

1

Gases **A** and **B** react as shown in the following equation.



The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

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

An incomplete table of data for the reaction between **A** and **B** is shown in the table.

Experiment	Initial [A] / mol dm ⁻³	Initial [B] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	4.2 × 10 ⁻³	2.8 × 10 ⁻³	3.3 × 10 ⁻⁵
2	7.9 × 10 ⁻³	2.8 × 10 ⁻³	
3		5.6 × 10 ⁻³	1.8 × 10 ⁻⁴

- (a) Use the data from Experiment 1 to calculate a value for the rate constant, *k*, at this temperature.
Deduce the units of *k*.

Calculation

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Units

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(3)

- (b) Use your value of *k* from (a) to complete the table for the reaction between **A** and **B**.
(If you have been unable to calculate an answer for (a), you may assume a value of 2.3.
This is **not** the correct answer.)

(2)

(c) The reaction is zero order with respect to **B**.

State the significance of this zero order for the mechanism of the reaction.

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(1)
(Total 6 marks)

2

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**.

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(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

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

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

$$k = \dots\dots\dots \text{Units} = \dots\dots\dots$$

(3)

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

$$\text{Initial rate} = \dots\dots\dots \text{mol dm}^{-3} \text{ s}^{-1}$$

(1)

(d) The rate equation for a reaction is

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

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 $k = 6.51 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3$ 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 $A = 2.57 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3$.

The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

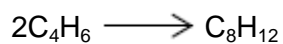
Activation energy =

(2)

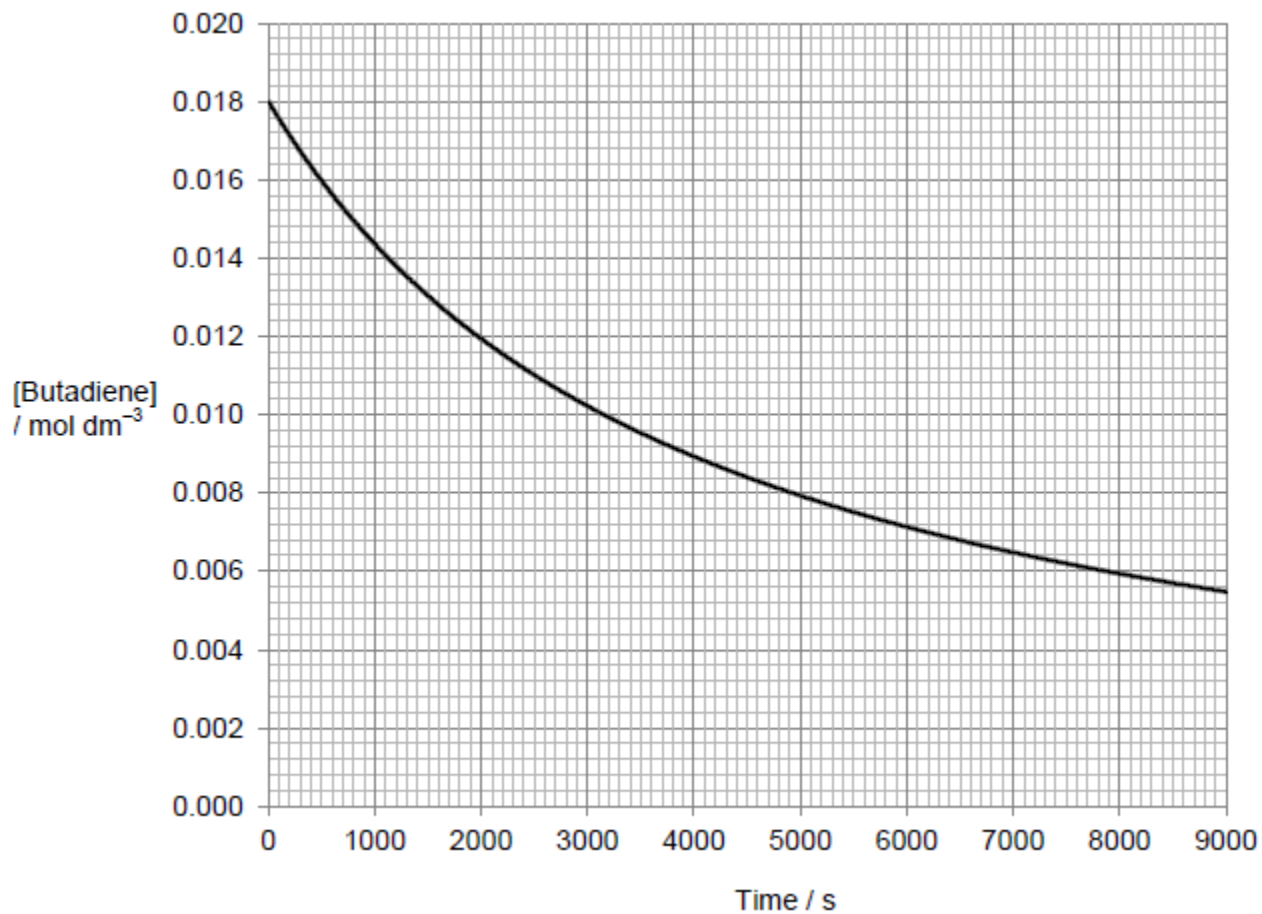
(Total 12 marks)

3

Butadiene dimerises according to the equation



The kinetics of the dimerisation are studied and the graph of the concentration of a sample of butadiene is plotted against time. The graph is shown below.



(a) Draw a tangent to the curve when the concentration of butadiene is 0.0120 mol dm⁻³.

(1)

(b) The initial rate of reaction in this experiment has the value $4.57 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Use this value, together with a rate obtained from your tangent, to justify that the order of the reaction is 2 with respect to butadiene.

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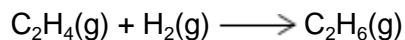
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(5)
(Total 6 marks)

4 The rate equation for the hydrogenation of ethene



is $\text{Rate} = k[\text{C}_2\text{H}_4][\text{H}_2]$

At a fixed temperature, the reaction mixture is compressed to triple the original pressure.

What is the factor by which the rate of reaction changes?

- A 6
- B 9
- C 12
- D 27

(Total 1 mark)

5

(a) The table shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B** dissolved in a given solvent.

All three experiments were carried out at the same temperature.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of A / mol dm ⁻³	1.60 × 10 ⁻²	2.40 × 10 ⁻²	3.60 × 10 ⁻²
Initial concentration of B / mol dm ⁻³	4.20 × 10 ⁻²	6.30 × 10 ⁻²	6.30 × 10 ⁻²
Initial rate / mol dm ⁻³ s ⁻¹	8.00 × 10 ⁻⁵	1.80 × 10 ⁻⁴	4.05 × 10 ⁻⁴

(i) Deduce the order of reaction with respect to **A**.
Tick (✓) **one** box.

Order of reaction with respect to A	Tick (✓)
0	
1	
2	

(1)

(ii) Deduce the order of reaction with respect to **B**.
Tick (✓) **one** box.

Order of reaction with respect to B	Tick (✓)
0	
1	
2	

(1)

- (b) The reaction between two different compounds, **C** and **D**, is studied at a given temperature. The rate equation for the reaction is found to be

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

- (i) When the initial concentration of **C** is $4.55 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of **D** is $1.70 \times 10^{-2} \text{ mol dm}^{-3}$, the initial rate of reaction is $6.64 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Calculate the value of the rate constant at this temperature and deduce its units.

Calculation

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Units of rate constant

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(3)

- (ii) The experiment in part (i) is repeated at the same temperature but after the addition of extra solvent so that the total volume of the mixture is doubled.

Deduce the new initial rate of reaction.

