

Please check the examination details below before entering your candidate information

Candidate surname

Other names

Pearson Edexcel
International
Advanced Level

Centre Number

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Candidate Number

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Friday 8 January 2021

Afternoon (Time: 1 hour 45 minutes)

Paper Reference **WCH14/01****Chemistry****International Advanced Level****Unit 4: Rates, Equilibria and Further Organic Chemistry**
(including synoptic assessment)**You must have:**

Data Booklet, scientific calculator, ruler

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.*
- Show all your working in calculations and include units where appropriate.

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.*
- In the question marked with an **asterisk** (*), marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ►

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 Which of these has the **highest** standard molar entropy at 298 K and 1 atm pressure?

- ☐ A carbon dioxide, CO_2
- ☐ B copper, Cu
- ☐ C ethanol, $\text{C}_2\text{H}_5\text{OH}$
- ☐ D hydrogen, H_2

(Total for Question 1 = 1 mark)

2 The entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, and the entropy change of the system, ΔS_{system} , for four different reactions are given.

Reaction	$\Delta S_{\text{surroundings}}$ / $\text{J K}^{-1} \text{mol}^{-1}$	ΔS_{system} / $\text{J K}^{-1} \text{mol}^{-1}$
P	+245	+34
Q	+350	-276
R	-482	+65
S	-563	-128

Which of these is thermodynamically feasible?

- ☐ A reaction **P** only
- ☐ B reactions **P** and **Q** only
- ☐ C reaction **R** only
- ☐ D reactions **R** and **S** only

(Total for Question 2 = 1 mark)

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

3 Which equation represents the standard enthalpy change of atomisation, $\Delta_{\text{at}}H$, of bromine?

- ☐ A $\frac{1}{2} \text{Br}_2(\text{l}) \rightarrow \text{Br}(\text{g})$
- ☐ B $\text{Br}_2(\text{l}) \rightarrow 2\text{Br}(\text{g})$
- ☐ C $\frac{1}{2} \text{Br}_2(\text{g}) \rightarrow \text{Br}(\text{g})$
- ☐ D $\text{Br}_2(\text{g}) \rightarrow 2\text{Br}(\text{g})$

(Total for Question 3 = 1 mark)

4 This question is about four ionic compounds.

(a) Which of these compounds would be expected to have the **least** exothermic lattice energy?

(1)

- ☐ A calcium chloride
- ☐ B magnesium chloride
- ☐ C potassium bromide
- ☐ D sodium bromide

(b) Which of these compounds would be expected to have the **largest** difference between their experimental (Born–Haber) and theoretical lattice energies?

(1)

- ☐ A calcium chloride
- ☐ B magnesium chloride
- ☐ C potassium bromide
- ☐ D sodium bromide

(Total for Question 4 = 2 marks)

5 The standard enthalpy change of solution of potassium chloride, KCl, is $+17 \text{ kJ mol}^{-1}$.

The solubility of potassium chloride in water at 298 K is 359 g dm^{-3} .

Which of these explains the solubility of potassium chloride in water?

- ☐ A the hydration enthalpy of K^+ and the lattice energy of KCl are exothermic
- ☐ B the hydration enthalpy of K^+ and the lattice energy of KCl are endothermic
- ☐ C the total entropy change when KCl dissolves is positive
- ☐ D the total entropy change when KCl dissolves is negative

- 6 The total entropy change, ΔS_{total} , of a reaction at 298 K is $-85.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

What is the value of the equilibrium constant for this reaction at 298 K?

$$[R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}]$$

- ☐ A 3.61×10^{-5}
- ☐ B 9.07×10^{-1}
- ☐ C 9.66×10^{-1}
- ☐ D 2.77×10^4

(Total for Question 6 = 1 mark)

- 7 Propanone reacts with iodine in the presence of a catalyst of dilute hydrochloric acid. The reaction occurs in aqueous solution.



The rate equation for this reaction is

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

Which is a possible mechanism for the reaction?

