1. The kinetics of the hydrolysis of the halogenoalkane \( \text{RCH}_2\text{Cl} \) with aqueous sodium hydroxide (where \( \text{R} \) is an alkyl group) was studied at 50 °C. The following results were obtained:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[( \text{RCH}_2\text{Cl} )]</th>
<th>[( \text{OH}^- )]</th>
<th>Initial rate/mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>0.10</td>
<td>(4.0 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>0.10</td>
<td>(1.2 \times 10^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.20</td>
<td>(1.6 \times 10^{-3})</td>
</tr>
</tbody>
</table>

(i) Deduce the order of reaction with respect to the halogenoalkane, \( \text{RCH}_2\text{Cl} \), and with respect to the hydroxide ion, \( \text{OH}^- \), giving reasons for your answers.

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(4)

(ii) Hence write the rate equation for the reaction.

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(1)

(iii) Calculate the value of the rate constant with its units for this reaction at 50 °C.

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(2)
(iv) Using your answer to part (ii), write the mechanism for this reaction.

2. In an experiment to determine the rate of the reaction between persulphate ions and iodide ions in aqueous solution

\[ \text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2 \]

the following data were obtained:

<table>
<thead>
<tr>
<th>Concentration/mol dm(^{-3})</th>
<th>Initial rate/mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{S}_2\text{O}_8^{2-})</td>
<td>(\text{I}^-)</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>0.200</td>
<td>0.100</td>
</tr>
<tr>
<td>0.200</td>
<td>0.200</td>
</tr>
</tbody>
</table>

(a) (i) Deduce the order of reaction with respect to each of the reagents and hence write the rate equation for the reaction.

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(Total 10 marks)
(ii) With reference to this reaction state what is meant by the **overall order** of a reaction.

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.........................................................................................................................................................  
......................................................................................................................................................... (1)

(iii) Calculate the rate constant including units.

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.........................................................................................................................................................  
......................................................................................................................................................... (2)

(iv) Explain why the rate equation cannot be written directly from the stoichiometric equation for the reaction.

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.........................................................................................................................................................  
......................................................................................................................................................... (1)

(b) (i) Suggest a suitable experimental technique that would enable you to determine the rate of the reaction given opposite.

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.........................................................................................................................................................  
......................................................................................................................................................... (1)

(ii) Suggest a necessary condition that would help to ensure accurate results.

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.........................................................................................................................................................  
......................................................................................................................................................... (1)
(iii) Suggest one advantage or disadvantage of your chosen experimental method.

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(Total 10 marks)

3. (a) (i) Explain what is meant by the following terms.

Rate of reaction ………………………………………………………………………
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Overall order of a reaction ……………………………………………………………
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(ii) Explain why the order of reaction cannot be deduced from the stoichiometric equation for a reaction.

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(1)
(b) Substitution reactions of halogenoalkanes, can proceed via an $S_N1$ or $S_N2$ mechanism. When 1-bromobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, 2-bromobutane, $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$, and 2-bromo-2-methylpropane, $\text{(CH}_3\text{)}_3\text{CBr}$, are reacted separately with aqueous sodium hydroxide solution each gives the corresponding alcohol.

(i) Give the mechanism for the $S_N1$ reaction between 2-bromobutane and hydroxide ions.

(ii) Explain why the product mixture is not optically active.

(iii) In an experiment designed to find the mechanism of the reaction between 2-bromo-2-methylpropane and hydroxide ions the following data were obtained at constant temperature.

<table>
<thead>
<tr>
<th>Initial concentration of 2-bromo-2-methylpropane /mol dm$^{-3}$</th>
<th>Initial concentration of OH$^-$ / mol dm$^{-3}$</th>
<th>Initial rate of reaction /mol dm$^{-3}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.20</td>
<td>0.10</td>
<td>$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.30</td>
<td>0.20</td>
<td>$3.6 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Use the data to deduce the rate equation for the reaction of 2-bromo-2-methylpropane with sodium hydroxide solution.

(c) Suggest, in outline, a method you could use to follow the progress of the reaction between a bromoalkane and aqueous sodium hydroxide.

