A-Level Chemistry

Rate Determining Step

Question Paper

Time available: 67 minutes
Marks available: 62 marks

1. Iodide ions are oxidised to iodine by hydrogen peroxide in acidic conditions.

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

The rate equation for this reaction can be written as

$$rate = k\,[H_2O_2]^a\,[I^-]^b\,[H^+]^c$$

In an experiment to determine the order with respect to $H^+(aq)$, a reaction mixture is made containing $H^+(aq)$ with a concentration of 0.500 mol dm^{-3}

A large excess of both H_2O_2 and I^- is used in this reaction mixture so that the rate equation can be simplified to

$$rate = k_1\,[H^+]^c$$

(a) Explain why the use of a large excess of H_2O_2 and I^- means that the rate of reaction at a fixed temperature depends only on the concentration of $H^+(aq)$.

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(2)

(b) Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $H^+(aq)$.

State and explain what must be done to each sample before it is titrated with alkali.

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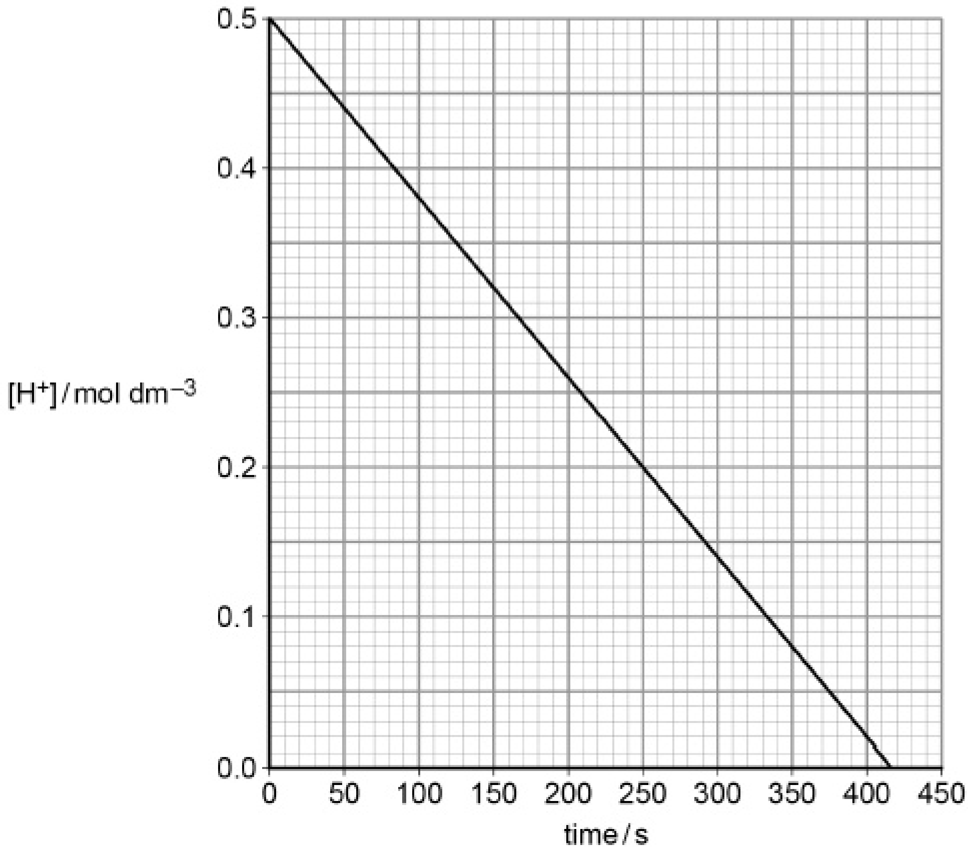
(2)

(c) A graph of the results is shown in **Figure 1**.

Figure 1



Explain how the graph shows that the order with respect to H^+(aq) is zero.

