Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

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

Wednesday 12 June 2013 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or 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 ▶

P41572A

6/5/7/7/7/7/

P 4 1 5 7 2 A 0 1 2 4

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 The overall equation for a reaction between two chemicals, M and N, is

$$M + 2N \rightarrow P + Q$$

(a) This reaction occurs spontaneously at room temperature. Which of the following **must** be true?

(1)

☒ **A** $\Delta H^{\ominus}_{reaction}$ is positive.

☒ **B** $\Delta H^{\ominus}_{reaction}$ is negative.

☒ **C** $\Delta S^{\ominus}_{total}$ is positive.

☒ **D** $\Delta S^{\ominus}_{total}$ is negative.

(b) The reaction above occurs in two stages via an intermediate, T.

$M + N \rightarrow T$ slow

$N + T \rightarrow P + Q$ fast

From this it can be deduced that the rate equation for the reaction between M and N is

(1)

☒ **A** rate = k[M][N]

☒ **B** rate = k[M][N]^2

☒ **C** rate = k[M][T]

☒ **D** rate = k[N][T]

(Total for Question 1 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

2 Calcium carbonate decomposes at high temperature to form calcium oxide and carbon dioxide:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Calcium carbonate is **thermodynamically** stable at room temperature because for this reaction

- ☒ **A** the activation energy is high.
- ☒ **B** the enthalpy change, ΔH, is positive.
- ☒ **C** entropy change of the system (ΔS_{system}) is positive.
- ☒ **D** entropy change of the system (ΔS_{system}) is negative.

(Total for Question 2 = 1 mark)

3 2-methylpropane has a smaller standard molar entropy at 298 K than butane. The best explanation for this is that 2-methylpropane has

- ☒ **A** a lower boiling temperature.
- ☒ **B** a higher standard molar enthalpy change of formation.
- ☒ **C** fewer ways of distributing energy quanta.
- ☒ **D** more ways of distributing energy quanta.

(Total for Question 3 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

4 (a) For the equilibrium reaction between hydrogen and iodine

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

increasing the pressure of the system

(1)

☒ **A** has no effect on the rate or the position of equilibrium.

☒ **B** increases the rate but does not affect the position of equilibrium.

☒ **C** increases the rate and shifts the equilibrium to the right.

☒ **D** increases the rate and shifts the equilibrium to the left.

(b) The equation for the equilibrium reaction between hydrogen and iodine may also be written as

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

This change to the equation, compared to that in part (a),

(1)

☒ **A** has no effect on the value of the equilibrium constant.

☒ **B** halves the value of the equilibrium constant.

☒ **C** doubles the value of the equilibrium constant.

☒ **D** square roots the value of the equilibrium constant.

(Total for Question 4 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

5 The first stage in the manufacture of nitric acid is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \quad \Delta H = -906 \text{ kJ mol}^{-1}$$

(a) In modern industrial plants this reaction is carried out at a pressure of around 3 atm. Which of the following statements is **incorrect**? The raised pressure

(1)

☒ **A** helps push the reactants through the reactor.

☒ **B** shifts the position of equilibrium to the right.

☒ **C** increases the cost of the reactor.

☒ **D** increases the energy cost of this part of the process.

(b) A platinum-rhodium alloy catalyst is used in this reaction. Which of the following statements is **incorrect**? The catalyst

(1)

☒ **A** lowers the activation energy of the reaction.

☒ **B** has no effect on the equilibrium constant for the reaction.

☒ **C** alters the enthalpy change of the reaction.

☒ **D** reduces the energy cost of this part of the process.

(c) The operating temperature of this reaction is about 900 °C. The use of a high temperature

(1)

☒ **A** increases the rate of the reaction and the equilibrium yield.

☒ **B** increases the rate of the reaction and decreases the equilibrium yield.

☒ **C** decreases the rate of the reaction and the equilibrium yield.

☒ **D** decreases the rate of the reaction and increases the equilibrium yield.

(Total for Question 5 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

6 Ammonium chloride decomposes on heating:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The equilibrium constant, K_p, for this reaction equals

☒ **A** $P_{NH_3} \times P_{HCl}$

☒ **B** $\dfrac{1}{P_{NH_3} \times P_{HCl}}$

☒ **C** $\dfrac{P_{NH_3} \times P_{HCl}}{P_{NH_4Cl}}$

☒ **D** $\dfrac{P_{NH_4Cl}}{P_{NH_3} \times P_{HCl}}$

(Total for Question 6 = 1 mark)

7 The dissociation constant of water, K_w, increases with increasing temperature. When the temperature increases, water

☒ **A** remains neutral.

