

1. The kinetics of the hydrolysis of the halogenoalkane RCH_2Cl with aqueous sodium hydroxide (where R is an alkyl group) was studied at 50°C . The following results were obtained:

Experiment	$[\text{RCH}_2\text{Cl}]$	$[\text{OH}^-]$	Initial rate/ $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.050	0.10	4.0×10^{-4}
2	0.15	0.10	1.2×10^{-3}
3	0.10	0.20	1.6×10^{-3}

- (i) Deduce the order of reaction with respect to the halogenoalkane, RCH_2Cl , and with respect to the hydroxide ion, OH^- , giving reasons for your answers.

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(4)

- (ii) Hence write the rate equation for the reaction.

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(1)

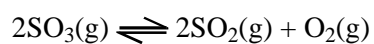
- (iii) Calculate the value of the rate constant with its units for this reaction at 50°C .

(2)

(iv) Using your answer to part (ii), write the mechanism for this reaction.

(3)
(Total 10 marks)

2. In the vapour phase sulphur trioxide dissociates:



(a) (i) Write an expression for K_p for this dissociation.

(1)

(ii) At a particular temperature, 75% of the sulphur trioxide is dissociated, producing a pressure of 10 atm. Calculate the value of K_p at this temperature paying attention to its units.

(5)

(b) Solid vanadium(V) oxide, V_2O_5 , is an effective catalyst for this reaction. State the effect of using double the mass of catalyst on:

(i) the position of the equilibrium;

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(1)

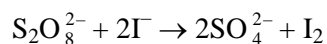
(ii) the value of K_p .

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(1)

(Total 8 marks)

3. In an experiment to determine the rate of the reaction between persulphate ions and iodide ions in aqueous solution



the following data were obtained:

Concentration/mol dm ⁻³		Initial rate /mol dm ⁻³ s ⁻¹
$S_2O_8^{2-}$	I^-	
0.100	0.100	0.36
0.200	0.100	0.72
0.200	0.200	1.44

(a) (i) Deduce the order of reaction with respect to each of the reagents and hence write the rate equation for the reaction.

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(3)

(ii) With reference to this reaction state what is meant by the **overall order** of a

reaction.

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(1)

(iii) Calculate the rate constant including units.

(2)

(iv) Explain why the rate equation cannot be written directly from the stoichiometric equation for the reaction.

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(1)

(b) (i) Suggest a suitable experimental technique that would enable you to determine the rate of the reaction given opposite.

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(1)

(ii) Suggest a necessary condition that would help to ensure accurate results.

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(1)

(iii) Suggest one advantage or disadvantage of your chosen experimental method.

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(1)

(Total 10 marks)

4. (a) (i) Explain what is meant by the following terms.

Rate of reaction

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Overall order of a reaction

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(2)

(ii) Explain why the order of reaction cannot be deduced from the stoichiometric equation for a reaction.

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(1)

(b) Substitution reactions of halogenoalkanes, can proceed via an S_N1 or S_N2 mechanism. When 1-bromobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, 2-bromobutane, $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$, and 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, are reacted separately with aqueous sodium hydroxide solution each gives the corresponding alcohol.

(i) Give the mechanism for the S_N1 reaction between 2-bromobutane and hydroxide ions.

(3)

(ii) Explain why the product mixture is not optically active.

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(2)

(iii) In an experiment designed to find the mechanism of the reaction between 2-bromo-2-methylpropane and hydroxide ions the following data were obtained at constant temperature.

Initial concentration of 2-bromo-2-methylpropane / mol dm^{-3}	Initial concentration of OH^- / mol dm^{-3}	Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
0.10	0.10	1.2×10^{-2}
0.20	0.10	2.4×10^{-2}
0.30	0.20	3.6×10^{-2}

Use the data to deduce the rate equation for the reaction of 2-bromo-2-methylpropane with sodium hydroxide solution.

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(3)

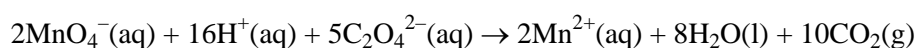
- (c) Suggest, in outline, a method you could use to follow the progress of the reaction between a bromoalkane and aqueous sodium hydroxide.

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(3)

(Total 14 marks)

5. Manganate(VII) ions react with ethanedioate ions in acidic solution.



- (a) In a particular experiment 200 cm^3 of aqueous potassium manganate(VII), KMnO_4 , of concentration $0.0500 \text{ mol dm}^{-3}$ were mixed with 50.0 cm^3 of ethanedioic acid, $\text{HOOC}-\text{COOH}$, of concentration $0.500 \text{ mol dm}^{-3}$, and 80 cm^3 of 1.0 mol dm^{-3} sulphuric acid.

- (i) Show by calculation that the starting concentration of the manganate(VII) ions was $3.03 \times 10^{-2} \text{ mol dm}^{-3}$.

(1)

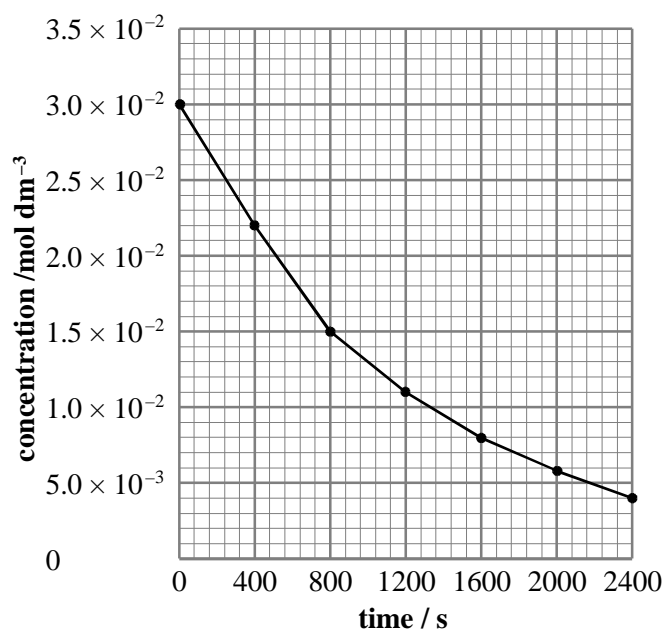
- (ii) The concentration of the manganate(VII) ions was determined over a period of time.

Time / s	Concentration of manganate(VII) ions/ mol dm ⁻³
0	3.03×10^{-2}
400	2.98×10^{-2}
800	2.86×10^{-2}
1200	2.75×10^{-2}
1600	1.90×10^{-2}
2000	7.50×10^{-3}
2400	2.50×10^{-3}

Plot a graph of the concentration of manganate(VII) ions against time and from it determine the initial rate of the reaction and the rate at 1600 s.

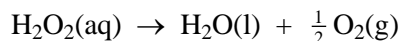
(5)

- (b) A second experiment was set up involving the same chemicals in the same concentrations as in experiment 1 but this time some solid manganese(II) sulphate was dissolved in the ethanedioic acid before the potassium manganate (VII) solution was poured in. The plot of the concentration of manganate(VII) ions against time is given below:



- (i) Determine the order of the reaction with respect to manganate(VII) ions by considering the time taken for the concentration to fall by half, using the concentrations at 0, 800 and 1600 s. (3)
- (ii) Compare this graph with the one you plotted in (a) (ii) and give two pieces of evidence that manganese(II) sulphate is a catalyst for this reaction. (2)
- (c) (i) Carrying out a flame test on potassium manganate(VII) gives a lilac flame. What does this show? (1)
- (ii) Describe how aqueous sodium hydroxide solution could be used to show that manganese(II) ions had been produced in the reaction between manganate (VII) ions and ethanedioate ions in acidic solution. (2)
- (Total 14 marks)

6. Hydrogen peroxide decomposes to form water and oxygen.



- (a) Suggest a method for following the rate of this reaction.
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- (2)
- (b) The reaction is first order with respect to hydrogen peroxide.
- (i) Explain what is meant by the term **first order**.
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- (1)
- (ii) The overall order of the reaction is one. Give the rate equation for the reaction.

Rate =

(1)

- (iii) How would you use a graph of hydrogen peroxide concentration against time to show that the reaction is first order?

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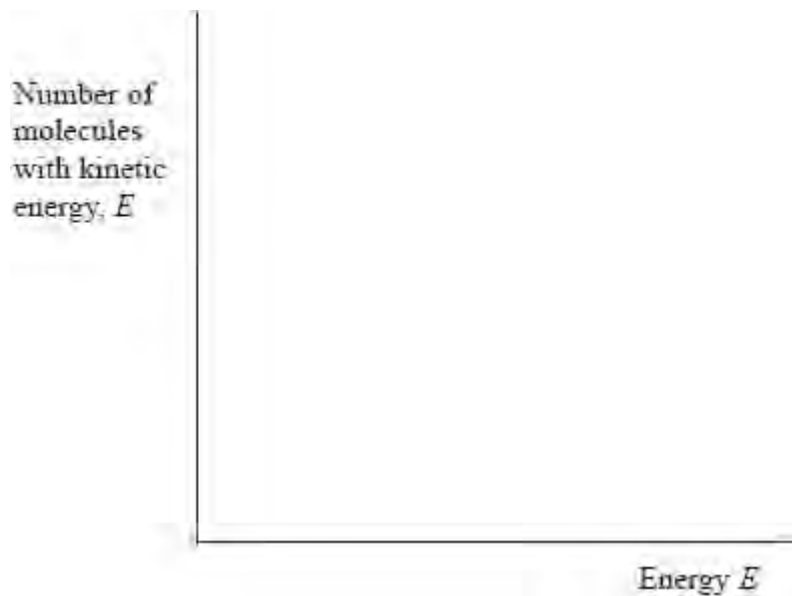
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(2)

- (c) The data in the table show the effect of temperature on the rate of this reaction.

T /K	Rate / mol dm ⁻³ s ⁻¹	1/T /K ⁻¹	ln(rate)
293	1.6 × 10 ⁻⁶	3.41 × 10 ⁻³	-13.3
302	4.2 × 10 ⁻⁶	3.31 × 10 ⁻³	-12.4
314	14.4 × 10 ⁻⁶	3.19 × 10 ⁻³	-11.1
323	33.8 × 10 ⁻⁶	3.10 × 10 ⁻³	-10.3

- (i) On the axes below, sketch graphs for two temperatures, T_1 and T_2 , where T_2 is greater than T_1 , and use them to explain why increasing temperature has a dramatic effect on the rate of this reaction.



