1 This is a question about how 'clock reactions' are used to study reaction kinetics.

The 'bromine clock' involves a reaction between bromide ions and bromate(V) ions in acid solution:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

In order to monitor this reaction, phenol and methyl orange are added to the reaction mixture.

- A small fixed amount of phenol is present which reacts immediately with the bromine as it is produced, thus removing it from solution.
- Once the bromine produced has reacted with all of the phenol present, then any further bromine produced will bleach the methyl orange solution providing a means to monitor the reaction rate.

(a) It is assumed that the **initial** rate of reaction is proportional to 1/time taken for the methyl orange to be bleached.

Explain why it is essential for the amount of phenol to be small compared to the amounts of the reactants for this assumption to be valid.

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(b) A series of experiments was carried out where only the concentration of bromide ions present was varied and the solution contained a large excess of BrO_3^- and H^+ ions. The total volume of the mixture was kept constant.

(i) Why was it important that the solution contained a large excess of BrO_3^- and H^+ ions?

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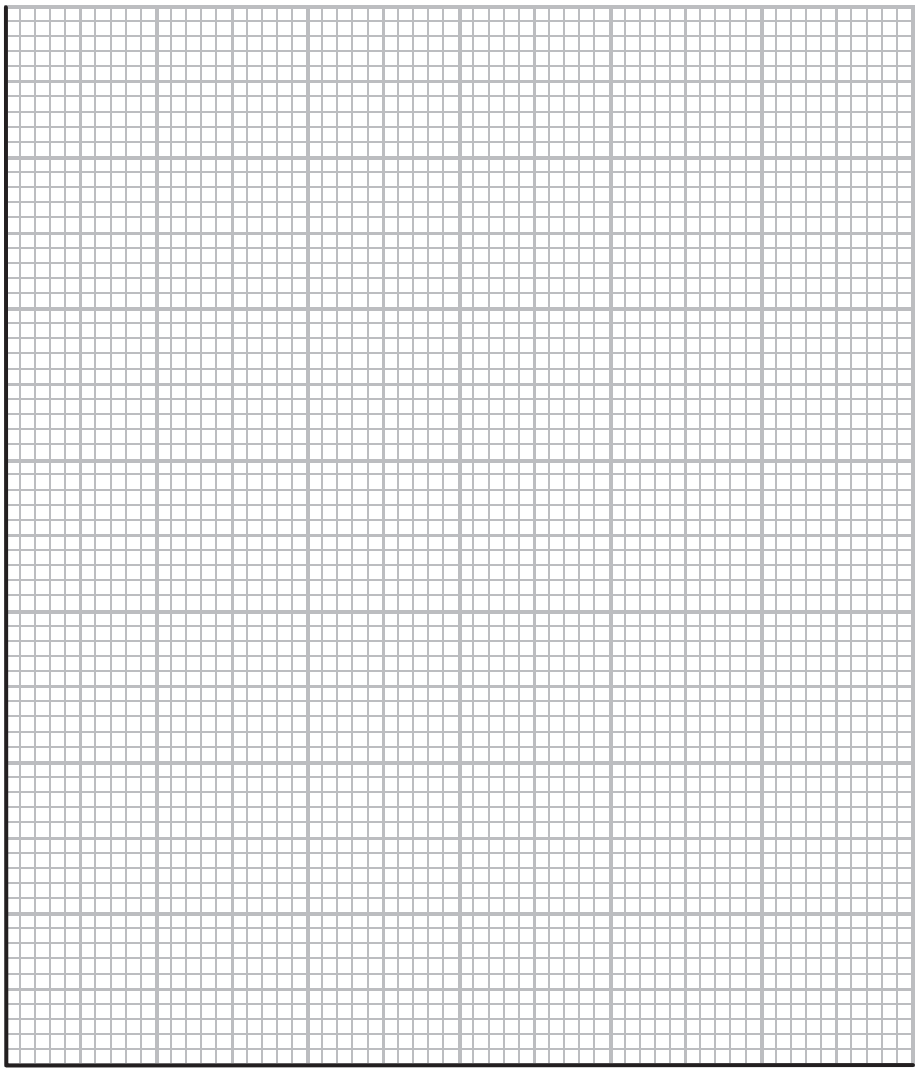
(ii) The following results were obtained.

Complete the table and use the results to plot a graph of 1/time on the vertical axis against the volume of bromide ions.

(4)

Volume of $Br^-(aq)$ / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time / s	180	226	300	364	444	900
(1/time) / 10^{-3} s^{-1}	5.56	4.42	3.33		2.25	1.11



(iii) Deduce the order of the reaction with respect to bromide ions.

Justify your answer.

(2)

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(iv) The reaction is first order with respect to bromate(V) ions and second order with respect to hydrogen ions. Write the overall rate equation for the 'bromine clock' reaction and deduce the units of the rate constant.

