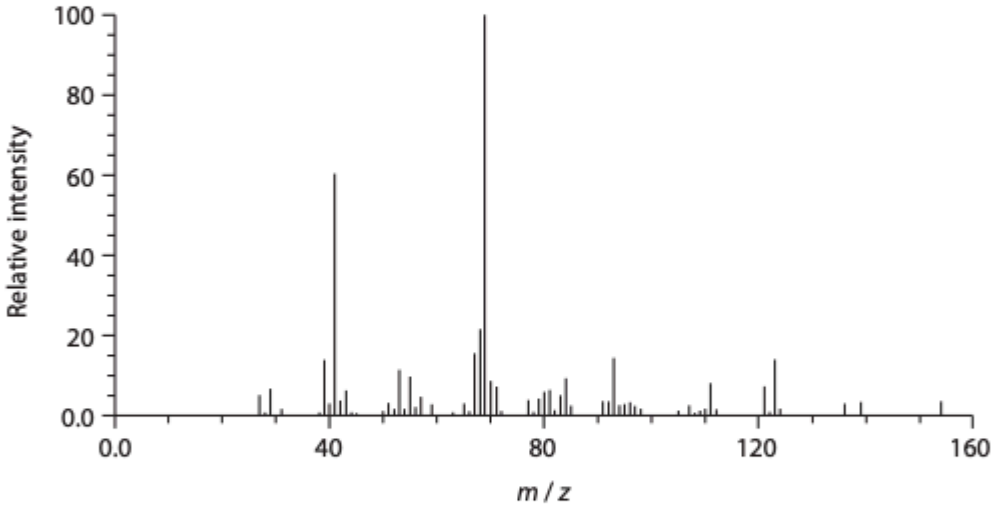
4 (a) The characteristic smell of pine wood is due, partly, to the presence of a group of compounds called terpenes. One of the simpler terpenes is a compound called geraniol, which is an oily liquid at room temperature and pressure. The structure of geraniol is



Deduce the molecular formula of geraniol. Use your answer to calculate the molar mass of geraniol in g mol^{-1}.

(2)

(b) The mass spectrum of geraniol is shown.



(i) Show that this mass spectrum can be used to confirm the molar mass of geraniol.

(1)

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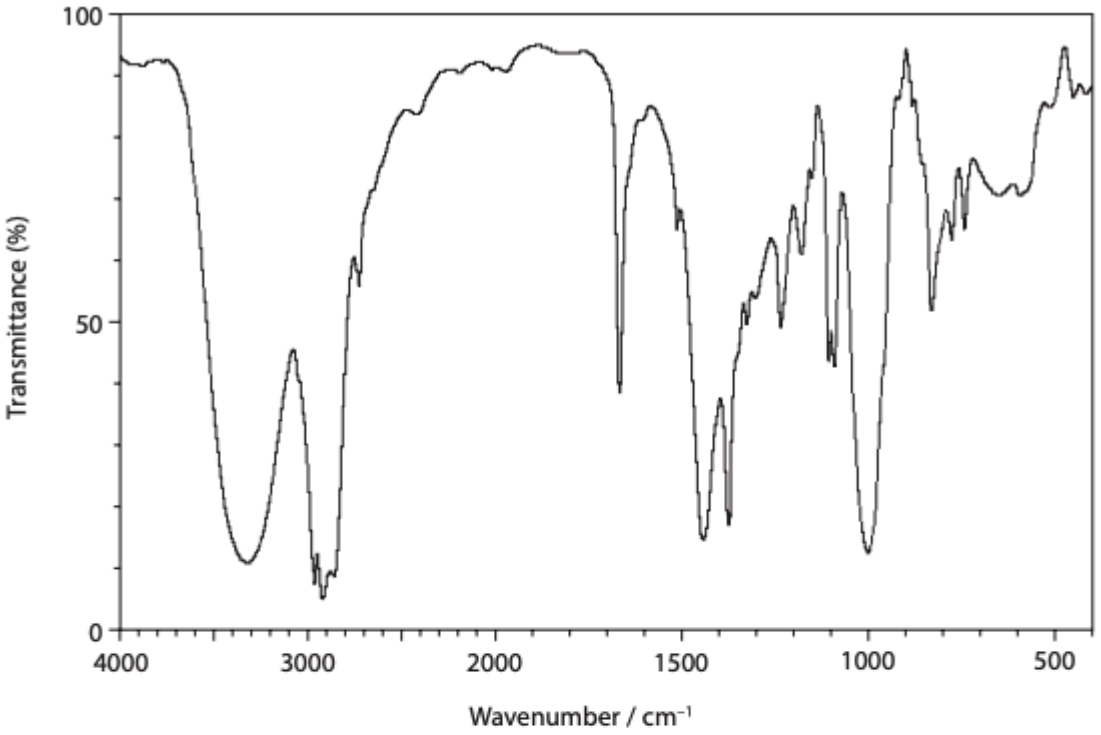
(ii) Identify an ion that could be responsible for the peak at $m/z = 69$.