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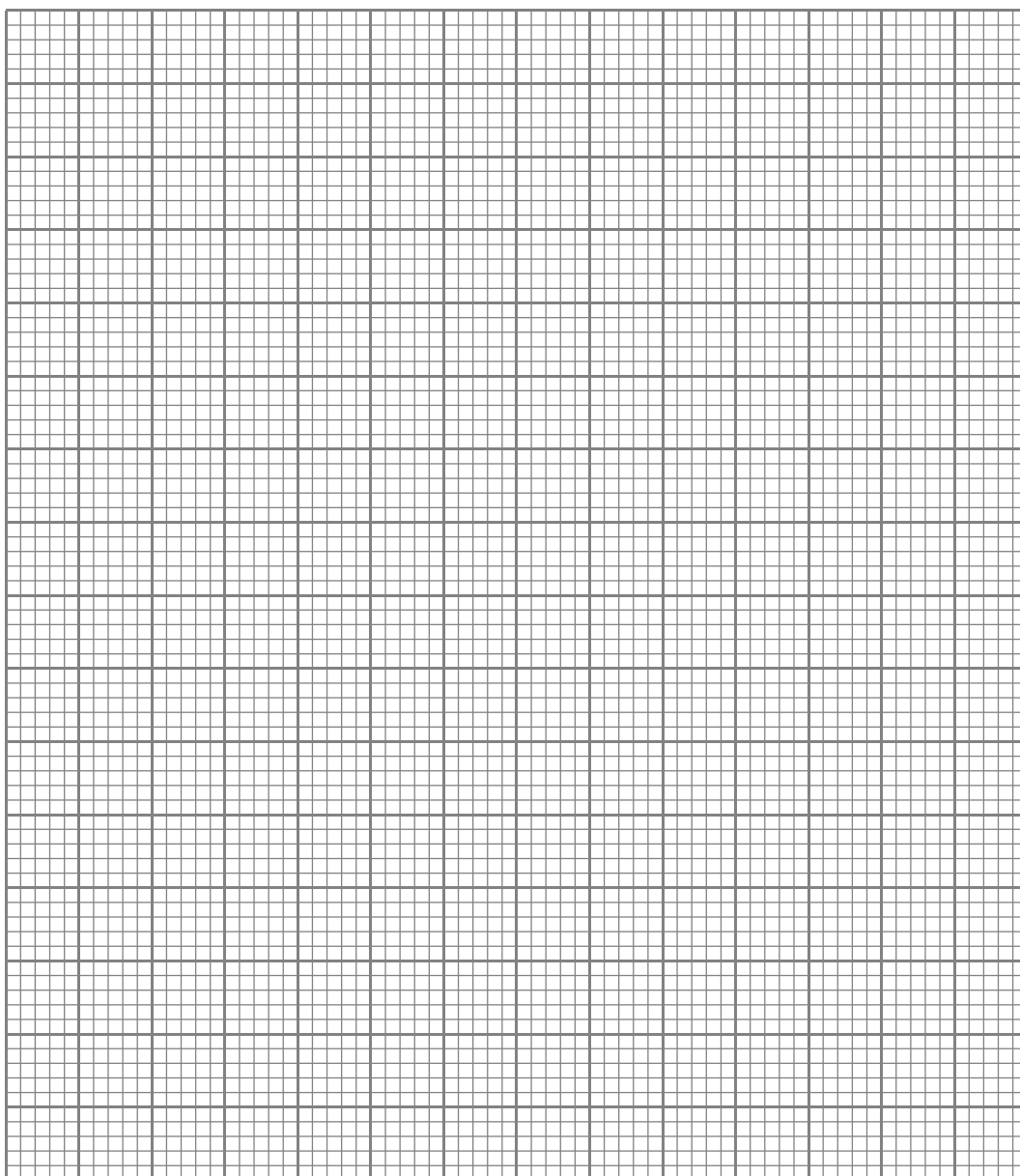
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(4)

- (ii) Plot a graph of $\ln(\text{rate})$, on the vertical axis, against $1/\text{temperature}$, on the horizontal axis, on the grid below.



(3)

- (iii) Use your graph and the equation below to calculate the activation energy, E_A , for this reaction.

$$\ln(\text{rate}) = \text{constant} \frac{E_A}{R} \left(1/T\right) \quad \text{where } R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

You should include the sign and units with your answer which should be given to two significant figures.

(3)
(Total 16 marks)

7. (a) In a rate of reaction experiment between two substances, A and B, the overall order of the reaction was found to be 2. Write three possible rate equations for such a second order reaction between A and B.

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(3)

- (b) At a certain temperature the rate of reaction between nitrogen monoxide, NO, and hydrogen, H₂, was investigated. The following data were obtained.

[NO]/mol dm ⁻³	[H ₂]/mol dm ⁻³	Rate/mol dm ⁻³ s ⁻¹
1.0	1.0	0.02
1.0	3.0	0.06
3.0	1.0	0.18

(i) Use the data above to deduce the rate equation for this reaction.

(3)

(ii) Use your answer to (b)(i) above to calculate the value of the rate constant, with units.

(2)

(c) The investigation described in part (b), above, was repeated, but at a higher temperature, and the rate of the reactions increased. Explain, in terms of particles, why an increase in temperature increases the rate of a reaction.

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(3)

- (d) State the effect of an increase in temperature on the value of the rate constant, k .

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(1)

- (e) Explain the effect of a catalyst on the rate of a reaction.

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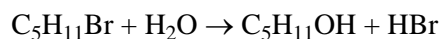
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(3)

(Total 15 marks)

8. This question is about the hydrolysis of 2-bromo-2-methylbutane.



- (a) 15 cm³ of water was mixed with 15 cm³ of ethanol. 1.0 cm³ of 2-bromo-2-methylbutane was added to this mixture. The conductivity of this mixture was measured and rose from 0 to 200 microsiemens in 600 s.

The experiment was repeated using equal volumes of water and ethanol, with 2.0 cm³ of 2-bromo-2-methylbutane in the 31 cm³ of mixture. The conductivity of the mixture rose from 0 to 400 microsiemens in 600 s.

- (i) Explain why the conductivity of the mixture increases during these reactions.

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(1)

- (ii) Why was an ethanol/water mixture used for this reaction rather than water on its own?

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(1)

- (iii) What is the effect on the rate of the reaction of doubling the concentration of 2-bromo-2-methylbutane?

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(1)

- (iv) Deduce the order of the reaction with respect to 2-bromo-2-methylbutane.

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(1)

- (v) Explain why this is the order of reaction with respect to 2-bromo-2-methylbutane and not the overall order of the reaction.

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(1)

- (b) The table below shows the results from another experiment where a solution of 2-bromo-2-methylbutane is reacted with varying concentrations of hydroxide ions.

A few drops of an acid-alkali indicator are added to the mixture and the time for the indicator to change to the acidic colour is measured.

$[\text{C}_5\text{H}_{11}\text{Br}]$ $/10^{-2} \text{ mol dm}^{-3}$	$[\text{OH}^-]$ $/10^{-3} \text{ mol dm}^{-3}$	Time /s
1.5	0.75	5
1.5	1.50	9
1.5	2.25	14

- (i) Calculate the rate of the reaction, in $\text{mol dm}^{-3} \text{s}^{-1}$, for each concentration of hydroxide ions.

(2)

- (ii) What effect does doubling the concentration of hydroxide ions have on the rate of the reaction?

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(1)

- (iii) What is the order of the reaction with respect to the hydroxide ions?

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(1)

- (c) When 2-bromo-2-methylbutane reacts with water, or hydroxide ions, the mechanism for the reaction is the same.

- (i) Use your answers to (a)(iv) and (b)(iii) to write the rate equation for the reaction with hydroxide ions.

Rate =

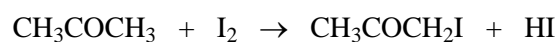
(1)

- (ii) Write a mechanism for the reaction which is consistent with your rate equation.

(2)

(Total 12 marks)

9. In an acidic solution, propanone reacts with iodine as follows:



The rate of this reaction can be followed by removing portions of the reaction mixture at known times, adding them to a solution of sodium hydrogen carbonate to stop the reaction and then titrating the mixture with standard sodium thiosulphate solution.

- (a) (i) Write the ionic equation for the reaction of thiosulphate ions with iodine in aqueous solution.

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(2)

- (ii) State which indicator is used in this titration, and describe what you would see at the end point.

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(2)

- (b) Use the following data to deduce the rate equation for the reaction of propanone with iodine in acidic solution, given that the order with respect to $[H^+]$ is one.

$[CH_3COCH_3]$ /mol dm ⁻³	$[I_2]$ /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1.0	0.10	3.2×10^{-3}
1.0	0.20	3.2×10^{-3}
2.0	0.10	6.4×10^{-3}

(3)

- (c) What is meant by:

- (i) order of reaction with respect to a particular reactant

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(1)

- (ii) overall order of reaction.

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(1)

- (d) What does the rate equation in (b) tell you about the involvement of iodine in the rate-determining step, and hence about the least number of steps in the reaction?

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(2)

- (e) Sodium hydroxide cannot be used to stop the reaction, because very alkaline conditions cause another reaction to occur between propanone and iodine.

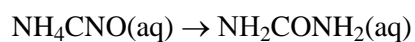
Write the equation for this reaction.

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(3)

(Total 14 marks)

10. This question is about the kinetics of the reaction in which ammonium cyanate, NH_4CNO , turns into urea, NH_2CONH_2 , in aqueous solution.



The table below shows the mass of urea, m_t , which formed at different times in a solution of ammonium cyanate of known starting concentration.

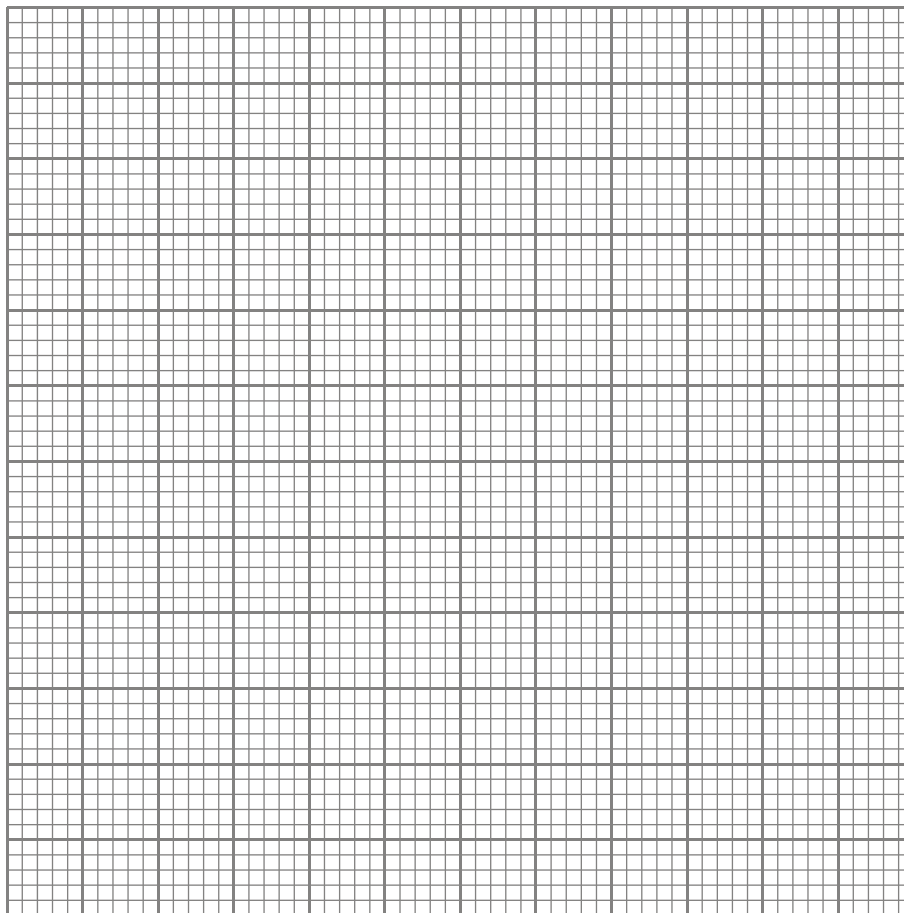
When the reaction stopped the mass of urea, m_{final} , was 20.3 g.

Time / min	Mass of urea, m_t / g	$m_{\text{final}} - m_t$ / g
0	0	20.3
25	12.5	7.8
50	15.7	4.6
75	17.1	3.2
100	17.5	2.8
150	18.7	1.6
200	19.1	
300	20.0	

- (a) Complete the final column of the table.

