Paper Reference(s)   **WCH04/01**

Pearson Edexcel
International Advanced Level

Chemistry
Advanced
Unit 4: General Principles of Chemistry I – Rates,
        Equilibria and Further Organic Chemistry
        (including synoptic assessment)

Tuesday 13 June 2017 – Afternoon

**Time: 1 hour 40 minutes plus your additional time
        allowance**

INSTRUCTIONS TO CANDIDATES
**Write your centre number, candidate number,
surname, other names and your signature in the
boxes below. Check that you have the correct
question paper.**

Centre No.					
Candidate No.					
Surname					
Other names					
Signature					
Paper Reference	W	C	H	0	4	/	0	1

P Pearson

- **Use BLACK ink or BLACK ball-point pen.**
- **Answer ALL questions.**
- **Answer the questions in the spaces provided – there may be more space than you need.**

MATERIALS REQUIRED FOR EXAMINATION
Data Booklet

ITEMS INCLUDED WITH QUESTION PAPERS
Periodic Table

INFORMATION FOR CANDIDATES
- **The total mark for this paper is 90.**
- **The marks for EACH question are shown in brackets – use this as a guide as to how much time to spend on each question.**
- **Questions labelled with an ASTERISK (*) are ones where the quality of your written communication will be assessed – you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.**
- **Candidates may use a scientific calculator.**
- **A Periodic Table is provided.**

ADVICE TO CANDIDATES
- **Read each question carefully before you start to answer it.**
- **Keep an eye on the time.**
- **Try to answer every question.**
- **Check your answers if you have time at the end.**

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1   When ethanoic acid is mixed with water, what are the Brønsted-Lowry conjugate acid-base pairs?

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

☐ A   acid 1 + base 1 $\rightleftharpoons$ acid 2 + base 2

☐ B   acid 1 + base 2 $\rightleftharpoons$ base 1 + acid 2

☐ C   acid 1 + base 2 $\rightleftharpoons$ acid 2 + base 1

☐ D   acid 2 + base 2 $\rightleftharpoons$ base 1 + acid 1

(TOTAL FOR QUESTION 1 = 1 MARK)

(Questions continue on next page)

2 **Which of these substances gives a solution with the HIGHEST pH when equal amounts are added to the same volume of water?**

☐ A CH_3COOH

☐ B $CH_2ClCOOH$

☐ C CH_3COONa

☐ D CH_3COCl

(TOTAL FOR QUESTION 2 = 1 MARK)

3 **The calibration of a pH meter is best carried out using**

☐ A solutions of an alkaline buffer and an acidic buffer.

☐ B solutions of a strong alkali and strong acid.

☐ C solutions of a weak acid and weak alkali.

☐ D deionised water.

(TOTAL FOR QUESTION 3 = 1 MARK)

(Questions continue on next page)

4   **What is the pH of the following solutions?**
     Use $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} where necessary.

     (a) **0.2 mol dm^{-3} nitric acid. (1 mark)**

     ☐ A   –0.7

     ☐ B   –0.2

     ☐ C   +0.2

     ☐ D   +0.7

     (b) **0.200 mol dm^{-3} barium hydroxide, Ba(OH)$_2$.**
          (1 mark)

     ☐ A   14.7

     ☐ B   14.0

     ☐ C   13.6

     ☐ D   13.3

(Question continues on next page)

(c) A mixture of $10.0\,cm^3$ of $1.00\,mol\,dm^{-3}$ hydrochloric acid and $20.0\,cm^3$ of $1.00\,mol\,dm^{-3}$ sodium hydroxide. (1 mark)

☐ A   13·5

☐ B   13·7

☐ C   14·0

☐ D   14·5

(d) A buffer solution prepared by mixing $20\,cm^3$ of $0.10\,mol\,dm^{-3}$ methanoic acid and $10\,cm^3$ of $0.10\,mol\,dm^{-3}$ sodium hydroxide, given that $pK_a = 3.8$ for methanoic acid. (1 mark)

☐ A   4·1

☐ B   3·8

☐ C   3·5

☐ D   3·3

(TOTAL FOR QUESTION 4 = 4 MARKS)

(Questions continue on next page)

