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Other names

Pearson Edexcel
International
Advanced Level

Centre Number

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Candidate Number

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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

Paper Reference

WCH04/01

You must have: Data Booklet

Candidates may use a scientific calculator.

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided – *there may be more space than you need.*

Information

- 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.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- 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.

Turn over ►

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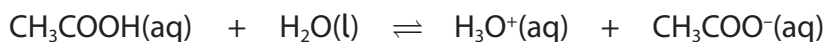


Pearson

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?



- 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)

- 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)

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

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

(1)

- A -0.7
- B -0.2
- C +0.2
- D +0.7

(b) $0.200 \text{ mol dm}^{-3}$ barium hydroxide, Ba(OH)_2 .

(1)

- A 14.7
- B 14.0
- C 13.6
- D 13.3

(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)

- 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 $\text{p}K_a = 3.8$ for methanoic acid.

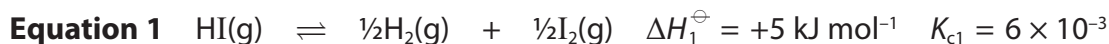
(1)

- A 4.1
- B 3.8
- C 3.5
- D 3.3

(Total for Question 4 = 4 marks)



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

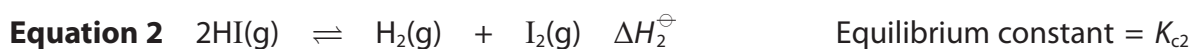


(a) What is the effect of raising the pressure of the reaction mixture on the reaction rate, equilibrium yield and value of K_{c1} ?

(1)

	Rate	Equilibrium yield	K_{c1}
<input type="checkbox"/> A	Increased	No change	No change
<input type="checkbox"/> B	No change	No change	Increased
<input type="checkbox"/> C	Increased	Increased	No change
<input type="checkbox"/> D	No change	Increased	Increased

(b) The equation can also be written as



Which combination of expressions is correct?

(1)

- A** $\Delta H_1^\ominus = \Delta H_2^\ominus$ and $K_{c1} = K_{c2}$
- B** $\Delta H_1^\ominus = \frac{1}{2}\Delta H_2^\ominus$ and $K_{c1} = \frac{1}{2}K_{c2}$
- C** $\Delta H_1^\ominus = \sqrt{\Delta H_2^\ominus}$ and $K_{c1} = \sqrt{K_{c2}}$
- D** $\Delta H_1^\ominus = \frac{1}{2}\Delta H_2^\ominus$ and $K_{c1} = \sqrt{K_{c2}}$

(Total for Question 5 = 2 marks)

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- 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)

- 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.



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)

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

- A $1 \text{ mol KCl(s)} + 2 \text{ mol of H}_2\text{O(l)} \rightarrow K^+(\text{aq}) + Cl^-(\text{aq})$
 B $1 \text{ mol KCl(s)} + \text{excess H}_2\text{O(l)} \rightarrow K^+(\text{aq}) + Cl^-(\text{aq})$
 C $1 \text{ mol KCl(g)} + 2 \text{ mol of H}_2\text{O(l)} \rightarrow K^+(\text{aq}) + Cl^-(\text{aq})$
 D $1 \text{ mol KCl(g)} + \text{excess H}_2\text{O(l)} \rightarrow K^+(\text{aq}) + Cl^-(\text{aq})$

(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?

	$\Delta H_{\text{solution}}^{\ominus}$	$\Delta H_{\text{hydration}}^{\ominus}$	Lattice energy
<input type="checkbox"/> A	negative	negative	positive
<input type="checkbox"/> B	positive	negative	negative
<input type="checkbox"/> C	negative	positive	negative
<input type="checkbox"/> 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)

- 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)

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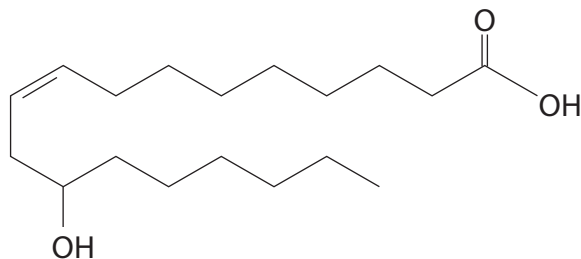
13 In a separation using high-performance liquid chromatography, the stationary phase was polar and the mobile phase was non-polar.