(1)

- (b) Plot a graph of $m_{\text{final}} - m_t$ (on the vertical axis) against time (on the horizontal axis).



(2)

(c) The graph can be used to work out a rate equation for the reaction.

What term in the rate equation for the reaction is proportional to $m_{\text{final}} - m_t$?

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(1)

- (d) (i) Show THREE successive half-life measurements on your graph, and give their values.

1. 2.

3.

(2)

- (ii) Use the half-lives to decide whether the reaction is zero order, first order or second order. Explain how you decided the order.

Order of reaction

Explanation

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(2)

(iii) Suggest a possible rate equation for the reaction.

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(1)

(e) A student thought that water might take part in the rate-determining step of the reaction.

(i) What is meant by the **rate-determining step**?

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(1)

- (ii) The solution of ammonium cyanate used in the experiment initially contained 0.35 moles of ammonium cyanate in approximately 1 dm³ (55.5 moles) of water.

Is the order you calculated in (d)(ii) an order with respect to ammonium cyanate, or could it include the water as well? Explain your answer.

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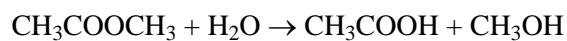
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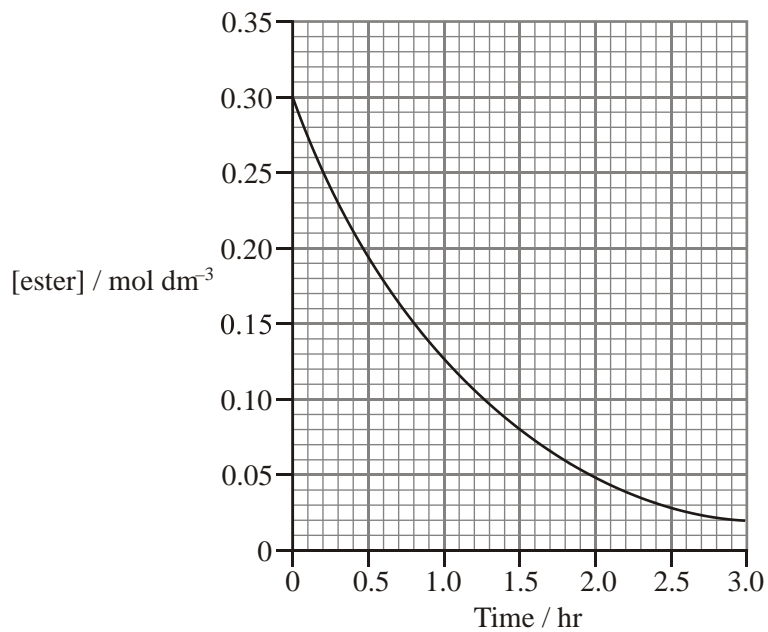
(Total 12 marks)

11. (a) The ester methyl ethanoate reacts with water as follows:



An experiment to investigate the kinetics of this hydrolysis showed that the concentration of methyl ethanoate varied as shown in the graph below.

The water in this reaction is not only a reagent but is also the solvent and is therefore in large excess.



- (i) Show, under these conditions, that the reaction is first order in methyl ethanoate.

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(2)

- (ii) Explain with a reason whether or not the overall order of reaction must also be one.

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(1)

- (iii) Assuming the reaction is first order, use the graph to calculate the rate constant, k . Include the units in your answer.

(3)

(iv) Suggest a method by which the progress of the reaction could be followed.

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(3)

(b) The Arrhenius equation

$$\ln k = \ln A - E_a/RT$$

relates the rate constant k to the activation energy E_a for a reaction. A is a constant, R is the gas constant.

- (i) Comment on the *relative* values of the rate constant k at a given arbitrary temperature T for two reactions, one of which has an activation energy of about 180 kJ mol^{-1} , the other of which has an activation energy of about 50 kJ mol^{-1} . No calculation is expected.

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(1)

- (ii) Suppose that these two different values of activation energy were for the same **overall** reaction at the same temperature. Suggest a way in which the conditions are different for the two reactions.

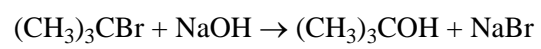
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(Total 11 marks)

12. 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide as shown in the equation below.



A series of experiments was carried out to investigate the kinetics of this reaction.

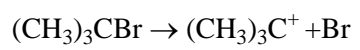
Initial concentration of $(\text{CH}_3)_3\text{CBr}$ / mol dm^{-3}	Initial concentration of NaOH / mol dm^{-3}	Initial rate of reaction / $\text{mol dm}^{-3} \text{s}^{-1}$
5.0×10^{-4}	2.0×10^{-2}	1.5×10^{-4}
1.5×10^{-3}	2.0×10^{-2}	4.5×10^{-4}
1.5×10^{-3}	4.0×10^{-2}	4.5×10^{-4}

- (a) (i) Give the order of the reaction with respect to
2-bromo-2-methylpropane
sodium hydroxide (2)
- (ii) Write the rate equation for this reaction.
..... (1)

- (b) Use one set of the data to calculate the rate constant for this reaction. Include the unit of the rate constant in your answer.

(2)

(c) The slowest step of the mechanism is the following reaction



Is your rate equation consistent with this information? Explain your answer.

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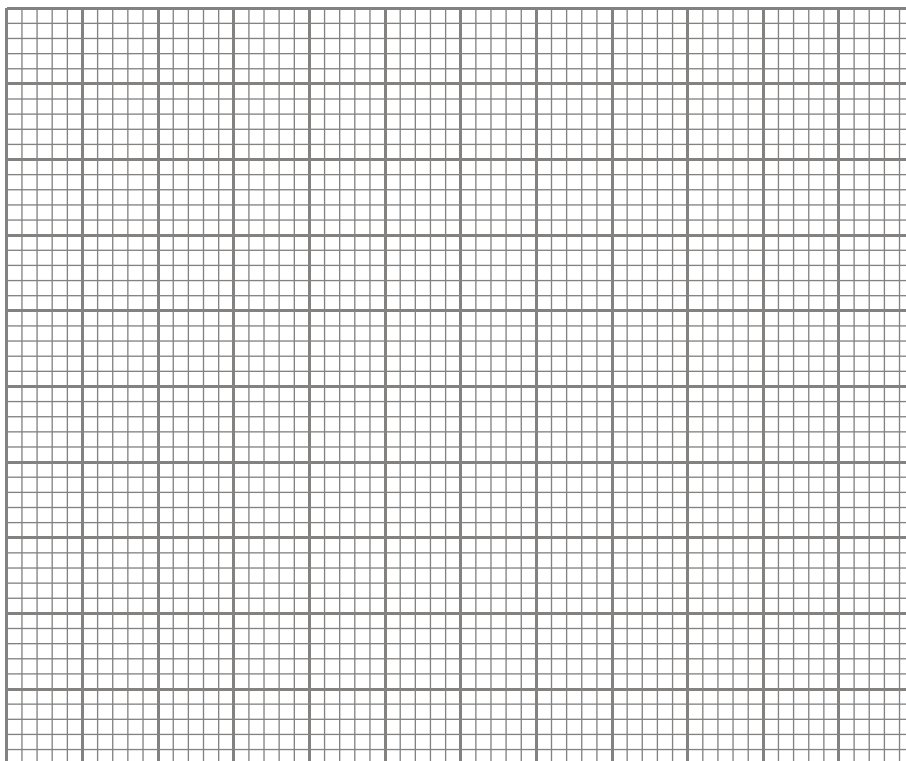
(1)

- (d) In another series of experiments, the rate of the reaction was measured at different temperatures. Complete the missing numbers in the table below.

temperature (T) /K	1/temperature ($1/T$) /K ⁻¹	rate /mol dm ⁻³ s ⁻¹	ln(rate)
300	3.33×10^{-3}	3.35×10^{-4}	-8.00
310	3.23×10^{-3}	7.47×10^{-4}	-7.20
320	3.13×10^{-3}	1.66×10^{-3}	-6.40
330	3.03×10^{-3}	4.09×10^{-3}	-5.50
340	2.94×10^{-3}	9.10×10^{-3}	-4.70
350		1.66×10^{-2}	

(2)

- (e) On the axes below plot a graph of $\ln(\text{rate})$ on the vertical axis against $1/T$ on the horizontal axis.



(2)

- (f) Use the Arrhenius equation

$$\ln(\text{rate}) = \text{constant} - \frac{E_{\text{A}}}{R} (1/T)$$

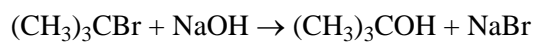
to calculate the value of the activation energy, E_{A} , for the reaction.

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

Show your working clearly and give your answer to 2 significant figures.

(2)
(Total 12 marks)

13. This question is about the kinetics of the reaction between 2-bromo-2-methylpropane and sodium hydroxide in a suitable solvent.



Equal volumes of $0.200 \text{ mol dm}^{-3}$ solutions of the two reactants were mixed together and maintained at a constant temperature of $30 \text{ }^\circ\text{C}$. The concentration of hydroxide ions was determined at different times. The results are shown in the table below.

$[\text{OH}^-]$ / mol dm^{-3}	Time /s
0.100	0
0.071	120
0.052	240
0.035	360
0.024	480
0.018	600

- (a) Describe how the concentration of hydroxide ions could be determined during the reaction.

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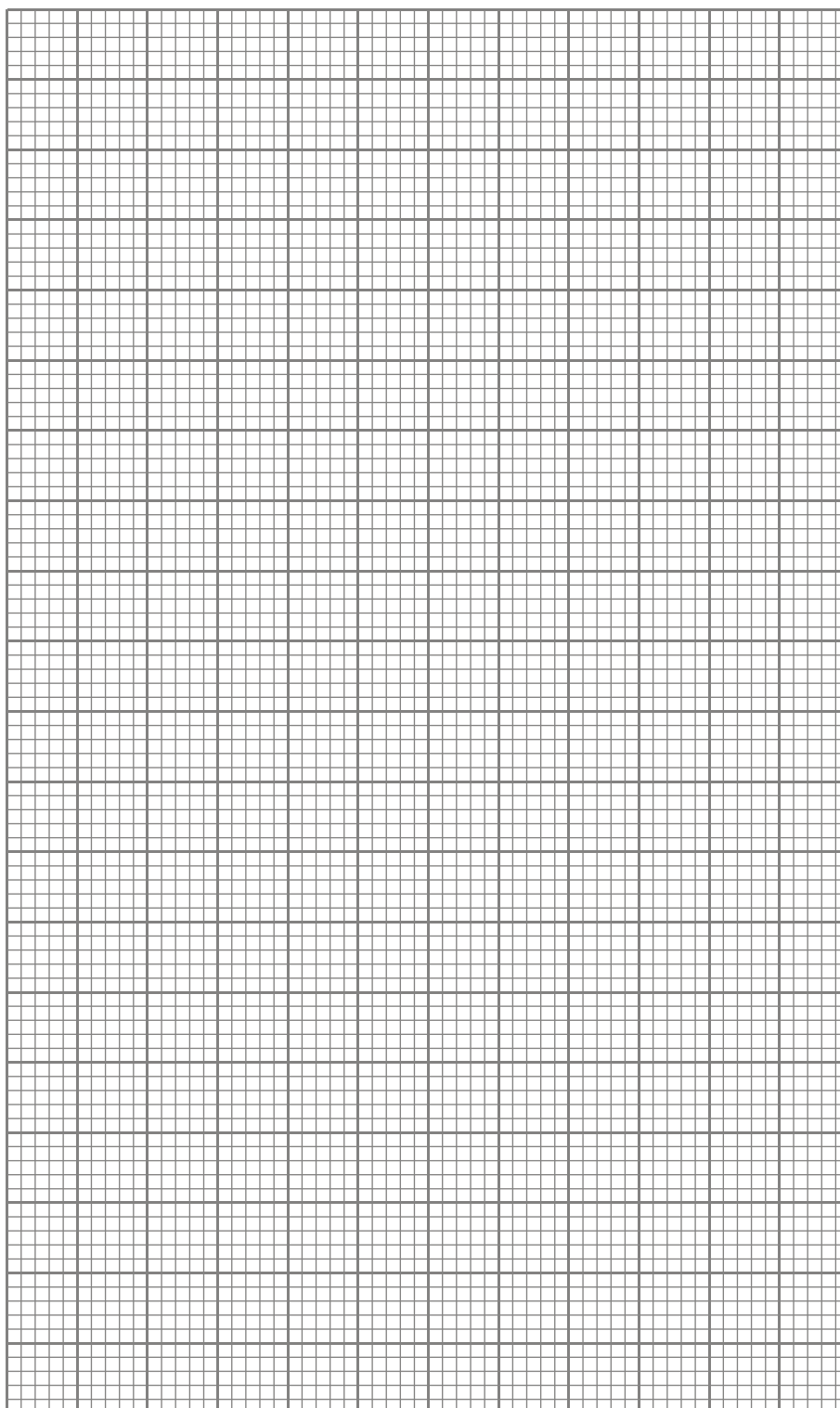
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(3)

- (b) (i) Plot a graph of hydroxide ion concentration (vertical axis) against time (horizontal axis) on the grid below.