☒ **B** dissociates less.

☒ **C** becomes acidic.

☒ **D** becomes alkaline.

(Total for Question 7 = 1 mark)

8 The reaction between concentrated sulfuric acid and pure ethanoic acid is

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$$

The Brønsted-Lowry acids in this equilibrium are

☒ **A** CH_3COOH and H_2SO_4

☒ **B** $CH_3COOH_2^+$ and HSO_4^-

☒ **C** H_2SO_4 and $CH_3COOH_2^+$

☒ **D** CH_3COOH and HSO_4^-

(Total for Question 8 = 1 mark)

9 An aqueous solution of ethanoic acid is gradually diluted. Which of the following statements is **incorrect**?

☒ **A** The pH decreases.

☒ **B** The value of K_a is unchanged.

☒ **C** The concentration of ethanoic acid molecules decreases.

☒ **D** The proportion of ethanoic acid molecules which dissociates increases.

(Total for Question 9 = 1 mark)

10 Methyl orange and phenolphthalein are both acid-base indicators. In the titration of a strong acid against a weak alkali

☒ **A** methyl orange is a suitable indicator but phenolphthalein is not.

☒ **B** phenolphthalein is a suitable indicator but methyl orange is not.

☒ **C** both phenolphthalein and methyl orange are suitable indicators.

☒ **D** neither phenolphthalein nor methyl orange is a suitable indicator.

(Total for Question 10 = 1 mark)

11 Select the word that best describes the effect of a chiral molecule on the plane of plane-polarized light. The plane of polarization of light is

☒ **A** reflected.

☒ **B** refracted.

☒ **C** resolved.

☒ **D** rotated.

(Total for Question 11 = 1 mark)

12 An organic compound reacts with **both** acidified potassium dichromate(VI) **and** lithium tetrahydridoaluminate (lithium aluminium hydride). The organic compound could be

☒ **A** a primary alcohol.

☒ **B** an aldehyde.

☒ **C** a ketone.

☒ **D** a carboxylic acid.

(Total for Question 12 = 1 mark)

13 Ketones react with

- ☒ **A** both 2,4-dinitrophenylhydrazine solution and Tollens' reagent.
- ☒ **B** 2,4-dinitrophenylhydrazine solution but not with Tollens' reagent.
- ☒ **C** Tollens' reagent but not with 2,4-dinitrophenylhydrazine solution.
- ☒ **D** neither Tollens' reagent nor 2,4-dinitrophenylhydrazine solution.

(Total for Question 13 = 1 mark)

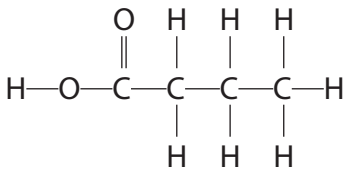
14 Ethanoic acid, CH_3COOH, may be prepared from ethanenitrile, CH_3CN. This reaction is best described as

- ☒ **A** reduction.
- ☒ **B** oxidation.
- ☒ **C** hydrolysis.
- ☒ **D** condensation.

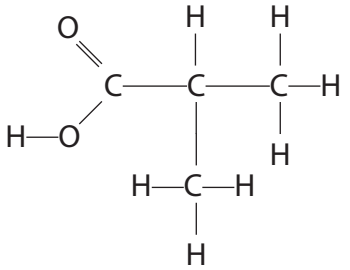
(Total for Question 14 = 1 mark)

15 Propanoic acid reacts with methanol to form an ester. The structure of the ester is

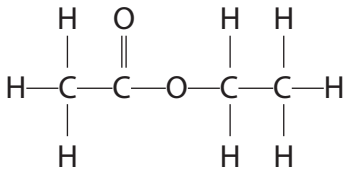
☒ **A**



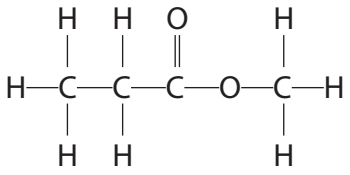
☒ **B**



☒ **C**



☒ **D**



(Total for Question 15 = 1 mark)

16 The boiling temperature of ethanoic acid is very much higher than that of butane although these molecules have similar numbers of electrons. This is because ethanoic acid has

☒ **A** stronger covalent bonds.

☒ **B** stronger ionic bonds.

