Q1.

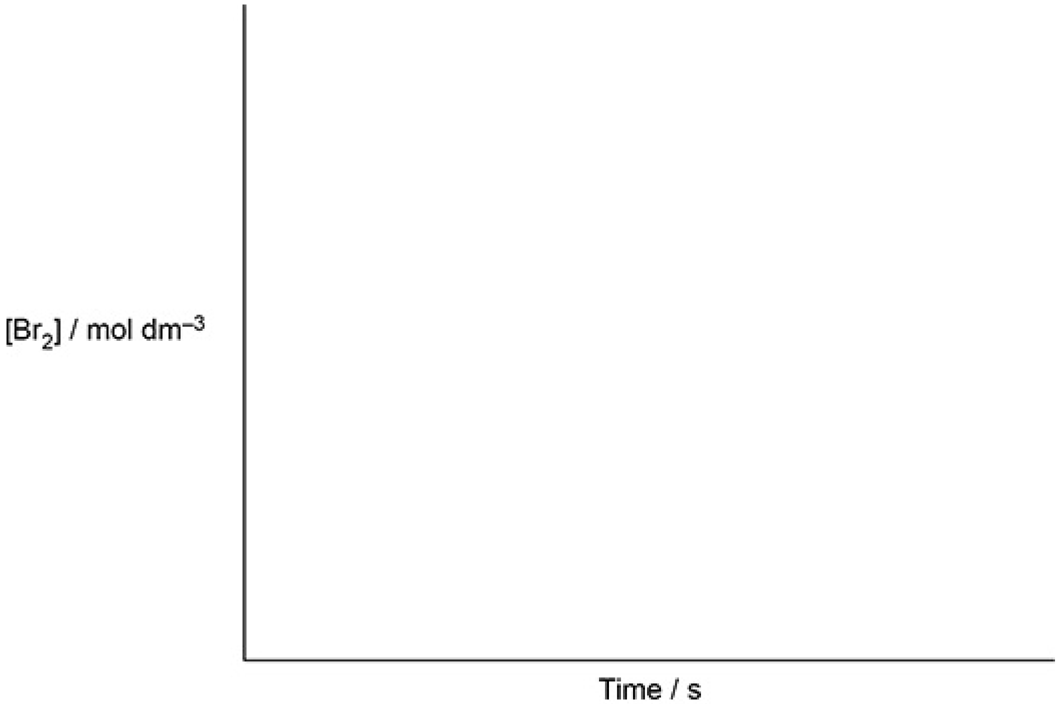
Propanone reacts with bromine in alkaline conditions.

$$CH_3COCH_3 + Br_2 + OH^- \longrightarrow CH_3COCH_2Br + Br^- + H_2O$$

The rate equation for this reaction is

$$\textit{Rate} = k\,[CH_3COCH_3]\,[OH^-]$$

(a) Sketch a graph on the axes provided to show how, at constant temperature, the concentration of bromine changes during this reaction.



(1)

(b) The table shows the initial rate of this reaction for experiments using different mixtures containing propanone, bromine and hydroxide ions.

Experiment	**$[CH_3COCH_3]$ / mol dm^{-3}**	**$[Br_2]$ / mol dm^{-3}**	**$[OH^-]$ / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	1.50×10^{-2}	2.50×10^{-2}	2.50×10^{-2}	2.75×10^{-11}
2	1.50×10^{-2}	2.50×10^{-2}		8.25×10^{-11}
3	3.75×10^{-3}	5.00×10^{-2}	1.00×10^{-1}	

Complete the table above.