(1)

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

(4)

Test and result for first functional group .....

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Test and result for second functional group .....

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5 This question concerns iodine monochloride, ICl, a red-brown solid which melts at 27 °C to form a red-brown liquid.

Iodine monochloride is used in measuring unsaturation in organic compounds.

Iodine monochloride gas can be produced by the reaction between iodine vapour and chlorine gas. The reaction is exothermic.

(b) Iodine monochloride is a polar molecule which adds rapidly to double bonds in a similar way to hydrogen chloride. This reaction can be used to determine the degree of unsaturation in oils.

(i) Add the dipole to a molecule of iodine monochloride.

(1)

I—Cl

(ii) Draw the mechanism for the addition of iodine monochloride to propene. You should include all curly arrows and relevant lone pairs and dipoles.

(3)

7 Halogenoalkanes react with water to produce alcohols and halide ions.

$$C_4H_9X + H_2O \rightarrow C_4H_9OH + X^- + H^+$$

(a) Test tube experiments can be carried out to investigate the relative rates of these substitution reactions.

The halogenoalkanes 1-chlorobutane, 1-bromobutane and 1-iodobutane can be used.

Some of the steps in these experiments are

- each halogenoalkane is added to a different tube containing 1 cm^3 of ethanol
- the test tubes are placed in the same beaker of hot water
- aqueous silver nitrate is added to each tube and the tubes are shaken
- a precipitate forms in each tube.

(i) State the purpose of adding ethanol to each of the test tubes.

(1)

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(ii) Give **one** reason why the test tubes were put in the same beaker of hot water.

(1)

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(iii) Give **one** reason why the test tubes were shaken after the addition of aqueous silver nitrate.

(1)

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(b) (i) State how the halogen atom present in each halogenoalkane can be identified using observations from this experiment in (a).

(1)

(ii) Identify further reagents that can be added, including relevant observations, to confirm the identity of the halogen atom present in each halogenoalkane.

(2)

*(c) Outline the method for a test tube experiment, **which expands on the steps in (a)**, to investigate how the rate of the substitution reaction depends on whether the halogenoalkane is primary, secondary or tertiary.

Your experiment should test a series of isomeric bromoalkanes reacting with water.

Your plan should include

- the chemicals you will use
- an outline of how the experiment will be carried out
- the observations or measurements you will make and how you will interpret them.

(6)

(d) Under different conditions, 2-chloro-2-methylpropane can react to produce 2-methylpropene, $(CH_3)_2C{=}CH_2$.

(i) State the reagent and conditions needed for this reaction.

(2)

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(ii) Draw the displayed formula for the repeat unit of a polymer that is made by the polymerisation of 2-methylpropene, $(CH_3)_2C{=}CH_2$.

(1)

(iii) Draw a mechanism for the addition of hydrogen bromide, HBr, to 2-methylpropene to form 2-bromo-2-methylpropane.
Include curly arrows, and any relevant dipoles and lone pairs.

(4)

(ii) A data book gives the standard enthalpy change of formation of ammonia as $-46.1\ kJ\,mol^{-1}$.

Give one reason for the difference between this value and the experiment value.