5 **The decomposition of hydrogen iodide at 500 K is an equilibrium reaction.**

EQUATION 1

$$HI(g) \rightleftharpoons \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \quad \Delta H_1^{\ominus} = +5 \text{ kJ mol}^{-1} \quad K_{c1} = 6 \times 10^{-3}$$

(a) **What is the effect of raising the pressure of the reaction mixture on the reaction rate, equilibrium yield and value of K_{c1}?** (1 mark)

	Rate	Equilibrium yield	K_{c1}
A	Increased	No change	No change
B	No change	No change	Increased
C	Increased	Increased	No change
D	No change	Increased	Increased

(Question continues on next page)

(b) The equation can also be written as

EQUATION 2

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H_2^{\ominus}$$

Equilibrium constant = K_{c2}

Which combination of expressions is correct? (1 mark)

☐ A $\quad \Delta H_1^{\ominus} = \Delta H_2^{\ominus}$ and $K_{c1} = K_{c2}$

☐ B $\quad \Delta H_1^{\ominus} = \frac{1}{2}\Delta H_2^{\ominus}$ and $K_{c1} = \frac{1}{2}K_{c2}$

☐ C $\quad \Delta H_1^{\ominus} = \sqrt{\Delta H_2^{\ominus}}$ and $K_{c1} = \sqrt{K_{c2}}$

☐ D $\quad \Delta H_1^{\ominus} = \frac{1}{2}\Delta H_2^{\ominus}$ and $K_{c1} = \sqrt{K_{c2}}$

(TOTAL FOR QUESTION 5 = 2 MARKS)

(Questions continue on next page)

6   The dissociation constant for water, K_w, increases with increasing temperature.

Which of these statements about the effect of increasing temperature is correct?

☐ A   Water becomes acidic.

☐ B   Water becomes alkaline.

☐ C   The pH of water decreases.

☐ D   In water, $[H_3O^+(aq)]$ increases and $[OH^-(aq)]$ decreases.

(TOTAL FOR QUESTION 6 = 1 MARK)

7   Ethanoyl chloride reacts with an equal amount of

☐ A   ammonia to form an amine.

☐ B   methylamine to form an amide.

☐ C   water to form a weakly acidic solution.

☐ D   methanol to form ethyl methanoate.

(TOTAL FOR QUESTION 7 = 1 MARK)

(Questions continue on next page)

8 **When an optically active isomer of 2-chlorobutane reacts with hydroxide ions to form butan-2-ol by an S_N1 mechanism, the product is NOT optically active.**

$$C_2H_5CHClCH_3 \ + \ OH^- \ \longrightarrow \ C_2H_5CH(OH)CH_3 \ + \ Cl^-$$

What is the best explanation for this?

☐ **A** **2-chlorobutane contains a chiral carbon atom.**

☐ **B** **The reaction is a nucleophilic substitution.**

☐ **C** **2-chlorobutane forms a transition state containing a chiral carbon at the reaction site.**

☐ **D** **2-chlorobutane forms a carbocation which is planar about the positively charged carbon.**

(TOTAL FOR QUESTION 8 = 1 MARK)

(Questions continue on next page)

(Turn over)

9 Which reaction has an enthalpy change equal to the enthalpy change of solution of potassium chloride?

☐ A 1 mol KCl(s) + 2 mol of H_2O(l) → K^+(aq) + Cl^-(aq)

☐ B 1 mol KCl(s) + excess H_2O(l) → K^+(aq) + Cl^-(aq)

☐ C 1 mol KCl(g) + 2 mol of H_2O(l) → K^+(aq) + Cl^-(aq)

☐ D 1 mol KCl(g) + excess H_2O(l) → K^+(aq) + Cl^-(aq)

(TOTAL FOR QUESTION 9 = 1 MARK)

10 An ionic solid dissolves in water. Which of the following statements about the signs of these standard enthalpy changes is possible?

	$\Delta H^{\ominus}_{solution}$	$\Delta H^{\ominus}_{hydration}$	Lattice energy
☐ A	negative	negative	positive
☐ B	positive	negative	negative
☐ C	negative	positive	negative
☐ D	positive	positive	positive

(TOTAL FOR QUESTION 10 = 1 MARK)

11 What is the main reason for hydrogenating vegetable oils for use as low-fat spreads?

☐ A To increase the melting temperature.