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(1)

(Total 6 marks)

6

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

(a) The data in this table were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of E / mol dm ⁻³	Initial concentration of F / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.42 × 10 ⁻³
2	0.45	0.24	3.78 × 10 ⁻³
3	0.90	0.12	7.56 × 10 ⁻³

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

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(1)

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

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(Space for working)
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(1)

- (b) The data in the following table were obtained in two experiments on the rate of the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of G / mol dm ⁻³	Initial concentration of H / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
4	3.8×10^{-2}	2.6×10^{-2}	8.6×10^{-4}
5	6.3×10^{-2}	7.5×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[G]^2[H]$$

- (i) Use the data from Experiment **4** to calculate a value for the rate constant k at this temperature. Deduce the units of k .

Calculation

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Units

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(3)

- (ii) Calculate a value for the initial rate of reaction in Experiment **5**.

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(1)

(Total 6 marks)

7

(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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(Extra space)

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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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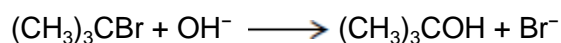
(1)

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

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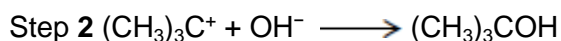
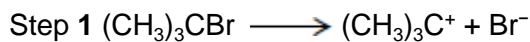
(1)

- (c) The compound (CH₃)₃CBr reacts with aqueous sodium hydroxide as shown in the following equation.



This reaction was found to be first order with respect to (CH₃)₃CBr but zero order with respect to hydroxide ions.

The following two-step process was suggested.



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

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(1)

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

(1)
(Total 8 marks)

8 Gases **P** and **Q** react as shown in the following equation.



The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

(a) Complete the table of data for the reaction between **P** and **Q**.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	2.5 × 10 ⁻²	1.8 × 10 ⁻²	5.0 × 10 ⁻⁵
2	7.5 × 10 ⁻²	1.8 × 10 ⁻²	
3	5.0 × 10 ⁻²		5.0 × 10 ⁻⁵
4		5.4 × 10 ⁻²	4.5 × 10 ⁻⁴

(Space for working)

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(3)

- (b) Use the data from Experiment 1 to calculate a value for the rate constant (k) at this temperature. Deduce the units of k .

Calculation

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Units

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(3)
(Total 6 marks)

9

The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

- (a) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] /mol dm ⁻³	Initial [Q] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	0.20	0.30	1.8 = 10 ⁻³
2	0.40	0.60	
3	0.60		5.4 = 10 ⁻³
4		0.90	12.2 = 10 ⁻³

(Space for working)

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(3)

- (b) Use the data from Experiment 1 to calculate a value for the rate constant k and deduce its units.

Calculation

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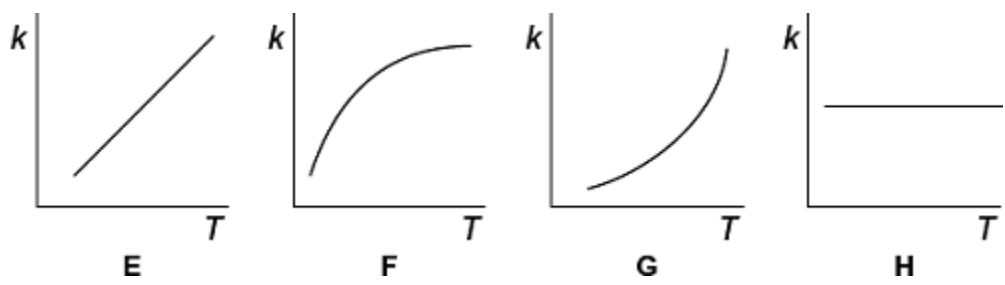
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Units

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(3)

- (c) Consider the graphs **E**, **F**, **G** and **H** below.



Write in the box below the letter of the graph that shows how the rate constant k varies with temperature.

(1)
(Total 7 marks)

10

- (a) In the presence of the catalyst rhodium, the reaction between NO and H₂ occurs according to the following equation.



The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The initial rate of reaction was $6.2 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of NO was $2.9 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of H₂ was $2.3 \times 10^{-2} \text{ mol dm}^{-3}$.

- (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation

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Units

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(3)

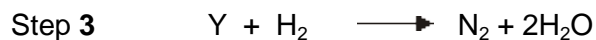
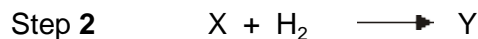
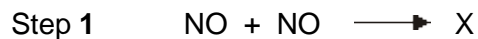
- (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H₂ both doubled from their original values.

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(1)

(b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.



Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step.....

Explanation

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(Extra space)

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(2)
(Total 6 marks)

11

The rate of hydrolysis of an ester **X** ($\text{HCOOCH}_2\text{CH}_2\text{CH}_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

(a) (i) Name ester **X**.

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(1)

(ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

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(1)

- (iii) When the initial concentration of **X** was $0.024 \text{ mol dm}^{-3}$ and the initial concentration of hydroxide ions was $0.035 \text{ mol dm}^{-3}$, the initial rate of the reaction was $8.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation

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Units

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(3)

- (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

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(1)

- (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part (a) (iii) and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

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(1)

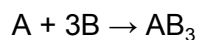
- (vi) State the effect, if any, on the value of the rate constant k when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect

Explanation

(2)

(b) Compound **A** reacts with compound **B** as shown by the overall equation



The rate equation for the reaction is

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

A suggested mechanism for the reaction is



Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step

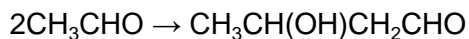
Explanation

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(2)
(Total 11 marks)

12

A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation. Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.



X

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k [\text{CH}_3\text{CHO}][\text{OH}^-]$$

(a) Give the IUPAC name of compound **X**.

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(1)

- (b) The initial rate of the reaction at 298K was found to be $2.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was $0.020 \text{ mol dm}^{-3}$. Calculate a value for the rate constant at this temperature and give its units.

Calculation

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Units

(3)

- (c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

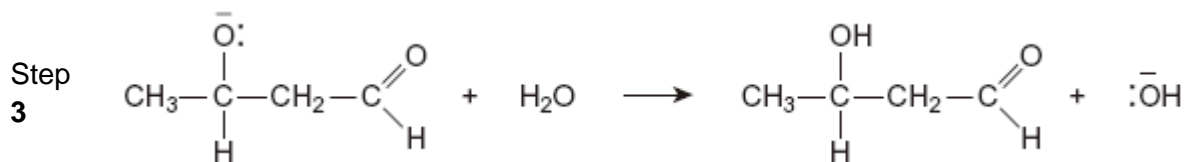
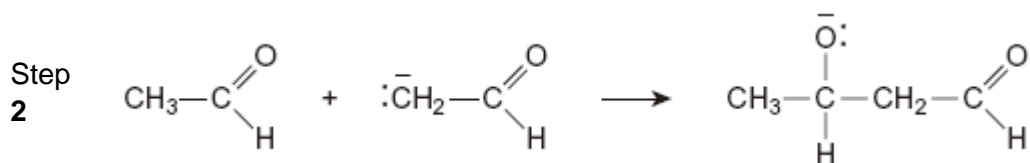
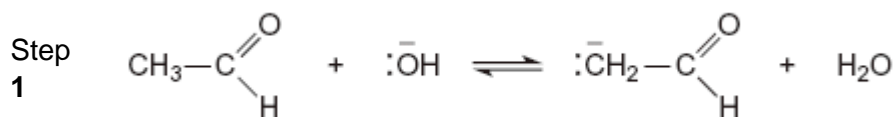
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(2)

- (d) A three-step mechanism has been proposed for this reaction according to the following equations.



- (i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step

Explanation

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(2)

(ii) Deduce the role of ethanal in Step 1.

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(1)

(iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step 2.

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(1)

(iv) In the space below draw out the mechanism of Step 2 showing the relevant curly arrows.

(2)

(e) In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

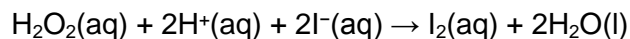
Deduce the structure of this trimer.

