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Candidate surname	Other names

Pearson Edexcel
International
Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Tuesday 2 June 2020

Afternoon (Time: 1 hour 40 minutes) | Paper Reference **WCH04/01**

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

Candidates must have: Scientific calculator
Data Booklet
Ruler

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.
- Show all your working in calculations and give units where appropriate.
- Check your answers if you have time at the end.

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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 Butanone is warmed with iodine in the presence of sodium hydroxide.
What is the formula of the crystalline solid that is formed?

☒ **A** CH_3I

☒ **B** CHI_3

☒ **C** $CH_2ICOC_2H_5$

☒ **D** C_2H_5COOH

(Total for Question 1 = 1 mark)

2 Dinitrogen tetroxide, N_2O_4, forms an equilibrium mixture with nitrogen dioxide, NO_2. Dinitrogen tetroxide is colourless and nitrogen dioxide is brown.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.2\,kJ\,mol^{-1}$$

(a) A mixture of dinitrogen tetroxide and nitrogen dioxide was placed in a gas syringe. The end of the syringe was sealed and the plunger pushed to increase the pressure. What would you see?

(1)

☒ **A** No change in colour.

☒ **B** The contents of the syringe initially turn darker and then go lighter in colour.

☒ **C** The contents of the syringe initially turn lighter and then go darker in colour.

☒ **D** The contents of the syringe just go lighter in colour.

(b) What happens to the mixture when the temperature of the equilibrium is raised by 50 °C?

(1)

☒ **A** The equilibrium moves to the right and the mixture darkens.

☒ **B** The equilibrium moves to the right and the mixture lightens.

☒ **C** The equilibrium moves to the left and the mixture darkens.

☒ **D** The equilibrium moves to the left and the mixture lightens.

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(c) What is the expression for the partial pressure of nitrogen dioxide gas?

(1)

☒ **A** Total pressure × moles of nitrogen dioxide gas

☒ **B** Total pressure × moles of nitrogen dioxide gas × 2

☒ **C** Total pressure × (moles of nitrogen dioxide gas ÷ total number of moles of gas)

☒ **D** Total pressure ÷ (moles of nitrogen dioxide gas ÷ total number of moles of gas)

(d) The equilibrium partial pressures of dinitrogen tetroxide and nitrogen dioxide are 0.67 atm and 0.33 atm respectively at 27 °C.

What is the value of K_p at 27 °C?

(1)

☒ **A** 2.030

☒ **B** 1.360

☒ **C** 0.493

☒ **D** 0.163

(Total for Question 2 = 4 marks)

3 When heated at 500 °C, magnesium carbonate decomposes in an endothermic reaction.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

What are the signs of the entropy changes at 500 °C?

	ΔS_{system}	$\Delta S_{surroundings}$
☒ **A**	negative	negative
☒ **B**	negative	positive
☒ **C**	positive	negative
☒ **D**	positive	positive

(Total for Question 3 = 1 mark)

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4 Different types of radiation are used in organic chemistry.

(a) Which of these types of radiation is used for initiating reactions?

(1)

☒ **A** Infrared

☒ **B** Microwave

☒ **C** Radio wave

☒ **D** Ultraviolet

(b) Which of these types of radiation is used in nuclear magnetic resonance, nmr?

(1)

☒ **A** Infrared

☒ **B** Microwave

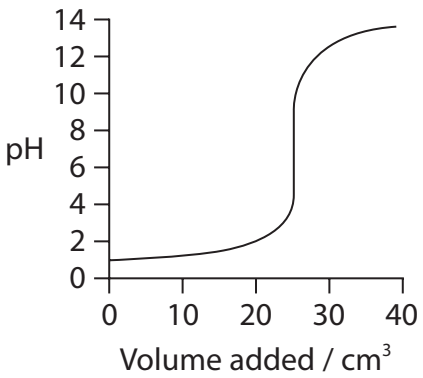
☒ **C** Radio wave

☒ **D** Ultraviolet

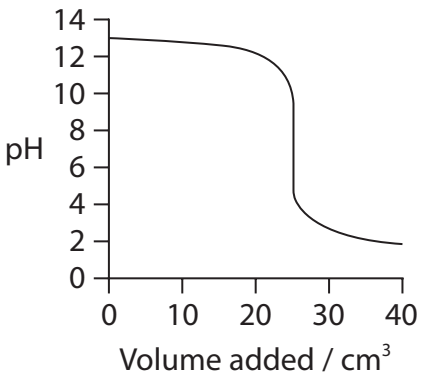
(Total for Question 4 = 2 marks)

5 The titration curves shown were obtained using different acids and bases, each with a concentration of 0.1 mol dm^{-3}.