☐ B To decrease the viscosity of the oil.

☐ C To prevent oxidation of carbon-carbon double bonds.

☐ D To decrease the cholesterol content.

(TOTAL FOR QUESTION 11 = 1 MARK)

(Questions continue on next page)

(Turn over)

12 **Which of the following statements is true?**

☐ **A** A trans fat has hydrogen atoms in the trans positions attached to the carbon-carbon double bonds.

☐ **B** Transesterification always produces esters with hydrogen atoms in the trans position attached to the carbon-carbon double bonds.

☐ **C** But-1-ene has cis and trans isomers.

☐ **D** 1-fluoro-1-chloro-2-bromo-2-iodoethane has cis and trans isomers.

(TOTAL FOR QUESTION 12 = 1 MARK)

(Questions continue on next page)

13   In a separation using high-performance liquid chromatography, the stationary phase was polar and the mobile phase was non-polar.

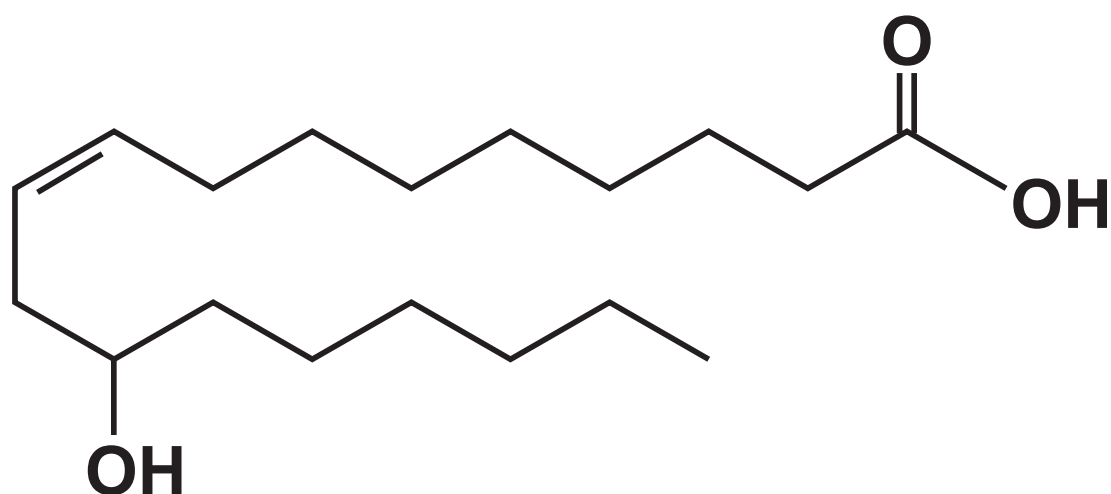Which compound would take the most time to travel through the column?

☐ A   1-bromopentane

☐ B   1-chloropentane

☐ C   1-iodopentane

☐ D   pentane

(TOTAL FOR QUESTION 13 = 1 MARK)

(Questions continue on next page)

14 Ricinoleic acid, found in castor oil, is a painkiller.

(a) What is the systematic name for ricinoleic acid?
(1 mark)

☐ A E-12-hydroxyoctadec-9-enoic acid

☐ B E-7-hydroxyoctadec-9-enoic acid

☐ C Z-7-hydroxyoctadec-9-enoic acid

☐ D Z-12-hydroxyoctadec-9-enoic acid

(Question continues on next page)

(b) The tallest peak in the mass spectrum of ricinoleic acid is at m/e = 55.

Which fragment produces this peak? (1 mark)

☐ A $COOH^+$

☐ B $C_4H_7^+$

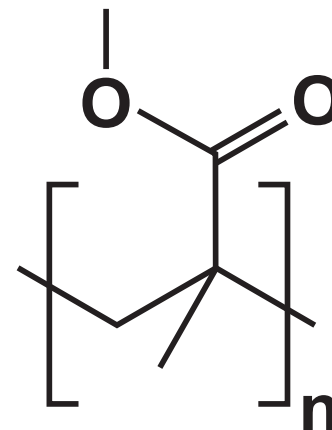☐ C $CH{=}CHCHOH^+$

☐ D $CH_2CO_2^+$

(TOTAL FOR QUESTION 14 = 2 MARKS)
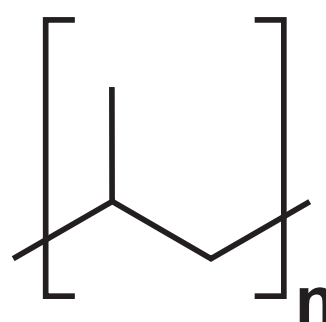
(Questions continue on next page)

