Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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11	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2015

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 10 June 2015 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

Time allowed
- 1 hour 45 minutes

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.
- 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 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

Do not write outside the box

Section A

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

1 Gases **A** and **B** react as shown in the following equation.

$$2\mathbf{A}(g) + \mathbf{B}(g) \longrightarrow \mathbf{C}(g) + \mathbf{D}(g)$$

The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{A}]^2$$

An incomplete table of data for the reaction between **A** and **B** is shown in **Table 1**.

Table 1

Experiment	Initial [A] / mol dm^{-3}	Initial [B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.2×10^{-3}	2.8×10^{-3}	3.3×10^{-5}
2	7.9×10^{-3}	2.8×10^{-3}	
3		5.6×10^{-3}	1.8×10^{-4}

1 (a) Use the data from Experiment **1** to calculate a value for the rate constant, *k*, at this temperature.
Deduce the units of *k*.

[3 marks]

Calculation ....

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Units ....

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1 (b) Use your value of *k* from Question **1(a)** to complete **Table 1** for the reaction between **A** and **B**.
(If you have been unable to calculate an answer for Question **1 (a)**, you may assume a value of 2.3 This is **not** the correct answer.)

[2 marks]

1 (c) The reaction is zero order with respect to **B**.

State the significance of this zero order for the mechanism of the reaction.

[1 mark]

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6

Turn over for the next question

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2 Sulfur dioxide reacts with oxygen to form sulfur trioxide according to the equation

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

2 (a) Write an expression for the equilibrium constant, K_c, for this reaction and deduce its units.

[2 marks]

K_c ....

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Units ....

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2 (b) Samples of sulfur dioxide, oxygen and sulfur trioxide were added to a flask of volume 1.40 dm^3 and allowed to reach equilibrium at a given temperature.
The flask contained 0.0550 mol of sulfur dioxide and 0.0720 mol of sulfur trioxide at equilibrium.
K_c has the numerical value of 27.9 under these conditions.

Calculate the amount, in moles, of oxygen gas in this equilibrium mixture.

[3 marks]

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2 (c) The experiment in Question **2 (b)** was repeated with the same amounts of sulfur dioxide, oxygen and sulfur trioxide at the same temperature but in a smaller flask.
The mixture was allowed to reach equilibrium.

2 (c) (i) State the effect, if any, of using a smaller flask on the value of K_c

[1 mark]

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2 (c) (ii) State the effect, if any, of using a smaller flask on the amount of sulfur trioxide at equilibrium.
Explain your answer.

[3 marks]

Effect ....

Explanation ....

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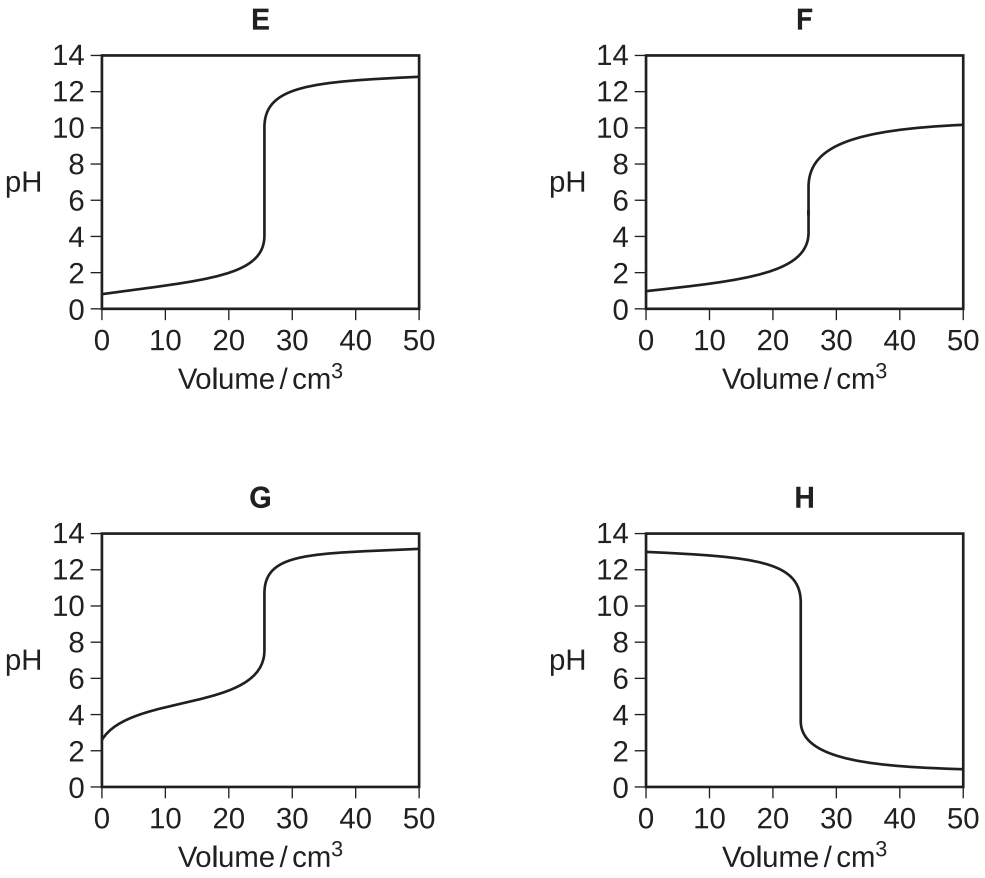
9