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(2)

(d) Use the graph in **Figure 1** to calculate the value of k_1

Give the units of k_1

k_1 ______________________

Units ______________________

(3)

(e) A second reaction mixture is made at the same temperature. The initial concentrations of $H^+(aq)$ and $I^-(aq)$ in this mixture are both 0.500 mol dm^{-3}

There is a large excess of H_2O_2

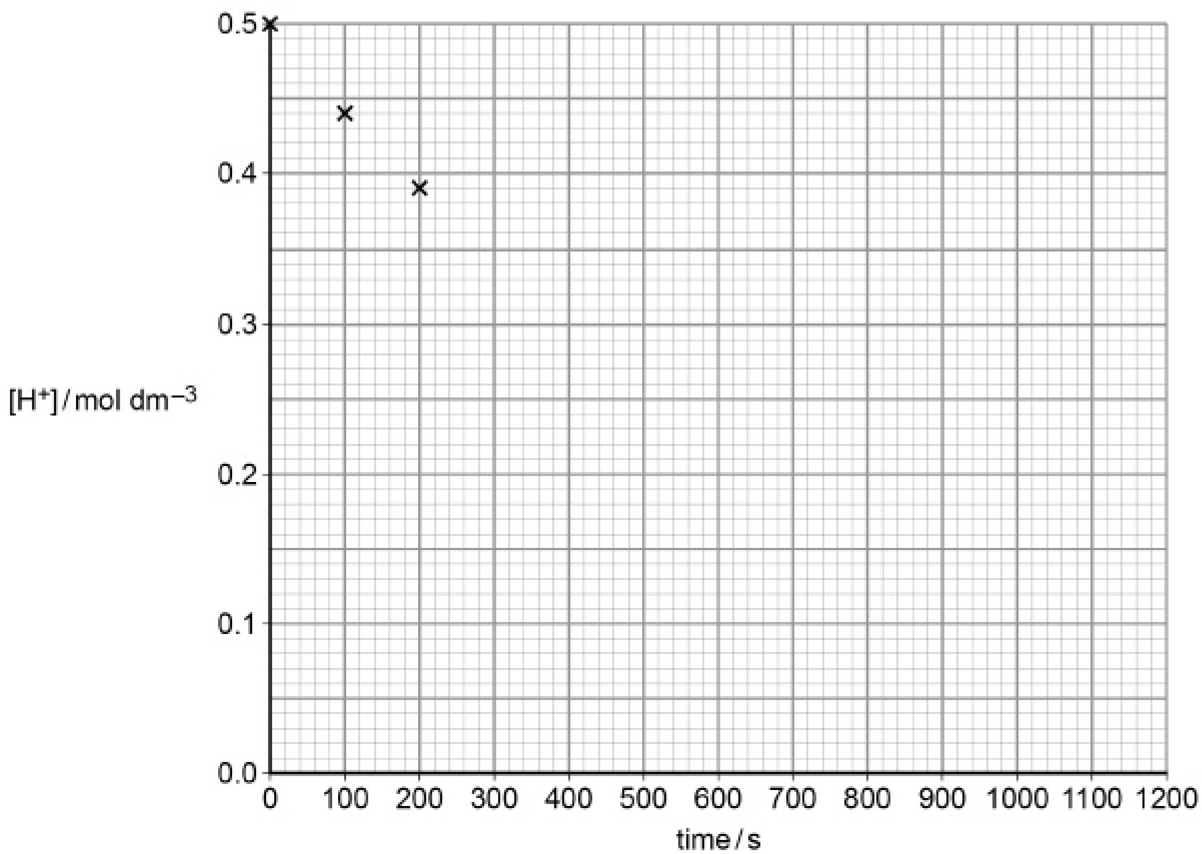
In this reaction mixture, the rate depends only on the concentration of $I^-(aq)$.

The results are shown in the table.

Time / s	0	100	200	400	600	800	1000	1200
$[H^+]$ / mol dm^{-3}	0.50	0.44	0.39	0.31	0.24	0.19	0.15	0.12

Plot these results on the grid in **Figure 2**. The first three points have been plotted.