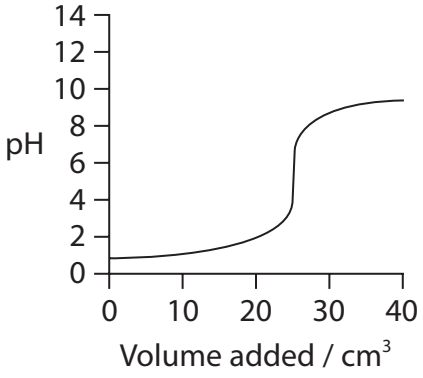
Curve **1**



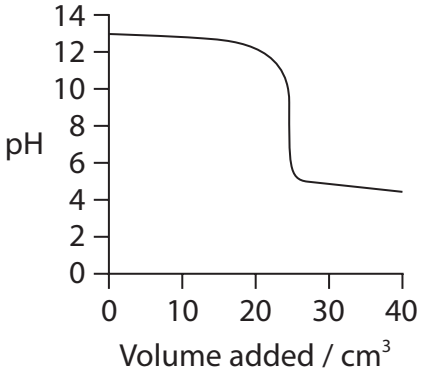
Curve **2**



Curve **3**



Curve **4**



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(a) Which curve shows the pH change when nitric acid is added to 25 cm^3 of sodium hydroxide?

(1)

☒ **A** Curve **1**

☒ **B** Curve **2**

☒ **C** Curve **3**

☒ **D** Curve **4**

(b) Which curve shows the pH change when ammonia is added to 25 cm^3 of hydrochloric acid?

(1)

☒ **A** Curve **1**

☒ **B** Curve **2**

☒ **C** Curve **3**

☒ **D** Curve **4**

(c) Which of these indicators would be **most** suitable for the titration shown by Curve **3**?

(1)

	Indicator	pK_{in}
☒ **A**	methyl violet	0.8
☒ **B**	methyl yellow	3.5
☒ **C**	bromocresol green	4.7
☒ **D**	phenol red	7.9

(Total for Question 5 = 3 marks)

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6 The expression for the ionic product of water is

☒ **A** $K_w = [H^+] \times [OH^-]$

☒ **B** $K_w = \dfrac{[H^+]}{[OH^-]}$

☒ **C** $K_w = \dfrac{[H^+] \times [OH^-]}{[H_2O]}$

☒ **D** $K_w = \dfrac{[H_2O]}{[H^+] \times [OH^-]}$

(Total for Question 6 = 1 mark)

7 This question concerns the kinetics of the reaction between nitrogen(II) oxide and hydrogen.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

This reaction is second order with respect to nitrogen(II) oxide and first order with respect to hydrogen and therefore third order overall.

(a) By what factor will the initial rate increase if the concentration of nitrogen(II) oxide is doubled and the concentration of hydrogen is tripled?

(1)

☒ **A** 3

☒ **B** 9

☒ **C** 12

☒ **D** 18

(b) The units of the rate constant *k* of this third order reaction are

(1)

☒ **A** $mol^3\,dm^{-9}\,s^{-1}$

☒ **B** $dm^9\,mol^{-3}\,s^{-1}$

☒ **C** $mol^2\,dm^{-6}\,s^{-1}$

☒ **D** $dm^6\,mol^{-2}\,s^{-1}$

(Total for Question 7 = 2 marks)