☒ **C** greater London forces.

☒ **D** hydrogen bonding.

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 The equation for the combustion of hydrogen is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

(a) Use the standard molar entropies on page 2 and page 25 of the data booklet to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of oxygen, $S^{\ominus}[\frac{1}{2}O_2(g)] = +102.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

(3)

(b) The standard enthalpy change for the combustion of hydrogen is $-285.8 \text{ kJ mol}^{-1}$. Use this value to calculate the entropy change of the surroundings for the combustion of hydrogen at 298 K. Give your answer to **3** significant figures and include a sign and units.

(3)

(c) Use your answers to (a) and (b) to calculate the total entropy change ($\Delta S^{\ominus}_{total}$) for the combustion of 1 mol of hydrogen. Include a sign and units in your answer.

(2)

*(d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

(2)

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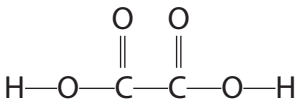
(Total for Question 17 = 10 marks)

18 Ethanedioic acid, $H_2C_2O_4$, is a dicarboxylic acid which occurs in many plants, for example in rhubarb leaves, and is used as a rust remover and strong descaler. The structure of ethanedioic acid is shown below.



Ethanedioic acid is a much stronger acid than carboxylic acids such as ethanoic acid, having a pK_a of 1.38. The hydrogenethanedioate ion, $HC_2O_4^-$, is a weaker acid than ethanedioic acid, having a pK_a of 4.28, although slightly stronger than ethanoic acid.

(a) (i) Write an equation for the reaction of the hydrogenethanedioate ion with water to form an acidic solution. Include state symbols in your equation.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, of the weak acid, $HC_2O_4^-$.

(1)

(iii) A solution containing hydrogenethanedioate ions behaves as a typical weak acid. Use your answer to (a)(ii) and the pK_a of the hydrogenethanedioate ion to calculate the pH of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate, $NaHC_2O_4$.

(3)

(b) (i) State **two** approximations used in the calculation of pH in (a)(iii).

(2)

1. .....

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2. .....

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*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

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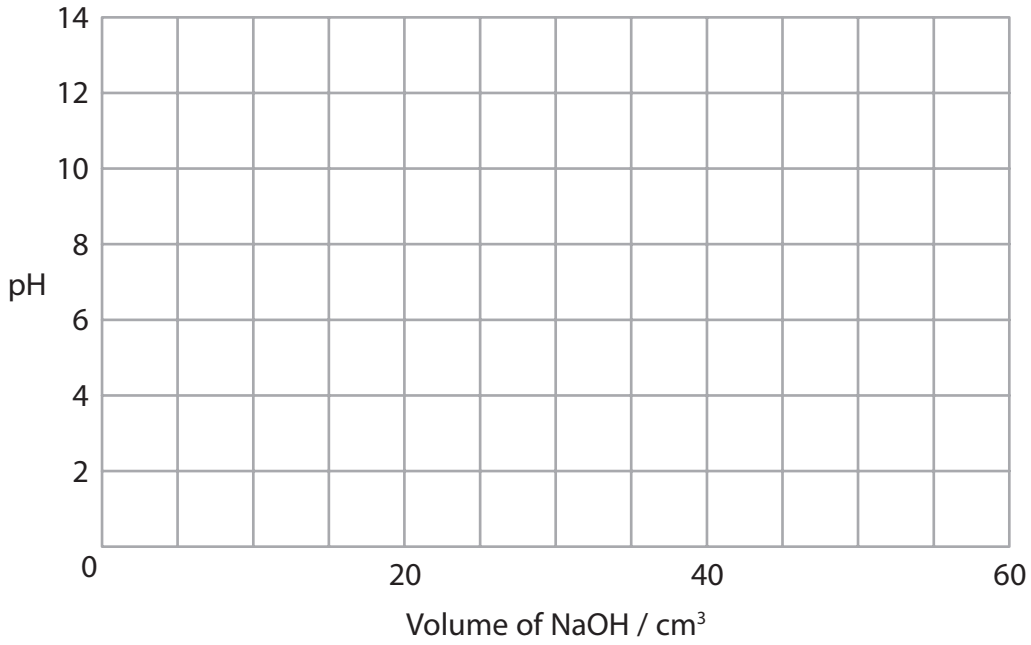
(c) 25 cm^3 of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



*(ii) When 25 cm^3 of a 0.050 mol dm^{-3} solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm^3.