Figure 2



(1)

(f) Draw a line of best fit on the grid in **Figure 2**.

(1)

(g) Calculate the rate of reaction when $[H^+] = 0.35$ mol dm^{-3}
Show your working using a suitable construction on the graph in **Figure 2**.

Rate ____________________ mol dm^{-3} s^{-1}

(2)

(h) A general equation for a reaction is shown.

A(aq) + **B**(aq) + **C**(aq) → **D**(aq) + **E**(aq)

In aqueous solution, **A**, **B**, **C** and **D** are all colourless but **E** is dark blue.

A reagent (**X**) is available that reacts rapidly with **E**. This means that, if a small amount of **X** is included in the initial reaction mixture, it will react with any **E** produced until all of the **X** has been used up.

Explain, giving brief experimental details, how you could use a series of experiments to determine the order of this reaction with respect to **A.** In each experiment you should obtain a measure of the initial rate of reaction.

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(6)

(Total 19 marks)

2. Iodine reacts slowly with propanone in the presence of an acid catalyst according to the equation

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time.The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time.

Five mixtures, **A**, **B**, **C**, **D** and **E**, are prepared as shown in **Table 1**.

Table 1

Mixture	**A**	**B**	**C**	**D**	**E**
Volume of 0.0200 mol dm^{-3} $I_2(aq)/cm^3$	40.0	40.0	40.0	40.0	40.0
Volume of 0.100 mol dm^{-3} $H_2SO_4(aq)/cm^3$	25.0	25.0	25.0	25.0	25.0
Volume of 1.00 mol dm^{-3} $CH_3COCH_3(aq)/cm^3$	25.0	20.0	15.0	10.0	6.5
Volume of distilled water/cm^3	0.0	5.0	10.0	15.0	18.5

(a) Calculate the initial concentration, in mol dm^{-3}, of the propanone in mixture **A**.

Concentration = __________ mol dm^{-3}

(2)

(b) State and explain why different volumes of water are added to mixtures **B**, **C**, **D** and **E**.

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(2)

(c) Calculate the volume of 0.0100 mol dm^{-3} sodium thiosulfate solution required to react with all of the iodine in a 10.0 cm^3 sample of mixture **E**, before the iodine reacts with propanone.

The equation for the reaction in the titration is

$$2Na_2S_2O_3(aq) + I_2(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq)$$

Volume = ____________________ cm^3

(4)

(d) The results for mixture **E** are shown in **Table 2**.

V is the volume of 0.0100 mol dm^{-3} sodium thiosulfate solution needed, at different times, **t**, to react with the iodine in a 10.0 cm^3 sample of **E**.

Table 2

t/min	5	10	20	30
V/cm^3	17.5	17.2	16.6	16.0

Use these data and your answer to part **(c)** to plot a graph of **V** (*y*-axis) against **t** (*x*-axis) for mixture **E**.

Draw a best-fit straight line through your points and calculate the gradient of this line.

gradient = ______________ cm^3 min^{-1}

(5)

(e) The gradients for similar graphs produced by mixtures **A**, **B**, **C** and **D** are shown in **Table 3**.
Each gradient is a measure of the rate of the reaction between iodine and propanone.

Table 3

Mixture	**A**	**B**	**C**	**D**
Gradient / cm^3 min^{-1}	−0.24	−0.20	−0.15	−0.10

Use information from **Table 1** and **Table 3** to deduce the order with respect to propanone.
Explain your answer.

(2)

(f) Each sample taken from the reaction mixtures is immediately added to an excess of sodium hydrogencarbonate solution before being titrated with sodium thiosulfate solution.

Suggest the purpose of this addition.
Explain your answer.

(2)
(Total 17 marks)

3. The rate of the reaction between substance **A** and substance **B** was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of **A** and **B**. These results were used to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

(a) What is meant by the term *order of reaction* with respect to **A**?