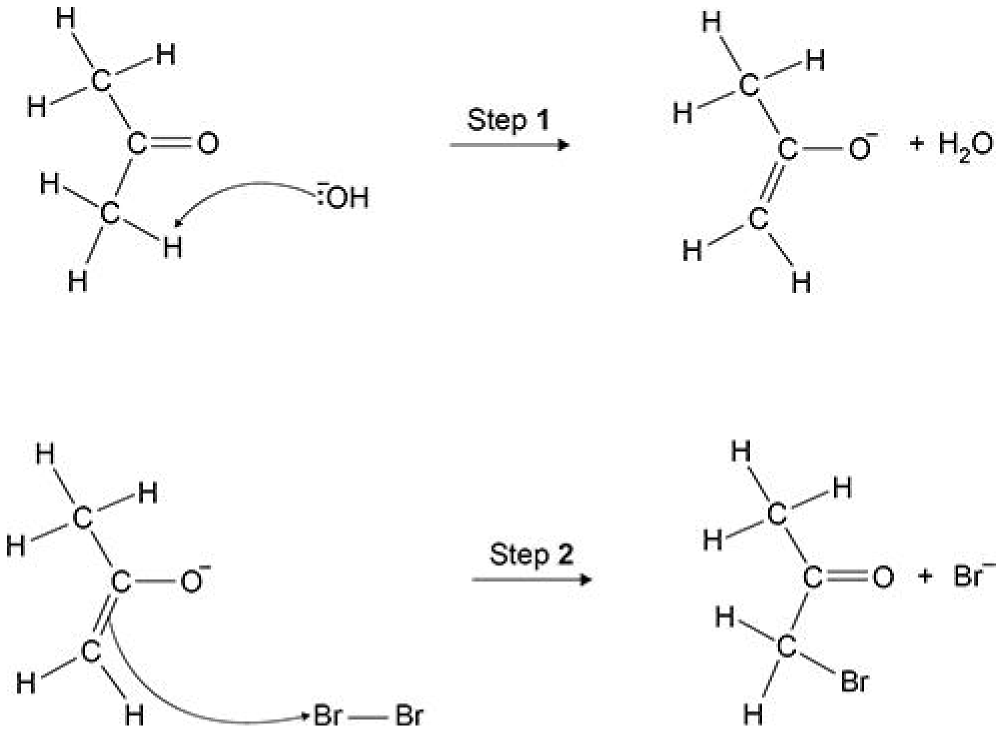
Use the data from experiment **1** to calculate the rate constant *k* for this reaction.

Give the units for the rate constant.

k ____________________ Units ____________________

(5)

(c) The figure below shows an incomplete mechanism for this reaction.



Complete the mechanism in the figure by adding four curly arrows and any relevant lone pair(s) of electrons.

(4)

(d) Use evidence from the rate equation to explain why Step **1** is the rate determining step.

____

____

(1)

(Total 11 marks)

Q2.

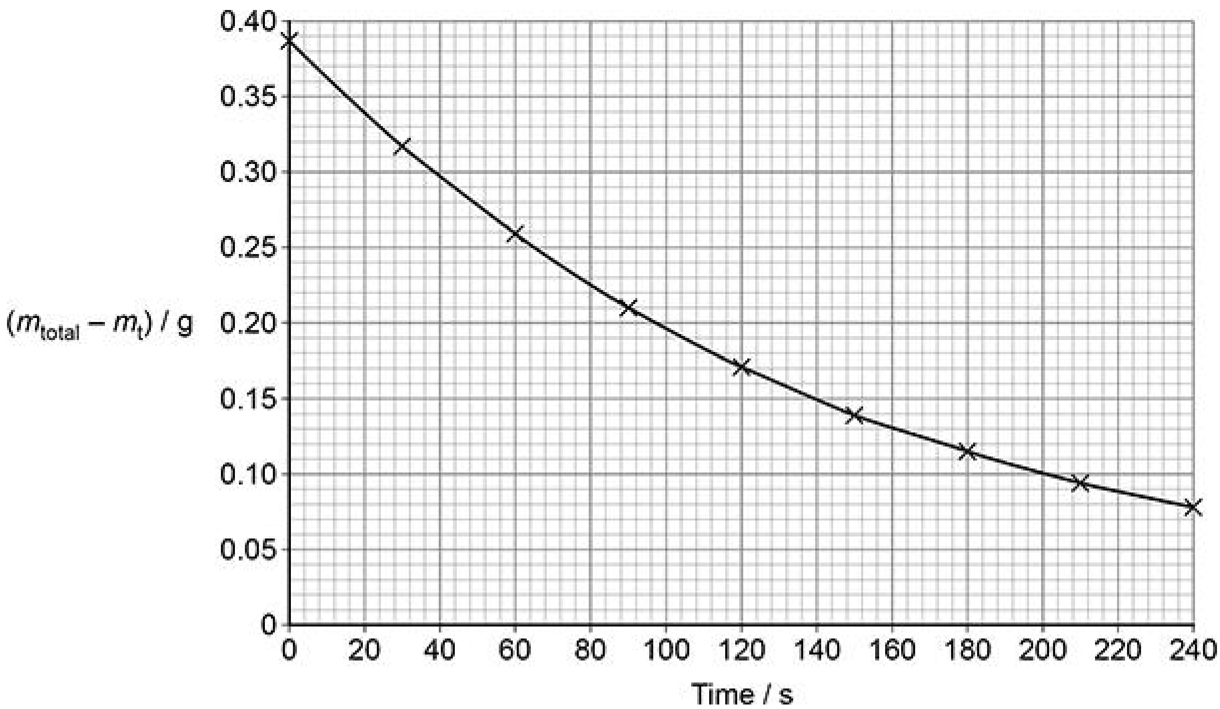
The rate of reaction between calcium carbonate and hydrochloric acid is investigated using a continuous monitoring method.