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)

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



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

(1)

- 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

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

Which fragment produces this peak?

(1)

- A COOH^+
- B C_4H_7^+
- C $\text{CH}=\text{CHCHOH}^+$
- D CH_2CO_2^+

(Total for Question 14 = 2 marks)

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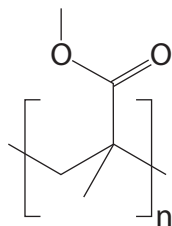
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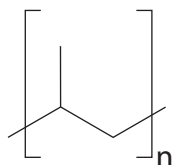


15 Which polymer is manufactured by a condensation polymerisation of a **single** substance?

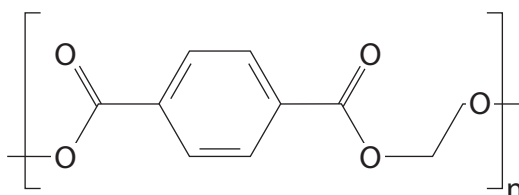
- A Poly(2-methylpropenoate)



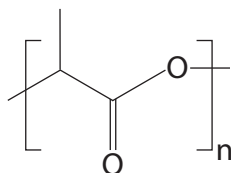
- B Poly(propene)



- C Poly(ethylene terephthalate)



- D Poly(lactic acid)



(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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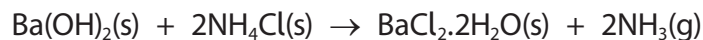
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SECTION B

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.



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

- (ii) Give a test, with the result, for $\text{NH}_3(\text{g})$. (1)

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

Include a sign and units in your answer.

The standard entropy of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ is $+202.9 \text{ J K}^{-1} \text{ mol}^{-1}$.

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

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

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(c) (i) The total standard entropy change, $\Delta S_{\text{total}}^{\ominus}$, is $+227.5 \text{ J K}^{-1} \text{ mol}^{-1}$.

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

Include a sign and units in your answer.

(3)

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

(1)

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(Total for Question 16 = 10 marks)



P 4 8 3 8 5 A 0 1 1 2 8

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)

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

(1)

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

(2)

(ii) Describe **two** observations you expect to make when this reaction occurs.

(2)



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- (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)

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- (ii) Draw the **skeletal** formula of the organic product of this reaction.

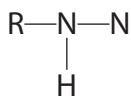
(1)

- (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)



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

(2)

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(e) (i) Propanone reacts with hydrogen cyanide to form a cyanohydrin, with structural formula $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$.

Give the fully displayed formula and the systematic name for this compound.

(2)

Fully displayed formula

Systematic name

(ii) Draw the mechanism for the reaction of propanone with hydrogen cyanide, in the presence of cyanide ions, to form the cyanohydrin, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$. Use curly arrows to show the movement of electron pairs.

(4)

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



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)

(Total for Question 17 = 22 marks)



P 4 8 3 8 5 A 0 1 5 2 8

(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)

(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)

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

(2)

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(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)

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(Total for Question 18 = 17 marks)

TOTAL FOR SECTION B = 49 MARKS

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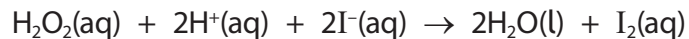


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SECTION C

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.



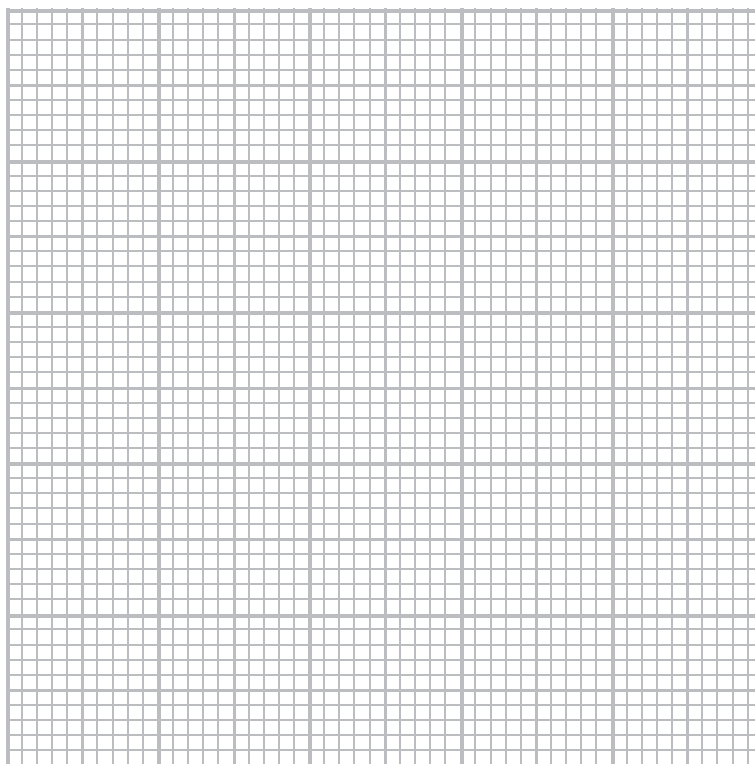
- (a) First, the concentration of hydrogen peroxide is measured at different times, while keeping the concentrations of iodide and hydrogen ions constant.