(1)

Reason 1

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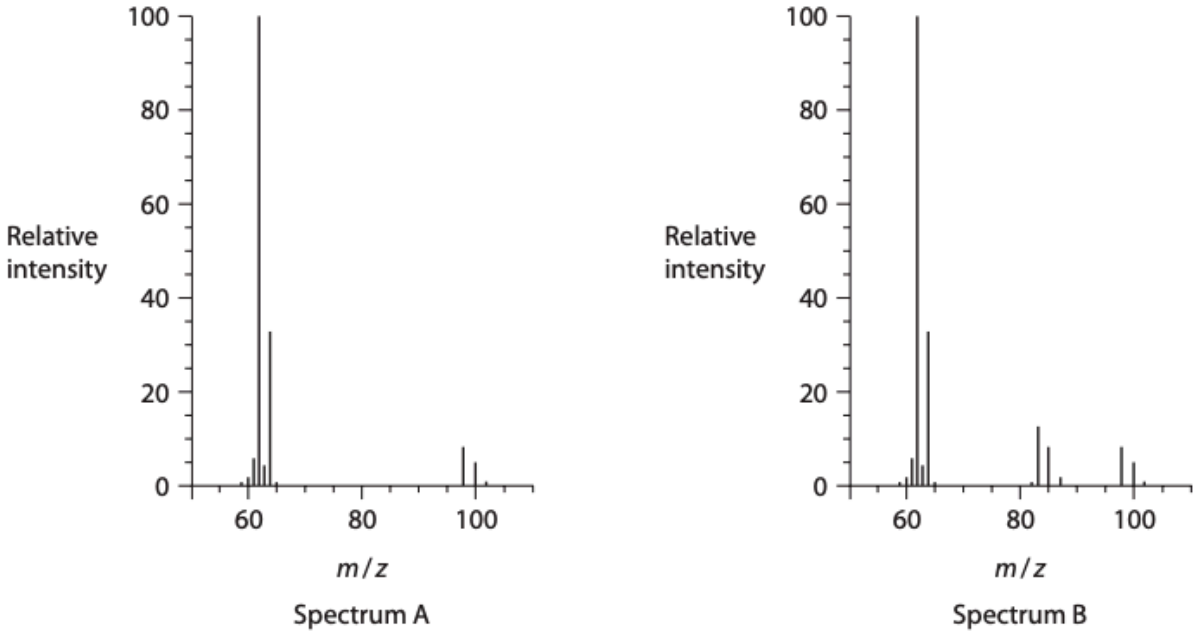
(iv) The mass spectra of the two isomers of dichloroethane are shown.



Deduce the molecular formulae of the species responsible for the molecular ion peaks at m/z 98, 100 and 102.
The molecular formulae for the species producing these peaks are the same in both spectra.

(2)

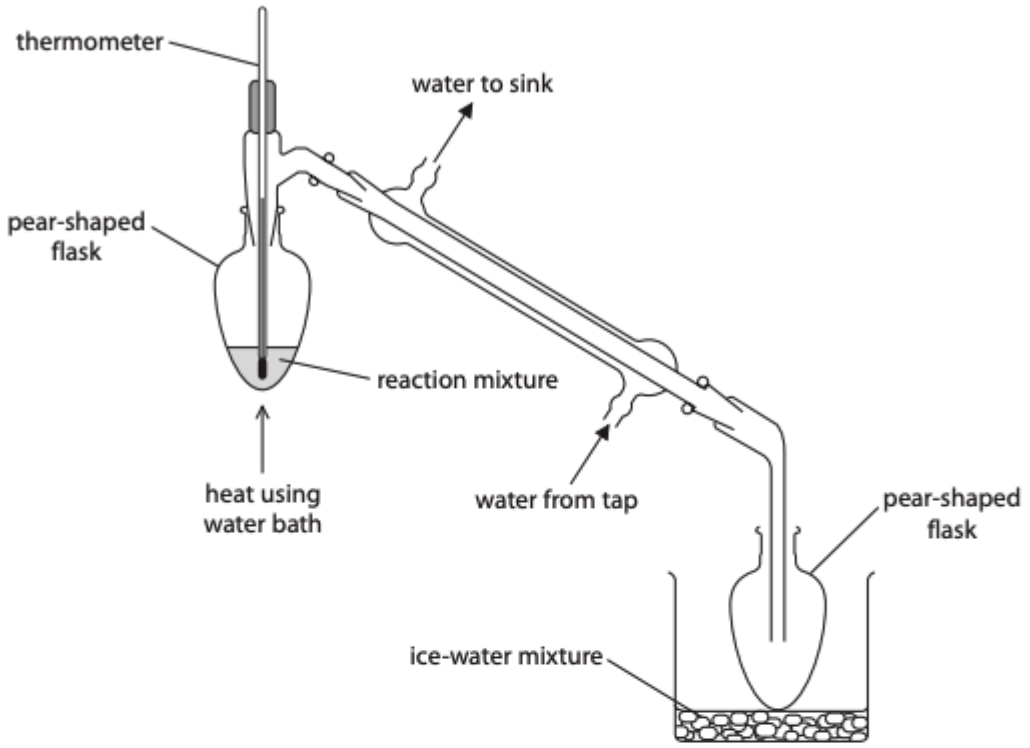
(v) State why in both spectra the peaks at 98, 100 and 102 have different relative intensities.