(Turn over)

15 Which polymer is manufactured by a condensation polymerisation of a SINGLE substance?
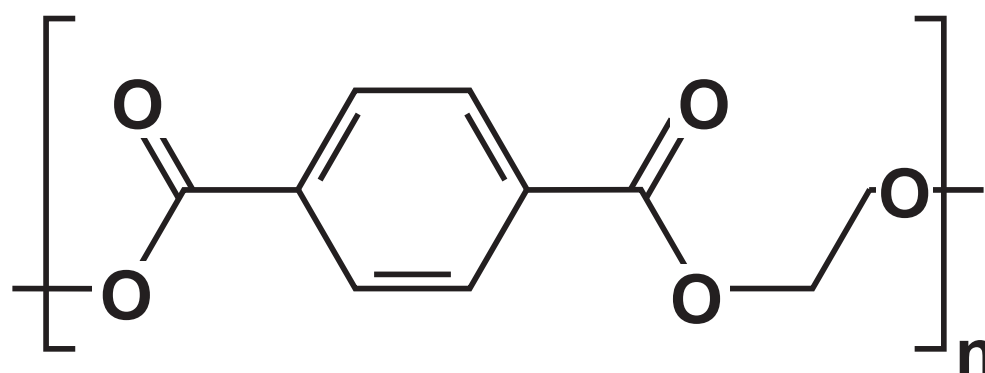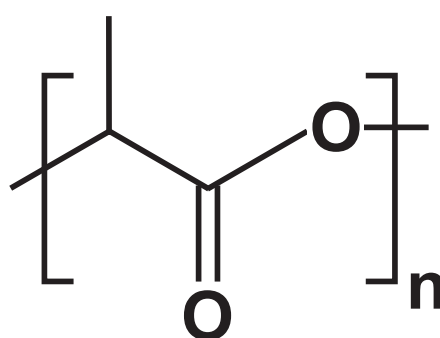
☐ A Poly(2-methylpropenoate)

☐ B Poly(propene)

☐ C Poly(ethylene terephthalate)

☐ D Poly(lactic acid)

(TOTAL FOR QUESTION 15 = 1 MARK)

TOTAL FOR SECTION A = 20 MARKS

(Section B begins on next page)

(Turn over)

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

16   This question is about the reaction between solid barium hydroxide and solid ammonium chloride. This reaction occurs at room temperature.

$$Ba(OH)_2(s) + 2NH_4Cl(s) \longrightarrow BaCl_2.2H_2O(s) + 2NH_3(g)$$

  (a) (i)   Suggest how you would speed up this reaction in the laboratory, without heating. (1 mark)

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       (ii) Give a test, with the result, for $NH_3(g)$. (1 mark)

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(Question continues on next page)

(Turn over)

(b) (i) Calculate the standard entropy change for the system, $\Delta S^{\ominus}_{system}$, for this reaction.

Include a sign and units in your answer.

The standard entropy of $BaCl_2.2H_2O(s)$ is $+202 \cdot 9$ J K^{-1} mol^{-1}.

Use your Data Booklet for the other values.
(3 marks)

(Question continues on next page)

(ii) Is the sign for the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, as you would expect? Justify your answer. (1 mark)

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(Question continues on next page)

(c) (i) The total standard entropy change, $\Delta S_{total}^{\ominus}$, is +227·5 J K^{-1} mol^{-1}.

Calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction at 298 K.

Include a sign and units in your answer.
(3 marks)

(ii) **State and explain how you would expect the temperature to change during this reaction. (1 mark)**

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(TOTAL FOR QUESTION 16 = 10 MARKS)

(Questions continue on next page)

(Turn over)

17 This question is about some reactions of propanone.

    (a) Iodine reacts with propanone, CH_3COCH_3, in two different ways depending on the conditions.