(1)

(Total 13 marks)

13

Hydrogen peroxide is a powerful oxidising agent. Acidified hydrogen peroxide reacts with iodide ions to form iodine according to the following equation.



The **initial rate** of this reaction is investigated by measuring the time taken to produce sufficient iodine to give a blue colour with starch solution.

A series of experiments was carried out, in which the concentration of iodide ions was varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue was recorded.

The initial rate of the reaction can be represented as $(\frac{1}{t})$, and the initial concentration of iodide ions can be represented by the volume of potassium iodide solution used.

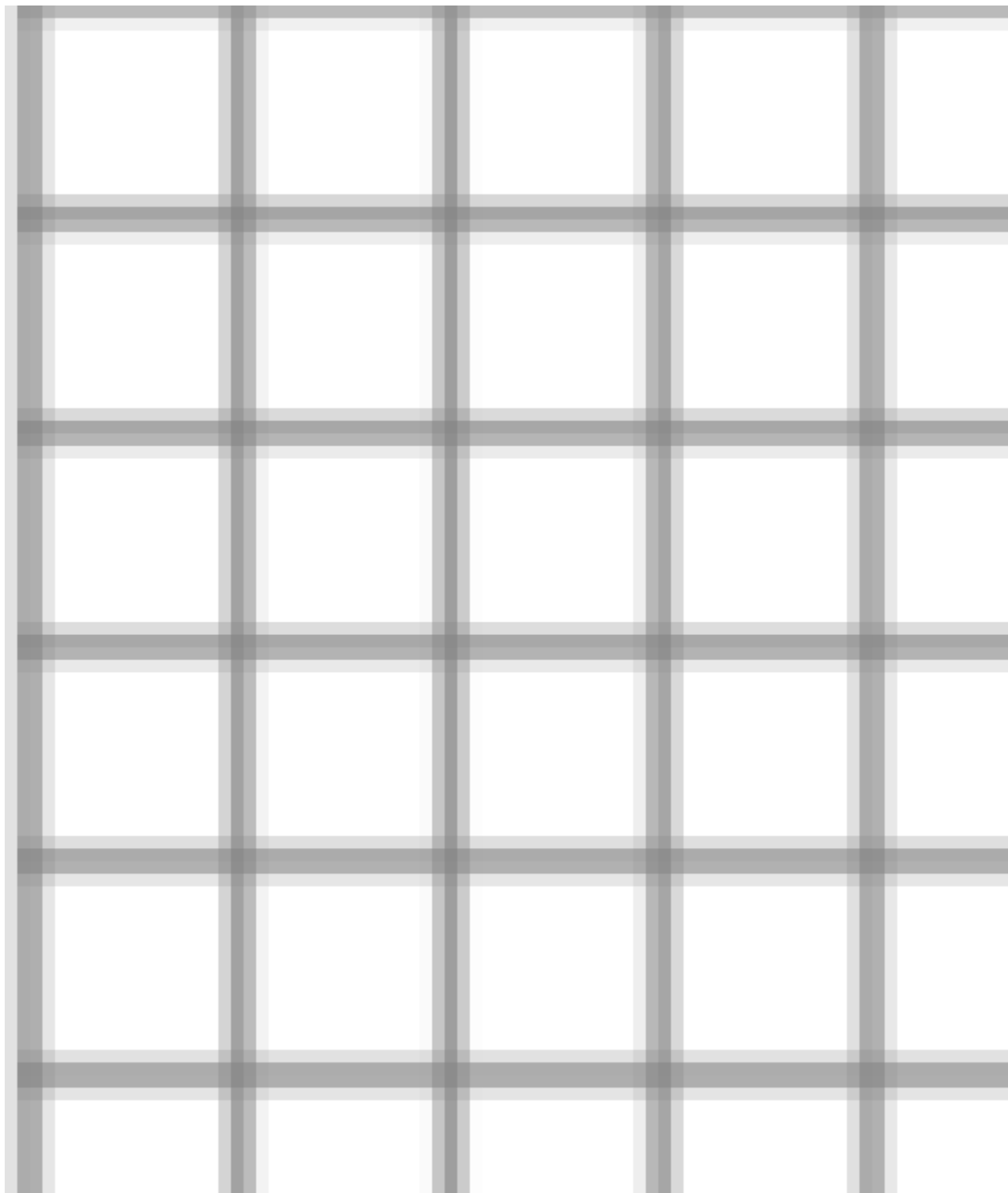
A graph of $\log_{10}(\frac{1}{t})$ on the y-axis against $\log_{10}(\text{volume of KI(aq)})$ is a straight line. The gradient of this straight line is equal to the order of the reaction with respect to iodide ions.

The results obtained are given in the table below. The time taken for each mixture to turn blue was recorded on a stopclock graduated in seconds.

Expt.	Volume of KI(aq) / cm ³	$\log_{10}(\text{volume of KI(aq)})$	Time / s	$\log_{10}(\frac{1}{t})$
1	5	0.70	71	-1.85
2	8	0.90	46	-1.66
3	10	1.00	37	-1.57
4	15	1.18	25	-1.40
5	20	1.30	19	-1.28
6	25	1.40	14	-1.15

- (a) Use the results given in the table to plot a graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y -axis against \log_{10} (volume of KI(aq)).

Draw a straight line of best fit on the graph, ignoring any anomalous points.



(5)

- (b) Determine the gradient of the line you have drawn. Give your answer to two decimal places. Show your working.

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(3)

- (c) Deduce the order of reaction with respect to iodide ions.

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(1)

- (d) A student carried out the experiment using a flask on the laboratory bench. The student recorded the time taken for the reaction mixture to turn blue. State **one** way this method could be improved, other than by repeating the experiment or by improving the precision of time or volume measurements. Explain why the accuracy of the experiment would be improved.

Improvement

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Explanation

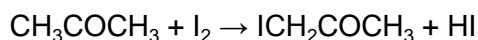
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(2)

(Total 11 marks)

14

Propanone and iodine react in acidic conditions according to the following equation.



A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

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

- (a) Give the overall order for this reaction.

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(1)

- (b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be $1.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3}
H^+	0.820

Use these data to calculate a value for the rate constant, k , for the reaction and give its units.

Calculation

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Units

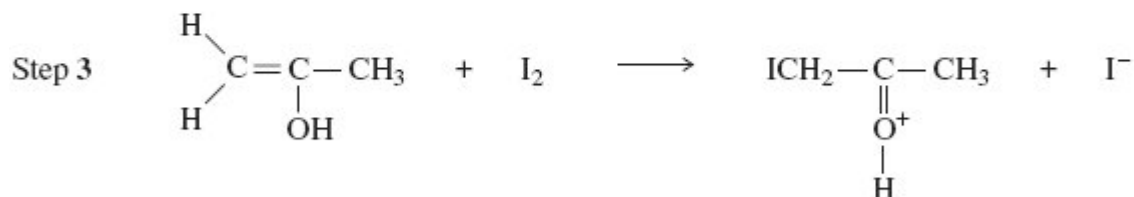
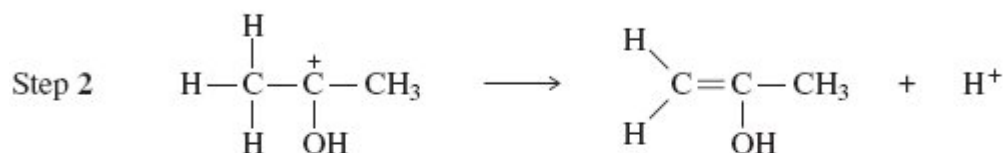
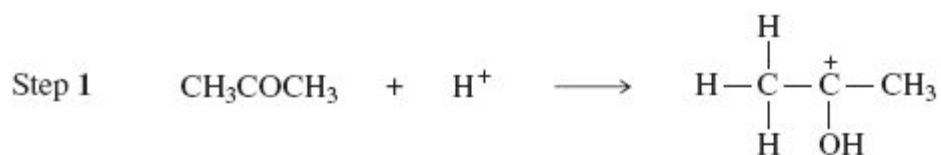
(3)

- (c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.