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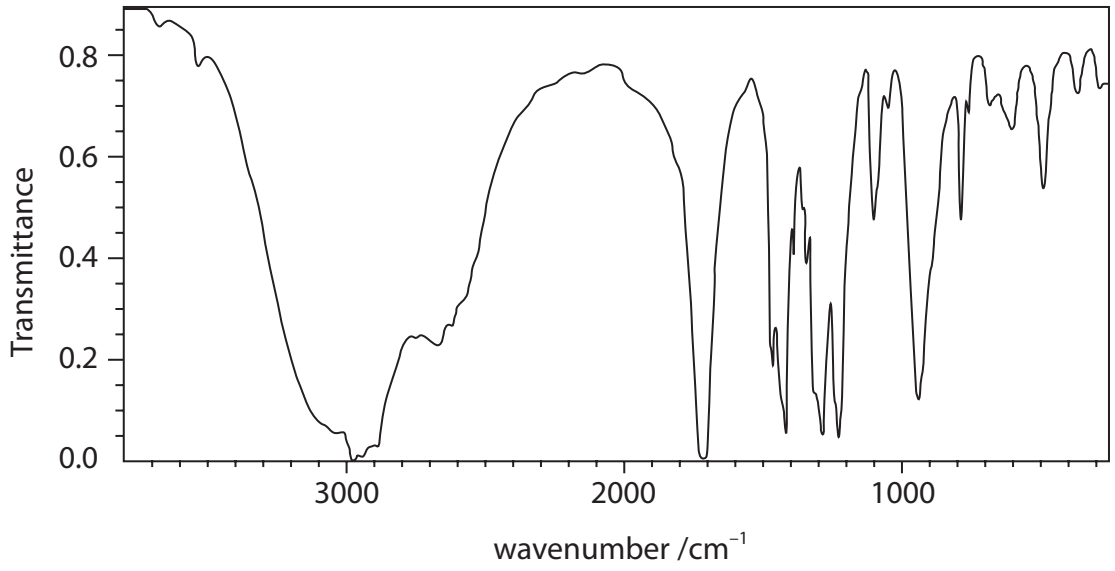
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8 Which interaction between propanone and water molecules contributes **most** to the solubility of propanone in water?

- ☒ **A** London forces
- ☒ **B** Dipole-dipole forces
- ☒ **C** Hydrogen bonds
- ☒ **D** Ion-dipole forces

(Total for Question 8 = 1 mark)

9 Which compound gives this infrared spectrum?



- ☒ **A** Propan-1-ol
- ☒ **B** Propanoic acid
- ☒ **C** Propanal
- ☒ **D** Propanone

(Total for Question 9 = 1 mark)

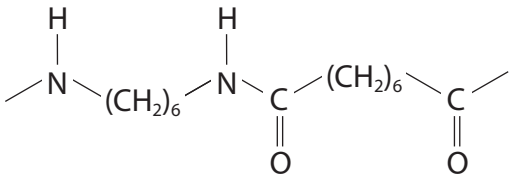
10 Ethanoyl chloride, CH_3COCl, reacts with

- ☒ **A** ammonia to form an amine.
- ☒ **B** water to form a halogenoalkane.
- ☒ **C** a halogenoalkane to form a ketone.
- ☒ **D** an alcohol to form an ester.

(Total for Question 10 = 1 mark)

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11 A section of a polymer is shown.



Which of these monomers would form this polymer?

☒ **A** $H_2N(CH_2)_6NH_2$ and $HO(CH_2)_6OH$

☒ **B** $H_2N(CH_2)_6NH_2$ and $ClOC(CH_2)_6COCl$

☒ **C** $HO(CH_2)_6NH_2$ and $HOOC(CH_2)_6COOH$

☒ **D** $H_2N(CH_2)_6COOH$ alone

(Total for Question 11 = 1 mark)

12 What is the enthalpy change of hydration for the ammonium ion?

Data

$\Delta H_{solution}$ $(NH_4Cl) = +20\,kJ\,mol^{-1}$

$\Delta H_{hydration}$ $(Cl^-) = -378\,kJ\,mol^{-1}$

Lattice Energy $(NH_4Cl) = -705\,kJ\,mol^{-1}$

☒ **A** $-307\,kJ\,mol^{-1}$

☒ **B** $+307\,kJ\,mol^{-1}$

☒ **C** $-347\,kJ\,mol^{-1}$

☒ **D** $+347\,kJ\,mol^{-1}$

(Total for Question 12 = 1 mark)

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13 Data for some ions are shown in the table.