Turn over for the next question

3 Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown in **Figure 1**.

All solutions have concentrations of 0.1 mol dm^{-3}.

Figure 1



3 (a) In this part of the question, write the appropriate letter in each box.

From the curves **E**, **F**, **G** and **H**, choose the curve produced by the addition of

3 (a) (i) sodium hydroxide to 25 cm^3 of ethanoic acid

[1 mark]

3 (a) (ii) ammonia to 25 cm^3 hydrobromic acid

[1 mark]

3 (a) (iii) hydrochloric acid to 25 cm^3 of potassium hydroxide

[1 mark]

3 (b) **Table 2** shows information about some acid-base indicators.

Table 2

Indicator	pH range	Lower pH colour	Higher pH colour
pentamethoxy red	1.2–3.2	violet	colourless
naphthyl red	3.7–5.0	red	yellow
4-nitrophenol	5.6–7.0	colourless	yellow
cresol purple	7.6–9.2	yellow	purple

3 (b) (i) Which indicator in **Table 2** could be used for the titration that produces curve **E** but **not** for the titration that produces curve **F**?

[1 mark]

Tick (✓) **one** box.

pentamethoxy red ☐

naphthyl red ☐

4-nitrophenol ☐

cresol purple ☐

3 (b) (ii) Give the colour change at the end point of the titration that produces curve **H** when naphthyl red is used as the indicator.

[1 mark]

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3 (b) (iii) A beaker contains 25 cm^3 of a buffer solution at pH = 6.0
Two drops of each of the four indicators in **Table 2** are added to this solution.

State the colour of the mixture of indicators in this buffer solution.
You should assume that the indicators do **not** react with each other.

[1 mark]

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6

Turn over ▶

Do not write outside the box

4 Water dissociates slightly according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, is given by the expression

$$K_w = [H^+][OH^-]$$

K_w varies with temperature as shown in **Table 3**.

Table 3

Temperature / °C	**K_w / mol^2 dm^{-6}**
25	1.00×10^{-14}
50	5.48×10^{-14}

4 (a) Explain why the expression for K_w does **not** include the concentration of water.

[2 marks]

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4 (b) Explain why the value of K_w increases as the temperature increases.

[2 marks]

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Do not write outside the box

4 (c) Calculate the pH of pure water at 50 ºC.
Give your answer to 2 decimal places.

[3 marks]

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4 (d) Calculate the pH of 0.12 mol dm^{-3} aqueous NaOH at 50 ºC.
Give your answer to 2 decimal places.

[3 marks]

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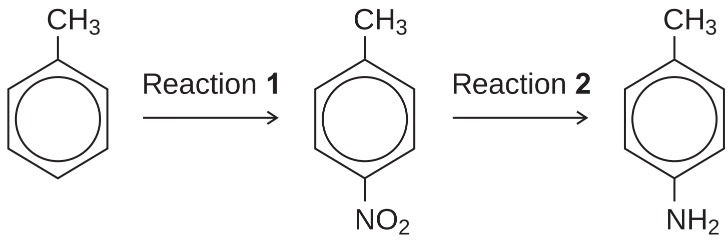
Turn over for the next question

Do not write outside the box

5 Consider the following reaction sequence starting from methylbenzene.



J

5 (a) Name the type of mechanism for reaction **1**.

