Write your name here

Surname	Other names

Pearson Edexcel
International
Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

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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P 4 8 3 8 5 A 0 1 2 8

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?

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

☒ **A** acid 1 + base 1 ⇌ acid 2 + base 2

☒ **B** acid 1 + base 2 ⇌ base 1 + acid 2

☒ **C** acid 1 + base 2 ⇌ acid 2 + base 1

☒ **D** acid 2 + base 2 ⇌ 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 $K_w = 1.00 \times 10^{-14}$ mol^2 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 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 pK_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.

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

(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)

	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

(b) The equation can also be written as

Equation 2 $2HI(g) \rightleftharpoons H_2(g) + I_2(g) \quad \Delta H_2^{\ominus}$ Equilibrium constant = K_{c2}

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.

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

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)

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 $H_2O(l) \rightarrow K^+(aq) + Cl^-(aq)$

☒ **B** 1 mol KCl(s) + excess $H_2O(l) \rightarrow K^+(aq) + Cl^-(aq)$

☒ **C** 1 mol KCl(g) + 2 mol of $H_2O(l) \rightarrow K^+(aq) + Cl^-(aq)$

☒ **D** 1 mol KCl(g) + excess $H_2O(l) \rightarrow K^+(aq) + Cl^-(aq)$

(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)

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

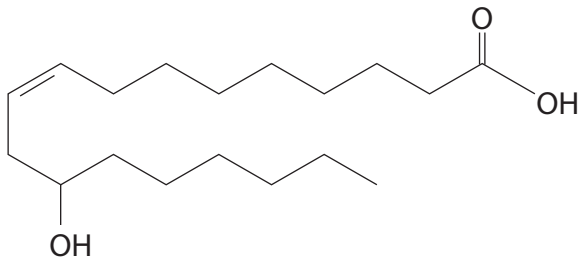
☒ **B** 1-chloropentane

☒ **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** $CH{=}CHCHOH^+$

☒ **D** $CH_2CO_2^+$

(Total for Question 14 = 2 marks)

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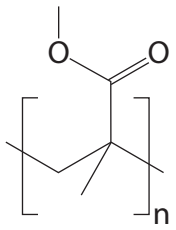
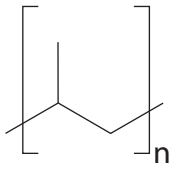
15 Which polymer is manufactured by a condensation polymerisation of a **single** substance?

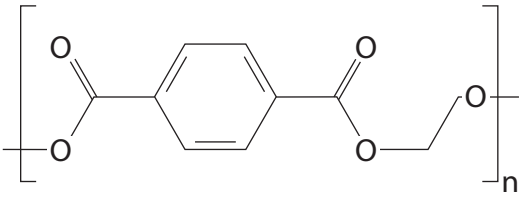
☒ **A** Poly(2-methylpropenoate)



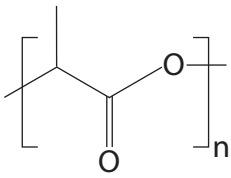
☒ **B** Poly(propene)



☒ **C** Poly(ethylene terephthalate)



☒ **D** Poly(lactic acid)



(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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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.

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

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

(1)

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

(1)

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(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 +202.9 J K^{-1} mol^{-1}.

Use your Data Booklet for the other values.

(3)

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

(1)

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(c) (i) The total standard entropy change, $\Delta S^{\ominus}_{total}$, 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)

(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)

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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)

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

(2)

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(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.

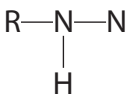
(1)

(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 $(CH_3)_2C(OH)CN$.

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, $(CH_3)_2C(OH)CN$.
Use curly arrows to show the movement of electron pairs.

(4)

*(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)

(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)

First reagent .....

.....

.....

Second reagent .....

.....

.....

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

(1)

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

(i) Give the structural formula of propanoic acid.

(1)

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

Step 1 **Step 2**

Propanoic acid ⟶ propanoyl chloride ⟶ propyl propanoate

Name the reagents for each step.

(2)

Step 1 .....

Step 2 .....

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(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)

(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)

(Total for Question 18 = 17 marks)

TOTAL FOR SECTION B = 49 MARKS

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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.