(2)

Rate equation:

Units of rate constant .....

(c) Another 'clock reaction' is the 'iodine clock' reaction, where hydrogen peroxide solution is mixed with a solution containing sodium thiosulfate, potassium iodide and starch.

The main reaction is

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

- The thiosulfate ions present react immediately with the iodine as it is produced, thus removing it from solution.
- Once all of the thiosulfate ions are used up, further iodine produced reacts with the starch present.

(i) Why are the potassium ions omitted from the above equation?

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(ii) State the observation made after all of the thiosulfate ions are used up and more iodine is produced.

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(d) 'Iodine clock' reactions can be used to determine the activation energy of a reaction using the equation:

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

(i) State the experimental measurements you would make to provide the numerical data for the calculation of the activation energy.

(1)

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(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

You should include

- how the data is processed
- the graph you would plot and its expected shape
- how the activation energy of the reaction can be determined from the graph produced.

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(Total for Question = 19 marks)

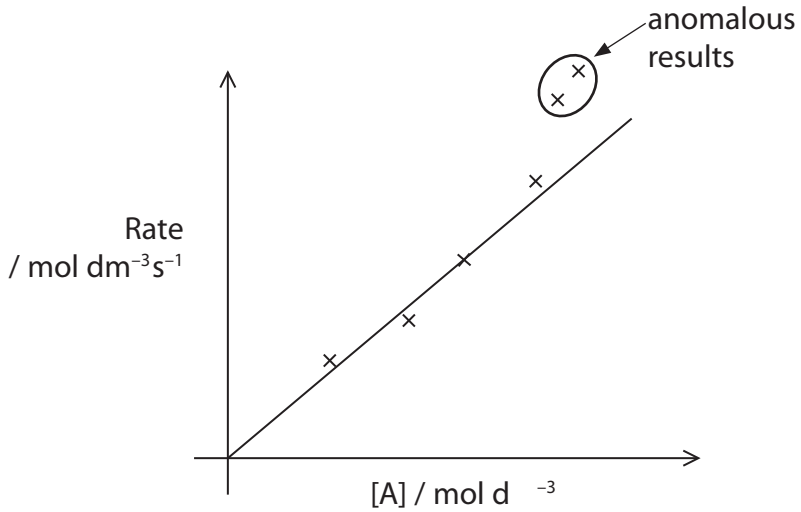
2 The kinetics of the fast reaction below were investigated in a series of experiments.

$$\mathbf{A} + \mathbf{B} \xrightarrow{\text{catalyst } \mathbf{X}} \mathbf{C} + \mathbf{D} \qquad \Delta H \text{ is negative}$$

(a) Outline a titrimetric method that could be used to measure the change in concentration of compound **A** with time. Compound **A** is an alkali, whereas compounds **B**, **C** and **D** are neutral.

(3)

(b) The rate of the reaction was measured at several different concentrations of **A**, in the presence of a large excess of compound **B** and a constant amount of catalyst **X**, to find the order of reaction with respect to **A**. The results are shown on the graph below.



(i) Explain how the graph confirms that the reaction is first order with respect to **A**.

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(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.

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(c) In a second series of experiments, further data were collected using an initial rates method. These results are summarised in the table below.

Experiment	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	A	**B**	**X**	
1	0.020	0.005	0.500	2.1×10^{-3}
2	0.040	0.005	0.500	4.2×10^{-3}
3	0.060	0.010	0.500	6.3×10^{-3}
4	0.080	0.010	0.250	4.2×10^{-3}

(i) Give **one** reason why obtaining these further data may be considered useful.

(1)

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(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer.

(5)

(iii) Use your answer from (c)(ii), and appropriate data from **Experiment 4**, to calculate the value of the rate constant, *k*. Include units in your answer.

(2)

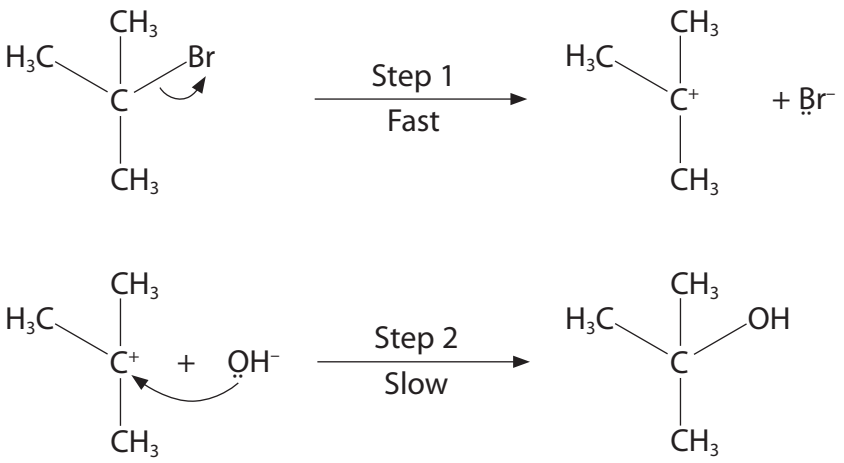
(d) A student carried out a similar investigation into the kinetics of the reaction between 2-bromomethylpropane and hydroxide ions. A summary of the student's findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is first order with respect to 2-bromomethylpropane

Suggested Mechanism

S_N2 - as two steps in process



Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest one feature of the summary, including the student's mechanism, that you agree with and two features you think are incorrect.