[1 mark]

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5 (b) Compound **J** is formed by reduction in reaction **2**.

5 (b) (i) Give a reducing agent for this reaction.

[1 mark]

....

5 (b) (ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

[1 mark]

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5 (b) (iii) Give a use for **J**.

[1 mark]

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Do not write outside the box

5 (c) Outline a mechanism for the reaction of bromomethane with an excess of compound **J**. You should represent **J** as RNH_2 in the mechanism.

[4 marks]

5 (d) Compound **K** ($C_6H_5CH_2NH_2$) is a structural isomer of **J**.

Explain why **J** is a weaker base than **K**.

[3 marks]

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11

Turn over ▶

Do not write outside the box

6 Esters are used as raw materials in the production of soaps and biodiesel.

6 (a) A student prepared an ester by two different methods.

Method **1** alcohol + acid anhydride

Method **2** alcohol + acyl chloride

6 (a) (i) An ester was prepared using method **1**, by reacting $(CH_3)_2CHOH$ with $(CH_3CO)_2O$

Write an equation for this reaction and give the IUPAC name of the ester formed.

[2 marks]

Equation

....

IUPAC name of the ester ....

6 (a) (ii) The same ester was prepared using method **2** by reacting $(CH_3)_2CHOH$ with CH_3COCl

Outline a mechanism for this reaction.

[4 marks]

Do not write outside the box

6 (b) The ester shown occurs in vegetable oils.
It can be hydrolysed to make soap and can also be used to produce biodiesel.

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

6 (b) (i) Write an equation for the reaction of this ester with sodium hydroxide to form soap.
[2 marks]

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

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6 (b) (ii) Give the formula of the biodiesel molecule with the highest M_r that can be produced by reaction of this ester with methanol.
[1 mark]

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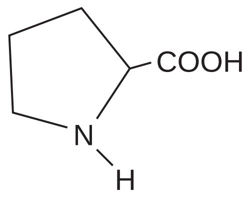
9

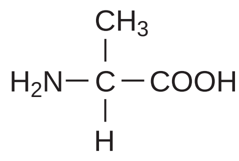
Turn over for the next question

Do not write outside the box

7 (a) The structures and common names of two amino acids are shown.



proline



alanine

7 (a) (i) Draw the structure of the zwitterion of proline.

[1 mark]

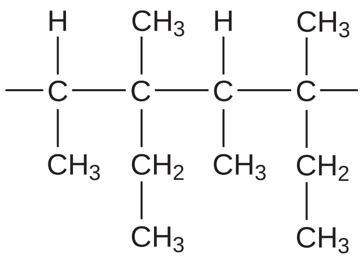
7 (a) (ii) Draw the structure of the tripeptide formed when a proline molecule bonds to two alanine molecules, one on each side.

[2 marks]

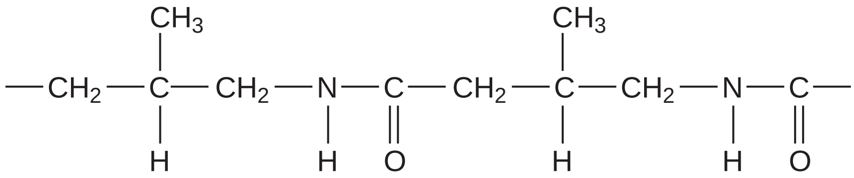
Do not write outside the box

7 (b) Sections of two polymers, **L** and **M**, are shown.

L



M



7 (b) (i) Give the IUPAC name of a monomer that forms polymer **L**.

[1 mark]

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7 (b) (ii) Give the IUPAC name of the monomer that forms polymer **M**.

[1 mark]

....

7 (b) (iii) Draw the section of a polymer made from a dicarboxylic acid and a diamine that is isomeric with the section of polymer **M** shown.

[1 mark]

7 (b) (iv) Explain why polymer **L** is non-biodegradable.