(2)

- (ii) Mark on your graph TWO consecutive half-lives. Measure their values and write them below.

First half-life

Second half-life

(1)

- (iii) What is the order of the reaction? Explain how you used your half-lives to arrive at your answer.

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(1)

- (iv) Explain why your answer to (iii) is an **overall** order.

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(1)

- (v) Suggest a rate equation for this reaction.

Rate =

(1)

- (c) (i) What mechanism is likely to be operating in this reaction? Justify your answer.

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(2)

- (ii) Write equations to show the steps involved in your chosen mechanism for this reaction.

(2)
(Total 13 marks)

14. (a) Define the terms

- (i) Overall order of reaction

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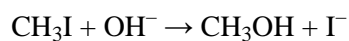
(1)

- (ii) Rate constant

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(1)

- (b) In a kinetic study of the reaction



At a certain temperature the following data were obtained:

Experiment	$[\text{CH}_3\text{I}]$ /mol dm ⁻³	$[\text{OH}^-]$ /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	0.1	0.1	1×10^{-5}
2	0.2	0.1	2×10^{-5}
3	0.1	0.2	2×10^{-5}

- (i) State the order of reaction with respect to CH_3I and with respect to OH^- ions. Give your reasons.

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(2)

- (ii) Write the rate equation for the reaction.

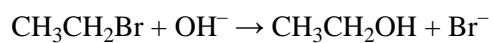
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(1)

- (iii) Calculate the value of the rate constant for this reaction, stating its units.

(2)

(c) The reaction



has an $\text{S}_{\text{N}}2$ mechanism that proceeds through a transition state.

(i) Draw the mechanism, showing the structure of the transition state.

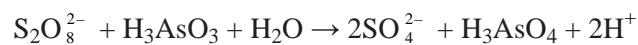
(3)

(ii) Draw a reaction profile for this exothermic reaction. Show the energy level of the transition state on the profile.

(2)

(Total 12 marks)

15. Persulphate ions, $\text{S}_2\text{O}_8^{2-}$ slowly oxidise arsenic(III) acid, H_3AsO_3 in aqueous solution according to the equation

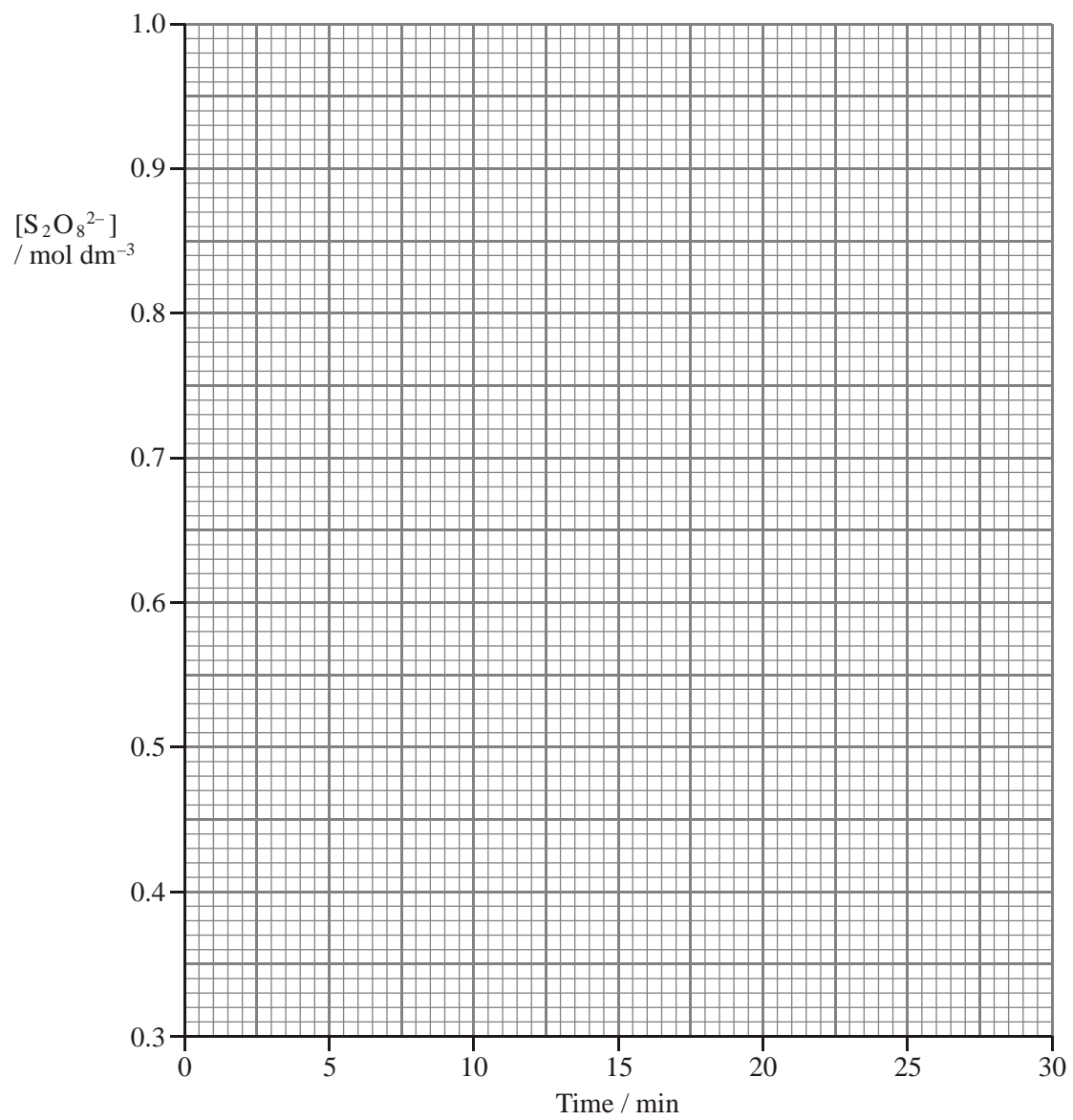


- 25 cm³ of a 1.0 mol dm⁻³ solution of potassium persulphate was mixed with 25 cm³ of a solution of arsenic(III) acid of the same concentration.
- At timed intervals, small portions of the reaction mixture were analysed to determine the concentration of persulphate ion, $[\text{S}_2\text{O}_8^{2-}]$.

The results are shown below.

Time / minutes	$[\text{S}_2\text{O}_8^{2-}]$ / mol dm ⁻³
0	1.0
5	0.76
10	0.62
15	0.52
20	0.44
30	0.35

- (a) (i) On the grid below, plot a graph of the concentration of persulphate ions against time.



(2)

- (ii) Draw a tangent to the curve at the point where $[\text{S}_2\text{O}_8^{2-}] = 0.50 \text{ mol dm}^{-3}$ and use it to calculate the slope of the curve at that point. Give your answer to **two** significant figures.

Slope:

(4)

- (b) The rate of the reaction at a particular concentration of reactant can be measured from the slope of the graph at that concentration.

The **initial** rate, which is the rate when the concentrations of persulphate ions, $\text{S}_2\text{O}_8^{2-}$, and arsenic(III) acid, H_3AsO_3 , are both 1.0 mol dm^{-3} , was found to be $0.060 \text{ mol dm}^{-3} \text{ min}^{-1}$.

- (i) Use your answer to (a)(ii) to show that the ratio of the initial rate to the rate when $[\text{S}_2\text{O}_8^{2-}]$ and $[\text{H}_3\text{AsO}_3]$ are 0.50 mol dm^{-3} is approximately 4:1. Use this ratio to deduce the **overall** order of reaction.

(3)

- (ii) Suggest TWO rate equations that agree with the order of the reaction that you have deduced in (i). How could the experiment be adapted to distinguish between these two rate equations?

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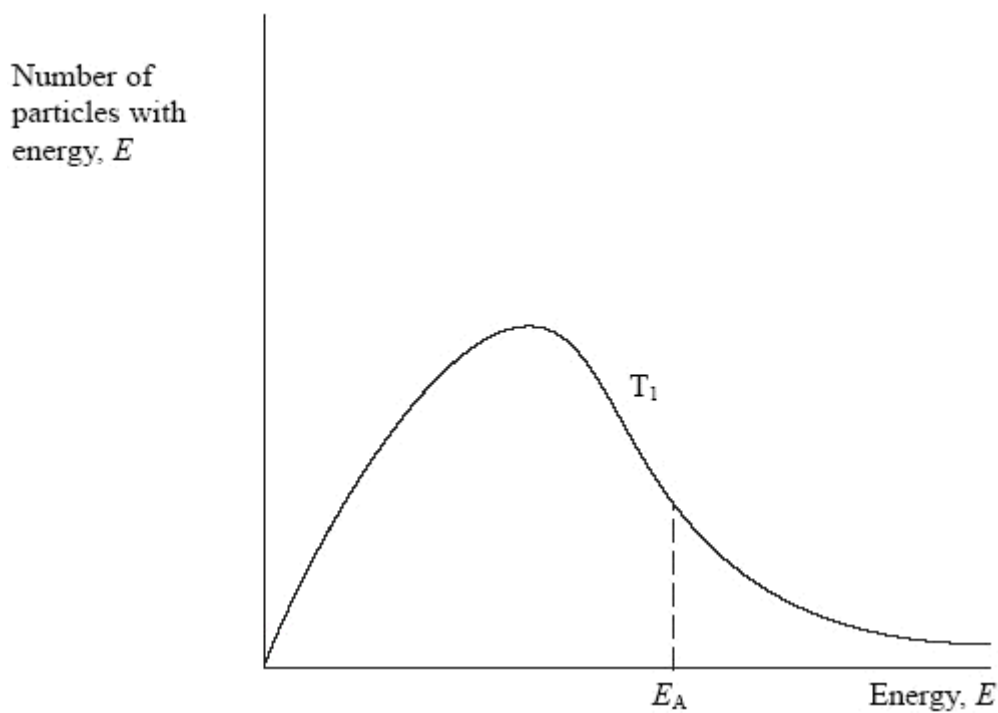
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(5)
(Total 14 marks)

16. (a) The distribution of the energy of particles in a gas at temperature T_1 is shown below.