4. Manganate(VII) ions react with ethanedioate ions in acidic solution.

\[ 2\text{MnO}_4^- (aq) + 16\text{H}^+ (aq) + 5\text{C}_2\text{O}_4^{2-} (aq) \rightarrow 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}(l) + 10\text{CO}_2(g) \]

(a) In a particular experiment 200 cm\(^3\) of aqueous potassium manganate(VII), KMnO\(_4\), of concentration 0.0500 mol dm\(^{-3}\) were mixed with 50.0 cm\(^3\) of ethanedioic acid, HOOC—COOH, of concentration 0.500 mol dm\(^{-3}\), and 80 cm\(^3\) of 1.0 mol dm\(^{-3}\) sulphuric acid.

(i) Show by calculation that the starting concentration of the manganate(VII) ions was 3.03 \times 10^{-2} \text{ mol dm}^{-3}.

(Total 14 marks)
(ii) The concentration of the manganate(VII) ions was determined over a period of time.

<table>
<thead>
<tr>
<th>Time / s</th>
<th>Concentration of manganate(VII) ions/ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.03 × 10$^{-2}$</td>
</tr>
<tr>
<td>400</td>
<td>2.98 × 10$^{-2}$</td>
</tr>
<tr>
<td>800</td>
<td>2.86 × 10$^{-2}$</td>
</tr>
<tr>
<td>1200</td>
<td>2.75 × 10$^{-2}$</td>
</tr>
<tr>
<td>1600</td>
<td>1.90 × 10$^{-2}$</td>
</tr>
<tr>
<td>2000</td>
<td>7.50 × 10$^{-3}$</td>
</tr>
<tr>
<td>2400</td>
<td>2.50 × 10$^{-3}$</td>
</tr>
</tbody>
</table>

Plot a graph of the concentration of manganate(VII) ions against time and from it determine the initial rate of the reaction and the rate at 1600 s.

(5)

(b) A second experiment was set up involving the same chemicals in the same concentrations as in experiment 1 but this time some solid manganese(II) sulphate was dissolved in the ethanedioic acid before the potassium manganate (VII) solution was poured in. The plot of the concentration of manganate(VII) ions against time is given below:
(i) Determine the order of the reaction with respect to manganate(VII) ions by considering the time taken for the concentration to fall by half, using the concentrations at 0, 800 and 1600 s.

(ii) Compare this graph with the one you plotted in (a) (ii) and give two pieces of evidence that manganese(II) sulphate is a catalyst for this reaction.

(c) (i) Carrying out a flame test on potassium manganate(VII) gives a lilac flame. What does this show?

(ii) Describe how aqueous sodium hydroxide solution could be used to show that manganese(II) ions had been produced in the reaction between manganate (VII) ions and ethanedioate ions in acidic solution.

5. Hydrogen peroxide decomposes to form water and oxygen.

\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \]

(a) Suggest a method for following the rate of this reaction.

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(b) The reaction is first order with respect to hydrogen peroxide.

(i) Explain what is meant by the term first order.

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(ii) The overall order of the reaction is one. Give the rate equation for the reaction.
Rate =

(iii) How would you use a graph of hydrogen peroxide concentration against time to show that the reaction is first order?

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(2)

(c) The data in the table show the effect of temperature on the rate of this reaction.

<table>
<thead>
<tr>
<th>T /K</th>
<th>Rate / mol dm$^{-3}$ s$^{-1}$</th>
<th>1/T /K$^{-1}$</th>
<th>ln(rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.6 $\times 10^{-6}$</td>
<td>3.41 $\times 10^{-3}$</td>
<td>−13.3</td>
</tr>
<tr>
<td>302</td>
<td>4.2 $\times 10^{-6}$</td>
<td>3.31 $\times 10^{-3}$</td>
<td>−12.4</td>
</tr>
<tr>
<td>314</td>
<td>14.4 $\times 10^{-6}$</td>
<td>3.19 $\times 10^{-3}$</td>
<td>−11.1</td>
</tr>
<tr>
<td>323</td>
<td>33.8 $\times 10^{-6}$</td>
<td>3.10 $\times 10^{-3}$</td>
<td>−10.3</td>
</tr>
</tbody>
</table>
(i) On the axes below, sketch graphs for two temperatures, \( T_1 \) and \( T_2 \), where \( T_2 \) is greater than \( T_1 \), and use them to explain why increasing temperature has a dramatic effect on the rate of this reaction.
(ii) Plot a graph of $\ln(\text{rate})$, on the vertical axis, against $1/\text{temperature}$, on the horizontal axis, on the grid below.
(iii) Use your graph and the equation below to calculate the activation energy, $E_A$, for this reaction.

$$\ln(\text{rate}) = \text{constant} \ \frac{E_A}{R} \ \frac{1}{(1/T)} \ \text{where } R = 8.31 \ \text{J K}^{-1} \ \text{mol}^{-1}$$

You should include the sign and units with your answer which should be given to two significant figures.