[1 mark]

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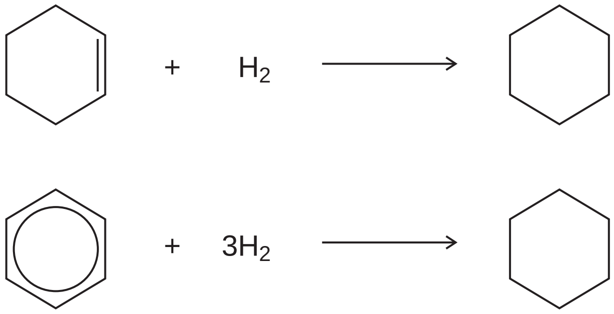
Turn over ▶

Do not write outside the box

8 Equations for the hydrogenation of cyclohexene and of benzene, together with the enthalpies of hydrogenation, are shown.



$\Delta H^\ominus = -120$ kJ mol^{-1}

$\Delta H^\ominus = -208$ kJ mol^{-1}

8 (a) (i) Use these data to show that benzene is 152 kJ mol^{-1} more stable than the hypothetical compound cyclohexa-1,3,5-triene.

[1 mark]

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8 (a) (ii) State, in terms of its bonding, why benzene is more stable than cyclohexa-1,3,5-triene.

[1 mark]

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8 (b) Three carbon-carbon bonds are labelled on the structures shown.
These bonds are of different lengths.

Write the letters **w**, **x** and **y** in order of **increasing** bond length.

[1 mark]

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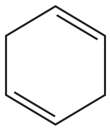
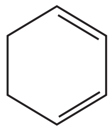
Do not write outside the box

8 (c) The structures of two cyclic dienes are shown.



cyclohexa-1,4-diene



cyclohexa-1,3-diene

8 (c) (i) Use the enthalpy of hydrogenation data given opposite to calculate a value for the enthalpy of hydrogenation of cyclohexa-1,4-diene.

[1 mark]

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8 (c) (ii) Predict a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene.

[1 mark]

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8 (c) (iii) Explain your answers to Questions **8 (c) (i)** and **8 (c) (ii)** in terms of the bonding in these two dienes.

[3 marks]

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Turn over ▶

Do not write outside the box

Section B

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

9 The acid dissociation constant, K_a, for ethanoic acid is given by the expression

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 ºC.

9 (a) A buffer solution is prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoic acid is 0.186 mol dm^{-3} and the concentration of sodium ethanoate is 0.105 mol dm^{-3}.

Calculate the pH of this buffer solution.
Give your answer to 2 decimal places.

[3 marks]

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9 (b) In a different buffer solution, the concentration of ethanoic acid is 0.251 mol dm^{-3} and the concentration of sodium ethanoate is 0.140 mol dm^{-3}.

A sample of hydrochloric acid containing 0.015 mol of HCl is added to 1000 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the hydrochloric acid has been added.
You should ignore any change in total volume.
Give your answer to 2 decimal places.

[5 marks]

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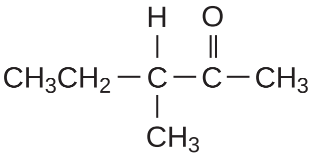
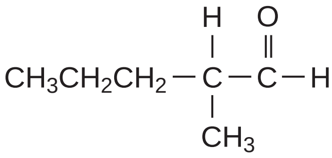
Turn over for the next question

Turn over ▶

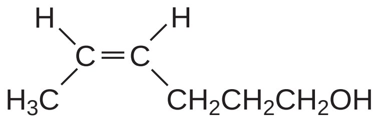
10 The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



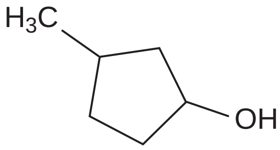
P



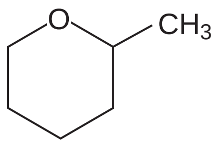
Q



R



S



T

10 (a) A simple test-tube reaction can be used to distinguish between isomers **P** and **S**.

Identify a reagent (or combination of reagents) you could use.
State what you would observe when both isomers are tested separately with this reagent or combination of reagents.

[3 marks]

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Do not write outside the box

10 (b) A simple test-tube reaction can be used to distinguish between isomer **Q** and all the other isomers.

Identify a reagent (or combination of reagents) you could use.
State what you would observe when **Q** is tested with this reagent or combination of reagents.

[2 marks]

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10 (c) State which **one** of the isomers, **P**, **Q**, **R**, **S** and **T**, has the least number of peaks in its ^{1}H n.m.r. spectrum.
Give the number of peaks for this isomer.