- (i) On the diagram above, draw the distribution of energy of particles at a **lower** temperature, T2.

(2)

- (ii) Use the diagram to explain why the rate of a reaction increases with an increase in temperature.

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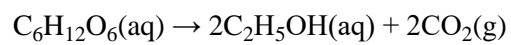
(3)

- (iii) Explain fully why a catalyst increases the rate of a reaction.

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(2)

- (b) The fermentation of glucose is an exothermic reaction and is catalysed by enzymes in yeast.



The reaction is slow at room temperature.

- (i) Describe, with the aid of a diagram, an experiment you could do to follow the progress of this reaction at different temperatures.

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(4)

- (ii) Would you expect ΔS_{system} to be positive or negative for this reaction? Justify your answer with TWO pieces of evidence.

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(2)

- (iii) Deduce the sign of $\Delta S_{\text{surroundings}}$. Show your reasoning.

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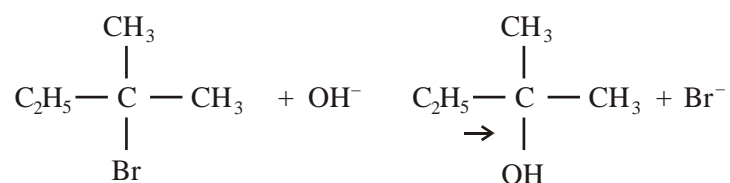
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(2)

(Total 15 marks)

17. 2-bromo-2-methylbutane reacts with aqueous sodium hydroxide in a substitution reaction.

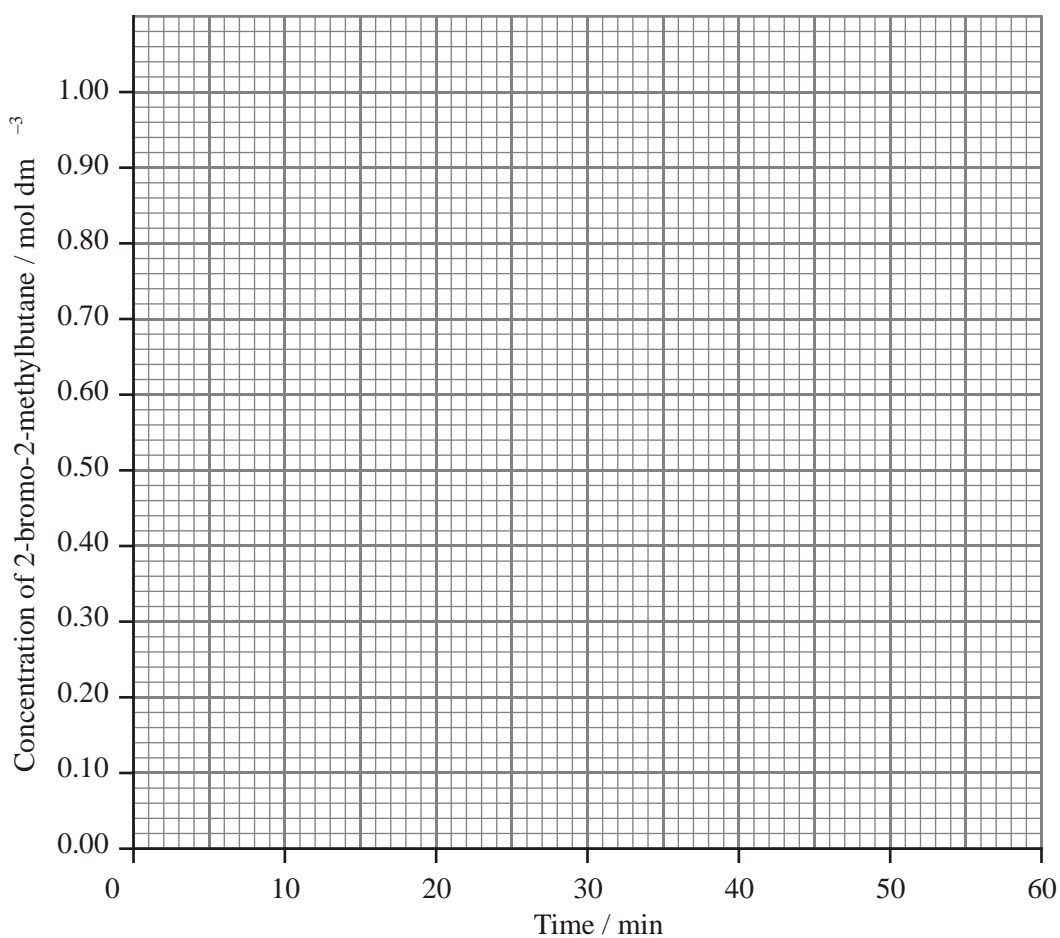


- (a) The rate of reaction can be followed by measuring the concentration of 2-bromo-2-methylbutane at various times.

In one such experiment, a known amount of 2-bromo-2-methylbutane was added to a **large** excess of aqueous sodium hydroxide. The following results were obtained.

Time/min	Concentration of 2-bromo-2-methylbutane/mol dm ⁻³
0	0.96
10	0.61
20	0.38
30	0.24
40	0.15
50	0.10

- (i) Plot a graph of the concentration of 2-bromo-2-methylbutane on the y (vertical) axis against time on the x (horizontal) axis.



(2)

- (ii) Show TWO successive half-life measurements on your graph and write their values below.

First half-life

Second half-life

(2)

- (iii) What is the order of reaction with respect to 2-bromo-2-methylbutane?
Give a reason for your answer.

Order

Reason

.....

(2)

- (b) When the reaction is repeated using equal concentrations of 2-bromo-2-methylbutane and aqueous sodium hydroxide, the same results are obtained.

- (i) What is the order of reaction with respect to hydroxide ions?

.....

(1)

- (ii) Write the rate equation for the reaction.

.....

(1)

(iii) Write a mechanism for the reaction which is consistent with your rate equation.

(3)

(c) The reaction between 2-bromobutane, $C_2H_5CHBrCH_3$, and aqueous sodium hydroxide proceeds by the same mechanism as in (b)(iii).

Use the mechanism to explain why the reaction of a single optical isomer of 2-bromobutane produces a mixture that is no longer optically active.

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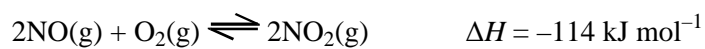
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(3)

(Total 14 marks)

18. One step in the manufacture of nitric acid is the reaction between nitrogen(II) oxide and oxygen to form nitrogen(IV) oxide.



- (a) (i) Use the equation to suggest the sign of ΔS_{system} for the forward reaction. Justify your answer.

.....

(2)

- (ii) What is the sign of $\Delta S_{\text{surroundings}}$ for the forward reaction? Justify your answer.

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(2)

- (b) (i) Write the expression for K_p for this reaction.
 What are the units of K_p in this reaction?

Units

(2)

- (ii) Suggest how the temperature and pressure could be altered to make nitrogen(IV) oxide more economically. Justify your suggestions by considering both yield and rate.

Temperature

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Pressure

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(4)

- (c) (i) What property would allow you to follow the progress of this reaction? Justify your answer.

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(2)

(ii) In a series of experiments, the following results were obtained.

Experiment	[NO(g)] /mol dm ⁻³	[O ₂ (g)] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	1.0 × 10 ⁻³	1.0 × 10 ⁻³	8.0 × 10 ⁻⁶
2	2.0 × 10 ⁻³	1.0 × 10 ⁻³	3.2 × 10 ⁻⁵
3	2.0 × 10 ⁻³	2.0 × 10 ⁻³	6.4 × 10 ⁻⁵

- What is the order of the reaction with respect to NO(g)? Justify your answer.

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(2)

- What is the order of the reaction with respect to O₂(g)?

.....

(1)

(iii) What is the rate equation for this reaction?

(1)

(iv) What is the overall order for this reaction?

.....

(1)

(v) Calculate the rate constant, k , for this reaction. Include units with your answer.

(2)

(d) Suggest why this reaction takes place quickly at room temperature and pressure.

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(1)

(Total 20 marks)

19. (a) Explain what is meant by the following terms.

Rate of reaction

.....

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Overall order of a reaction

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.....

(2)

- (b) Two gases, A and B, react according to the equation



A series of experiments carried out at 298 K gave the following results.

Experiment	Initial concentration of A / mol dm ⁻³	Initial concentration of B / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ min ⁻¹
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.200	0.100	0.00399

- (i) State the order of reaction with respect to each of the reactants. Justify your answer.

Reactant A

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Reactant B

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(3)

- (ii) Write the rate equation for the reaction between A and B.

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(1)

- (iii) Use the experimental data from **Experiment 1** to calculate the rate constant, including units.

(2)

- (iv) Suggest a possible mechanism for the reaction between A and B, leading to the formation of AB₃. Identify the rate-determining step.

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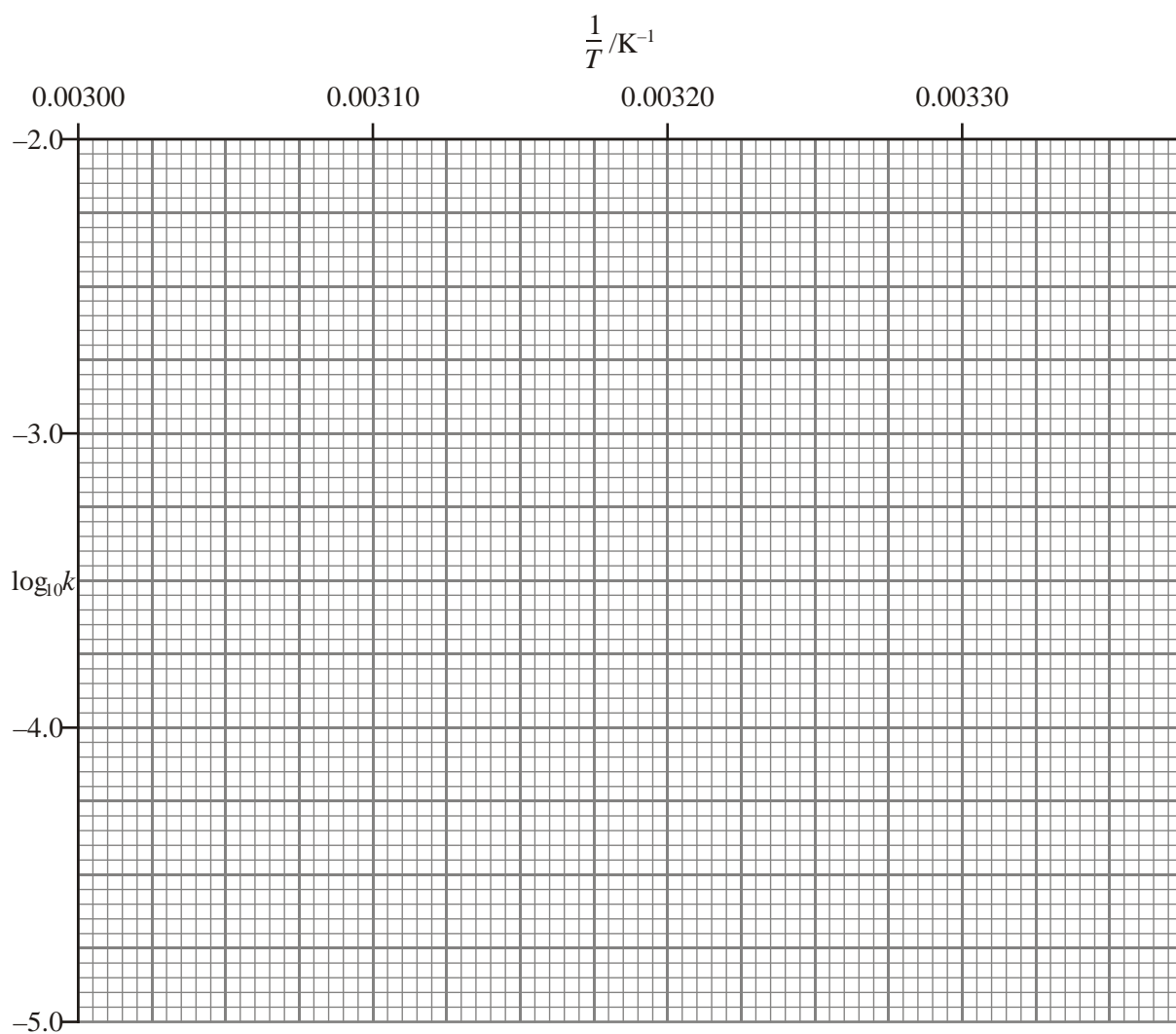
(3)

- (c) The rate constant, k , for the reaction in (b) was measured at different temperatures.