Ion	Ionic radius/nm	Ionic charge
W	0.072	+2
X	0.102	+1
Y	0.100	+2
Z	0.138	+1

Which of these ions has the hydration enthalpy of the greatest magnitude?

☒ **A** W

☒ **B** X

☒ **C** Y

☒ **D** Z

(Total for Question 13 = 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.

14 This question is about carbonic acid. It is a weak acid that dissociates as shown.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

(a) (i) Calculate the pH of a solution of carbonic acid with a concentration of $0.00125\ mol\ dm^{-3}$. Assume there is no dissociation of the HCO_3^- ion.

[pK_a for carbonic acid = 6.35]

(3)

(ii) State **two** further assumptions you have made when calculating the pH in (a)(i).

(2)

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(b) Blood is buffered by a mixture of carbonic acid (H_2CO_3) and hydrogencarbonate ions (HCO_3^-).

(i) The pH of blood is maintained at 7.4. Calculate the hydrogen ion concentration in the blood and hence the ratio of carbonic acid to hydrogencarbonate ions.

(3)

*(ii) Explain how this buffer solution resists a change in pH when extra hydrogen ions enter the blood.

(3)

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15 An organic compound **A** contains only carbon, hydrogen and oxygen.

(a) (i) On analysis, **A** was found to contain 54.55% carbon and 9.09% hydrogen by mass. Show by calculation that the empirical formula of **A** is C_2H_4O.

(3)

(ii) The molar mass of **A** is 88 g mol^{-1}. Deduce the molecular formula of **A**.

(1)

*(b) The results of tests carried out on separate samples of **A** are shown.

	Test	Results
1	Addition of sodium	Effervescence Gas burns with a squeaky pop
2	Addition of sodium hydrogencarbonate solution	No visible reaction
3	Addition of 2,4-dinitrophenylhydrazine	Red precipitate formed
4	Addition of Tollens' reagent and warm	No visible reaction

Explain what can be deduced about the functional groups present in **A** from each of these test results.

(4)

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(c) The high resolution proton nmr spectrum of **A** gives four peaks, **P**, **Q**, **R** and **S**.

Peak	**P**	**Q**	**R**	**S**
Number of hydrogen atoms	2	1	2	3
Splitting pattern	triplet	singlet	triplet	singlet

(i) Draw a structure for **A** which is consistent with these data and **all** the information from (a) and (b), labelling the hydrogen environments responsible for peaks **Q** and **S**.

(3)

(ii) State the further information that you need to assign the hydrogen environments responsible for peaks **P** and **R**.

(1)

(iii) Explain the splitting pattern for **one** of the triplets.

(1)

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16 This question is about the production of ammonia by the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92.2\,kJ\,mol^{-1}$$

(a) (i) Using your Data Booklet, calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction.
Include a sign and units in your answer.

(3)

[note that Data Booklet values for the standard molar entropy, $S^{\ominus}$, of elements are per atom]

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

(1)

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(b) (i) Calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 400 K. Include a sign and units in your answer.

(2)

(ii) Using your answers from (a)(i) and (b)(i), calculate the total standard entropy change, $\Delta S^{\ominus}_{\text{total}}$, at 400 K and explain whether or not the reaction is feasible at this temperature.

(2)

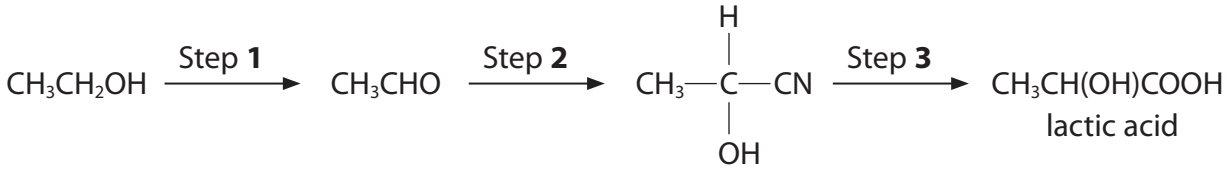
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(Total for Question 16 = 8 marks)

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17 This question is about carboxylic acids. A sequence of reactions for the formation of lactic acid is shown.