- ☐ A $\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ fast
 $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{OH})=\text{CH}_2 + \text{H}^+$ slow
 $\text{CH}_3\text{C}(\text{OH})=\text{CH}_2 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ fast
- ☐ B $\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ fast
 $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{OH})=\text{CH}_2 + \text{H}^+$ fast
 $\text{CH}_3\text{C}(\text{OH})=\text{CH}_2 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ slow
- ☐ C $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{COCH}_2^- + \text{H}^+$ slow
 $\text{I}_2 \rightarrow \text{I}^+ + \text{I}^-$ slow
 $\text{CH}_3\text{COCH}_2^- + \text{I}^+ \rightarrow \text{CH}_3\text{COCH}_2\text{I}$ fast
- ☐ D $\text{I}_2 \rightarrow \text{I}^+ + \text{I}^-$ slow
 $\text{CH}_3\text{COCH}_3 + \text{I}^- \rightarrow \text{CH}_3\text{COCH}_2^- + \text{HI}$ slow
 $\text{CH}_3\text{COCH}_2^- + \text{I}^+ \rightarrow \text{CH}_3\text{COCH}_2\text{I}$ fast

(Total for Question 7 = 1 mark)

8 The rate equation for a reaction is

$$\text{rate} = k[A]^2[B]^0$$

The initial rate of reaction is $9.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when $[A] = 0.30 \text{ mol dm}^{-3}$ and $[B] = 0.20 \text{ mol dm}^{-3}$.

What is the value of the rate constant in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$?

- ☐ A 8.1×10^{-6}
- ☐ B 3.0×10^{-4}
- ☐ C 1.0×10^{-3}
- ☐ D 5.0×10^{-3}

(Total for Question 8 = 1 mark)

9 This question is about weak acids.

pK_a of ethanoic acid, $\text{CH}_3\text{COOH} = 4.8$

pK_a of chloroethanoic acid, $\text{CH}_2\text{ClCOOH} = 2.9$

(a) What is the pH of a $0.100 \text{ mol dm}^{-3}$ solution of chloroethanoic acid?

(1)

- ☐ A 0.27
- ☐ B 1.95
- ☐ C 2.90
- ☐ D 3.90

(b) Which is the acid-conjugate base pair in the reaction between ethanoic acid and chloroethanoic acid?

(1)

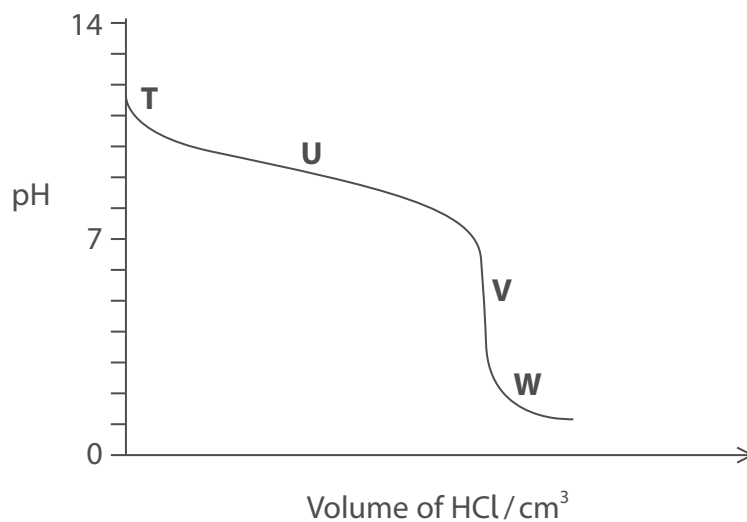
	Acid	Conjugate base
☐ A	CH_3COOH	CH_3COO^-
☐ B	CH_3COOH	$\text{CH}_3\text{COOH}_2^+$
☐ C	CH_2ClCOOH	$\text{CH}_2\text{ClCOO}^-$
☐ D	CH_2ClCOOH	$\text{CH}_2\text{ClCOOH}_2^+$

(Total for Question 9 = 2 marks)

- 10 A titration was carried out by adding 0.1 mol dm^{-3} hydrochloric acid to 0.1 mol dm^{-3} aqueous ammonia.



The titration curve is shown.



- (a) Which region of the graph represents the most effective buffer solution?

(1)

- ☐ A region T
- ☐ B region U
- ☐ C region V
- ☐ D region W

- (b) Which of these is the best indicator to use in this titration?