        (i) Write the equation for the reaction between iodine and propanone in the presence of an acid catalyst. State symbols are not required. (1 mark)

        (ii) Suggest why the rate of this reaction increases as the reaction proceeds. (1 mark)

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(Question continues on next page)

(b) (i) Identify, by names or formulae, the organic products of the reaction between iodine and propanone in alkaline conditions. (2 marks)

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(ii) Describe TWO observations you expect to make when this reaction occurs. (2 marks)

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(Question continues on next page)

(c) (i) **When propanone reacts with lithium tetrahydridoaluminate(III), water is not a suitable solvent.**

**Explain why water is unsuitable and name the solvent that should be used. (2 marks)**

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(ii) **Draw the SKELETAL formula of the organic product of this reaction. (1 mark)**

(Question continues on next page)

(d) **Propanone reacts with 2,4-dinitrophenylhydrazine to form an organic product which is a crystalline solid and water.**

    (i) **Complete the formula of the crystalline solid.**

        The formula of 2,4-dinitrophenylhydrazine can be simplified to $RNHNH_2$ (1 mark)

$$R\text{—}N\text{—}N$$
$$\ \ \ \ \ \ |$$
$$\ \ \ \ \ \ H$$
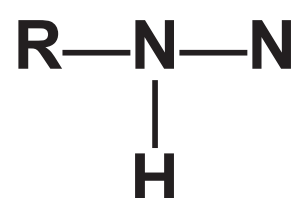
(Question continues on next page)

(Turn over)

**(ii) What are the TWO uses of
2,4-dinitrophenylhydrazine in the laboratory?
(2 marks)**

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(Question continues on next page)

(e) (i) Propanone reacts with hydrogen cyanide to form a cyanohydrin, with structural formula $(CH_3)_2C(OH)CN$.

Give the fully displayed formula and the systematic name for this compound.
(2 marks)

Fully displayed formula

Systematic name_____

(Question continues on next page)

(Turn over)

(ii) Draw the mechanism for the reaction of propanone with hydrogen cyanide, in the presence of cyanide ions, to form the cyanohydrin, $(CH_3)_2C(OH)CN$. Use curly arrows to show the movement of electron pairs. (4 marks)

(Question continues on next page)

(Turn over)

*(iii) When hydrogen cyanide and propanone react in ethanol solution to form the cyanohydrin, an equilibrium is set up.

$$CH_3COCH_3 + HCN \rightleftharpoons (CH_3)_2C(OH)CN$$

When $100\,cm^3$ of $0.10\,mol\,dm^{-3}$ propanone solution is mixed with $100\,cm^3$ of $0.20\,mol\,dm^{-3}$ hydrogen cyanide solution, the equilibrium concentration of the cyanohydrin is $0.034\,mol\,dm^{-3}$.

Calculate the equilibrium constant K_c for this reaction.

Include units with your answer, which should be given to TWO significant figures. (4 marks)

(Continue your answer on next page)

(TOTAL FOR QUESTION 17 = 22 MARKS)

18 (a) Propanal is an isomer of propanone.

It reacts with at least three reagents which do NOT react with propanone.

(i) Identify TWO of these reagents, in each case stating what you would SEE when the reaction takes place. **(4 marks)**

First reagent_____

_____

_____

_____

_____

Second reagent _____

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(Question continues on next page)

(ii)   Each reaction is of the same type. State the type of reaction. (1 mark)

_____

(b) Propanoic acid can be formed in the reactions in (a).

(i)   Give the structural formula of propanoic acid. (1 mark)

(Question continues on next page)

(ii) Propyl propanoate can be made from propanoic acid in two steps.

	Step 1		Step 2	

Propanoic acid $\longrightarrow$ propanoyl chloride $\longrightarrow$ propyl propanoate

NAME the reagents for each step. (2 marks)

Step 1 _____

Step 2 _____

(iii) Explain why the two step process given in b(ii) gives a higher yield than synthesising propyl propanoate from propanoic acid in one step. (1 mark)

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(Question continues on next page)

(c) Propanal and propanone can be easily distinguished from each other by proton nmr (nuclear magnetic resonance spectroscopy) or IR (infrared) spectroscopy.