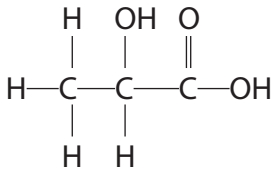
When methyl yellow indicator is used, the colour changes at around 25 cm^3.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

(Total for Question 18 = 15 marks)

19 2-hydroxypropanoic acid, lactic acid, is a chiral molecule which is found in muscles and in sour milk. The 2-hydroxypropanoic acid formed in muscles is optically active but that in sour milk is not.



2-hydroxypropanoic acid

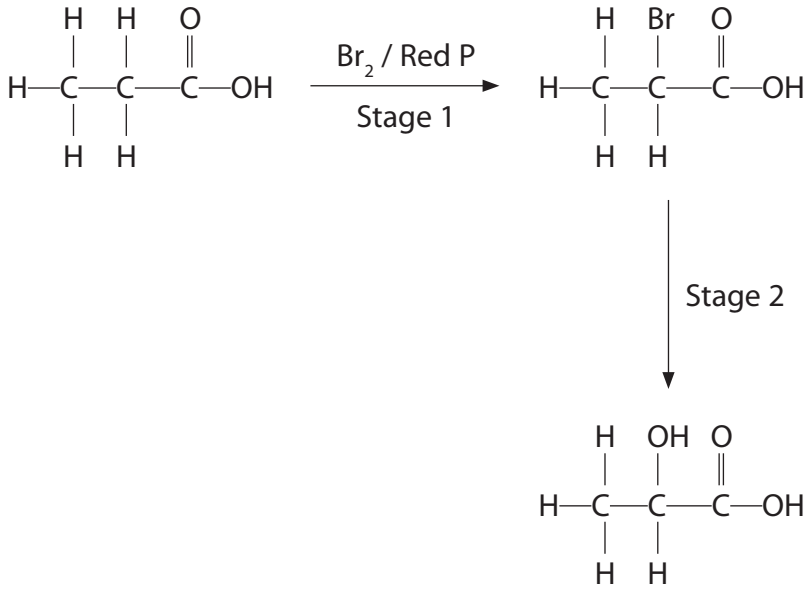
(a) (i) Explain the term **chiral**, stating the feature of 2-hydroxypropanoic acid that makes it chiral. Label this feature on the formula above.

(3)

(ii) What is the difference between the 2-hydroxypropanoic acid formed in muscles and that found in sour milk which gives rise to the difference in optical activity?

(2)

(b) 2-hydroxypropanoic acid may be prepared in the laboratory from propanoic acid in a two-stage sequence in which 2-bromopropanoic acid is formed as an intermediate:



(i) Stage 2 of this sequence was carried out in two steps. Identify the reagent required for each step in Stage 2.

(2)

First step .....

Second step .....

(ii) When an optically active isomer of 2-bromopropanoic acid is used in Stage 2, the resulting 2-hydroxypropanoic acid is also optically active. State and explain what this indicates about the mechanism of the first reaction in Stage 2.

(3)

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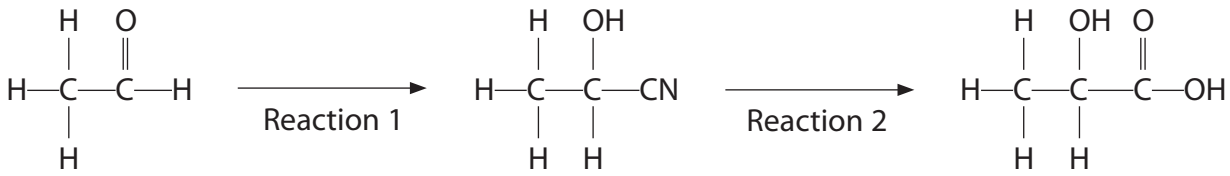
(c) 2-hydroxypropanoic acid may also be prepared from ethanal in the following sequence:



(i) Name the mechanism and type of reaction occurring in Reaction 1.

(2)

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(ii) Identify the attacking species in Reaction 1.

(1)

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(iii) Give the first step of the mechanism of Reaction 1, showing the formation of the intermediate.

(2)

*(iv) Explain, by referring to the mechanism in (c)(iii), why the 2-hydroxypropanoic acid formed from ethanal shows no optical activity.