The following data were obtained.

$\log_{10} k$	$\frac{1}{T} / \text{K}^{-1}$
-2.70	0.00303
-3.39	0.00315
-4.09	0.00327
-4.43	0.00333

- (i) Plot a graph of $\log_{10} k$ against $\frac{1}{T}$, on the grid below.



(2)

(ii) The Arrhenius equation can be written

$$\log_{10} k = \text{constant} - \frac{E_a}{2.30R} \left(\frac{1}{T} \right)$$

where $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

A graph of $\log_{10} k$ against $\frac{1}{T}$ has a gradient of $\frac{-E_a}{2.30R}$.

Calculate the gradient of the graph and hence calculate the value of activation energy, E_a .

(2)

(Total 15 marks)

20. This question is about the reaction between calcium carbonate and hydrochloric acid.



One method of studying the kinetics of this reaction is to measure the volume of carbon dioxide given off at various timed intervals when using an excess of calcium carbonate.

- (a) Suggest TWO other methods for following this reaction. Explain your choices.

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(2)

- (b) Suggest why the volume of carbon dioxide given off in the first few seconds of the reaction is an unreliable measure of the initial rate of the reaction.

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(1)

- (c) In an experiment, the following results were obtained.

Time / s	Volume of CO ₂ V _t /cm ³	(V _{final} - V _t) / cm ³
5	3	85
35	42	46
65	62	26
95	72	
125	79	
155	84	
185	87	

- (i) What was the final volume, V_{final}?

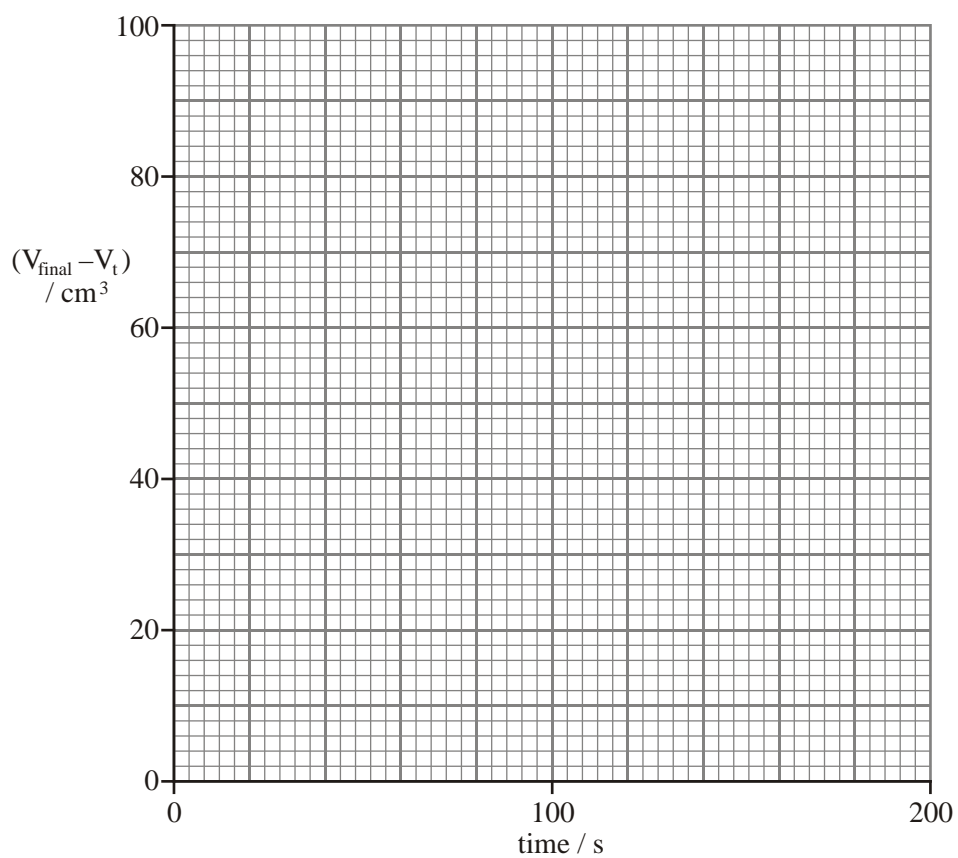
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(1)

(ii) Complete the table. (1)

(iii) To what is $(V_{\text{final}} - V_t)$ proportional?
 (1)

(iv) Plot these results on the grid below.



(2)

- (v) On your graph measure and record THREE successive half-lives. Deduce the order of the reaction. Justify your answer.

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(3)

- (vi) Give the rate equation for this reaction.

(1)

- (vii) What are the units of the rate constant?

.....

(1)

- (d) What would you expect the signs of ΔS_{system} and ΔS_{total} to be for the reaction between calcium carbonate and hydrochloric acid? Justify your answers.

ΔS_{system}

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ΔS_{total}

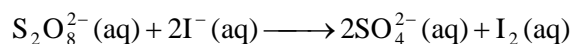
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(4)
(Total 17 marks)

21. The reaction between peroxodisulphate and iodide ions occurs as follows:



Initial rates for this reaction can be determined by a method known as an 'iodine clock'.

A mixture of potassium iodide, sodium thiosulphate and starch is made up, and a clock started when a solution of potassium peroxodisulphate is added. When enough iodine has been formed to react with all the sodium thiosulphate, the excess iodine suddenly forms a blue-black complex with the starch. At this point the clock is stopped, and the time taken.

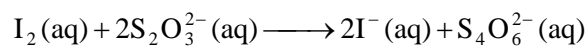
- (a) In one particular experiment, the volumes of the reactants used were as follows:

Volume of $\text{K}_2\text{S}_2\text{O}_8(\text{aq})$ / cm^3	Volume of $\text{KI}(\text{aq})$ / cm^3	Volume of $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ / cm^3	Volume of starch solution / cm^3	Volume of water / cm^3	Time taken / s
10.0	10.0	5.0	1.0	14.0	5

- (i) The concentration of the sodium thiosulphate used was $0.010 \text{ mol dm}^{-3}$. Calculate the number of moles of thiosulphate ions, $\text{S}_2\text{O}_3^{2-}$, in the mixture.

(1)

(ii) Iodine reacts with thiosulphate ions as shown below:



Calculate the number of moles of iodine which had reacted when the clock was stopped.

(1)

(iii) Calculate the rate of formation of iodine in $\text{mol dm}^{-3} \text{ s}^{-1}$.

(2)

(b) Further experiments were carried out and the results are shown below.

Experiment	$[\text{S}_2\text{O}_8^{2-}(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0100	0.0200	2.74×10^{-5}
2	0.0100	0.0400	5.47×10^{-5}
3	0.0300	0.0800	3.28×10^{-4}

(i) What is the order of reaction with respect to iodide ions, I^- ?

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(1)

(ii) Deduce the order of reaction with respect to peroxodisulphate ions, $\text{S}_2\text{O}_8^{2-}$. Show how you arrived at your answer.

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(1)

(iii) Use your answers to (i) and (ii) to write an overall rate equation for the reaction.

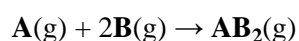
(1)

(iv) Use the data from **experiment 1** to calculate the rate constant for this reaction.
Give the units for the rate constant.

(2)

(Total 9 marks)

22. Two gases, **A** and **B**, react according to the equation



A series of kinetics experiments performed at constant temperature gave the following results:

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	0.0500	0.100	1.00 × 10 ⁻⁴
2	0.0500	0.200	3.92 × 10 ⁻⁴
3	0.1000	0.100	1.95 × 10 ⁻⁴

(a) (i) Calculate, showing your working, the order of reaction with respect to **A** and to **B**.

(3)

(ii) Write the rate equation for the reaction.

.....

(1)

(iii) Calculate the rate constant, k , for the reaction in **experiment 3**, stating its units.

(2)

- (b) (i) Explain, in terms of collision theory, why the rate of reaction increases with an increase in temperature.

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(3)

- (ii) Suggest, with an explanation, the least number of steps which is *likely* to exist in the mechanism of the reaction between **A** and **B**.

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(2)

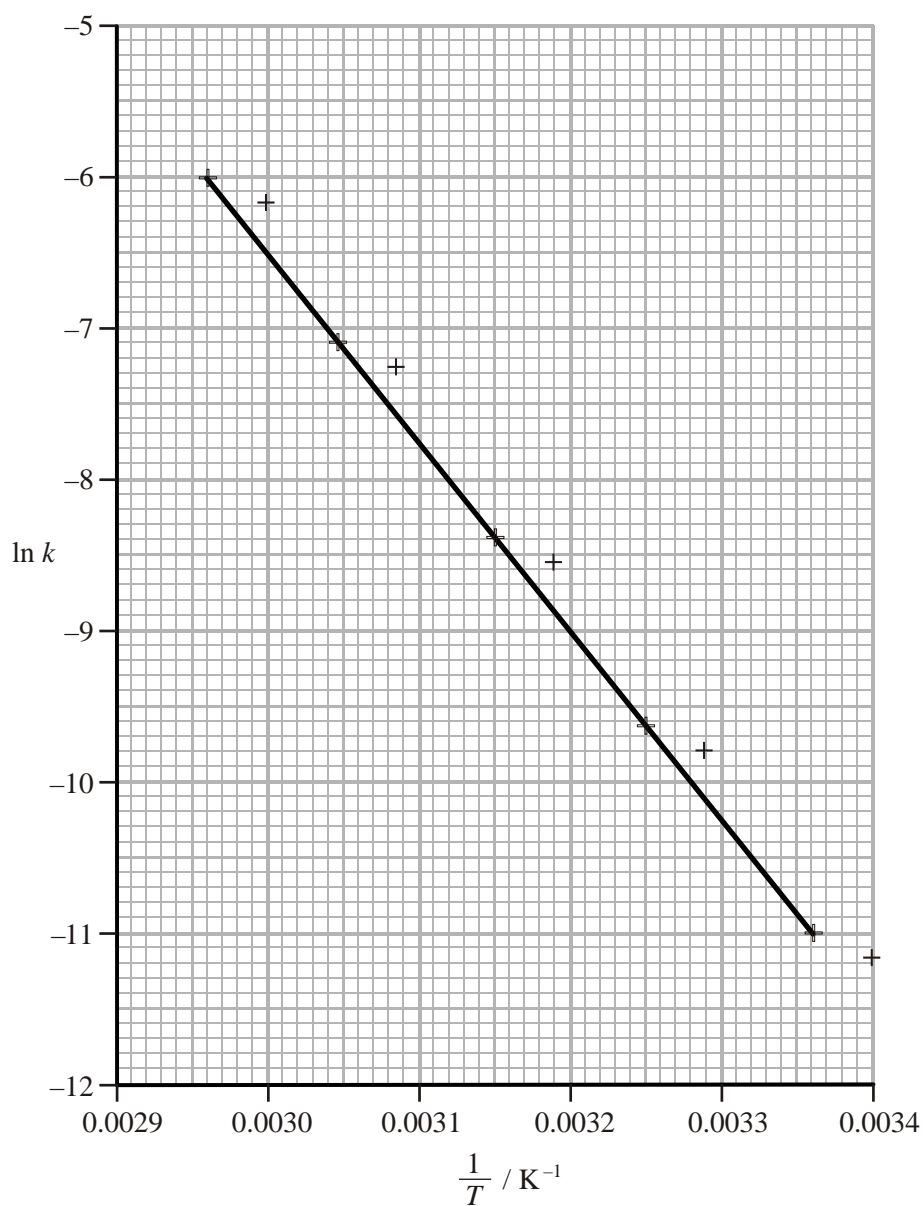
- (c) The variation of the rate constant, k , with change in temperature is given by the Arrhenius equation:

$$\ln k = \left(\frac{-E_a}{R} \right) \frac{1}{T} + \ln A$$

where A is a constant.