Method

- Place a conical flask on a balance and add approximately 20 g of large marble chips.
- Add 50 cm^3 of 0.4 mol dm^{-3} hydrochloric acid.
- Place a loose cotton wool plug in the neck of the flask.
- Zero the mass reading on the balance.
- Start a timer.
- Record the loss in mass (m_t) every 30 seconds for 4 minutes.
- Wait for the reaction to finish and record the total mass loss (m_{total}).
- Plot a graph of ($m_{total} - m_t$) against time.

Figure 1 shows a graph of the results obtained during the first 240 s

Figure 1



(a) Suggest why a loose cotton wool plug is placed in the neck of the flask, instead of leaving the flask open or inserting a bung.

Instead of leaving the flask open ________________________

____

Instead of inserting a bung ________________________

____

(2)

(b) 20 g of large marble chips is a large excess of calcium carbonate.

Suggest why using a large excess of calcium carbonate means that the rate is only affected by the changing concentration of the hydrochloric acid.

___

___

(1)

(c) The mass of carbon dioxide produced in time *t* is equal to m_t.

The total mass of CO_2 produced during the reaction is equal to m_{total}.

Explain why $(m_{total} - m_t)$ is proportional to the concentration of hydrochloric acid remaining in the flask at time *t*.

___

___

___

___

___

(2)

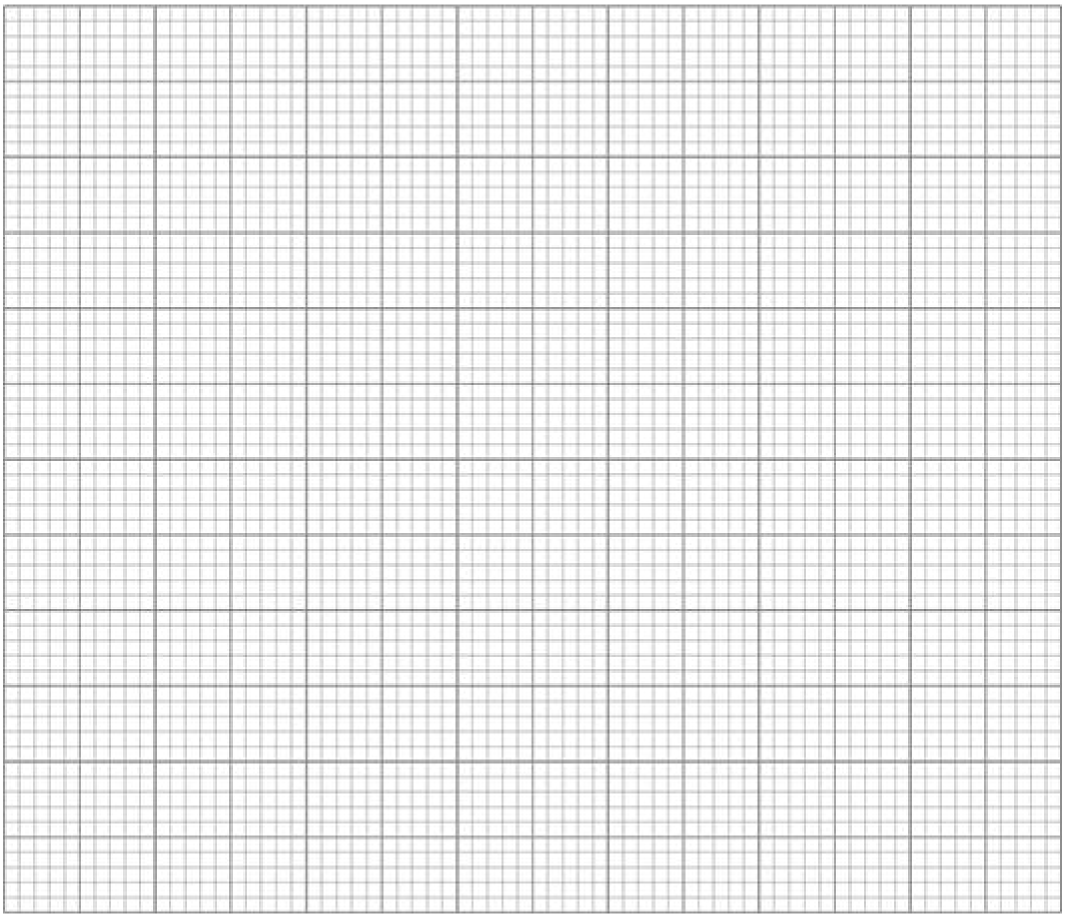
(d) The table below shows the rate of reaction, calculated from the gradient of the curve, at five different times.