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(1)

(d) The following mechanism for the overall reaction has been proposed.



Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

Rate-determining step

Explanation

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(2)

(e) Use your understanding of reaction mechanisms to predict a mechanism for Step 2 by adding one or more curly arrows as necessary to the structure of the carbocation below.



(1)

(Total 8 marks)

15

Kinetic studies enable chemists to suggest mechanisms for reactions.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

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	0.15	0.32 × 10 ⁻³
2	0.36	0.15	2.88 × 10 ⁻³
3	0.72	0.30	11.52 × 10 ⁻³

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

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

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(2)

- (b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0 × 10 ⁻²	2.0 × 10 ⁻²	6.5 × 10 ⁻⁴
5	6.5 × 10 ⁻²	3.4 × 10 ⁻²	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (i) Use the data from Experiment **4** to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of *k*

.....

Units of *k*

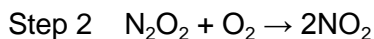
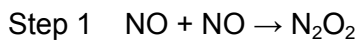
.....

- (ii) Calculate a value for the initial rate in Experiment **5**.

.....

.....

- (iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.



Which did the scientist suggest was the rate-determining step?

.....

(5)
(Total 7 marks)

16

The hydrolysis of methyl propanoate was studied in acidic conditions at 25°C and the rate equation was found to be

$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{COOCH}_3][\text{H}^+]$$

- (a) Use the data below to calculate the value of the rate constant, k , at this temperature. Deduce its units.

Initial rate of reaction / mol dm ⁻³ s ⁻¹	Initial concentration of methyl propanoate / mol dm ⁻³	Initial concentration of hydrochloric acid / mol dm ⁻³
1.15 × 10 ⁻⁴	0.150	0.555

Rate constant

.....

.....

Units

.....

(3)

- (b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

.....

.....

(1)

- (c) A third experiment was carried out at a different temperature. Some data from this experiment are shown in the table below.

Initial rate of reaction / mol dm ⁻³ s ⁻¹	Value of rate constant at this different temperature	Initial methyl propanoate / mol dm ⁻³
4.56 × 10 ⁻⁵	8.94 × 10 ⁻⁴	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

.....

.....

.....

.....

(3)
(Total 7 marks)

17

The initial rate of the reaction between the gases NO and H₂ was measured in a series of experiments at a constant temperature and the following rate equation was determined.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

- (a) Complete the table of data below for the reaction between NO and H₂

Experiment	Initial [NO] / mol dm ⁻³	Initial [H ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	3.0 × 10 ⁻³	1.0 × 10 ⁻³	1.8 × 10 ⁻⁵
2	3.0 × 10 ⁻³		7.2 × 10 ⁻⁵
3	1.5 × 10 ⁻³	1.0 × 10 ⁻³	
4		0.50 × 10 ⁻³	8.1 × 10 ⁻⁵

(3)

- (b) Using the data from experiment 1, calculate a value for the rate constant, k , and state its units.

.....
.....
.....
.....
.....
.....

(3)
(Total 6 marks)

18

- (a) Compound **A**, $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$, is an ester. Name this ester and write an equation for its reaction with aqueous sodium hydroxide.

Name

Equation

(2)

- (b) The initial rate of reaction between ester **A** and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm ⁻³	Initial concentration of A / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

Order with respect to **A**

Order with respect to NaOH

Initial rate in Experiment 4

.....

(3)

- (c) In a further experiment at a different temperature, the initial rate of reaction was found to be 9.0×10^{-3} mol dm⁻³ s⁻¹ when the initial concentration of **A** was 0.020 mol dm⁻³ and the initial concentration of NaOH was 2.00 mol dm⁻³.

Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

- (i) Write a rate equation for the reaction under these new conditions.

.....

- (ii) Calculate a value for the rate constant under these new conditions and state its units.

Calculation

.....

.....

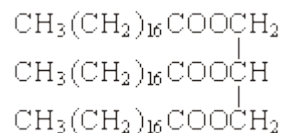
Units

- (iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

.....
.....
.....

(6)

- (d) A naturally-occurring triester, shown below, was heated under reflux with an excess of aqueous sodium hydroxide and the mixture produced was then distilled. One of the products distilled off and the other was left in the distillation flask.



- (i) Draw the structure of the product distilled off and give its name.

Structure

Name

- (ii) Give the formula of the product left in the distillation flask and give a use for it.

Formula

Use

(4)
(Total 15 marks)

19

(a) The following table shows the results of three experiments carried out at the same temperature to investigate the rate of the reaction between compounds **P** and **Q**.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of P /mol dm ⁻³	0.50	0.25	0.25
Initial concentration of Q /mol dm ⁻³	0.36	0.36	0.72
Initial rate/mol dm ⁻³ s ⁻¹	7.6 × 10 ⁻³	1.9 × 10 ⁻³	3.8 × 10 ⁻³

Use the data in the table to deduce the order with respect to **P** and the order with respect to **Q**.

Order with respect to **P**

Order with respect to **Q**

(2)

(b) In a reaction between **R** and **S**, the order of reaction with respect to **R** is one, the order of reaction with respect to **S** is two and the rate constant at temperature T_1 has a value of $4.2 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.

(i) Write a rate equation for the reaction. Calculate a value for the initial rate of reaction when the initial concentration of **R** is 0.16 mol dm^{-3} and that of **S** is 0.84 mol dm^{-3} .

Rate equation

Calculation

(ii) In a second experiment performed at a different temperature, T_2 , the initial rate of reaction is $8.1 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of **R** is 0.76 mol dm^{-3} and that of **S** is 0.98 mol dm^{-3} . Calculate the value of the rate constant at temperature T_2 .

.....
.....
.....

(iii) Deduce which of T_1 and T_2 is the higher temperature.

.....

(6)
(Total 8 marks)

20

- (a) The initial rate of the reaction between compounds **A** and **B** was measured in a series of experiments at a fixed temperature. The following rate equation was deduced.

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

- (i) Complete the table of data below for the reaction between **A** and **B**.

Expt	Initial [A] /mol dm ⁻³	Initial [B] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	4.80 × 10 ⁻²	6.60 × 10 ⁻²	10.4 × 10 ⁻³
2	4.80 × 10 ⁻²	3.30 × 10 ⁻²	
3		13.2 × 10 ⁻²	5.20 × 10 ⁻³
4	1.60 × 10 ⁻²		10.4 × 10 ⁻³

- (ii) Using the data for experiment 1, calculate a value for the rate constant, *k*, and state its units.

Calculation

.....

Units

(6)

- (b) State how the value of the rate constant, *k*, would change, if at all, if the concentration of **A** were increased in a series of experiments.

.....

(1)

(Total 7 marks)

21

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

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	0.15	0.32 × 10 ⁻³
2	0.36	0.15	2.88 × 10 ⁻³
3	0.72	0.30	11.52 × 10 ⁻³

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

.....
.....

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

.....
.....

(2)

- (b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0 × 10 ⁻²	2.0 × 10 ⁻²	6.5 × 10 ⁻⁴
5	6.5 × 10 ⁻²	3.4 × 10 ⁻²	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (i) Use the data from experiment 4 to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of *k*

.....

.....

Units of *k*

.....

- (ii) Calculate a value for the initial rate in experiment 5.

.....

.....

.....

(4)
(Total 6 marks)

22

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**?

.....

.....

(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.

.....

(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

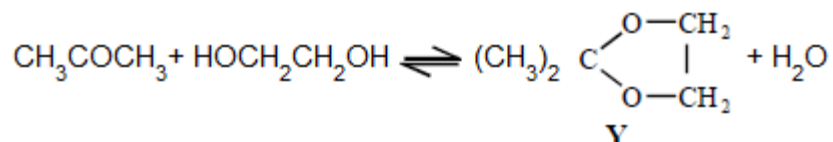
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(4)

(Total 6 marks)

23

This question is about the reaction between propanone and an excess of ethane-1,2-diol, the equation for which is given below.