6. (a) In a rate of reaction experiment between two substances, A and B, the overall order of the reaction was found to be 2. Write three possible rate equations for such a second order reaction between A and B.

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(b) At a certain temperature the rate of reaction between nitrogen monoxide, NO, and hydrogen, $\text{H}_2$, was investigated. The following data were obtained.

<table>
<thead>
<tr>
<th>[NO]/mol dm$^{-3}$</th>
<th>[H$_2$]/mol dm$^{-3}$</th>
<th>Rate/mol dm$^{-3}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.02</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.06</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>0.18</td>
</tr>
</tbody>
</table>
(i) Use the data above to deduce the rate equation for this reaction.

(ii) Use your answer to (b)(i) above to calculate the value of the rate constant, with units.

(c) The investigation described in part (b), above, was repeated, but at a higher temperature, and the rate of the reactions increased. Explain, in terms of particles, why an increase in temperature increases the rate of a reaction.

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(d) State the effect of an increase in temperature on the value of the rate constant, \( k \).

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(1)

(e) Explain the effect of a catalyst on the rate of a reaction.

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(3)

(Total 15 marks)

7. This question is about the hydrolysis of 2-bromo-2-methylbutane.

\[ \text{C}_5\text{H}_{11}\text{Br} + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_{11}\text{OH} + \text{HBr} \]

(a) 15 cm\(^3\) of water was mixed with 15 cm\(^3\) of ethanol. 1.0 cm\(^3\) of 2-bromo-2-methylbutane was added to this mixture. The conductivity of this mixture was measured and rose from 0 to 200 microsiemens in 600 s.

The experiment was repeated using equal volumes of water and ethanol, with 2.0 cm\(^3\) of 2-bromo-2-methylbutane in the 31 cm\(^3\) of mixture. The conductivity of the mixture rose from 0 to 400 microsiemens in 600 s.

(i) Explain why the conductivity of the mixture increases during these reactions.

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(1)

(ii) Why was an ethanol/water mixture used for this reaction rather than water on its own?

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(1)
(iii) What is the effect on the rate of the reaction of doubling the concentration of 2-bromo-2-methylbutane?

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(1)

(iv) Deduce the order of the reaction with respect to 2-bromo-2-methylbutane.

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(1)

(v) Explain why this is the order of reaction with respect to 2-bromo-2-methylbutane and not the overall order of the reaction.

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(1)

(b) The table below shows the results from another experiment where a solution of 2-bromo-2-methylbutane is reacted with varying concentrations of hydroxide ions.

A few drops of an acid-alkali indicator are added to the mixture and the time for the indicator to change to the acidic colour is measured.

<table>
<thead>
<tr>
<th>[C₅H₁₁Br] /10⁻² mol dm⁻³</th>
<th>[OH⁻] /10⁻³ mol dm⁻³</th>
<th>Time /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.75</td>
<td>5</td>
</tr>
<tr>
<td>1.5</td>
<td>1.50</td>
<td>9</td>
</tr>
<tr>
<td>1.5</td>
<td>2.25</td>
<td>14</td>
</tr>
</tbody>
</table>
(i) Calculate the rate of the reaction, in mol dm$^{-3}$ s$^{-1}$, for each concentration of hydroxide ions.

(ii) What effect does doubling the concentration of hydroxide ions have on the rate of the reaction?

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

(1)

(iii) What is the order of the reaction with respect to the hydroxide ions?

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

(1)

(c) When 2-bromo-2-methylbutane reacts with water, or hydroxide ions, the mechanism for the reaction is the same.

(i) Use your answers to (a)(iv) and (b)(iii) to write the rate equation for the reaction with hydroxide ions.

Rate =
(ii) Write a mechanism for the reaction which is consistent with your rate equation.

8. In an acidic solution, propanone reacts with iodine as follows:

$$\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$$

The rate of this reaction can be followed by removing portions of the reaction mixture at known times, adding them to a solution of sodium hydrogen carbonate to stop the reaction and then titrating the mixture with standard sodium thiosulphate solution.