$(m_{total} - m_t)$ is proportional to the concentration of unreacted HCl at time t.

Rate of reaction / g s^{-1}	23.0×10^{-4}	19.0×10^{-4}	15.7×10^{-4}	11.5×10^{-4}	6.67×10^{-4}
$(m_{total} - m_t)$ / g	0.340	0.280	0.225	0.170	0.100

On the grid in **Figure 2** plot the rate of reaction (y-axis) against $(m_{total} - m_t)$ (x-axis).

Figure 2



(3)

(e) State how the graph in **Figure 2** confirms that the rate equation for this reaction is

$$Rate = k[HCl]$$

____

____

____

(1)

(f) In this experiment the variable measured is mass loss.

The rate of this reaction at a constant temperature can be investigated in other ways.

Suggest **two** other variables that can be measured instead of mass loss.

1 ____

2 ____

(2)

(Total 11 marks)

Q3.

The thermal decomposition of but-3-en-1-ol is investigated at different temperatures (T).

$$CH_2{=}CHCH_2CH_2OH \rightarrow CH_2{=}CHCH_3 + HCHO$$

The results from the investigation are used to calculate the rate constant, k, at each temperature.

The table below shows some of the results.

T / K	$\frac{1}{T}$ / K^{-1}	k / s^{-1}	ln k
553	1.81×10^{-3}	4.6×10^{-4}	–7.68
563	1.78×10^{-3}	8.4×10^{-4}	–7.08
573		15.6×10^{-4}	
583	1.72×10^{-3}	28.0×10^{-4}	–5.88
593	1.69×10^{-3}	49.9×10^{-4}	–5.30

(a) Complete the table with the missing values at 573 K

(1)

(b) The overall order of the reaction can be deduced from a piece of information in one of the column headings in the table.

Identify this piece of information and deduce the overall order.