(3)

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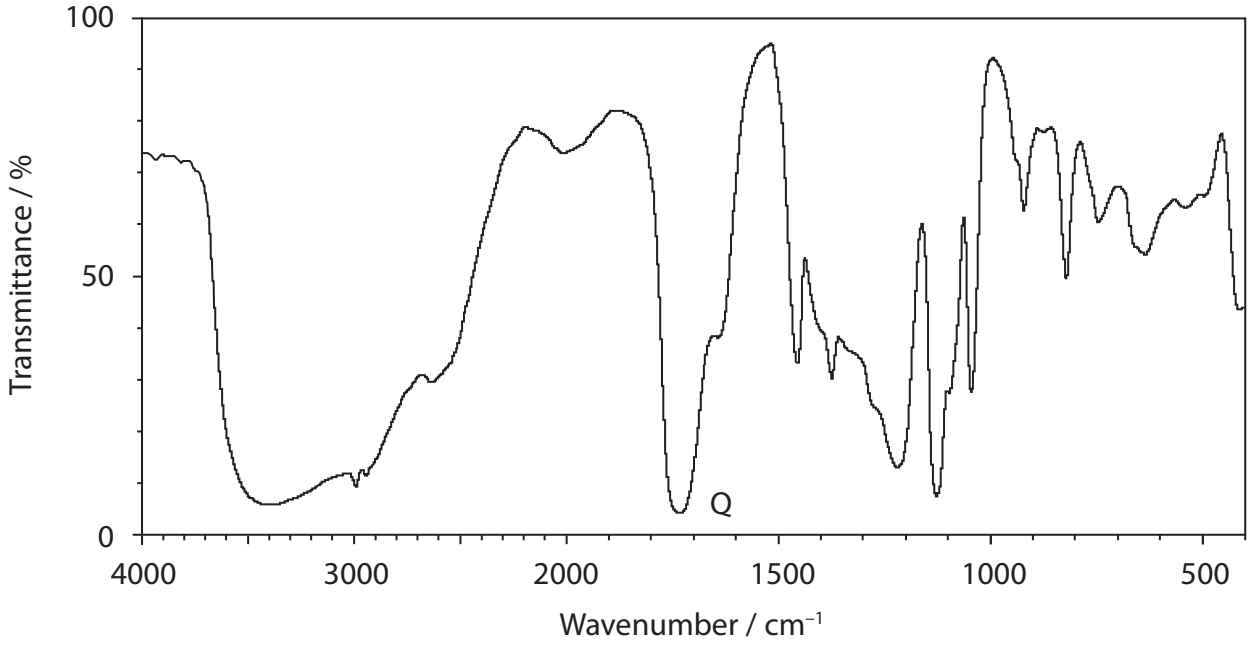
(d) The infrared spectrum of 2-hydroxypropanoic acid is shown below.



(i) Give the wavenumber of the peak that is present in the infrared spectrum of 2-hydroxypropanoic acid but will not be present in the infrared spectrum of ethanal, identifying the group most likely to be responsible for this peak. Use the data on pages 5 and 6 of the data booklet.

(1)

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*(ii) Identify the bond responsible for absorption peak Q in the spectrum. By considering the wavenumber of this peak, and the data on pages 5 and 6 of the data booklet, explain whether this peak **alone** can be used to distinguish between ethanal and 2-hydroxypropanoic acid.

(3)

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(e) Ethanal and 2-hydroxypropanoic acid can be distinguished by the use of chemical tests. Give two suitable tests **not** involving indicators. For each test, state the observation associated with a positive result.

(4)

Test which is positive for ethanal but not for 2-hydroxypropanoic acid.

Test which is positive for 2-hydroxypropanoic acid but not for ethanal.

(Total for Question 19 = 26 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

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

20 The ionic equation for the reaction of ammonium peroxodisulfate (persulfate), $(NH_4)_2S_2O_8$, with potassium iodide, KI, is

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(a) In a series of experiments to determine the rate equation for this reaction, 10 cm^3 of 0.0050 mol dm^{-3} sodium thiosulfate was mixed with 20 cm^3 of $(NH_4)_2S_2O_8$ solution and 5 drops of starch solution. 20 cm^3 of KI solution was added with mixing and the time taken for the solution to darken was noted. The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions and the times for the mixture to darken are shown below.

Experiment Number	Initial concentration / mol dm^{-3}		Time for solution to darken / s
	$S_2O_8^{2-}$	I^-	
1	0.10	0.20	35
2	0.05	0.20	69
3	0.10	0.10	70

(i) Explain the purpose of the sodium thiosulfate solution.