[Refer to the Data Booklet]

(1)

- ☐ A methyl red
- ☐ B phenol red
- ☐ C phenolphthalein
- ☐ D thymol blue

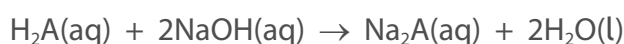
(c) What is the approximate pH of an ammonium chloride solution?

(1)

- ☐ **A** 2.0
- ☐ **B** 5.8
- ☐ **C** 9.7
- ☐ **D** 11.3

(Total for Question 10 = 3 marks)

11 A diprotic acid, H_2A , was titrated with sodium hydroxide solution.



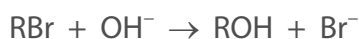
A 25.0 cm^3 portion of 0.100 mol dm^{-3} sodium hydroxide solution required 12.80 cm^3 of the solution of the diprotic acid for complete neutralisation.

What is the concentration of H_2A in mol dm^{-3} ?

- ☐ **A** 2.56×10^{-2}
- ☐ **B** 9.77×10^{-2}
- ☐ **C** 1.95×10^{-1}
- ☐ **D** 3.91×10^{-1}

(Total for Question 11 = 1 mark)

12 A sample of a bromoalkane, RBr , containing a single optical isomer reacts with hydroxide ions in an $\text{S}_{\text{N}}1$ mechanism.



The alcohol formed is a racemic mixture.

From this information, it can be deduced that RBr is most likely to be

- ☐ **A** primary only
- ☐ **B** secondary only
- ☐ **C** tertiary only
- ☐ **D** primary, secondary or tertiary

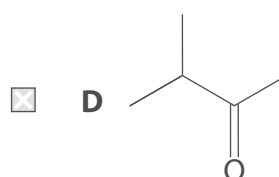
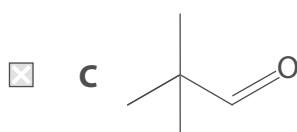
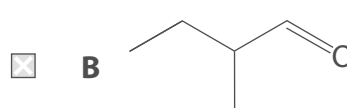
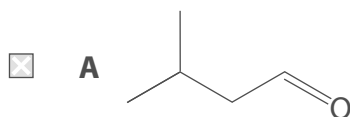
(Total for Question 12 = 1 mark)

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

13 A compound **X**, with molecular formula $C_5H_{10}O$, gave an orange precipitate with 2,4-dinitrophenylhydrazine.

X gave a silver mirror with Tollens' reagent.

Which of these could **not** be **X**?



(Total for Question 13 = 1 mark)

14 Propyl ethanoate, $CH_3COOCH_2CH_2CH_3$, is hydrolysed with aqueous sodium hydroxide.

Which products are formed?

- ☐ **A** CH_3COOH and $CH_3CH_2CH_2OH$
- ☐ **B** CH_3COOH and $CH_3CH_2CH_2ONa$
- ☐ **C** CH_3COONa and $CH_3CH_2CH_2OH$
- ☐ **D** CH_3COONa and $CH_3CH_2CH_2ONa$

(Total for Question 14 = 1 mark)

15 2.95 g of ethanoic acid is produced from 2.50 g of ethanol.

What is the percentage yield of ethanoic acid?

[Molar masses in $g\ mol^{-1}$: ethanoic acid = 60 ethanol = 46]

- ☐ **A** 65.0 %
- ☐ **B** 84.7 %
- ☐ **C** 90.5 %
- ☐ **D** 118 %

(Total for Question 15 = 1 mark)

16 A mixture of organic compounds was analysed using thin-layer chromatography.

The R_f value was 0.92 for one of the components in the mixture.

What can be deduced about the attractions between that component and the stationary and mobile phases?

		Attraction between component and stationary phase	Attraction between component and mobile phase
☐	A	strong	strong
☐	B	strong	weak
☐	C	weak	weak
☐	D	weak	strong

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

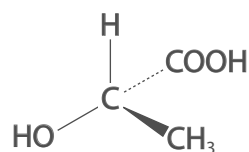
Answer ALL the questions.

Write your answers in the spaces provided.

17 This question is about carboxylic acids and their derivatives.

- (a) Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, is produced in muscles as a result of anaerobic respiration.

- (i) The structure of lactic acid is



Give a reason why lactic acid shows optical isomerism.

