

Centre Number						Candidate Number				
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Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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10	
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**.



J U N 1 5 C H E M 4 0 1

WMP/Jun15/CHEM4/E5

# CHEM4

**Section A**

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

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



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

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

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

**Table 1**

Experiment	Initial [A] / mol dm <sup>-3</sup>	Initial [B] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
<b>1</b>	$4.2 \times 10^{-3}$	$2.8 \times 10^{-3}$	$3.3 \times 10^{-5}$
<b>2</b>	$7.9 \times 10^{-3}$	$2.8 \times 10^{-3}$	
<b>3</b>		$5.6 \times 10^{-3}$	$1.8 \times 10^{-4}$

- 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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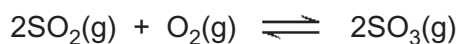
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Turn over for the next question

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



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  $1.40 \text{ dm}^3$  and allowed to reach equilibrium at a given temperature. The flask contained  $0.0550 \text{ mol}$  of sulfur dioxide and  $0.0720 \text{ mol}$  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]**

.....

**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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**Turn over for the next question**

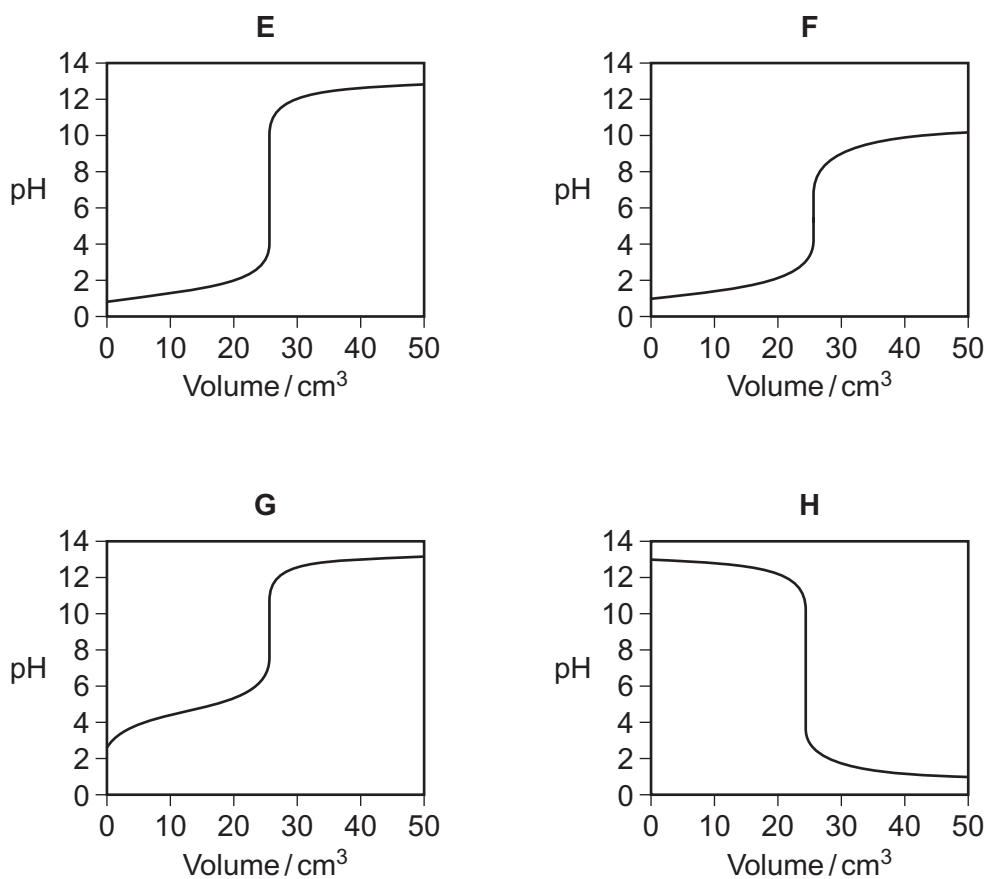
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3 Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown in **Figure 1**.

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

**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  $25 \text{ cm}^3$  of ethanoic acid

[1 mark]

3 (a) (ii) ammonia to  $25 \text{ cm}^3$  hydrobromic acid

[1 mark]

3 (a) (iii) hydrochloric acid to  $25 \text{ cm}^3$  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<sup>3</sup> of a buffer solution at pH = 6.0  
Two drops of each of the four indicators in **Table 2** are added to this solution.