(2)

(ii) Use the data in the table to deduce the rate equation for the reaction between $S_2O_8^{2-}$ and I^- ions. Explain, by referring to the data, how you arrived at your answer.

(3)

(b) A further experiment was carried out to confirm the order of the reaction with respect to iodide ions. $(NH_4)_2S_2O_8$ was mixed with KI to form a solution in which the initial concentration of $(NH_4)_2S_2O_8$ was 2.0 mol dm^{-3} and that of KI was 0.025 mol dm^{-3}. The concentration of iodine was measured at various times until the reaction was complete.

(i) Outline a method, **not** involving sampling the mixture, which would be suitable for measuring the iodine concentrations in this experiment. Experimental details are not required but you should state how you would use your measurements to obtain iodine concentrations.

(3)

(ii) Explain why the initial concentration of $(NH_4)_2S_2O_8$ is much higher than that of KI.

(1)

(iii) State how the initial rate of reaction may be obtained from the results of this type of experiment.

(2)

(iv) In such an experiment a student calculated the initial rate of reaction to be 8.75×10^{-5} mol dm^{-3} s^{-1}. Use this value, the initial concentrations in (b) and the rate equation that you obtained in (a)(ii), to calculate the rate constant for this reaction. Include units in your answer.

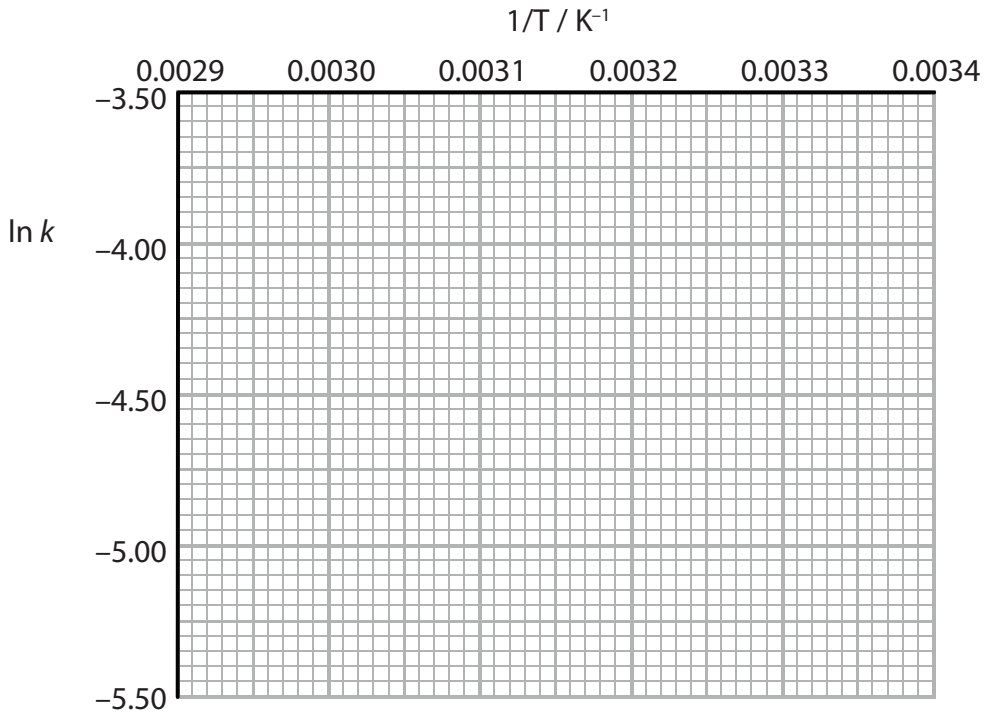
(2)

(c) Using the method outlined in (b), the rate constant for this reaction was determined at various temperatures. The data from these experiments are shown in the table below. Note that none of the temperatures corresponds to that used in (b) and that the rate constant is given in appropriate units.

Temperature T / K	Rate constant k	ln k	1/T / K^{-1}
300	0.00513	–5.27	0.00333
310	0.00833	–4.79	0.00323
320	0.0128	–4.36	0.00313
330	0.0201	–3.91	0.00303
340	0.0301	–3.50	0.00294

(i) Use the data in the table to plot a graph of ln *k* (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points.

(2)



(ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a, of the reaction, stating the units.

(4)

The rate constant of a reaction, *k*, is related to the temperature, T, by the expression

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

(Total for Question 20 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

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 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

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
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

* Lanthanide series

* Actinide series