The following results are obtained.

$t / 10^3 \text{ s}$	$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$
0	0.20
2	0.14
4	0.09
6	0.06
8	0.04
10	0.03

- (i) Plot a graph of $[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$ against $t / 10^3 \text{ s}$.

(2)



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

Show your working on your graph, together with their values.

(2)

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

Justify your answer.

(2)

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

Mixtures are prepared using 0.10 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 / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	3.0	3.0	3.0	1.0	1.06×10^{-4}
2	2.0	3.0	3.0	2.0	7.00×10^{-5}
3	1.0	3.0	3.0	3.0	3.50×10^{-5}
4	3.0	3.0	2.0	2.0	1.08×10^{-4}
5	3.0	3.0	1.0	3.0	1.05×10^{-4}

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

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

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(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)

Iodide ions

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Hydrogen ions

.....



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

(1)

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

(1)

(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)

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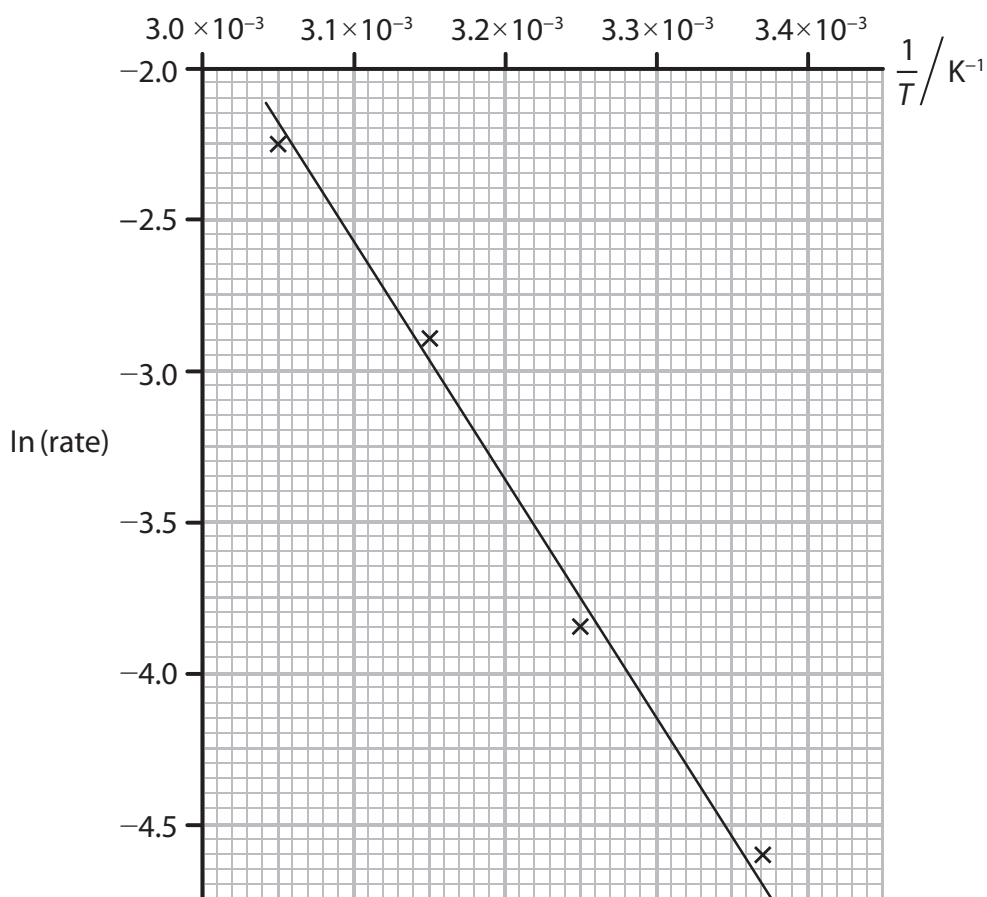
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- (c) (i) The activation energy for this reaction is found by keeping the concentrations of reactants constant and repeating the reaction at different temperatures.