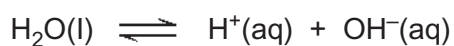
State the colour of the mixture of indicators in this buffer solution.  
You should assume that the indicators do **not** react with each other.

[1 mark]

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4 Water dissociates slightly according to the equation:



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

$$K_w = [\text{H}^+][\text{OH}^-]$$

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

**Table 3**

Temperature / °C	$K_w$ / mol <sup>2</sup> dm <sup>-6</sup>
25	$1.00 \times 10^{-14}$
50	$5.48 \times 10^{-14}$

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

[3 marks]

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- 4 (d) Calculate the pH of 0.12 mol dm<sup>-3</sup> aqueous NaOH at 50 °C.  
Give your answer to 2 decimal places.

[3 marks]

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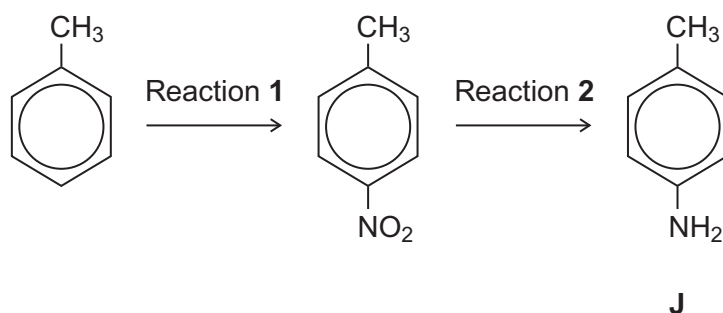
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Turn over for the next question

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5 Consider the following reaction sequence starting from methylbenzene.



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]

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

[1 mark]

.....

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

[1 mark]

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- 5 (c)** Outline a mechanism for the reaction of bromomethane with an excess of compound **J**. You should represent **J** as  $\text{RNH}_2$  in the mechanism.

**[4 marks]**

- 5 (d)** Compound **K** ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ) is a structural isomer of **J**.

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

**[3 marks]**

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**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  $(\text{CH}_3)_2\text{CHOH}$  with  $(\text{CH}_3\text{CO})_2\text{O}$

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

**[2 marks]**

Equation

.....

IUPAC name of the ester .....

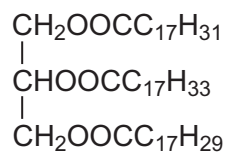
**6 (a) (ii)** The same ester was prepared using method 2 by reacting  $(\text{CH}_3)_2\text{CHOH}$  with  $\text{CH}_3\text{COCl}$

Outline a mechanism for this reaction.

**[4 marks]**

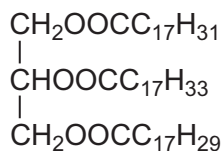


- 6 (b)** The ester shown occurs in vegetable oils.  
It can be hydrolysed to make soap and can also be used to produce biodiesel.



- 6 (b) (i)** Write an equation for the reaction of this ester with sodium hydroxide to form soap.

**[2 marks]**



- 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]**

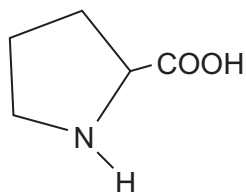
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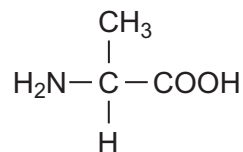
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7 (a) The structures and common names of two amino acids are shown.



proline



alanine

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

[1 mark]

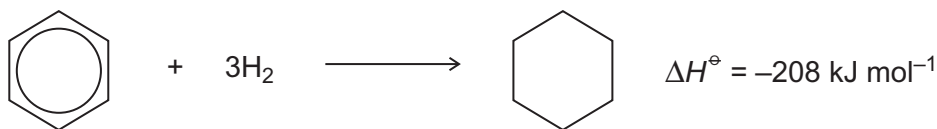
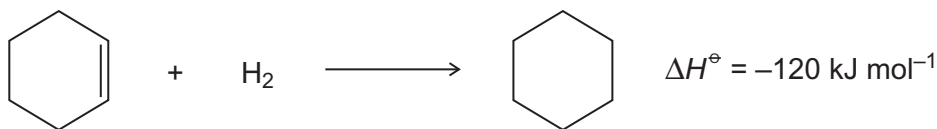
7 (a) (ii) Draw the structure of the tripeptide formed when a proline molecule bonds to two alanine molecules, one on each side.

[2 marks]





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



- 8 (a) (i) Use these data to show that benzene is  $152 \text{ kJ mol}^{-1}$  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.