(1)

- (ii) A laboratory sample of lactic acid does **not** rotate the plane of plane-polarised monochromatic light.

Give a reason for this observation.

(1)

- (iii) Give the structure of the organic product formed when lactic acid reacts with concentrated phosphoric(V) acid, H_3PO_4 .

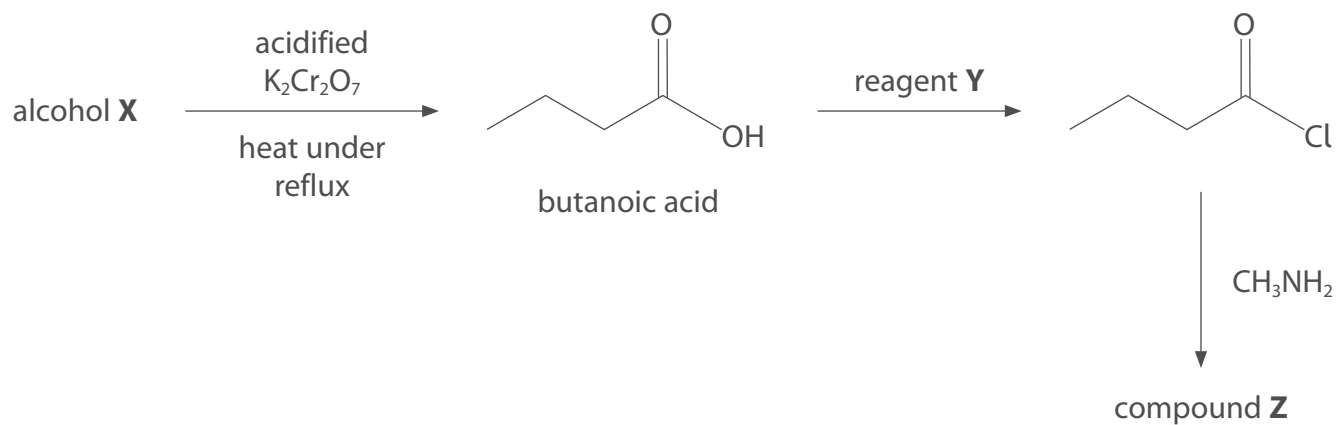
(1)

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(b) A reaction scheme involving butanoic acid is shown.



Identify **X**, **Y** and **Z** by name or formula.

(3)

Alcohol **X**

Reagent **Y**

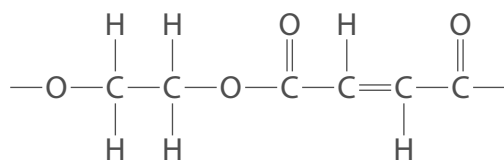
Compound **Z**

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(c) The repeat unit of a polyester is shown.



Give the structures of the two monomers that could form this polyester.

(2)

Monomer 1	Monomer 2

(d) An organic compound **E** contains carbon, hydrogen and oxygen only.

- (i) The accurate relative atomic masses, A_r , of the three elements in **E** are shown in the table.

Element	A_r
hydrogen	1.0078
carbon	12.0000
oxygen	15.9949

E contains five carbon atoms and gives a molecular ion peak at $m/z = 102.0678$ in its mass spectrum.

Deduce the molecular formula of **E**.

(1)

- (ii) Aqueous sodium hydrogencarbonate is added to a sample of **E**.
No effervescence occurs.

State what can be deduced by this observation.

(1)

- (iii) The infrared spectrum of **E** has an absorption in the range $1750 - 1735 \text{ cm}^{-1}$.

Name the functional group in **E**.

(1)

- (iv) Data from the high resolution proton NMR spectrum of **E** is shown.

Peak	Chemical shift, δ / ppm for TMS	Splitting pattern	Relative peak area
A	4.02	triplet	2
B	2.05	singlet	3
C	1.65	sextet	2
D	0.95	triplet	3

Deduce the structure of **E**.

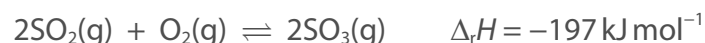
Justify your answer by labelling the protons responsible for each peak.

(3)

(Total for Question 17 = 14 marks)

18 This question is about sulfuric acid and its salts.

(a) The manufacture of sulfuric acid involves the equilibrium



(i) A catalyst of vanadium(V) oxide is used in this reaction.

