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

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

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

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

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

**(2)**

.....

.....

.....

.....

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

**(3)**

.....

.....

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

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

**(3)**

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

**(1)**

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

**(2)**

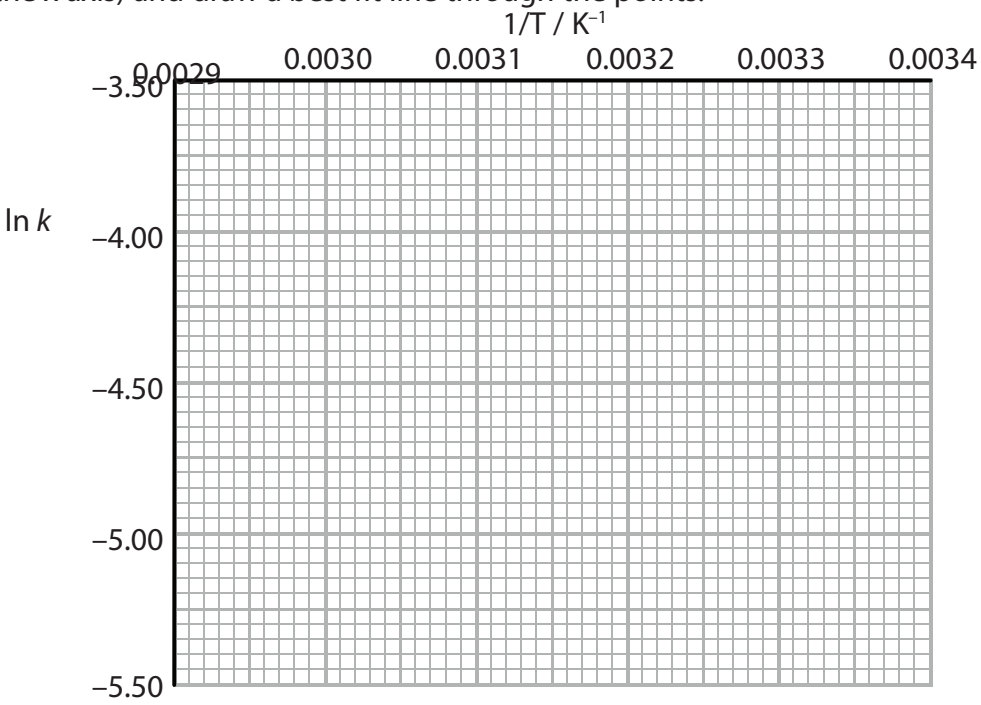
(iv) In such an experiment a student calculated the initial rate of reaction to be $8.75 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$. Use this value, the initial concentrations in (b) and the rate equation that you obtained in (a)(ii), to calculate the rate constant for this reaction. Include units in your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

**(2)**

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

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

(i) Use the data in the table to plot a graph of ln *k* (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points. **(2)**




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

**(4)**

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

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

**(Total for Question = 19 marks)**

**2** Iodine reacts with propanone in the presence of an acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

An experiment was carried out to investigate the kinetics of this reaction by monitoring the concentration of iodine. The progress of the reaction was followed by mixing together the reagents, removing samples of the mixture every five minutes, quenching the reaction and then titrating to find the concentration of iodine at a given time.

(a) (i) Suggest a suitable reagent with which you could titrate the iodine.

**(1)**

.....

(ii) State and explain how you would quench the reaction.

**(2)**

.....

.....

.....