Piece of information ____

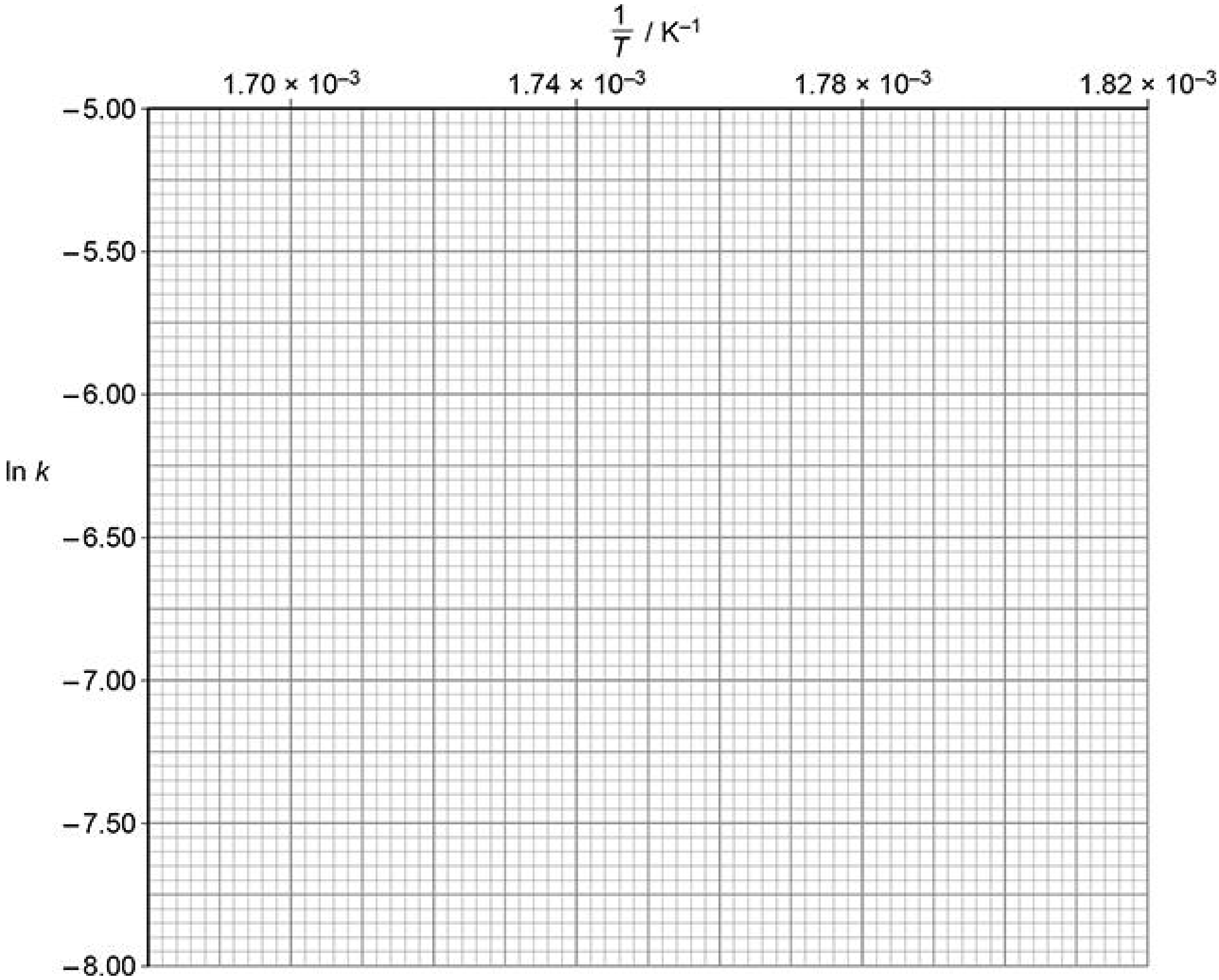
Overall order ____

(2)

(c) The Arrhenius equation can be written in the form shown.

$$\ln k = \ln A - \frac{E_a}{RT}$$

On the grid in below figure plot a graph of ln k against $\frac{1}{T}$



(2)

(d) Use your graph from part (c) to calculate a value for E_a, in kJ mol^{-1}, for the thermal decomposition of but-3-en-1-ol.

The gas constant, R = 8.31 J K^{-1} mol^{-1}

E_a ____________________ kJ mol^{-1}

(3)

(e) 2-Methylpent-4-en-2-ol decomposes in a similar way to but-3-en-1-ol, to produce an alkene and a carbonyl compound.

Deduce the structures of the alkene and the carbonyl compound.

$CH_2{=}CHCH_2C(CH_3)_2OH$ → ____________________ + ____________________

alkene carbonyl compound

(2)

(Total 10 marks)

Q4.

A and B react together in the presence of an acid catalyst.

$$A(aq) + 2\,B(aq) \rightarrow C(aq) + D(aq)$$

The rate equation for this reaction is

$$rate = k[B]^2[H^+]$$

The table below shows how the values of the relative initial rate vary with different concentrations of each reagent at the same temperature.

Experiment	**[A] / mol dm^{-3}**	**[B] / mol dm^{-3}**	**[H^+] / mol dm^{-3}**	**Relative initial rate**
1	0.40	0.20	0.10	1.00
2	0.50	0.20	0.10	
3	0.40		0.10	0.64
4	0.50	0.30	0.06	

(a) Complete the table by calculating the missing values.

(3)

(b) A suggested mechanism for the reaction is shown.

Step 1 $B + H^+ \rightarrow BH^+$

Step 2 $BH^+ + B \rightarrow B_2H^+$

Step 3 $B_2H^+ + A \rightarrow C + D$

Deduce the rate-determining step for this reaction.

Give a reason for your answer.

Rate-determining step ______________________________

Reason ______________________________

____

____

(2)

(Total 5 marks)

Q5.

This question is about ethanoic anhydride.

In the gas phase, ethanoic anhydride $(CH_3CO)_2O$ decomposes to form ethenone.

The equation is

$$(CH_3CO)_2O \rightarrow \underset{\text{Ethenone}}{H_2C{=}C{=}O} + CH_3COOH$$

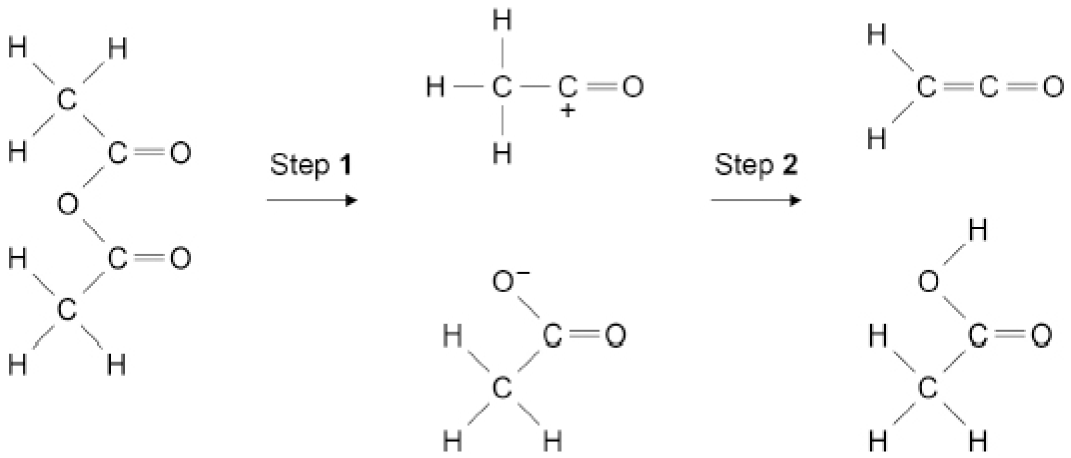
(a) Ethenone is the simplest member of the ketene homologous series. Ketones all contain one C=C double bond and one C=O double bond.