*(i) Draw the displayed formula of propanal and label the different proton environments. Indicate the relative areas and splitting pattern for each peak in the high resolution proton nmr spectrum.

Chemical shifts are not required. (3 marks)

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(Continue your answer on next page)

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(Question continues on next page)

(ii) State and explain the appearance of the high resolution nmr spectrum of propanone. (2 marks)

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(Question continues on next page)

(iii) Use your Data Booklet to identify TWO absorptions in the IR spectrum of propanal that would distinguish it from propanone.

How would the IR spectrum of propanone be different from propanal?

Identify the wavenumber of each absorption and the bond responsible. (3 marks)

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(Continue your answer on next page)

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(TOTAL FOR QUESTION 18 = 17 MARKS)

TOTAL FOR SECTION B = 49 MARKS

(Section C begins on next page)

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

19 The kinetics of the reaction between hydrogen peroxide and iodide ions in the presence of sulfuric acid is investigated.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow 2H_2O(l) + I_2(aq)$$

(a) First, the concentration of hydrogen peroxide is measured at different times, while keeping the concentrations of iodide and hydrogen ions constant.
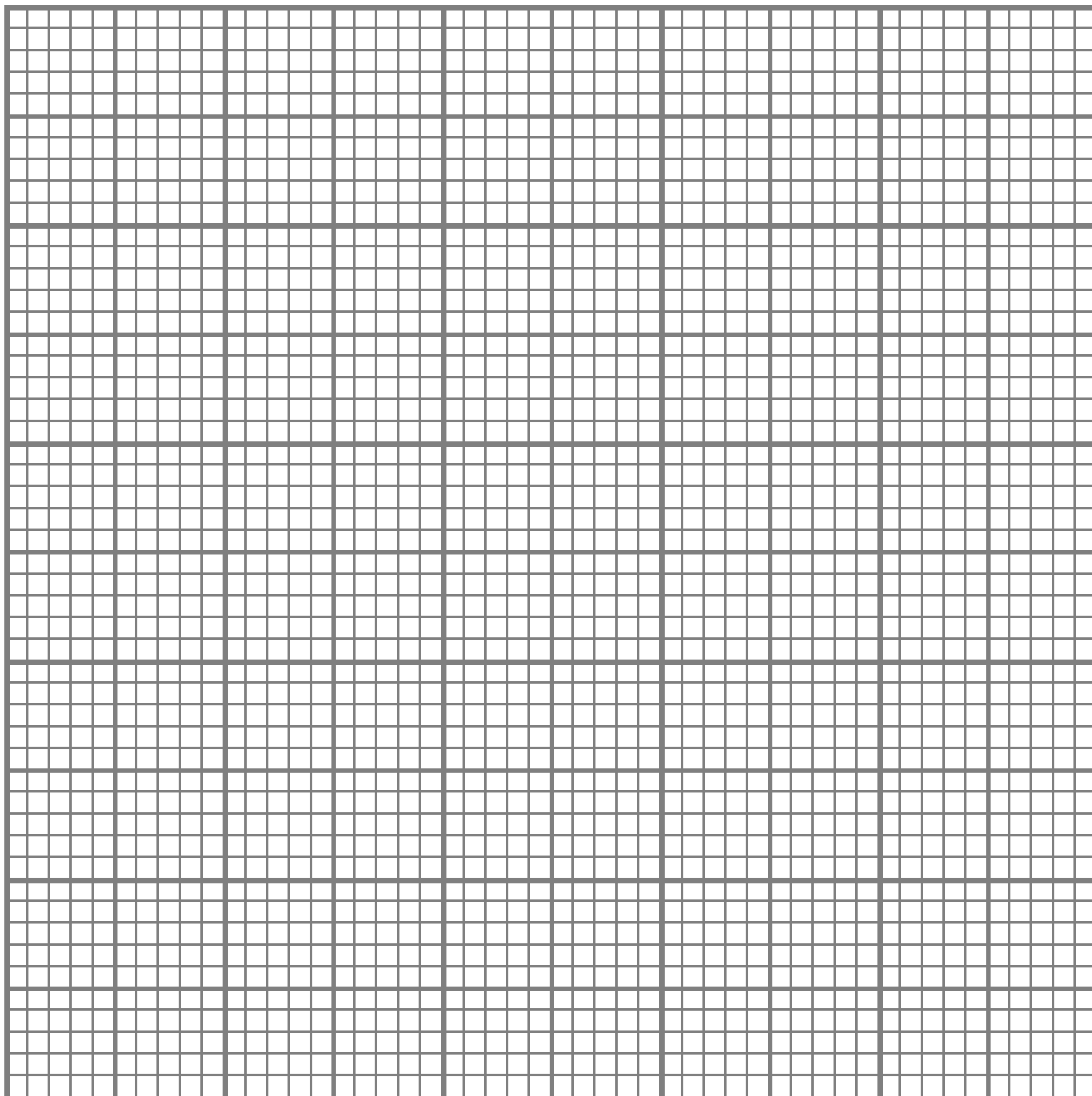
The following results are obtained.