(a) A mixture of hydrogen cyanide and cyanide ions is required for Step **2**.

Draw the mechanism for Step **2**. Include curly arrows, and any relevant dipoles and lone pairs of electrons.

(4)

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(b) (i) The reaction in (a) is carried out at a carefully controlled pH.

Given that hydrogen cyanide is a weak acid, suggest why this reaction occurs more slowly at both high and low concentrations of hydrogen ions.

(2)

High concentration .....

.....

Low concentration .....

.....

(ii) The product formed in Step **2** exists as two optical isomers.
Draw a diagram of these two isomers to illustrate their optical isomerism.

(1)

*(iii) By referring to your mechanism, explain whether or not the product formed in Step **2** would show optical activity.

(2)

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(c) (i) Name the type of reaction in Step **3**.

(1)

.....

(ii) Give the systematic name of lactic acid.

(1)

.....

(d) Lactic acid is a weak acid. Explain what is meant by the terms 'weak' and 'acid'.

(2)

Weak .....

.....

Acid .....

.....

(e) Propanoic acid, another carboxylic acid, reacts with methanol in the presence of an acid catalyst to produce an ester.

$$CH_3CH_2COOH(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2COOCH_3(l) + H_2O(l)$$

Name the ester formed and draw its **skeletal** formula.

(2)

Name	Skeletal formula

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(f) In an experiment to determine the equilibrium constant, K_c, for this reaction, 1.0 mol of propanoic acid was mixed with 1.0 mol of methanol and 2.0 mol of water.

A small quantity of hydrochloric acid was also added to catalyse the reaction. The mixture was left for a week to reach equilibrium.

After this time, 0.52 mol of propanoic acid was present. The total volume of the equilibrium mixture was 134 cm^3.

(i) Write the expression for the equilibrium constant, K_c, for the reaction in (e).

(1)

(ii) Using the expression in (f)(i), calculate the value of K_c for this reaction. Give your answer to two significant figures and include units if appropriate.

(4)

(Total for Question 17 = 20 marks)

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SECTION C

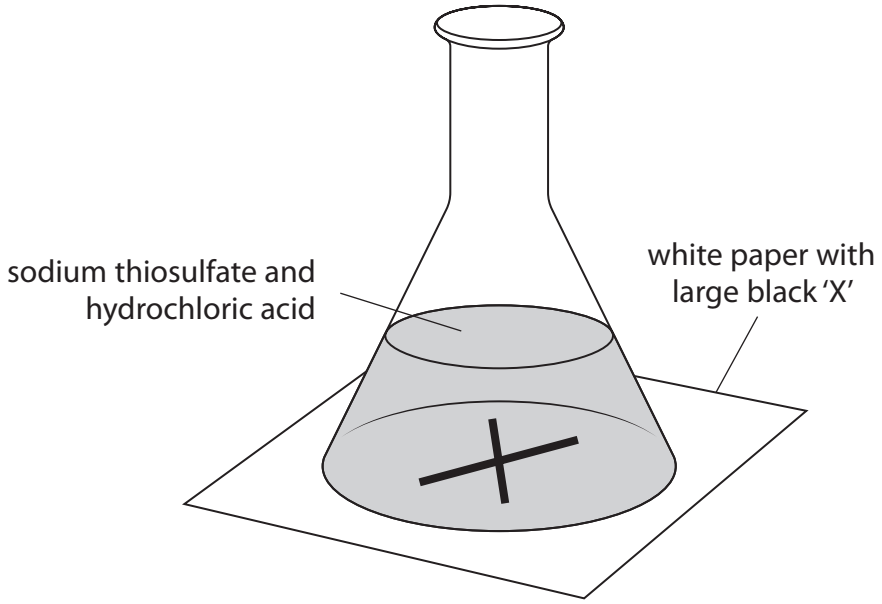
Answer ALL the questions. Write your answers in the spaces provided.