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

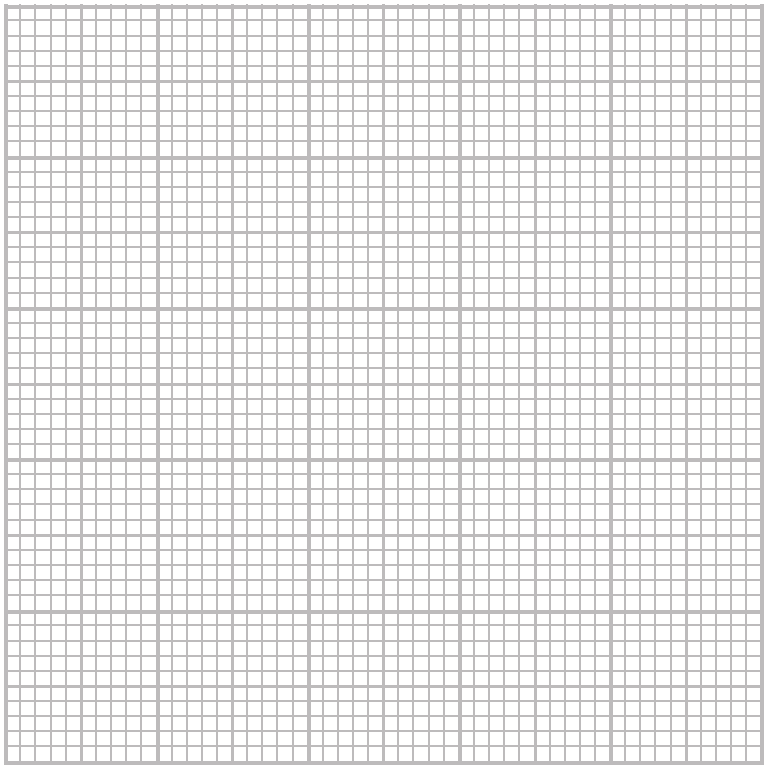
(a) First, the concentration of hydrogen peroxide is measured at different times, while keeping the concentrations of iodide and hydrogen ions constant.

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

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

(2)



(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 /mol dm^{-3} 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 .....

.....

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).

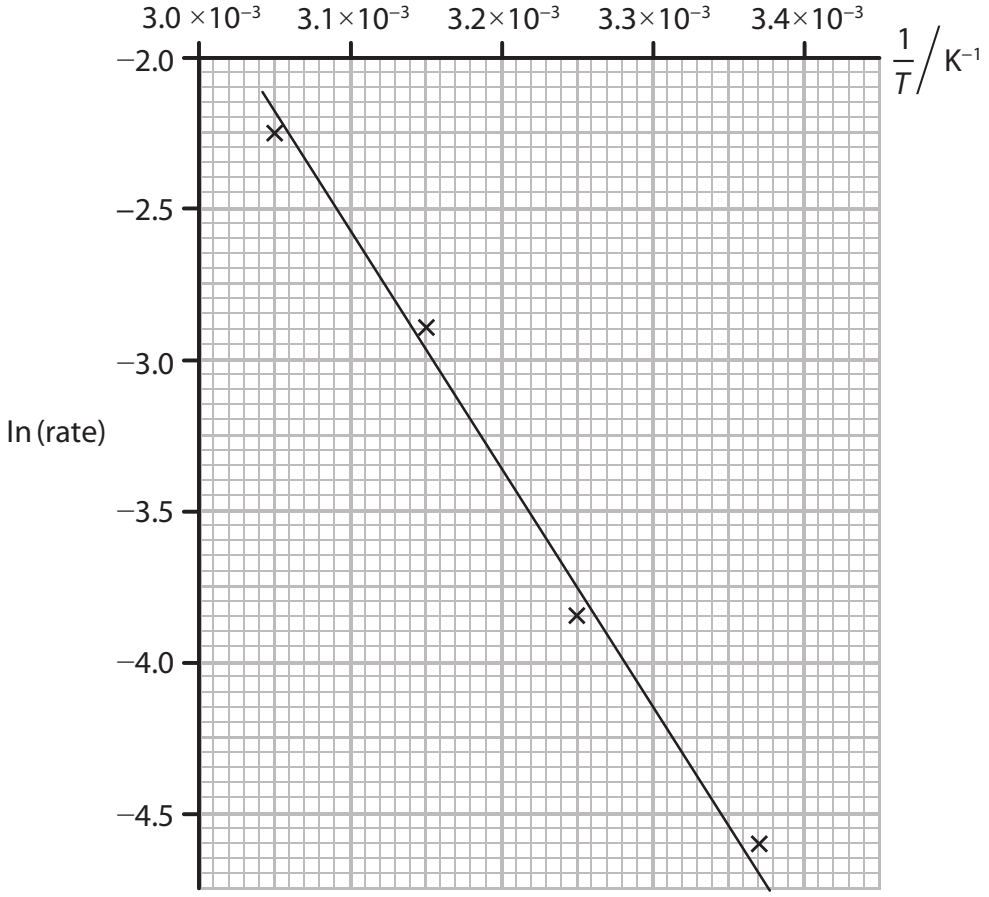
(1)

(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)

(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.

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

Include a sign and units with your answer.

(3)

*(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)
							1.0 H hydrogen 1										(18)
																	4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

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

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103