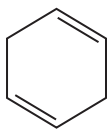
[1 mark]

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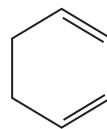




**8 (c)** The structures of two cyclic dienes are shown.



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 ►



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

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

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

The value of  $K_a$  for ethanoic acid is  $1.74 \times 10^{-5} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ .

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

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  $0.251 \text{ mol dm}^{-3}$  and the concentration of sodium ethanoate is  $0.140 \text{ mol dm}^{-3}$ .

A sample of hydrochloric acid containing  $0.015 \text{ mol}$  of  $\text{HCl}$  is added to  $1000 \text{ cm}^3$  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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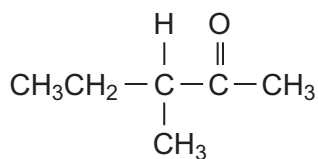
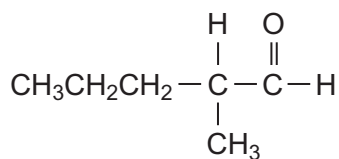
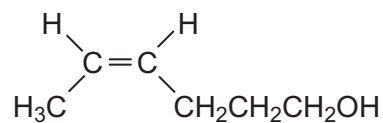
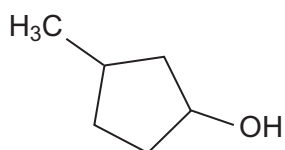
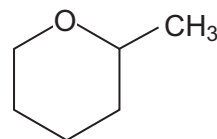
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- 10 The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.

**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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**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  $^1\text{H}$  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  $^{13}\text{C}$  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**

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

Figure 2

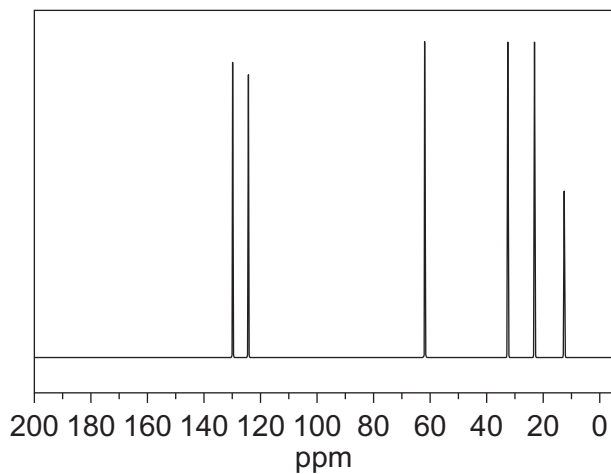
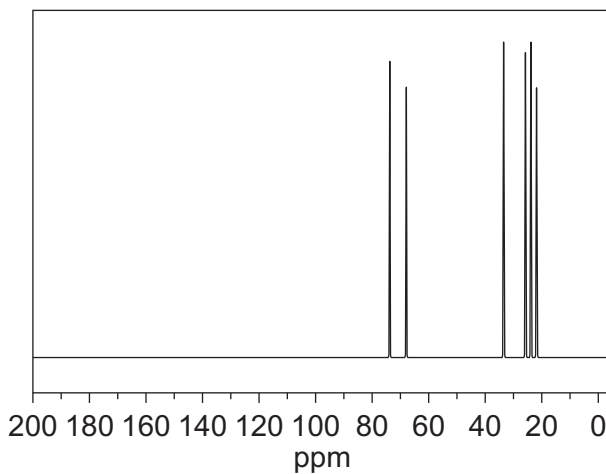
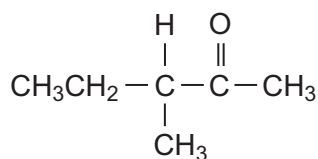


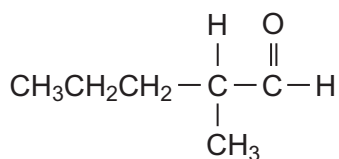
Figure 3



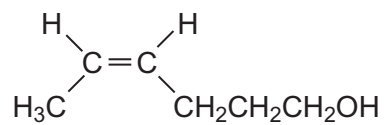
The structures of the five isomers are repeated to help you answer this question.



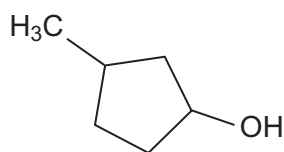
P



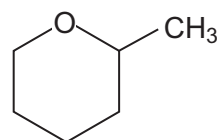
Q



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  $^1\text{H}$  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**