(1)

(vi) Explain how the presence of the peaks at 83, 85 and 87 in Spectrum B allows the identification of the isomer responsible for this spectrum.

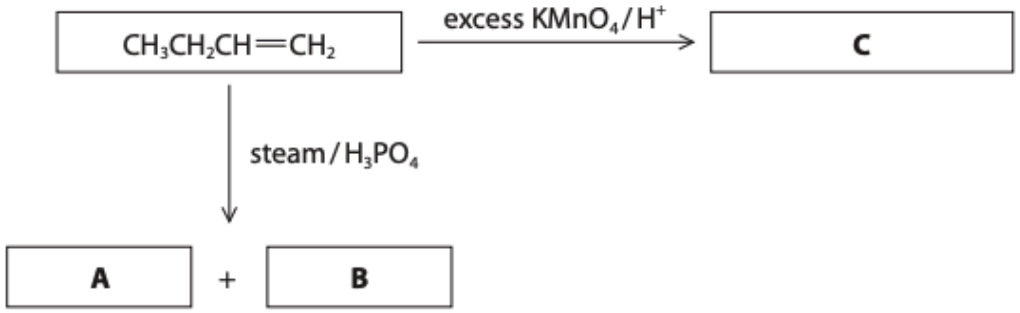
(2)

*(ii) A diagram of the distillation apparatus is shown.



Discuss the improvements that should be made to the set-up of the apparatus. Include the likely effect of the errors identified on the yield or purity of the product.
Assume the apparatus is suitably clamped.

(6)



A and **B** are structural isomers. **A** is butan-1-ol.

(i) Draw the fully **displayed** formula of isomer **B**.

(1)

(ii) Draw the **structural** formula of product **C**, which is formed by the reaction of but-1-ene with potassium manganate(VII) in acid conditions.

(1)

4 This question is about halogenoalkanes and some of their reactions.

(a) **X**, **Y** and **Z** are three different halogenoalkanes.

X is 1-chloropropane

Y is 1-bromopropane

Z is 1-iodopropane

An experiment is carried out to compare the rates of hydrolysis of these compounds.

Outline procedure:

1 cm^3 of each of the three halogenoalkanes, **X**, **Y** and **Z**, is added to separate test tubes, each containing 5 cm^3 of ethanol and 5 cm^3 of aqueous silver nitrate solution, in a water bath at 50 °C.

The time taken for a precipitate to form in each test tube is measured.

(i) Give **three** reasons why these reaction **conditions** are specified.

(3)

(ii) Explain why a precipitate forms.

(2)

(iii) The three halogenoalkanes were placed in order of **increasing** rate of reaction.

Which is the correct sequence?

(1)

(b) The results table shows the time taken to produce a precipitate when three bromoalkanes react with aqueous ethanolic silver nitrate solution.

Halogenoalkane	Time to produce a precipitate / s
1-bromobutane	58
2-bromobutane	33
2-bromo-2-methylpropane	2

Give a reason why the times taken to produce a precipitate for these isomeric bromoalkanes are different.

(1)

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(d) 1-bromopropane undergoes reactions when heated with different reagents.

(i) Give **two** reasons why organic reactions are often heated for a long time but the yield is frequently low.

(2)

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*(iv) Describe, including practical details, how a sample of butanoic acid (boiling temperature 166 °C) could be prepared from butan-1-ol (boiling temperature 117 °C) using acidified potassium dichromate(VI).
Include labelled diagrams of the apparatus you would use for the reaction, and for collecting the product.
You may assume that all necessary safety precautions are observed.

(6)