Deduce the general formula for the ketene homologous series.

____

(1)

(b) The figure below shows an incomplete suggested mechanism for the decomposition of ethanoic anhydride.



Complete the mechanism in the figure above by adding three curly arrows and any relevant lone pairs of electrons.

(3)

(c) For a chemical reaction the relationship between the rate constant, k, and the temperature, T, is shown by the Arrhenius equation.

$$k = \mathrm{A}e^{\frac{-E_a}{RT}}$$

For the decomposition of gaseous ethanoic anhydride

the activation energy, E_a = 34.5 kJ mol^{-1}
the Arrhenius constant, A = 1.00×10^{12} s^{-1}

At temperature T_1 the rate constant, $k = 2.48 \times 10^{8}$ s^{-1}

Calculate T_1

The gas constant, R = 8.31 J K^{-1} mol^{-1}

T_1 ____________________ K

(3)

(d) Sketch the Maxwell–Boltzmann distribution of molecular energies for gaseous ethanoic anhydride at temperature T_1 and at a higher temperature T_2

Include a label for each axis, and mark on the appropriate axis a typical position for the activation energy.

Explain why the rate of reaction is faster at T_2

Explanation

____

____

____

(5)

(Total 12 marks)

Q6.

An acidified solution of butanone reacts with iodine as shown.

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

(a) Draw the displayed formula for $CH_3CH_2COCH_2I$

Give the name of $CH_3CH_2COCH_2I$

Displayed formula

Name ____

(2)

(b) The rate equation for the reaction is

$$rate = k[CH_3CH_2COCH_3][H^+]$$

Table 1 shows the initial concentrations used in an experiment.

Table 1

	$CH_3CH_2COCH_3$	I_2	H^+
Initial concentration / mol dm^{-3}	4.35	0.00500	0.825

The initial rate of reaction in this experiment is 1.45×10^{-4} mol dm^{-3} s^{-1}

Calculate the value of the rate constant, *k*, for the reaction and give its units.

k ____________________

Units ____________________

(3)

(c) Calculate the initial rate of reaction when all of the initial concentrations are halved.

Initial rate of reaction ____________________ mol dm^{-3} s^{-1}

(1)

(d) An experiment was done to measure the time, *t*, taken for a solution of iodine to react completely when added to an excess of an acidified solution of butanone.

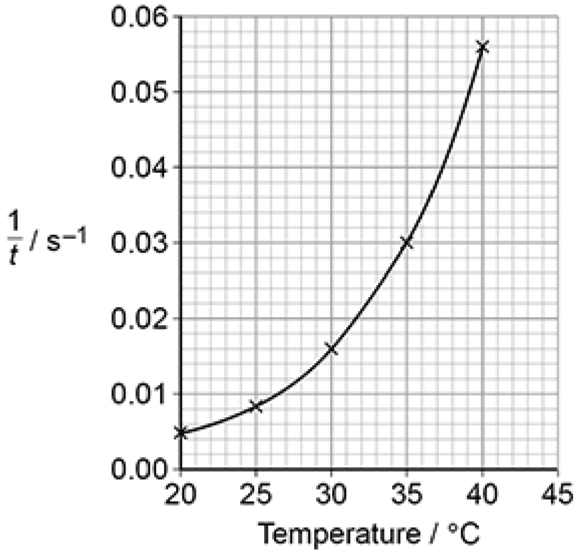
Suggest an observation used to judge when all the iodine had reacted.

____

____

The experiment was repeated at different temperatures.

The graph below shows how $\frac{1}{t}$ varied with temperature for these experiments.



(1)

(e) Describe and explain the shape of the graph above.

____

____

____

____

____

____

____

(3)

(f) Deduce the time taken for the reaction at 35 °C

Time ________________ s

(1)

(g) For a different reaction, **Table 2** shows the value of the rate constant at different temperatures.