$t / 10^3 \, s$	$[H_2O_2] / mol \, dm^{-3}$
0	0·20
2	0·14
4	0·09
6	0·06
8	0·04
10	0·03

(Question continues on next page)

(Turn over)

(i) Plot a graph of $[H_2O_2]$ / mol dm^{-3} against t / 10^3 s.
    (2 marks)

(Question continues on next page)

(ii) **Find TWO successive half-lives from your graph.**

Show your working on your graph, together with their values. (2 marks)

(iii) **Deduce the order of the reaction with respect to hydrogen peroxide.**

Justify your answer. (2 marks)

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(Question continues on next page)

(b) The experiment is repeated using an initial rate method.

Mixtures are prepared using $0 \cdot 10 \, mol \, dm^{-3}$ solutions of each reactant, $2 \, cm^3$ of sodium thiosulfate solution mixed with starch and varying amounts of water so that the total volume is always $12 \, cm^3$.

The time for the mixtures to change colour is recorded and the initial rate calculated.

Run	Volume KI / cm^3	Volume H_2O_2 / cm^3	Volume H_2SO_4 / cm^3	Volume of water / cm^3	Initial rate / $mol \, dm^{-3} \, s^{-1}$
1	3·0	3·0	3·0	1·0	$1 \cdot 06 \times 10^{-4}$
2	2·0	3·0	3·0	2·0	$7 \cdot 00 \times 10^{-5}$
3	1·0	3·0	3·0	3·0	$3 \cdot 50 \times 10^{-5}$
4	3·0	3·0	2·0	2·0	$1 \cdot 08 \times 10^{-4}$
5	3·0	3·0	1·0	3·0	$1 \cdot 05 \times 10^{-4}$

(Question continues on next page)

(i) Explain why it is necessary to keep the total volume of each mixture the same. (1 mark)

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(Question continues on next page)

(Turn over)

(ii) **The reciprocal of time can be used as an approximate measure of rate. What assumption does this approximation depend on? (1 mark)**

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(Question continues on next page)

(iii) Use the results in the table to deduce the order of reaction with respect to iodide ions and hydrogen ions.

Justify each answer by referring to relevant data from the table. (3 marks)

Iodide ions _____

_____

_____

Hydrogen ions _____

_____

_____

(iv) Write the overall rate equation for this reaction using your answers to (a)(iii) and (b)(iii).
(1 mark)

(Question continues on next page)

(v) Calculate the actual concentrations of hydrogen peroxide and iodide ions in the MIXTURE used in Run 1 from the table in (b). (1 mark)

(vi) Calculate a value for the rate constant using Run 1 from the table in (b) and your answers to parts (b)(iv) and (b)(v). Include units for the rate constant. (2 marks)

(Question continues on next page)

(c) (i) The activation energy for this reaction is found by keeping the concentrations of reactants constant and repeating the reaction at different temperatures.