State the effect, if any, of the catalyst on the value of the equilibrium constant, K_p .

(1)

(ii) The temperature used for this reaction in industry is 700 K.

Explain, in terms of the equilibrium constant and the equilibrium position, the effect of an increase in temperature on the equilibrium yield of sulfur trioxide.

(2)

(iii) Write the expression for the equilibrium constant, K_p , for this equilibrium.
State symbols are not required.

(1)

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- (iv) A mixture of 2.00 mol of sulfur dioxide and 1.00 mol of oxygen is allowed to reach equilibrium at 5.00 atm pressure.
1.60 mol of sulfur trioxide is formed.

Calculate the value of K_p .

Include units and give your answer to an appropriate number of significant figures.

(4)

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(b) Sulfur trioxide is used to produce sulfuric acid.

- (i) Commercial concentrated sulfuric acid contains 98.5 % H_2SO_4 and 1.5 % water by mass.

The density of concentrated sulfuric acid is 1800 g dm^{-3} .

Calculate the concentration of this sulfuric acid in mol dm^{-3} .

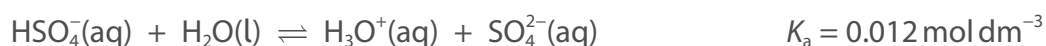
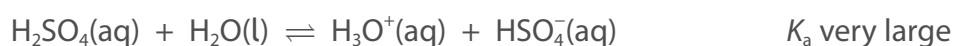
(2)

- (ii) The pH of a 0.10 mol dm^{-3} solution of sulfuric acid at 25°C is 0.97.

Calculate the concentration of hydrogen ions, in mol dm^{-3} , in this solution.

(1)

- (iii) In an aqueous solution of sulfuric acid, the following equilibria exist.



Explain, in terms of these equilibria, why the concentration of hydrogen ions in a 0.10 mol dm^{-3} solution of sulfuric acid is **not** 0.20 mol dm^{-3} .

No calculation is required.

(2)

.....

.....

.....

.....

.....

(c) A buffer solution is made from HSO_4^- and SO_4^{2-} ions.

- (i) Write two ionic equations involving HSO_4^- and SO_4^{2-} ions to show how this solution acts as a buffer.
State symbols are not required.

(2)

- (ii) A buffer solution is formed by mixing

25.0 cm³ of a solution that is 0.150 mol dm⁻³ with respect to SO_4^{2-} ions with
75.0 cm³ of a solution that is 0.100 mol dm⁻³ with respect to HSO_4^- ions.

Calculate the pH of this buffer solution.

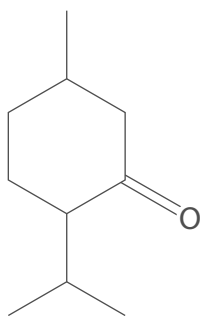
[K_a for HSO_4^- ions = 0.012 mol dm⁻³]

(5)

(Total for Question 18 = 20 marks)

19 This question is about carbonyl compounds.

(a) The skeletal formula of menthone is shown.



Give the molecular formula of menthone.

(1)

(b) Ethanal, CH_3CHO , reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxypropanenitrile.

Draw the mechanism for this reaction.

Include curly arrows, and any relevant lone pairs and dipoles.

(4)

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(c) A carbonyl compound, **F**, has the molecular formula $C_6H_{12}O$.

(i) **F** reacts with iodine in an alkaline solution to give a pale yellow precipitate.

Give the name or formula of the group in **F** identified by this test.

(1)

(ii) Draw the **skeletal** formulae of the four possible structures of carbonyl compound **F**.

(2)

(iii) The carbon-13 (^{13}C) NMR spectrum of **F** has four peaks.

Identify **F** by drawing its **displayed** formula.

Justify your answer by labelling the carbon atoms or groups of carbon atoms responsible for the four peaks in the spectrum.

(2)

- *(d) Explain, in terms of all the intermolecular forces involved, why butanal has a higher boiling temperature than pentane but a lower boiling temperature than propanoic acid.

Substance	Boiling temperature / °C
butanal	76
pentane	36
propanoic acid	141

(6)

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(Total for Question 19 = 16 marks)

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SECTION C

Answer ALL the questions.