In a typical procedure, a mixture of 1.00 g of propanone, 5.00 g of ethane-1,2-diol and 0.100 g of benzenesulphonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, is heated under reflux in an inert solvent. Benzenesulphonic acid is a strong acid.

When the concentration of benzenesulphonic acid is doubled, the rate of the reaction doubles. It can be deduced that

- A** the reaction is first order overall.
- B** the reaction is third order overall.
- C** the reaction is acid-catalysed.
- D** units for the rate constant, k , are $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$.

(Total 1 mark)

24

- (a) The initial rate of the reaction between substances **P** and **Q** was measured in a series of experiments and the following rate equation was deduced.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (i) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.30	4.8 × 10 ⁻³
2	0.10	0.10	
3	0.40		9.6 × 10 ⁻³
4		0.60	19.2 × 10 ⁻³

- (ii) Using the data from experiment 1, calculate a value for the rate constant, *k*, and deduce its units.

.....
.....
.....
.....
.....

(6)

- (b) What change in the reaction conditions would cause the value of the rate constant to change?

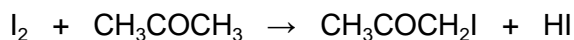
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(1)

(Total 7 marks)

25

Iodine and propanone react in acid solution according to the equation



The rate equation for the reaction is found to be

$$\text{rate} = k [CH_3COCH_3][H^+]$$

- (a) Deduce the order of reaction with respect to iodine and the overall order of reaction.

Order with respect to iodine

Overall order

(2)

- (b) At the start of the experiment, the rate of reaction was found to be $2.00 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the concentrations of the reactants were as shown below.

Reactant	Concentration / mol dm ⁻³
CH ₃ COCH ₃	1.50
I ₂	2.00×10^{-2}
H ⁺	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

Rate constant

.....

.....

Units

(3)

- (c) How can you tell that H⁺ acts as a catalyst in this reaction?

.....

.....

.....

(2)

- (d) Calculate the initial rate of reaction if the experiment were to be repeated at the same temperature and with the same concentrations of iodine and propanone as in part (b) but at a pH of 1.25

.....

.....

.....

.....

.....

.....

(3)
(Total 10 marks)

26

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.45 × 10 ⁻⁵
2	0.30	0.24	0.90 × 10 ⁻⁵
3	0.60	0.48	7.20 × 10 ⁻⁵

- (i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to **A**.

.....

.....

- (ii) Deduce the order with respect to **B**.

.....

.....

(2)

- (b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	0.75	1.50	9.30 × 10 ⁻⁵
5	0.20	0.10	To be calculated

The rate equation for this reaction is

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

- (i) Use the data from Experiment 4 to calculate a value for the rate constant, k , at this temperature. State the units of k .

Value for k

.....

.....

Units of k

.....

- (ii) Calculate the value of the initial rate in Experiment 5.

.....

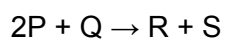
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.....

(4)
(Total 6 marks)

27

The equation and rate law for the reaction of substance P with substance Q are given below.



$$\text{rate} = k[P]^2[H^+]$$

Under which one of the following conditions, all at the same temperature, would the rate of reaction be slowest?

	[P] / mol dm ⁻³	pH
A	0.1	0
B	1	2
C	3	3
D	10	4

(Total 1 mark)

28

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

Correct units for the rate constant in the rate equation above are

- A** mol dm⁻³ s⁻¹
- B** mol⁻¹ dm⁻³ s⁻¹
- C** mol² dm⁻⁶ s⁻¹
- D** mol⁻² dm⁶ s⁻¹

(Total 1 mark)

Mark schemes

1

(a) $k = \text{rate} / [\text{A}]^2$ or $\frac{3.3 \times 10^{-5}}{(4.2 \times 10^{-3})^2}$ 1

= 1.87 or 1.9

Answer scores 2

1.90 scores first mark only (incorrect rounding)

1

$\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

Any order and independent of calculation

1

(b) Expt 2 rate = $1.167 \times 10^{-4} - 1.2 \times 10^{-4}$ ($\text{mol dm}^{-3} \text{s}^{-1}$)

If answers in table are not those given here, check their value of k in part (a) or use of alternative k.

1

Expt 3 [A] = $9.7 \times 10^{-3} - 9.8(1) \times 10^{-3}$ (mol dm^{-3})

If their k is incorrect in part (a) mark this part consequentially e.g. if $k = 7.9 \times 10^{-3}$ due to lack of squaring in (a)

Using alternative value for k

expt 2 4.9×10^{-7}

Expt 2 rate = $1.4(4) \times 10^{-4}$ ($\text{mol dm}^{-3} \text{s}^{-1}$)

expt 3 1.5×10^{-1}

Expt 3 [A] = 8.85×10^{-3} (mol dm^{-3})

(expt 2 $6.24 \times 10^{-5} \times \text{their } k$)

(expt 3 $0.0134 / \sqrt{k}$)

1

(c) Slow step or rds involves only A

OR

B does not appear in the slow step or the rds

OR

B only appears after the slow step or the rds

Not B has no effect on the rate or B is not in the rate equation

Allow "it" for B

1

[6]

2

(a) Consider experiments 1 and 2: [B constant]

[A] increases $\times 3$: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases $\times 2$: rate should increase $\times 2^2$ but only increases $\times 2$

Therefore, halving [B] halves rate and so 1st order with respect to B

Rate equation: rate = $k[A]^2[B]$

(b) rate = $k[C]^2[D]$ therefore $k = \text{rate} / [C]^2[D]$

$$k = \frac{7.2 \times 10^{-4}}{(1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2})} = 57.0$$

Allow consequential marking on incorrect transcription

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

(c) rate = $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} \text{ (mol dm}^{-3} \text{ s}^{-1})$