A graph of ln(rate) of the reaction against reciprocal of temperature is given below.
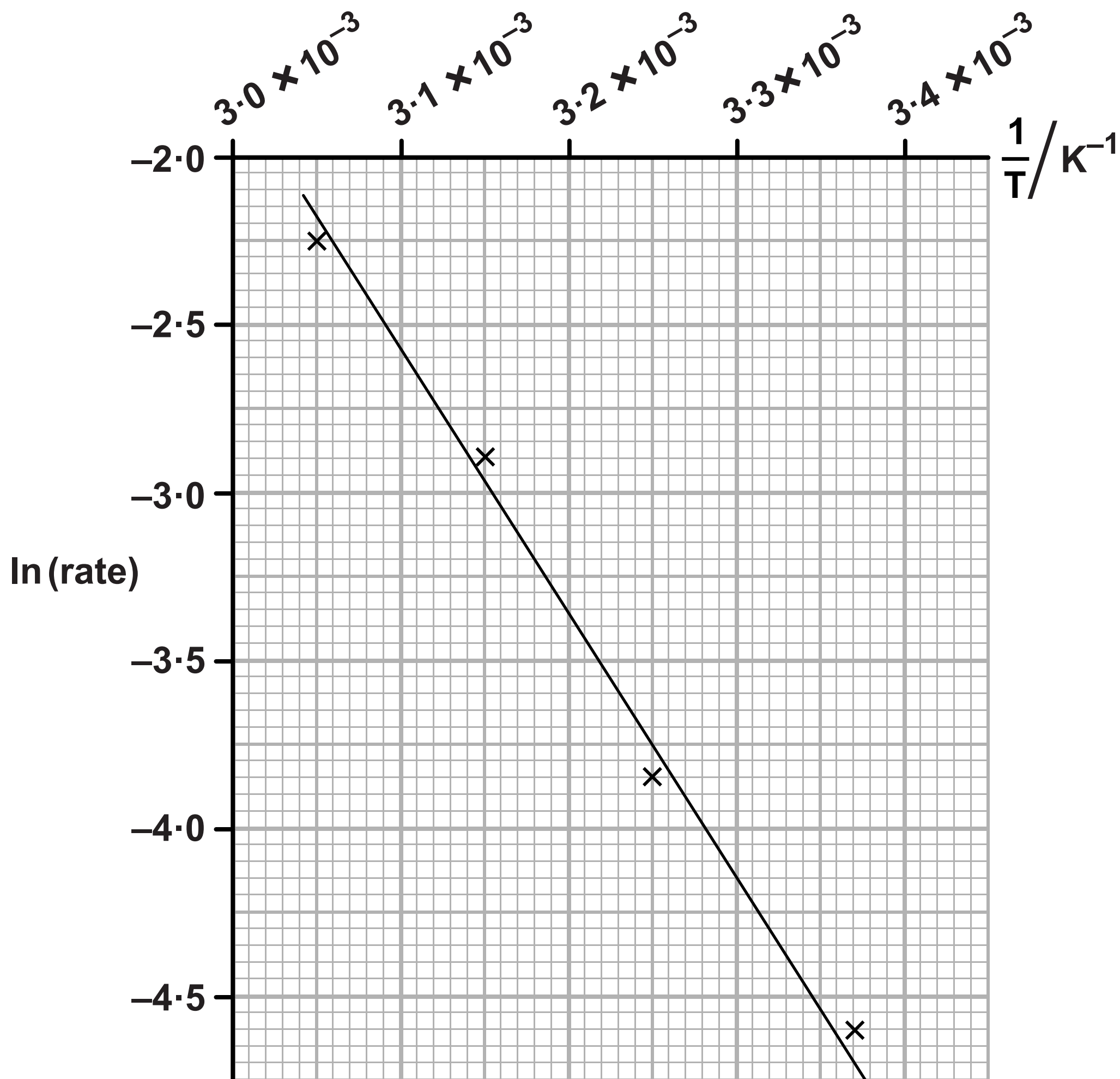
Calculate the gradient of the graph.

Use your value of the gradient and the equation below to calculate the activation energy of the reaction.

$$\ln (\text{rate}) = \frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad [R = 8{\cdot}31 \text{ J K}^{-1} \text{ mol}^{-1}]$$

Include a sign and units with your answer.
(3 marks)

(Question continues on next page)

*(ii) **If the same reaction is carried out in the presence of a catalyst of ammonium molybdate, the activation energy is found to be much lower.**

Sketch a Maxwell-Boltzmann distribution of molecular energies.

Use your sketch to explain why this reduction in activation energy increases the rate of the reaction. (3 marks)

Explanation

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(TOTAL FOR QUESTION 19 = 21 MARKS)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS
END