In a series of experiments performed at various temperatures T to determine the rate constant, k , for the decomposition of a gas X , a graph of $\ln k$ against $1/T$ gave a straight

line of slope $\frac{-E_a}{R}$:



Use the graph to calculate the value of the activation energy, in kJ mol^{-1} , for the decomposition of **X**. The value of the gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

(4)
(Total 15 marks)

23. In the presence of hydrogen ions, H^+ , glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, can be oxidised by a solution of potassium manganate(VII), KMnO_4 , which is purple in colour.

A series of experiments was carried out to determine the rate of reaction and the results are shown below.

Experiment	Initial concentration of $\text{C}_6\text{H}_{12}\text{O}_6$ / mol dm^{-3}	Initial concentration of KMnO_4 / mol dm^{-3}	Initial concentration of H^+ / mol dm^{-3}	Rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	1.0	0.01	0.5	2.0×10^{-5}
2	1.0	0.005	0.5	1.0×10^{-5}
3	0.5	0.005	0.5	1.0×10^{-5}
4	1.0	0.02	1.0	8.0×10^{-5}

- (a) Describe how the rate of this reaction may have been measured.

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(2)

- (b) (i) Give the order of reaction with respect to each reactant. In the case of potassium manganate(VII) and hydrogen ions explain how you arrived at your answer.

Glucose

Potassium manganate(VII)

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Hydrogen ions

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(3)

- (ii) Write the rate equation for this reaction.

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(1)

- (iii) Using the data from **experiment 1**, calculate the rate constant for the reaction. Include the units of the rate constant in your final answer.

(2)

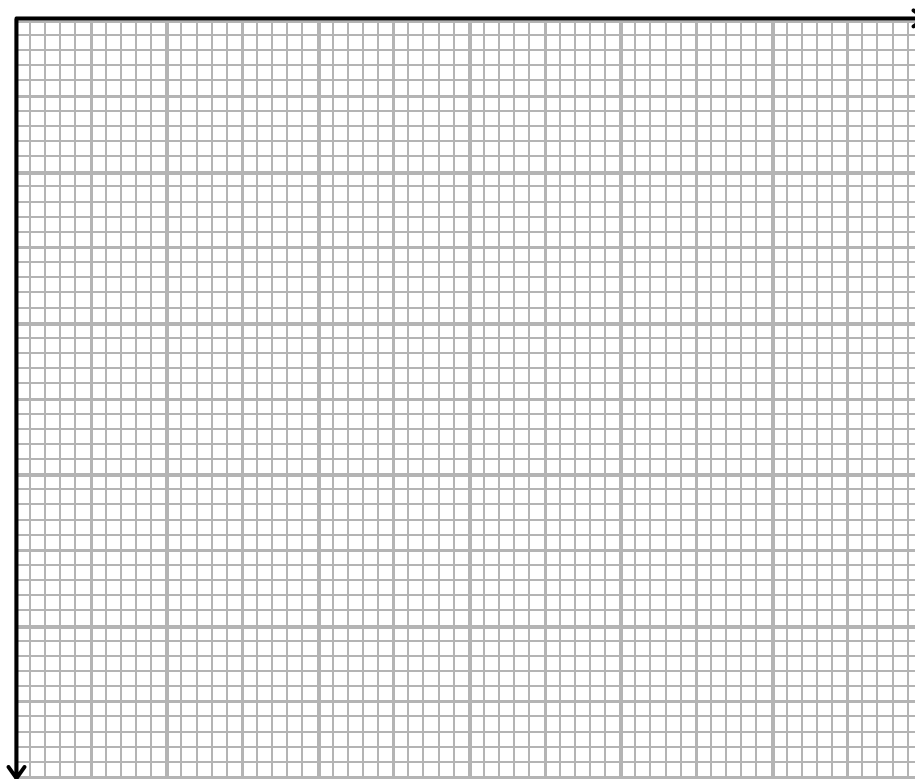
- (c) Additional experiments were carried out to investigate the effect of temperature on the rate of reaction.

- (i) Complete the missing data in the table below.

Temperature (T) / K	1/ temperature (1/T) / K ⁻¹	Rate constant	ln (rate constant)
295	3.39×10^{-3}	2.88×10^{-3}	-5.85
305	3.28×10^{-3}	1.01×10^{-2}	-4.60
311		1.83×10^{-2}	
320	3.13×10^{-3}	4.98×10^{-2}	-3.00
333	3.00×10^{-3}	2.02×10^{-1}	-1.60

(1)

- (ii) Plot a graph of $\ln(\text{rate constant})$ on the vertical axis against $1/T$ on the horizontal axis using the axes below.



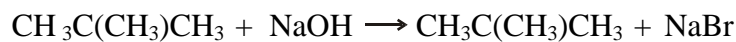
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- (iii) Use the Arrhenius equation $\ln(\text{rate}) = \frac{-E_A}{R} \times \frac{1}{T} + \text{constant}$, together with your graph to calculate a value of the activation energy, E_A , for this reaction. Show all steps in your working. Include units in your final answer, which should be given to **two** significant figures.
[Gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$]

(2)

(Total 13 marks)

24. The principal reaction occurring when 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide is as follows:



Several experiments were carried out in order to follow the kinetics of this alkaline hydrolysis. A few drops of phenolphthalein were added to a sample of sodium hydroxide, and, after the addition of a measured amount of 2-bromo-2-methylpropane, the mixture was vigorously shaken and a clock was immediately started. The time was taken when the pink colour due to the indicator disappeared.

This experiment was repeated twice using different concentrations of the two reactants. All experiments were carried out at the same temperature.

The results are shown in the table below.

Experiment	2-bromo-2-methylpropane / mol dm ⁻³	Sodium hydroxide / mol dm ⁻³	Time /s
A	0.011	8.0×10^{-4}	33
B	0.022	8.0×10^{-4}	16
C	0.022	1.2×10^{-3}	24

- (a) (i) Identify the attacking species responsible for this alkaline hydrolysis.

.....

(1)

- (ii) Assuming that the final concentration of sodium hydroxide is zero, calculate the average rates of reaction in mol dm⁻³ s⁻¹ for experiments **A** and **B**.

A mol dm⁻³ s⁻¹

B mol dm⁻³ s⁻¹

(2)

- (iii) Deduce the order of reaction with respect to 2-bromo-2-methylpropane. Justify your answer.

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(1)

- (iv) By comparing the average rates of reaction between experiments **B** and **C**, deduce the order of reaction with respect to sodium hydroxide.

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(2)

- (v) Write the rate equation for the reaction.

Rate =

(1)

- (vi) From your rate equation, suggest how this reaction proceeds by giving a possible mechanism.

(3)

- (b) Explain briefly why 1-bromobutane, an isomer of 2-bromo-2-methylpropane, reacts by a different mechanism when it is hydrolysed.

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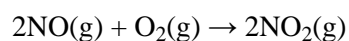
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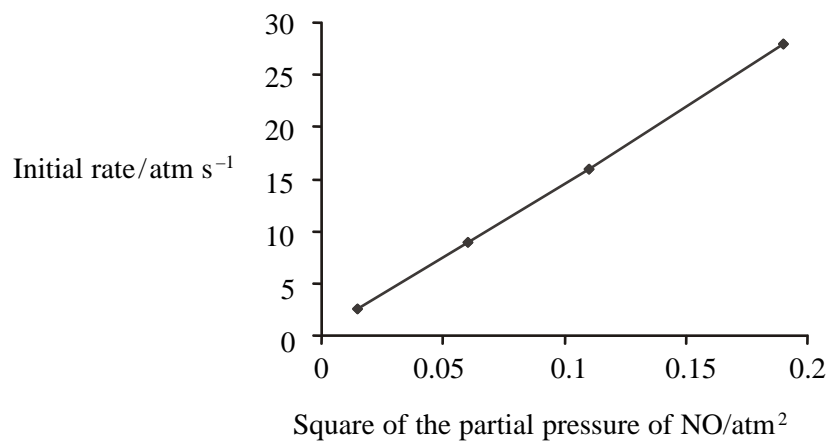
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(2)
(Total 12 marks)

25. This question concerns the reaction between nitrogen monoxide and oxygen:



- (a) In a series of experiments designed to find the rate equation for this reaction, the following data were obtained. In each experiment the partial pressure of oxygen was the same.



- (i) What is the order of reaction with respect to nitrogen monoxide?

Justify your answer.

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(2)

- (ii) A new series of readings is taken with the partial pressure of oxygen doubled. The gradient of the line doubles.

State, with a reason, the order of reaction with respect to oxygen.

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(1)

- (iii) Hence write the rate equation for the reaction.

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(1)

- (iv) State the units of the rate constant.

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(1)

- (b) The rate of the decomposition of nitrous oxide



has been studied at different temperatures. The rate constant k was determined at each temperature.

The relationship between the rate constant and the temperature T is given by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

where E_a is the activation energy for the reaction, R is the gas constant, and k is the rate constant at temperature T .

- (i) Given values of k at different temperatures T , what graph would you plot and how would you use it to determine the activation energy?

.....

(2)

- (ii) A plot of the data gave a straight line with gradient $-2.95 \times 10^4 \text{ K}^{-1}$.

Find the activation energy for the reaction, in kJ mol^{-1} , to **three** significant figures.

[The value of R is $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

(2)

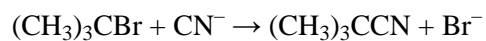
(iii) What is the oxidation number of nitrogen in nitrous oxide, N_2O ?

Put a cross (☒) in the box of the correct answer. If you change your mind about an answer, put a line through the box (~~☒~~) and then mark your new answer with a cross (☒).

A	+2	☒
B	+1	☒
C	-1	☒
D	-2	☒

(1)
(Total 10 marks)

26. Cyanide ions react with 2-bromo-2-methylpropane in the following way:



The rate equation for this reaction is

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

(i) What information does this rate equation give about the mechanism of this reaction?