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(1)

(b) When the concentrations of **A** and **B** were both doubled, the initial rate increased by a factor of 4. Deduce the **overall** order of the reaction.

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(1)

(c) In another experiment, the concentration of **A** was increased by a factor of three and the concentration of **B** was halved. This caused the initial rate to increase by a factor of nine.

(i) Deduce the order of reaction with respect to **A** and the order with respect to **B**.

Order with respect to ***A*** ____

Order with respect to ***B*** ____

(ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

Rate equation ____

Units for the rate constant ____

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(4)

(Total 6 marks)

4. (a) The data in the following table were obtained in two experiments about the rate of the reaction between substances **B** and **C** at a constant temperature.

Experiment	Initial concentration of **B** / mol dm^{-3}	Initial concentration of **C** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.2×10^{-2}	2.6×10^{-2}	8.4×10^{-5}
2	6.3×10^{-2}	7.8×10^{-2}	To be calculated

The rate equation for this reaction is known to be

$$\text{rate} = k[\mathbf{B}]^2[\mathbf{C}]$$

(i) Use the data from Experiment **1** to calculate a value for the rate constant *k* at this temperature and deduce its units.

Calculation ____

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Units ____

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(3)

(ii) Calculate a value for the initial rate in Experiment **2**.

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(1)

(b) The data in the following table were obtained in a series of experiments about the rate of the reaction between substances **D** and **E** at a constant temperature.

Experiment	Initial concentration of **D** / mol dm^{-3}	Initial concentration of **E** / mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
3	0.13	0.23	0.26×10^{-3}
4	0.39	0.23	2.34×10^{-3}
5	0.78	0.46	9.36×10^{-3}

(i) Deduce the order of reaction with respect to **D**.

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(1)

(ii) Deduce the order of reaction with respect to **E**.

(1)

(c) The compound $(CH_3)_3CBr$ reacts with aqueous sodium hydroxide as shown in the folfollowing equation.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

This reaction was found to be first order with respect to $(CH_3)_3CBr$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.

Step **1** $(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$

Step **2** $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3COH$

(i) Deduce the rate-determining step in this two-step process.

(1)

(ii) Outline a mechanism for this step using a curly arrow.

(1)

(Total 8 marks)

5. This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in **Table 1** were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Table 1

Experiment	**Initial concentration of A / mol dm^{-3}**	**Initial concentration of B / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	0.12	0.26	2.10×10^{-4}
2	0.36	0.26	1.89×10^{-3}
3	0.72	0.13	3.78×10^{-3}

(a) Show how these data can be used to deduce the rate expression for the reaction between **A** and **B**.

(3)

The data in **Table 2** were obtained in two experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Table 2

Experiment	**Initial concentration of C / mol dm^{-3}**	**Initial concentration of D / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
4	1.9×10^{-2}	3.5×10^{-2}	7.2×10^{-4}
5	3.6×10^{-2}	5.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[\mathbf{C}]^2[\mathbf{D}]$$

(b) Use the data from experiment **4** to calculate a value for the rate constant, *k*, at this temperature. Deduce the units of *k*.

k = ________________ Units = ________________

(3)

(c) Calculate a value for the initial rate in experiment **5**.

Initial rate = ________________ mol dm^{-3} s^{-1}

(1)

(d) The rate equation for a reaction is

$$rate = k[\mathbf{E}]$$

Explain qualitatively why doubling the temperature has a much greater effect on the rate of the reaction than doubling the concentration of **E**.

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(3)

(e) A slow reaction has a rate constant $k = 6.51 \times 10^{-3}$ mol^{-1} dm^{3} at 300 K.

Use the equation $\ln k = \ln A - E_a / RT$ to calculate a value, in kJ mol^{-1}, for the activation energy of this reaction.

The constant $A = 2.57 \times 10^{10}$ mol^{-1} dm^{3}.
The gas constant $R = 8.31$ J K^{-1} mol^{-1}.

Activation energy = _______________

(2)
(Total 12 marks)