OR

Their $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

(d) Reaction occurs when molecules have $E \geq E_a$

Doubling T by 10 °C causes many more molecules to have this E

Whereas doubling [E] only doubles the number with this E

(e) $E_a = RT(\ln A - \ln k) / 1000$

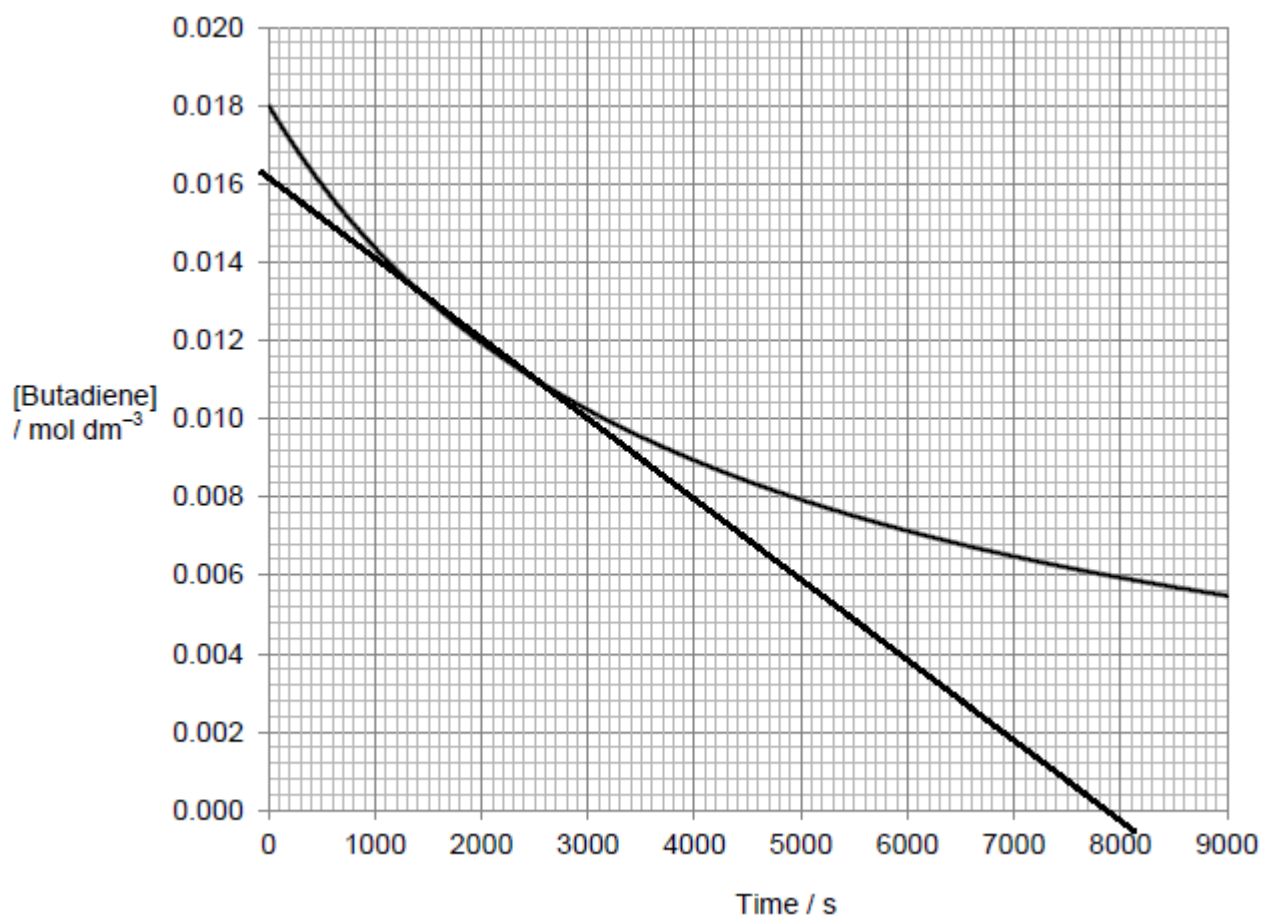
Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

$$E_a = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 \text{ (kJ mol}^{-1})$$

[12]

3

(a) Gradient drawn on graph



Line must touch the curve at 0.012 but must not cross the curve.

1

(b) Stage 1: Rate of reaction when concentration = $0.0120 \text{ mol dm}^{-3}$

From the tangent

Change in [butadiene] = $-0.0160 - 0$ and change in time = $7800 - 0$ *Extended response*

1

Gradient = $-(0.0160 - 0) / (7800 - 0) = -2.05 \times 10^{-6}$ Rate = $2.05 \times 10^{-6} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$

1

Stage 2: Comparison of rates and concentrations

Initial rate / rate at $0.0120 = (4.57 \times 10^{-6}) / (2.05 \times 10^{-6}) = 2.23$ *Marking points in stage 2 can be in either order*

1

Initial concentration / concentration at point where tangent drawn = $0.018 / 0.012 = 1.5$

1

Stage 3: Deduction of order

If order is 2, rate should increase by factor of $(1.5)^2 = 2.25$ this is approximately equal to 2.23 therefore order is 2nd with respect to butadiene

1
[6]

4 B

[1]

5 (a) (i) 2

1

(ii) 0

1

(b) (i)
$$K = \frac{6.64 \times 10^{-5}}{(4.55 \times 10^{-2}) \times (1.70 \times 10^{-2})^2}$$

Correct answer for k with or without working scores 2.

First mark is for insertion of numbers into a correctly rearranged rate equ, k = etc.

1

= 5.05 (range allowed 5.03–5.07)

AE (-1) for copying numbers wrongly or swapping two numbers.

1

mol⁻² dm⁺⁶ s⁻¹

Mark units separately, ie only these units but can be in any order.

1

(ii) 8.3×10^{-6} (mol dm⁻³ s⁻¹)

Allow 0.83×10^{-5} .

Ignore units.

OR if not 8.3×10^{-6} , look at their k in part(i) and if not 5.05

Allow ecf for their (incorrect) $k \times (1.64 \times 10^{-6})$

1

[6]

6 (a) (i) 2 or two or second or [E]²

1

(ii) 1 or one or first or [F]¹ or [F]

1

(b) (i) $k = \frac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$
mark is for insertion of numbers into a correctly rearranged rate equation, k = etc.
AE (-1) for copying numbers wrongly or swapping two numbers.

1

= 22.9 (Allow 22.9 – 24 after correct rounding)

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order.

1

(ii) $6.8(2) \times 10^{-3} \text{ (mol dm}^{-3} \text{s}^{-1}\text{)}$
OR if their k is wrong, award the mark consequentially
 a quick check can be achieved by using
their answer = 2.9768×10^{-4} Allow $2.9 - 3.1 \times 10^{-4}$ for the mark
 their k

Allow 6.8×10^{-3} to 6.9×10^{-3}

Ignore units.

1

[6]

7

(a) (i) $k = \frac{8.4 \times 10^{-5}}{(4.2 \times 10^{-2})^2 \times 2.6 \times 10^{-2}}$ **OR** $\frac{8.4 \times 10^{-5}}{(1.76 \times 10^{-3}) \times 2.6 \times 10^{-2}}$

Mark is for insertion of numbers into a correctly rearranged rate equation, k = etc.

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

= 1.8(3)

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

If k calculation wrong, allow units consequential to their k = expression

1

(ii) $5.67 \times 10^{-4} \text{ (mol dm}^{-3} \text{s}^{-1}\text{)}$ **OR** their k $\times 3.1 \times 10^{-4}$

Allow 5.57×10^{-4} to 5.7×10^{-4}

1

(b) (i) 2 or second or $[D]^2$

1

(ii) 0 or zero or $[E]^0$

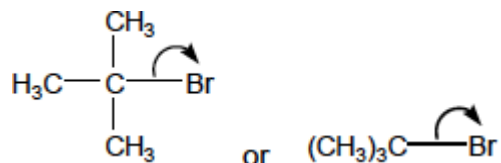
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(c) (i) Step 1 or equation as shown

Penalise Step 2 but mark on

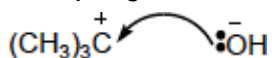
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(ii)



Ignore correct partial charges, penalise full / incorrect partial charges

If Step 2 given above, can score the mark here for



allow: OH^- (must show lp)

If $\text{S}_{\text{N}}2$ mechanism shown then no mark (penalise involvement of :OH^- in step 1)

Ignore anything after correct step 1

1

[8]

8

(a) Exp 2 4.5×10^{-4}

Min 2sf

1

Exp 3 4.5×10^{-3}

If three wrong answers, check their value of k in (b).

1

Exp 4 0.043 OR 4.3×10^{-2} OR 0.044 OR 4.4×10^{-2}

They can score all 3 if they have used their (incorrect) value of k . see below.

$$\text{Exp 2 rate} = k \times (1.0125 \times 10^{-4})$$

$$\text{Exp 3 } [Q] = 0.02/k$$

$$\text{Exp 4 } [P] = 0.0913/k$$

1

(b) $k = \frac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$

Mark is for insertion of numbers into a correctly rearranged rate equation, $k = \text{etc}$

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

$= 4.4(4)$ (allow 40/9)

1

$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

Any order

If k calculation wrong, allow units conseq to their k expression

1

[6]

9

(a) Exp 2 $14.(4) \times 10^{-3}$ **OR** $1.4(4) \times 10^{-2}$ or 0.014

Allow 2sf

1

Exp 3 0.1(0)

1

Exp 4 0.3(0)

If three wrong answers, check their value of k in 1(b).

They can score all 3 if they have used their (incorrect) value of k.

see below.