A graph of $\ln(\text{rate})$ 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.

$$\ln(\text{rate}) = \frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad [R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}]$$

Include a sign and units with your answer.

(3)



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*(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)

Explanation

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(Total for Question 19 = 21 marks)

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



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The Periodic Table of Elements

1	2	3	4	5	6	7	0 (8)										
(1) 6.9 Li lithium 3 23.0 Na sodium 11 39.1 K potassium 19 85.5 Rb rubidium 37 132.9 Cs caesium 55 [223] Fr francium 87	(2) 9.0 Be beryllium 4 24.3 Mg magnesium 12 40.1 Ca calcium 20 87.6 Sr strontium 38 137.3 Ba barium 56 [226] Ra radium 88	(3) 45.0 Sc scandium 21 88.9 Y yttrium 39 138.9 La* lanthanum 57 [227] Ac* actinium 89	(4) 47.9 Ti titanium 22 91.2 Zr zirconium 40 178.5 Hf hafnium 72 [261] Rf rutherfordium 104	(5) 50.9 V vanadium 23 92.9 Nb niobium 41 180.9 Ta tantalum 73 [262] Db dubnium 105	(6) 52.0 Cr chromium 24 95.9 Mo molybdenum 42 183.8 W tungsten 74 [266] Sg seaborgium 106	(7) 54.9 Mn manganese 25 [98] Tc technetium 43 186.2 Re rhenium 75 [264] Bh bohrium 107	(8) 55.8 Fe iron 26 101.1 Ru ruthenium 44 190.2 Os osmium 76 [277] Hs hassium 108	(9) 58.9 Co cobalt 27 102.9 Rh rhodium 45 192.2 Ir iridium 77 [268] Mt meitnerium 109	(10) 58.7 Ni nickel 28 106.4 Pd palladium 46 195.1 Pt platinum 78 [271] Ds darmstadtium 110	(11) 63.5 Cu copper 29 107.9 Ag silver 47 197.0 Au gold 79 [272] Rg roentgenium 111	(12) 65.4 Zn zinc 30 65.4 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(13) 10.8 B boron 5 27.0 Al aluminium 13 28.1 Si silicon 14 72.6 Ge germanium 31 72.6 Ga gallium 32 74.9 As arsenic 33 74.9 Se selenium 34 79.0 Br bromine 35 79.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(14) 12.0 C carbon 6 12.0 N nitrogen 7 14.0 O oxygen 8 16.0 S sulfur 16 32.1 P phosphorus 15 31.0 S sulfur 16 32.1 Cl chlorine 17 35.5 Ar argon 18 39.9 Br bromine 35 79.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(15) 14.0 N nitrogen 7 14.0 O oxygen 8 16.0 S sulfur 16 32.1 P phosphorus 15 31.0 S sulfur 16 32.1 Cl chlorine 17 35.5 Ar argon 18 39.9 Br bromine 35 79.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(16) 16.0 O oxygen 8 16.0 S sulfur 16 32.1 P phosphorus 15 31.0 S sulfur 16 32.1 Cl chlorine 17 35.5 Ar argon 18 39.9 Br bromine 35 79.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(17) 19.0 F fluorine 9 19.0 Cl chlorine 17 35.5 Ar argon 18 39.9 Br bromine 35 79.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]	(18) 4.0 He helium 2 20.2 Ne neon 10 20.2 Ar argon 18 39.9 Kr krypton 36 83.8 Xe xenon 54 126.9 I iodine 53 127.6 Te tellurium 52 127.6 Sb antimony 51 121.8 Sn tin 50 118.7 In indium 49 114.8 Cd cadmium 48 112.4 Hg mercury 80 200.6 Pb lead 82 207.2 Tl thallium 81 204.4 Bi bismuth 83 209.0 Po polonium 84 [209] At astatine 85 [210] Rn radon 86 [222]

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series

* Actinide series