(3)

One feature you agree with.

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Two features you think are incorrect.

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(Total for Question = 18 marks)

3 Persulfate ions, $S_2O_8^{2-}$, oxidize iodide ions in aqueous solution to form iodine and sulfate ions, SO_4^{2-}.

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) The effect of persulfate ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to the potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium persulfate, but the same volumes and concentrations of sodium thiosulfate solution and potassium iodide solution.

The rates of the reaction were compared using the reciprocal of the time (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

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(ii) What would happen if the reaction was carried out without the addition of sodium thiosulfate?

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(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)

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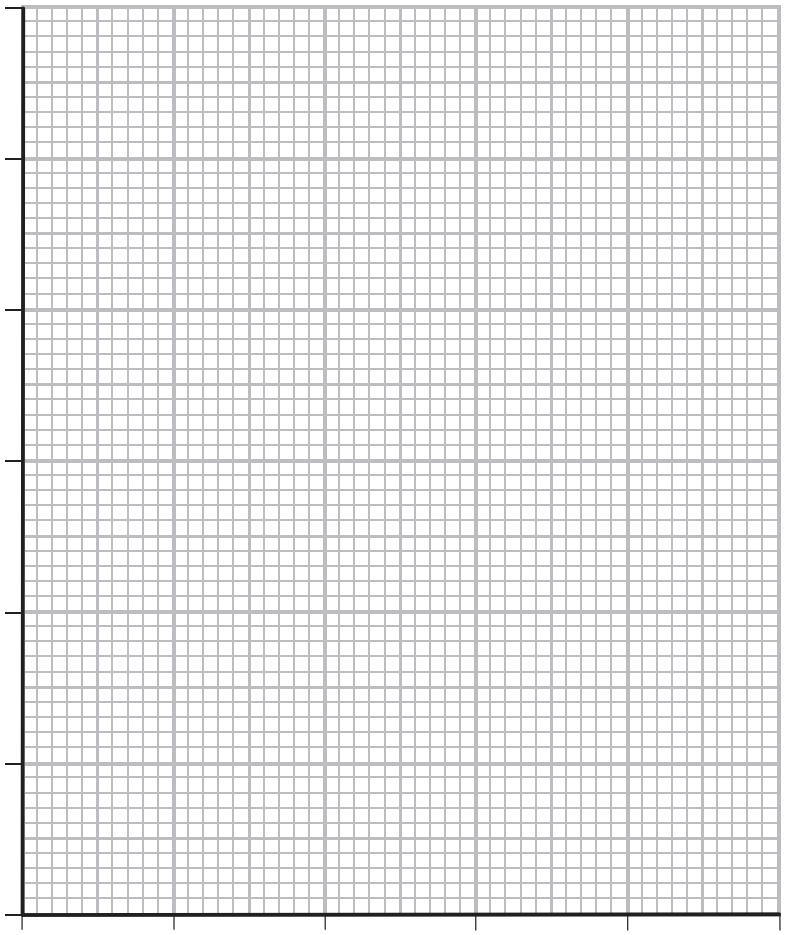
(c) The results obtained from the experiment in part (b) were tabulated as follows.

$[S_2O_8^{2-}]$ /mol dm^{-3}	Time /s	1/time /s^{-1}
0.0100	40.0	0.0250
0.0090	44.4	0.0225
0.0075	53.3	0.0188
0.0060	66.7	0.0150

(i) Plot a graph of 1/time on the vertical axis against the concentration of the persulfate ions.

(2)



(ii) 1/time is a measure of the initial rate of the reaction.

Deduce the order of the reaction with respect to persulfate ions.

Justify your answer.

(2)

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(iii) The reaction is first order with respect to iodide ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

(2)

Rate =

Units for the rate constant .....

(d) The reaction in part (b) is repeated at two different temperatures, keeping the initial volumes and concentrations of the solutions constant.

T (Temperature) /K	1/time /s^{-1}	1/T /K^{-1}	ln(1/time)
293	0.0250	3.41×10^{-3}	−3.69
303	0.0500	3.30×10^{-3}	−3.00

(i) Calculate, without drawing a graph, the activation energy of the reaction. Remember to give a sign and units with your answer.

(3)

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

(ii) Suggest how the reliability of the activation energy determination could be improved, without changing the apparatus, solutions or method.

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(Total for Question = 14 marks)