Write your answers in the spaces provided.

20 This question is about some compounds of bromine.

(a) Potassium bromate(V) decomposes to form potassium bromide and oxygen.



The standard molar entropies of these substances are given in the table.

Substance	KBrO ₃ (s)	KBr(s)	O ₂ (g)
$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$	149.2	95.9	205.0

Calculate the total entropy change, ΔS_{total} , for this reaction at 298 K.

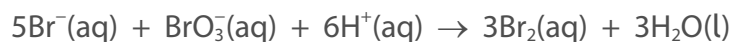
(5)

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(b) Bromide ions react with bromate(V) ions in acidic solution.



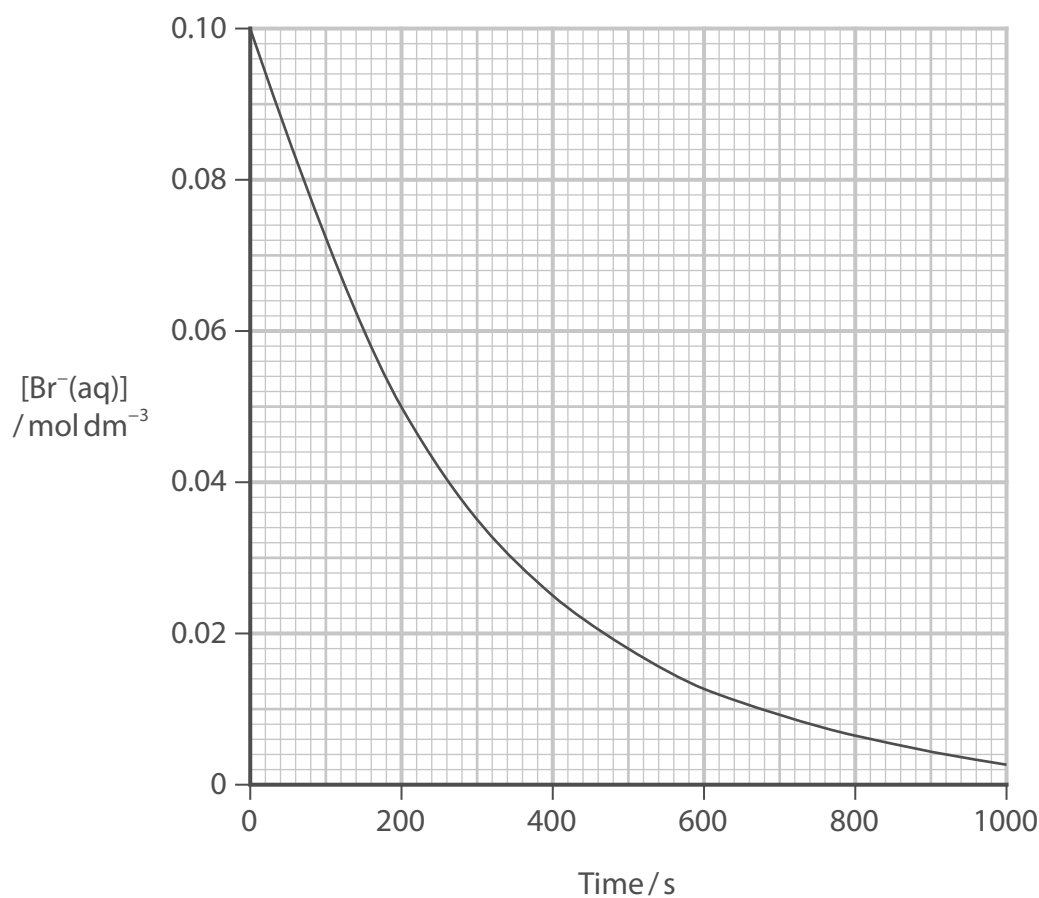
Two experiments are carried out.

(i) **Experiment 1**

The concentration of Br^- ions is determined at different times.

The concentrations of BrO_3^- ions and H^+ ions are in large excess and effectively constant.

The graph of concentration of Br^- ions against time is shown.



Determine the order of the reaction with respect to bromide ions.
Show your working on the graph.