Table 2

Experiment	**Temperature / K**	**Rate constant / s^{-1}**
1	T_1 = 303	k_1 = 1.55 ×10^{-5}
2	T_2 = 333	k_2 = 1.70 ×10^{-4}

This equation can be used to calculate the activation energy, E_a

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Calculate the value, in kJ mol^{-1}, of the activation energy, E_a

The gas constant, R = 8.31 J K^{-1} mol^{-1}

E_a ________________ kJ mol^{-1}

(5)

(h) Name and outline the mechanism for the reaction of butanone with KCN followed by dilute acid.

Name of mechanism ______________________________

Outline of mechanism

(5)
(Total 21 marks)

Q7.

Hydrogen peroxide solution decomposes to form water and oxygen.

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

The reaction is catalysed by manganese(IV) oxide.

A student determines the order of this reaction with respect to hydrogen peroxide. The student uses a continuous monitoring method in the experiment.

The student places hydrogen peroxide solution in a conical flask with the catalyst and uses a gas syringe to collect the oxygen formed. The student records the volume of oxygen every 10 seconds for 100 seconds.

(a) Explain why the reaction is fastest at the start.

____

____

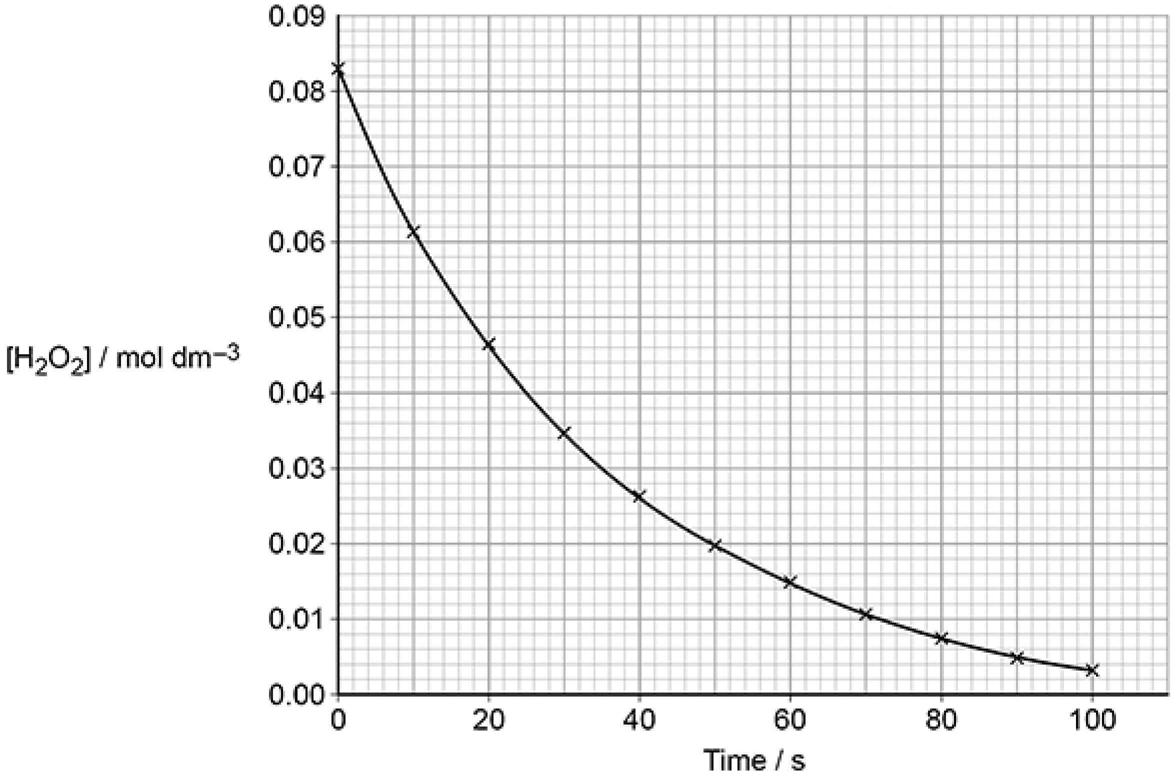
____

____

(2)

(b) The graph in **Figure 1** shows how the concentration of hydrogen peroxide changes with time in this experiment.

Figure 1



Tangents to the curve in **Figure 1** can be used to determine rates of reaction.

Draw a tangent to the curve when the concentration of hydrogen peroxide solution is 0.05 mol dm^{-3}

Use your tangent to calculate the gradient of the curve at this point.