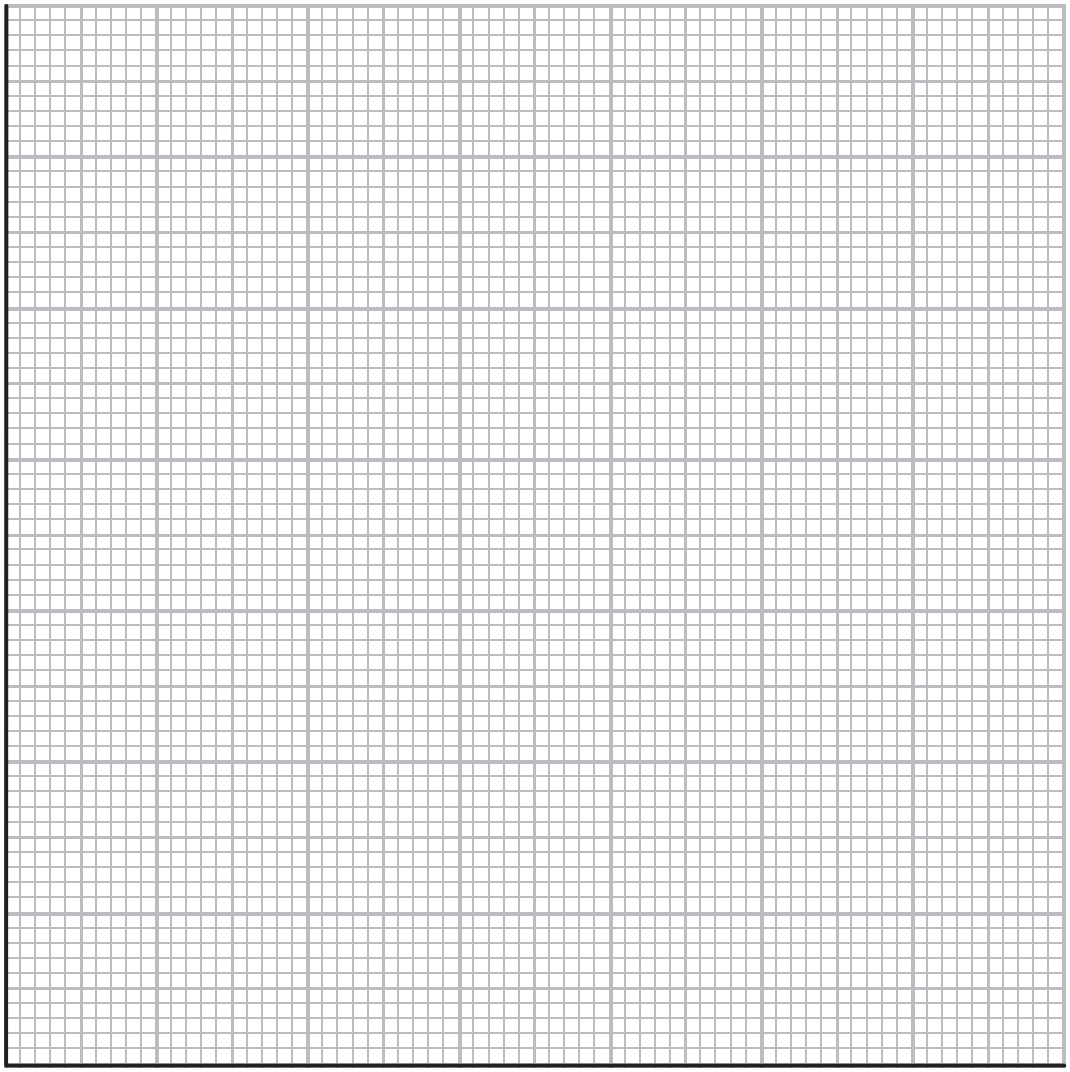
.....

(b) (i) Data obtained from the experiment are shown in the table below. Use the data to plot a suitable graph to determine the order of the reaction with respect to iodine and state this order.

**(3)**

| Time / mins | $[I_2(aq)]$ / mol $dm^{-3}$ |
|---|---|
| 5 | $9.74 \times 10^{-4}$ |
| 10 | $9.50 \times 10^{-4}$ |
| 15 | $9.25 \times 10^{-4}$ |
| 20 | $9.03 \times 10^{-4}$ |
| 25 | $8.80 \times 10^{-4}$ |
| 30 | $8.55 \times 10^{-4}$ |

$[I_2(aq)]$ / mol $dm^{-3}$



Order with respect to iodine .....