(3)

(ii) Experiment 2

The initial concentrations of BrO_3^- ions and H^+ ions are changed and the initial rate of reaction is determined.

The initial concentration of Br^- ions is constant and in large excess.

Run	$[\text{BrO}_3^-(\text{aq})]$ $/\text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})]$ $/\text{mol dm}^{-3}$	Initial rate $/\text{mol dm}^{-3} \text{s}^{-1}$
1	0.1	0.1	3.6×10^{-3}
2	0.2	0.1	7.2×10^{-3}
3	0.3	0.2	4.3×10^{-2}

Determine the order of reaction with respect to BrO_3^- ions and to H^+ ions.

You must explain your working.

(3)

(iii) Give the overall rate equation for this reaction.
Include the units for the rate constant.

(2)

- (c) The rate constant for the reaction between bromoalkane and cyanide ions is determined at five different temperatures.

The results are given in the table.

Temperature (T) /K	1/Temperature ($1/T$) /K ⁻¹	Rate constant (k) /s ⁻¹	ln k
300	3.33×10^{-3}	3.72×10^{-5}	-10.20
310	3.23×10^{-3}	1.34×10^{-4}	-8.92
320	3.13×10^{-3}	5.48×10^{-4}	-7.51
330	3.03×10^{-3}	2.01×10^{-3}	-6.21
340	2.93×10^{-3}	7.23×10^{-3}	-4.93

Plot a graph of ln k against $1/T$ and use it to determine the activation energy, E_a .

Include the sign and units of the gradient and the activation energy.

(7)

The Arrhenius equation can be expressed as

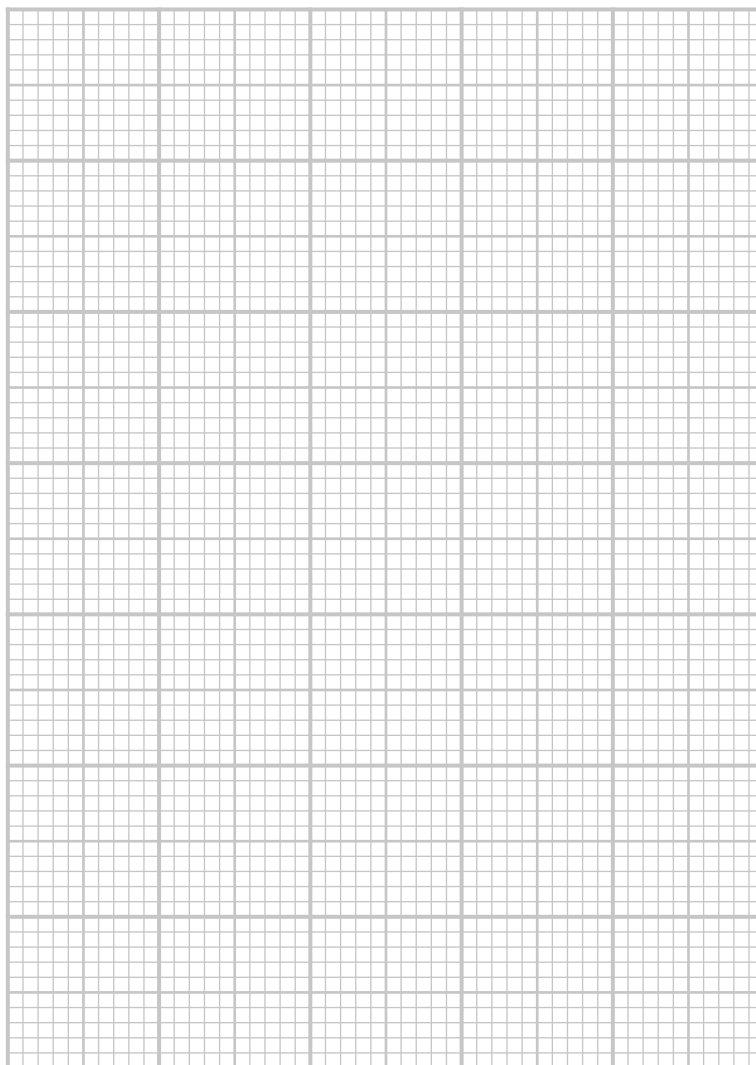
$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

[$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]

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TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