Exp 2 rate = $0.096 \times k$

Exp 3 **[Q]** = $0.015/k$

Exp 4 **[P]** = $0.116/k$

1

(b)
$$K = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$$

mark is for insertion of numbers into a correctly rearranged rate equ

, k = etc

1

= 0.15 (min 2sfs) (allow $\frac{3}{20}$)

if upside down, score only units mark

AE (-1) for copying numbers wrongly or swapping two numbers

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

If k calculation wrong, allow units conseq to their k

1

(c) G

1

[7]

10

(a) (i) $k = \frac{6.2 \times 10^{-6}}{(2.9 \times 10^{-2})^2 \times 2.3 \times 10^{-2}}$

mark is for insertion of numbers into a correctly

rearranged rate equ, k = etc

AE (-1) for copying numbers wrongly or swapping two numbers

1

= 0.32 (min 2sfs)

1

mol⁻² dm⁶ s⁻¹ Units must be conseq to their k

Any order

If k calculation wrong, allow units conseq to their k

1

(ii) 4.95×10^{-5} to 4.97×10^{-5} or 5.0×10^{-5} (min 2 sfs)

(ignore units)

rate = their k \times 1.547×10^{-4}

1

(b) Step 2

If wrong no further mark

1

One H₂ (and two NO) (appear in rate equation)

or species (in step 2) in ratio/proportion as in the rate equation

1

[6]**11**

(a) (i) propyl methanoate

must be correct spelling

1

(ii) rate = k[X][OH⁻]

allow HCOOCH₂CH₂CH₃ (or close) for X

allow () but penalise missing minus

1

(iii) $k = \frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$

In (a)(iii), if wrong orders allow

mark is for insertion of numbers in correct expression for k

If expression for k is upside down, only score units conseq to their expression

1

$= 0.10(12)$ 2sf minimum

1 for conseq answer

1

$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

1 for conseq units

any order

1

(iv) $2.1(3) \times 10^{-5}$

or $2.1(2) \times 10^{-5}$ ignore units

allow 2 sf

NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k

See * below

1

(v) $1.3 \times 10^{-4} (1.28 \times 10^{-4})$

allow (1.26×10^{-4}) to (1.3×10^{-4}) ignore units

allow 2 sf

NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k

See ** below

1

For example, if orders given are 1st in X and second in OH⁻

[The mark in a(ii) and also first mark in a(iii) have already been lost]

So allow mark * in (iv) for rate = their $k \times (0.012)(0.0175)^2 = \text{their } k \times (3.7 \times 10^{-6})$
(allow answer to 2sf)

** in (v) for rate = their $k \times (0.012)(0.105)^2 = \text{their } k \times (1.32 \times 10^{-4})$
(allow answer to 2sf)

The numbers will of course vary for different orders.

(vi) Lowered
if wrong, no further mark 1

fewer particles/collisions have energy $> E_a$
OR
fewer have sufficient (activation) energy (to react)
not just fewer successful collisions 1

(b) Step 2 1

(this step with previous) involves one mol/molecule/particle
A and two Bs

or 1:2 ratio or same amounts (of reactants) as in rate equation
if wrong, no further mark 1

[11]

12

(a) 3-hydroxybutanal
ignore number 1 i.e. allow 3-hydroxybutan-1-al
not hydroxyl 1

(b) $k = \frac{2.2 \times 10^{-3}}{(0.10)(0.02)}$ 1

= 1.1 1

$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ 1

(c) planar or flat C=O or molecule
allow planar molecule 1

equal probability of attack from above or below
must be equal; not attack of OH⁻ 1

(d) (i) Step 1 if wrong – no mark for explanation. 1

involves ethanal and OH⁻ or species/ “molecules”
in rate equation 1

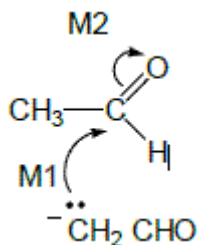
(ii) (B-L) acid or proton donor
not Lewis acid

1

(iii) nucleophilic addition
QOL

1

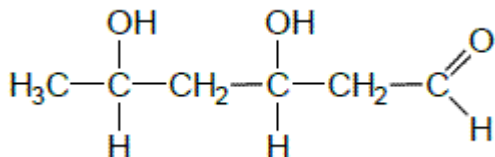
(iv)



not allow M2 before M1, but allow M1 attack on C+ after non-scoring carbonyl arrow
ignore error in product

2

(e)



1

[13]

13

(a) Log (1 / time) on the y-axis + log (vol) on x-axis

If axes unlabelled use data to decide that log (1 / time) is on the y-axis

1

Sensible scales

Lose this mark if the plotted points do not cover at least half of the paper

Lose this mark if the graph plot goes off the squared paper

Lose this mark if plots a non-linear / broken scale

Lose this mark if uses an ascending y-axis of negative numbers

1

Plots points correctly \pm one square

1

Line through the points is smooth

Lose this mark if the candidate's line is doubled

1

Line through the points is best fit – ignores last point

Must recognise that point at 25 cm³ is an anomaly

If wrong graph, mark consequentially on anomaly if correctly plotted.

*A kinked graph loses smooth **and** best fit marks*

1

(b) Uses appropriate *x* and *y* readings

Allow taken from table or taken or drawn on graph

Must show triangle on graph or such as $\frac{1.65 - 1.2}{1.4 - 0.9}$

1

Correctly calculates gradient 0.95 ± 0.02

Ignore positive or negative sign

Correct answer only with no working scores this mark

1

Answer given to 2 decimal places

1

(c) First order or order is 1

Allow consequential answer from candidate's results

1

(d) Thermostat the mixture / constant temperature / use a water bath
or Colorimeter / uv-visible spectrometer / light sensor to monitor colour change

1

Reaction / rate affected by temperature change

or Eliminates human error in timing / more accurate time of colour change

1

[11]

14

(a) 2 or two or second

1

(b) $k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$

mark is for insertion of numbers into a correctly rearranged rate equ, $k = \text{etc}$

if upside down, (or use of I_2 data) score only units mark

1

$= 3.44 \times 10^{-5}$ (min 3sfs)

1

$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

any order

1

(c) no change or no effect or stays the same or 1.24×10^{-4}

1

(d) 1 or 2 or 1 and 2

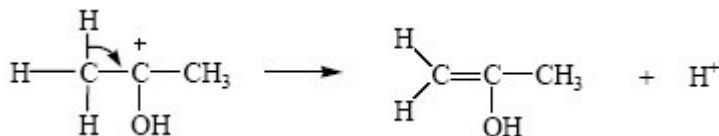
if wrong no further mark but mark on from no answer

1

rate equ doesn't involve I_2 or only step which includes 2 species in rate equ

1

(e)



any second arrow loses the mark

1

[8]

15

(a) (i) 2

1

(ii) 0

1

(b) (i) $\text{rate}/[\text{NO}_2]^2[\text{O}_2]$

1

13

1

mol dm^{-3}

1

(ii) 1.9×10^{-3}

1

(iii) Step 2

1

[7]

16

(a) $k = \text{rate}/[\text{CH}_3\text{CH}_2\text{COOCH}_3][\text{H}^+]$

1

or

$$= \frac{1.15 \times 10^{-4}}{(0.150)(0.555)}$$

$$= 1.38 \times 10^{-3} \text{ to } 1.4 \times 10^{-3}$$

1

$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

1

(b) $\text{ans} = \text{rate constant} \times (\frac{1}{2} \times 0.150) \times (\frac{1}{2} \times 0.555)$

ignore units

$$= \text{rate constant} \times 0.0208$$

$$2.88 \times 10^{-5} \quad (1.38 \times 10^{-3} \text{ gives } 2.87 \times 10^{-5})$$

Allow 2.87 – 2.91 $\times 10^{-5}$ (1.4 $\times 10^{-3}$ gives 2.91 $\times 10^{-5}$)