Gradient _______________ mol dm^{-3} s^{-1}

(2)

(c) The concentration of hydrogen peroxide solution at time *t* during the experiment can be calculated using this expression.

$$[H_2O_2]_t = [H_2O_2]_{initial}\left(\frac{V_{max} - V_t}{V_{max}}\right)$$

$[H_2O_2]_t$ = concentration of hydrogen peroxide solution at time *t* / mol dm^{-3}

$[H_2O_2]_{initial}$ = concentration of hydrogen peroxide solution at the start / mol dm^{-3}

V_{max} = total volume of oxygen gas collected during the whole experiment / cm^3

V_t = volume of oxygen gas collected at time *t* / cm^3

In this experiment, V_{max} = 100 cm^3

Use **Figure 1** and the expression to calculate $[H_2O_2]_t$ when 20 cm^3 of oxygen has been collected.

$[H_2O_2]_t$ _______________ mol dm^{-3}

(2)

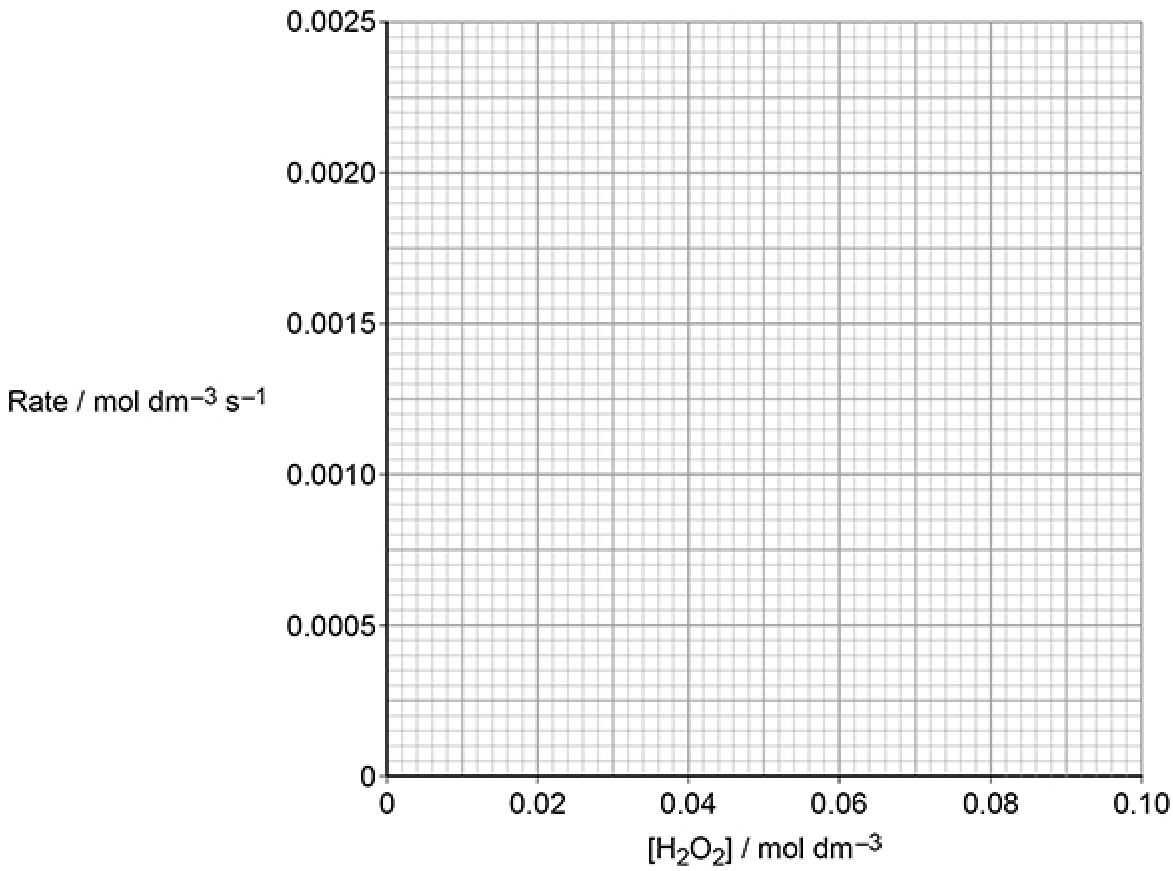
The table below shows data from a similar experiment.

[H_2O_2] / mol dm^{-3}	0.02	0.03	0.05	0.07	0.09
Rate / mol dm^{-3} s^{-1}	0.00049	0.00073	0.00124	0.00168	0.00219

(d) Plot the data from the table above on the grid in **Figure 2**.

Draw a line of best fit.

Figure 2



(2)

(e) Use **Figure 2** to determine the order of reaction with respect to H_2O_2

State how the graph shows this order.

Order ____

How the graph shows this order __________________________

____

____

(2)

(Total 10 marks)