18 This question is about the reaction between sodium thiosulfate solution and hydrochloric acid.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$

(a) A series of experiments was carried out at different temperatures to determine the activation energy of the reaction, using the apparatus shown. The time taken (t) for the solution to become cloudy and obscure the cross was recorded.

The reciprocal of time ($1/t$) was used as a measure of the rate of the reaction.



(i) State why the solution becomes cloudy.

(1)

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(ii) Explain why $1/t$ can be used as a measure of the rate.

(2)

(b) The results obtained in this experiment are shown.

Temperature (T) / K	$1/T$ / K^{-1}	Time (t) / s	$1/t$ / s^{-1}	ln($1/t$)
298	3.36×10^{-3}	58	0.0172	–4.06
308	3.25×10^{-3}	36	0.0278	–3.58
317	3.15×10^{-3}	23	0.0435	–3.14
328	3.05×10^{-3}	14	0.0714	–2.64
338		9		

(i) Complete the table.

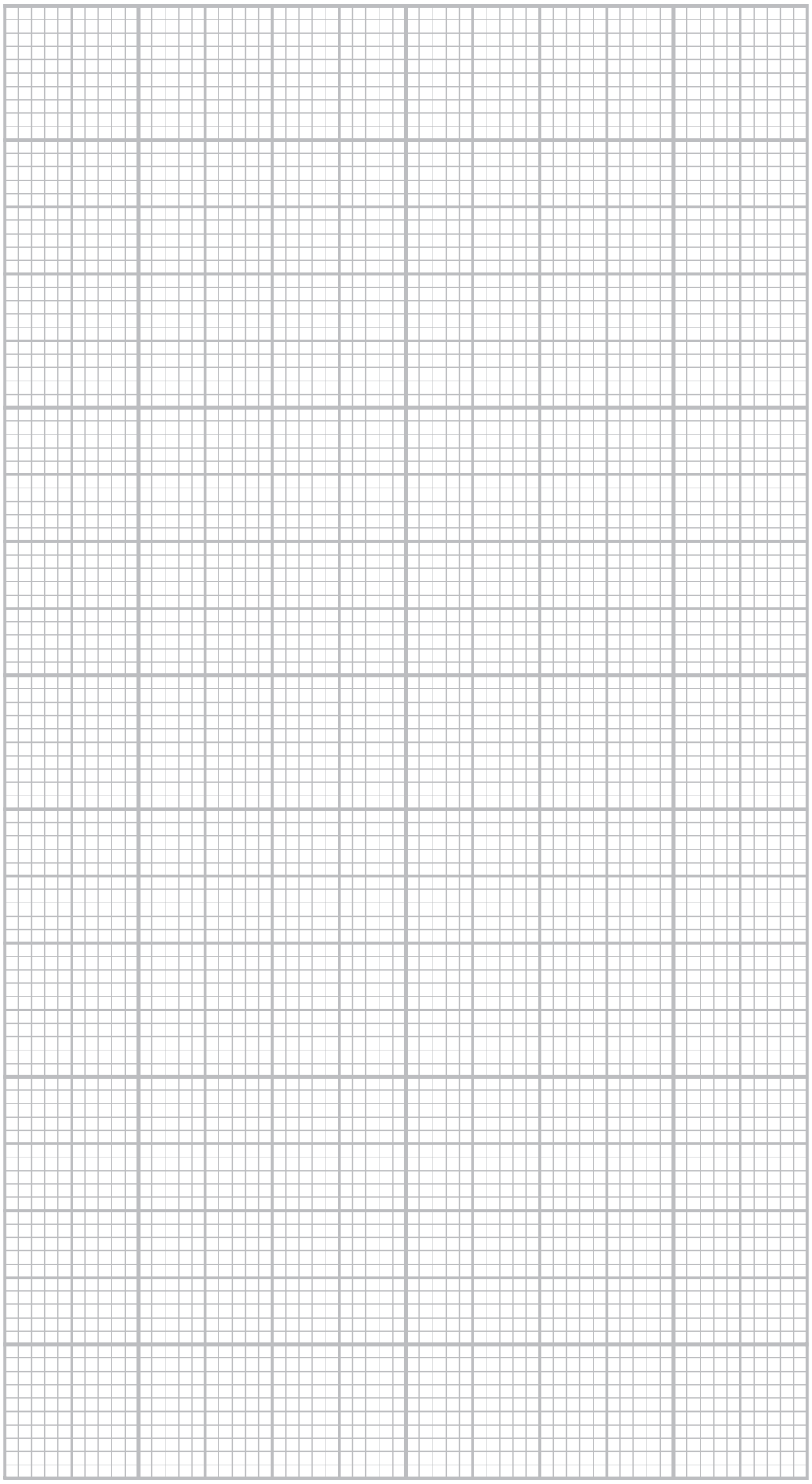
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(ii) On the grid, plot ln(1/*t*) against 1/*T*.