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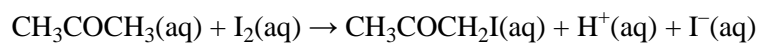
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(2)

- (ii) Give the mechanism for this reaction consistent with the rate equation.

(3)
(Total 5 marks)

27. This question is about the reaction of iodine with propanone.



- (a) Suggest, **in outline**, THREE different methods for following the rate of this reaction. State which of the reactants or products could be measured by each method you choose.

Method 1

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Method 2

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Method 3

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(3)

- (b) The reaction is extremely slow at room temperature in the absence of H^+ ions as a catalyst.

Suggest how you would quench the reaction before carrying out a titration method to determine the concentration of iodine at different times.

Justify your answer.

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(2)

- (c) A series of experiments was carried out, varying the concentrations of the reactants and the catalyst. The following results were obtained.

Experiment	$[\text{CH}_3\text{COCH}_3]$ /mol dm ⁻³	$[\text{I}_2]$ /mol dm ⁻³	$[\text{H}^+]$ /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	1.00	0.010	0.10	2.8×10^{-6}
2	1.00	0.010	0.20	5.6×10^{-6}
3	1.50	0.010	0.20	8.4×10^{-6}
4	1.50	0.020	0.10	4.2×10^{-6}

The reaction is first order with respect to hydrogen ions, H^+ .

- (i) Deduce the order of the reaction with respect to propanone, CH_3COCH_3 . Justify your answer.

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(3)

- (ii) Deduce the order of the reaction with respect to iodine, I_2 .

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(1)

- (iii) Hence give the rate equation for this reaction.

(1)

- (iv) Which species are involved in the rate-determining step?

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(1)

- (v) Suggest an equation for the reaction between the species in the rate-determining step.

Explain why this step is likely to take place.

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(2)

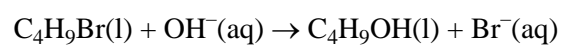
(Total 13 marks)

28. This question involves the following techniques which can be used to follow chemical reactions in order to investigate their kinetics.

- A collecting and measuring the volume of a gas
- B colorimetry
- C measuring the electrical conductivity
- D titration with standard acid solution

Select, from A to D, the technique **most** appropriate to investigate:

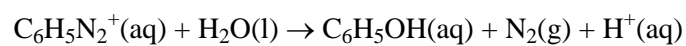
- (a) the hydrolysis of 1-bromobutane using hydroxide ions



- A
- B
- C
- D

(1)

- (b) the decomposition of the benzenediazonium ion



- A
- B
- C
- D

(1)

- (c) the reaction of acidified potassium manganate(VII) with propan-2-ol to give propanone and manganese(II) sulfate.

A

B

C

D

(1)

- (d) the catalytic decomposition of hydrogen peroxide.

A

B

C

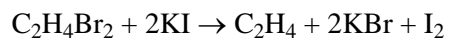
D

(1)

(Total 4 mark)

(2)

- (iii) Use the Arrhenius equation $\ln(\text{rate}) = \frac{-E_A}{R} \times \frac{1}{T}$ 29. 1,2-dibromoethane reacts with potassium iodide dissolved in methanol according to the equation:



The rate equation for this reaction is

- A rate = $k[\text{KI}]^2[\text{C}_2\text{H}_4\text{Br}_2]$
 B rate = $k[\text{KI}]^2$
 C rate = $k[\text{C}_2\text{H}_4\text{Br}_2]$
 D not possible to deduce from this information

(Total 1 mark)

+ constant, together with your graph to calculate a value of the activation energy, E_A , for this reaction. Show all steps in your working. Include units in your final answer, which should be given to **two** significant figures.

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

(2)
(Total 13 marks)

30. For the reaction between sodium bromate(V) and sodium bromide in acidic solution, the rate equation is:

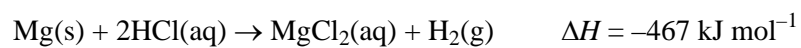
$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

When the concentrations of all three reactants are doubled, the rate will increase by a factor of

- A 4
- B 6
- C 8
- D 16

(Total 1 mark)

31. This question is about the reaction of magnesium with hydrochloric acid which takes place rapidly at room temperature.



- (a) Rewrite the equation omitting spectator ions.

(1)

(b) Suggest the sign of the following entropy changes for this reaction. Justify each of your answers.

(i) ΔS_{system}

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(2)

(ii) $\Delta S_{\text{surroundings}}$

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(2)

(iii) ΔS_{total}

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(1)

(c) A student carried out this experiment at five different temperatures in order to calculate the activation energy of the reaction. The student's laboratory record is shown below.

Method

Clean a strip of magnesium weighing 0.100 g with sand paper. Measure the temperature of 20 cm³ of 1.00 mol dm⁻³ hydrochloric acid in a 100 cm³ beaker. Add the magnesium ribbon, stir continuously, and time how long it takes for the magnesium to disappear. Repeat the experiment at four other temperatures.

Assumption: the initial rate of reaction is proportional to 1/time.

Results

Temperature /°C	Temperature /K	1/T /K ⁻¹	time /s	1/time /s ⁻¹	ln 1/time
24	297	3.37 × 10 ⁻³	45	0.0222	-3.81
33	306	3.27 × 10 ⁻³	25	0.0400	-3.22
45	318	3.14 × 10 ⁻³	11	0.0909	-2.40
56	329	3.04 × 10 ⁻³	6	0.1667	-1.79
10	283	3.53 × 10 ⁻³	122	0.0082	-4.80

The Arrhenius equation is $\ln k = -E_a/R \times (1/T) + \text{constant}$

$\ln 1/\text{time}$ is proportional to $\ln k$ and so a graph of $\ln 1/\text{time}$ will have the same gradient as that of the Arrhenius plot of $\ln k$ against $1/\text{Temperature}$

The student plotted the graph of $\ln 1/\text{time}$ against $1/\text{Temperature}$ and from this the activation energy, E_A , was calculated as $+ 51.3 \text{ kJ mol}^{-1}$.

- (i) Suggest the reason for cleaning the magnesium ribbon with sand paper.

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(1)

- (ii) Calculate the number of moles of hydrochloric acid used up when all the magnesium reacts in one experiment. Hence comment on whether the change in concentration during the reaction will have a significant effect on the validity of the assumption that the initial rate of reaction is proportional to $1/\text{time}$. How would you overcome this potential error?

[Take the relative atomic mass of magnesium as 24 in this and subsequent calculations.]

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- (iii) Use the value of ΔH and other information given in the question to calculate the temperature change in an experiment assuming no energy is lost to the surroundings. Hence comment on whether this change in temperature will have a significant effect. How would you overcome this potential error?

$$[\Delta H = -467 \text{ kJ mol}^{-1}]$$

heat produced = mass \times specific heat capacity \times change in temperature.

Assume that the specific heat capacity of the solution is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$

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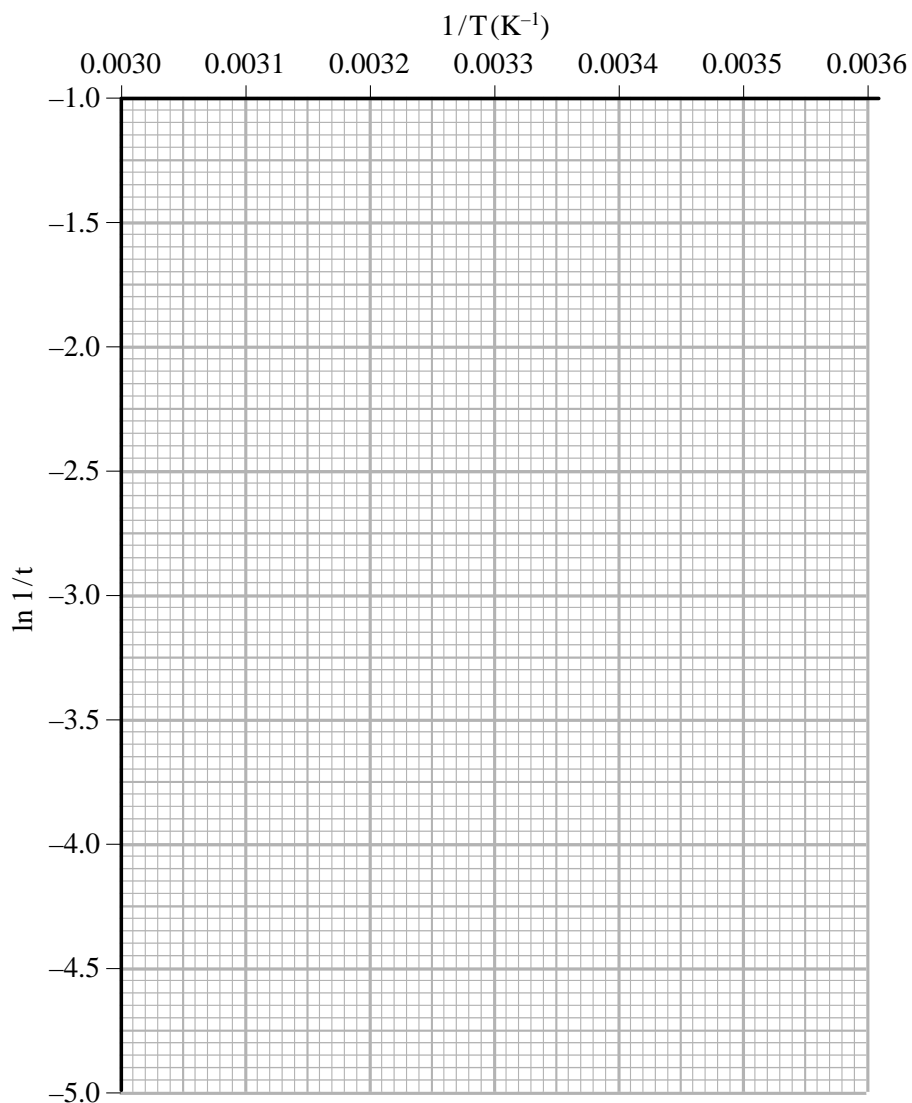
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(4)

- (iv) The most difficult thing to measure accurately is the time it takes for the magnesium to disappear and the time measured can be up to 2 seconds out. Assuming this error, calculate the shortest time at 56 °C **and** the longest time at 10 °C for this reaction.

Complete the table for these times. Plot the two points on the grid below and join them with a straight line. From the gradient, which equals $-E_A/R$, of this line calculate another value for the activation energy.

Temperature / °C	Temperature /K	1/T /K ⁻¹	time /s	1/time /s ⁻¹	ln 1/time
56	329	3.04×10^{-3}			
10	283	3.53×10^{-3}			



- (v) If the reaction mixture is not stirred, the magnesium tends to float on the surface of the acid.

Suggest how this would affect the measurements of the rate of the reaction.

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(1)

- (vi) Suggest **two** other improvements the student could do to this experiment to improve the accuracy or validity of the results.

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(2)

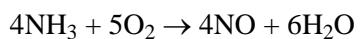
- (vii) If ethanoic acid of the same concentration and at the same temperature is used instead of hydrochloric acid, explain how the rate would differ.

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(1)

(Total 24 marks)

32. One step in the production of nitric acid is the oxidation of ammonia.



This is carried out at 900 °C over a platinum-rhodium catalyst and is an example of heterogeneous catalysis.

Explain in terms of collision frequency and collision energy how the rate would change if the temperature were increased, and which of these causes the greater effect.

What is the difference between a heterogeneous and a homogeneous catalyst? Suggest **one** advantage of using a heterogeneous catalyst in processes such as this.

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(Total 6 marks)