Time / minutes

(ii) Explain how you determined the order using your graph.

**(2)**

.....

.....

.....

.....

(c) State an alternative practical procedure that could be used to monitor the concentration of iodine.

**(1)**

.....

**(Total for Question 9 marks)**

**3** Nitrogen(IV) oxide, $NO_2$, is a brown gas which is a pollutant in air. It is produced in the reaction below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) The table below shows the results of a series of experiments to measure the rate of this reaction at 298 K.

| Experiment number | Initial concentration / mol $dm^{-3}$ | | Initial rate / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| | $[O_2(g)]$ | $[NO(g)]$ | |
| 1 | 0.0050 | 0.0125 | $5.10 \times 10^{4}$ |
| 2 | 0.0100 | 0.0125 | $10.2 \times 10^{4}$ |
| 3 | 0.0100 | 0.0250 | $40.8 \times 10^{4}$ |

(i) State, with reasons, the order of reaction with respect to oxygen and the order of reaction with respect to nitrogen(II) oxide, NO.

**(2)**

.....

.....

.....

.....

(ii) Write the rate equation for the reaction.

**(1)**

(iii) Calculate the value of the rate constant. Include units in your answer.

**(2)**

(b) Nitrogen(IV) oxide in air reacts with carbon monoxide in car exhausts. The following two-step reaction mechanism has been suggested.

**Step 1:** $2NO_2(g) \rightarrow NO(g) + NO_3(g)$ Slow

**Step 2:** $NO_3(g) + 2CO(g) \rightarrow NO(g) + 2CO_2(g)$ Fast

(i) Write the equation for the overall reaction which takes place.

**(1)**

(ii) The overall reaction is second order. Suggest a rate equation for this reaction, justifying your answer.

**(2)**

.....

.....

**(Total for Question 8 marks)**

**4** A bromoalkane has the molecular formula $C_4H_9Br$. The ionic equation for the hydrolysis of this compound with aqueous sodium hydroxide is shown below.

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

(a) The rate of hydrolysis was investigated by mixing a large excess of the bromoalkane with aqueous sodium hydroxide, and measuring the time taken for **all** the hydroxide ions to be used up. This was carried out with different initial concentrations of the bromoalkane and the hydroxide ions. The results are shown in the table below.

| Experiment | $[C_4H_9Br]$ /mol $dm^{-3}$ | $[OH^-]$ /mol $dm^{-3}$ | Time for $OH^-$ to be used up/s | Initial rate /mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|---|
| 1 | 0.017 | 0.0012 | 42 | $2.9 \times 10^{-5}$ |
| 2 | 0.034 | 0.0012 | 21 | $5.7 \times 10^{-5}$ |
| 3 | 0.034 | 0.0020 | 35 | |

(i) Complete the missing value of the initial rate in the table.

**(1)**

(ii) State the order of the reaction with respect to $C_4H_9Br$ and to $OH^-$. Justify each answer by reference to the concentrations of both reactants.

**(3)**

Order with respect to $C_4H_9Br$

Reason

Order with respect to $OH^-$

Reason

(iii) Deduce the rate equation for the reaction.

**(1)**

**Rate** =

(iv) Use the results for the first experiment in the table to calculate the rate constant and give its units.

**(2)**

**Units**

(b) What evidence supports the theory that there is more than one step in the reaction mechanism?

**(1)**

(c) Write the mechanism for the hydrolysis of $C_4H_9Br$ which is consistent with your rate equation. Show the structure of $C_4H_9Br$ clearly in your mechanism.

**(3)**

*(d) Explain why primary and tertiary bromoalkanes are hydrolysed by different mechanisms.

**(2)**

**(Total for Question = 13 marks)**