[2 marks]

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10 (d) Write the **molecular** formula of the standard used in ^{13}C n.m.r. spectroscopy.
Give **two** reasons why this compound is used.

[3 marks]

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Question 10 continues on the next page

Turn over ▶

10 (e) **Figure 2** and **Figure 3** show the ^{13}C n.m.r. spectra of two of the five isomers.

Figure 2

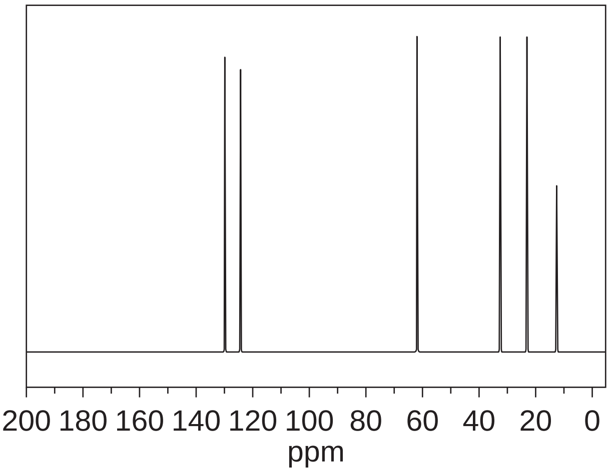
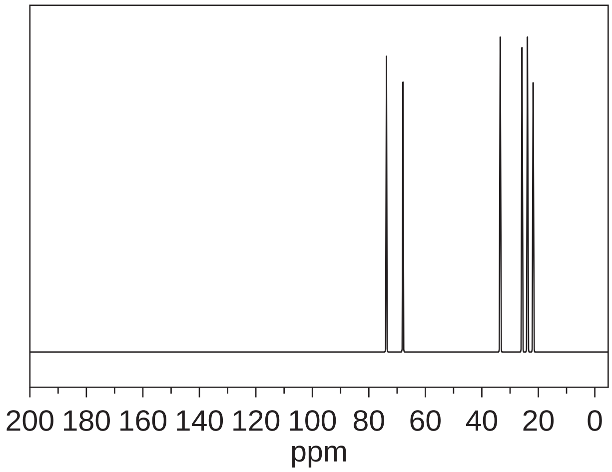
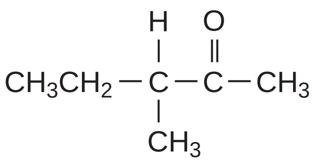


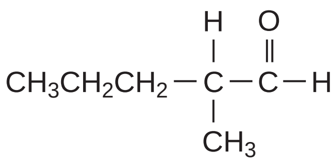
Figure 3



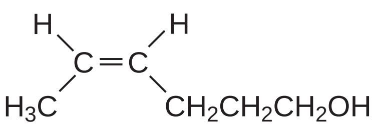
The structures of the five isomers are repeated to help you answer this question.



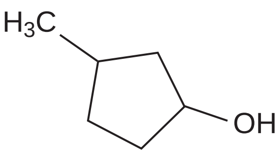
P



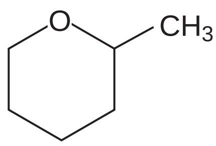
Q



R



S



T

State which isomer produces the spectrum in **Figure 2** and which isomer produces the spectrum in **Figure 3**.

Explain your answer.

You do not need to identify every peak in each spectrum.
Use **Table C** on the Data Sheet to answer the question.

[5 marks]

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10 (f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.
The ^{1}H n.m.r. spectrum of **U** consists of two singlets.
V is a cyclic alcohol that exists as optical isomers.

Draw the structure of **U** and the structure of **V.**

[2 marks]

U **V**

17

Turn over ▶

Do not write outside the box

11 The N-substituted amide $C_6H_{13}NO$ can be formed from but-2-ene in a three-step synthesis.

$$H_3CCH{=}CHCH_3 \xrightarrow{\text{Reaction } \mathbf{1}} C_4H_9Br \xrightarrow{\text{Reaction } \mathbf{2}} C_4H_{11}N \xrightarrow{\text{Reaction } \mathbf{3}} C_6H_{13}NO$$

For each reaction

- state a reagent
- give the structure of the product
- name the mechanism of the reaction.

Detailed mechanisms are **not** required.

[9 marks]

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END OF QUESTIONS