1

(c) $[\text{H}^+] = \text{rate}/ k[\text{CH}_3\text{COOCH}_2\text{CH}_3]$

1

$$= \frac{4.56 \times 10^{-5}}{(8.94 \times 10^{-4})(0.123)}$$

$$= 0.415 \text{ (0.4146)}$$

1

pH = 0.38 mark independently

$$[\text{H}^+] = 0.41 \text{ gives } \text{pH} = 0.39$$

1

[7]

17

(a) exp2 4.0×10^{-3}

1

exp3 0.45×10^{-5}

1

exp4 9.0×10^{-3}

1

(b) $\frac{1.8 \times 10^{-5}}{(3.0 \times 10^{-3})^2 (1.0 \times 10^{-3})}$

1

2000

1

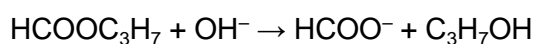
$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

1

[6]

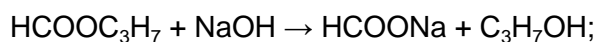
18

(a) propyl methanoate;



1

OR



1

(b) order wrt A = 1;

1

order wrt NaOH = 1;

1

Initial rate in Exp 4 = 2.4×10^{-3} ;

1

(c) (i) $r(\text{ate}) = k[\text{A}]$

OR

$$r(\text{ate}) = k[\text{A}][\text{NaOH}]^0;$$

(penalise missing [] but mark on)

(penalise missing [] once per paper)

(if wrong order, allow only units mark conseq on their rate eqs)

(penalise k_a or k_w etc)

1

(ii) $k = \frac{9.0 \times 10^{-3}}{0.02};$

1

= 0.45;

1

s^{-1} ;

1

(iii) (large) excess of OH^- or $[\text{OH}^-]$ is large/high; 1

$[\text{OH}^-]$ is (effectively) constant

OR

$[\text{A}]$ is the limiting factor *(Q of L mark)* 1

(d) (i)
$$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
 1

propan(e)-1,2,3-triol

OR

1,2,3-propan(e)triol

OR

Glycerol; 1

(ii) $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$ or $\text{C}_{17}\text{H}_{35}\text{COONa}$ or $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$; 1
(ignore 3 in front of formula but not if indicating trimer)

(not just anion and penalise Na shown as covalently bonded) soap -
allow with detergent but not detergent alone; 1

[15]

19

(a) order with respect to **P** is 2 1

order with respect to **Q** is 1 1

- (b) (i) rate = $k[R][S]^2$
(if wrong expression, no further marks)

1

$$\text{rate} = (4.2 \times 10^{-4}) \times 0.16 \times 0.84^2$$

1

$$= 4.7 \times 10^{-5} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$$

ignore units even if wrong

1

(ii) $k = \frac{\text{rate}}{[R][S]^2} = \frac{8.1 \times 10^{-5}}{0.76 \times 0.98^2}$

1

$$= 1.1 \times 10^{-4}$$

1

- (iii) T_1

**If calculated value for $k > 4.2 \times 10^{-4}$, then answer to (iii) is T_2*

1

[8]

20

- (a) (i) Experiment 2 2.60×10^{-3}

1

Experiment 3 0.60×10^{-2}

1

Experiment 4 11.4×10^{-2}

1

(ii) $k = \frac{10.4 \times 10^{-3}}{(4.80 \times 10^{-2})(6.60 \times 10^{-2})^2}$

1

$$= 49.7$$

(Allow 49.8 and 50)

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

1

(b) No change

1

[7]

21

(a) (i) 2 (1)

(ii) 0 (1)

2

(b) (i) Value of k : $k = \frac{\text{rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{8.5 \times 10^{-4}}{(5.012 \times 10^{-2})^2 (2.0 \times 10^{-2})} = 13$

Units of k : $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ (1)

(ii) $\text{rate} = 13 (6.5 \times 10^{-2})^2 (3.4 \times 10^{-2})$
 $= 1.9 \times 10^{-3} \quad (\text{mol dm}^{-3} \text{s}^{-1})$ (1)

*If k wrong, the mark in (ii) may be gained conseq for their
 $k \times 1.437 \times 10^{-4}$*

4

[6]

22

(a) Power (or index or shown as x in $[\]^x$) of concentration term
(in rate equation) (1)

1

(b) 2 (1)

1

(c) (i) Order with respect to **A**: 2 (1)

Order with respect to **B**: 0 (1)

(ii) Rate equation: (rate =) $k [\text{A}]^2$ (1)

Allow conseq on c(i)

Units for rate constant: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1)

conseq on rate equation

4

[6]

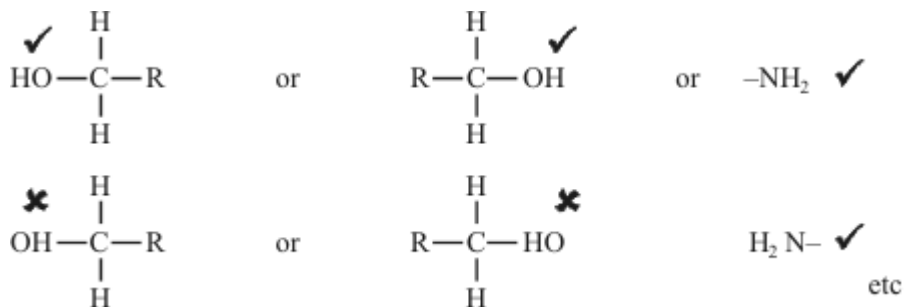
Organic points

- (1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



- (2) Structures

penalise sticks (i.e. $\begin{array}{c} | \\ \text{---C---} \\ | \end{array}$) once per paper



Penalise once per paper

allow CH₃- or -CH₃ or $\begin{array}{c} \text{CH}_3 \\ | \end{array}$ or H₃C-

23

[1]

24

- (a) (i) Experiment 2: $0.4(0) \times 10^{-3}$ (1)
Experiment 3: 0.15 (1)
Experiment 4: 0.28 (1)

(ii) $k = \frac{4.8 \times 10^{-3}}{(0.20)^2 \times (0.30)} = 0.4(0) \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$
(1) (1) (1)

6

(b) (change in) temperature (1)

1

[7]

25

(a) Order with respect to iodine: 0 (1)
Overall order: 2 (1)

2

(b) Rate constant: $k = \frac{2 \times 10^{-5}}{(1.5) \times (3 \times 10^{-2})} = 4.4(4) \times 10^{-4}$ (1)

Units: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1)

3

(c) Appears in rate equation (1)

OR implied by mention of concentration or order

does not appear in (stoichiometric / overall) equation (1)

2

(d) $\text{pH} = -\log_{10} [\text{H}^+]$ (1)
 $= 1.25$

$[\text{H}^+] = 0.056(2)$ (1)

$\therefore \text{rate} = (4.44 \times 10^{-4}) \times (1.50) \times (0.0562)$

$= 3.75 \times 10^{-5}$ (1) ($\text{mol dm}^3 \text{s}^{-1}$)

(3.7 — 3.8)

Can score all 3 conseq on k from part (b)

3

[10]

26

(a) (i) (Experiment 1 \rightarrow 2) [A] doubled, ([B] constant,) rate doubled (1)

stated or shown numerically

(ii) 2 (1)

or shown as ... $[\text{B}]^2$

2

$$(b) \quad (i) \quad k = \frac{9.30 \times 10^{-5}}{(0.75)^2 \times (1.50)} = 1.1(0) \times 10^{-4}$$

(1) (1)

units of k: mol⁻² dm⁶ s⁻¹ (1)

$$(ii) \quad \text{rate} = (1.10 \times 10^{-4}) \times (0.20)^2 \times (0.10)$$

$$= 4.4(1) \times 10^{-7} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$$

(1) for the answer

Ignore units

Conseq on (i)

Upside down expression for k scores zero in (i) for 9073

but rate = 9073 × (0.2)² × (0.1) = 36(.3)

conseq scores (1) in (ii)

4

[6]

C
27

[1]

D
28

[1]