(3)



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(iii) State the meaning of the term 'activation energy'.

(1)

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(iv) From the graph, determine the gradient of the line.
Include a sign and units in your answer.

(2)

(v) Calculate the activation energy for this reaction.
Include a sign and units in your answer.

The Arrhenius equation for this experiment can be expressed as

$$\ln(1/t) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(2)

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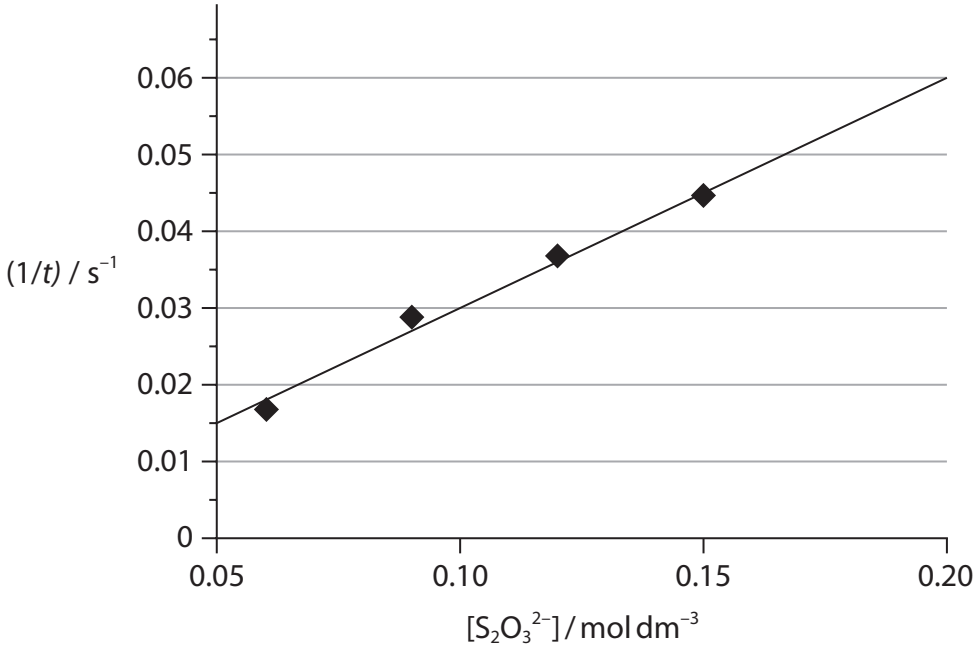
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(c) Another series of experiments was carried out at constant temperature to determine the order of reaction with respect to thiosulfate ions, $S_2O_3^{2-}$.

The time taken (*t*) for the solution to become cloudy and obscure the cross was recorded.

A graph was drawn from the data, using reciprocal time (1/*t*) as a measure of rate.



(i) In these experiments, suggest why the acid was in considerable excess.

(1)

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(ii) State the order of reaction with respect to sodium thiosulfate and justify your answer by referring to the graph in (c).

(2)

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(d) Further experiments were carried out to determine the order of reaction with respect to H^+ ions and hence to identify the species involved in the rate-determining step.

(i) State what is meant by the term 'rate-determining step'.

(1)

.....

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(ii) The reaction is first order with respect to H^+ ions. Using this fact and your answer to (c)(ii), suggest the **formula** of the intermediate formed during the rate-determining step.

(1)

(Total for Question 18 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li thium 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 odium 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 tassium 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 bidium 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
32.9 Cs esium 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 ancium 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

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