(a) (i) Write the ionic equation for the reaction of thiosulphate ions with iodine in aqueous solution.

.................................................................................................................................................................................. (2)

(ii) State which indicator is used in this titration, and describe what you would see at the end point.

.................................................................................................................................................................................. (2)
(b) Use the following data to deduce the rate equation for the reaction of propanone with iodine in acidic solution, given that the order with respect to \([H^+]\) is one.

<table>
<thead>
<tr>
<th>([\text{CH}_3\text{COCH}_3]) /mol dm(^{-3})</th>
<th>([\text{I}_2]) /mol dm(^{-3})</th>
<th>Initial rate /mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>3.2 \times 10^{-3}</td>
</tr>
<tr>
<td>1.0</td>
<td>0.20</td>
<td>3.2 \times 10^{-3}</td>
</tr>
<tr>
<td>2.0</td>
<td>0.10</td>
<td>6.4 \times 10^{-3}</td>
</tr>
</tbody>
</table>

(c) What is meant by:

(i) order of reaction with respect to a particular reactant
...............................................................................................................................
...............................................................................................................................
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............................................................................................................................. (1)

(ii) overall order of reaction.
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............................................................................................................................. (1)

(d) What does the rate equation in (b) tell you about the involvement of iodine in the rate-determining step, and hence about the least number of steps in the reaction?
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............................................................................................................................. (2)
(e) Sodium hydroxide cannot be used to stop the reaction, because very alkaline conditions cause another reaction to occur between propanone and iodine.

Write the equation for this reaction.

.................................................................................................................................................................................. (3)

(Total 14 marks)

9. This question is about the kinetics of the reaction in which ammonium cyanate, \( \text{NH}_4\text{CNO} \), turns into urea, \( \text{NH}_2\text{CONH}_2 \), in aqueous solution.

\[
\text{NH}_4\text{CNO}(\text{aq}) \rightarrow \text{NH}_2\text{CONH}_2(\text{aq})
\]

The table below shows the mass of urea, \( m_t \), which formed at different times in a solution of ammonium cyanate of known starting concentration.

When the reaction stopped the mass of urea, \( m_{\text{final}} \), was 20.3 g.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Mass of urea, ( m_t )/g</th>
<th>( m_{\text{final}} - m_t )/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>20.3</td>
</tr>
<tr>
<td>25</td>
<td>12.5</td>
<td>7.8</td>
</tr>
<tr>
<td>50</td>
<td>15.7</td>
<td>4.6</td>
</tr>
<tr>
<td>75</td>
<td>17.1</td>
<td>3.2</td>
</tr>
<tr>
<td>100</td>
<td>17.5</td>
<td>2.8</td>
</tr>
<tr>
<td>150</td>
<td>18.7</td>
<td>1.6</td>
</tr>
<tr>
<td>200</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>20.0</td>
<td></td>
</tr>
</tbody>
</table>

(a) Complete the final column of the table. (1)
(b) Plot a graph of $m_{\text{final}} - m_t$ (on the vertical axis) against time (on the horizontal axis).

(c) The graph can be used to work out a rate equation for the reaction.

What term in the rate equation for the reaction is proportional to $m_{\text{final}} - m_t$?

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(1)

(d) (i) Show THREE successive half-life measurements on your graph, and give their values.

1. ...........................................................   2. .........................................................

3. ...........................................................

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(2)
(ii) Use the half-lives to decide whether the reaction is zero order, first order or second order. Explain how you decided the order.

Order of reaction ...........................................................................................................
Explanation ..................................................................................................................
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(2)

(iii) Suggest a possible rate equation for the reaction.
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(1)

(e) A student thought that water might take part in the rate-determining step of the reaction.
(i) What is meant by the rate-determining step?
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(1)

(ii) The solution of ammonium cyanate used in the experiment initially contained 0.35 moles of ammonium cyanate in approximately 1 dm$^3$ (55.5 moles) of water.

Is the order you calculated in (d)(ii) an order with respect to ammonium cyanate, or could it include the water as well? Explain your answer.
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(2)

(Total 12 marks)

10. (i) Experiments 1 & 2, [R–CH$_2$–Cl] × 3, Rate × 3 (1)
    \[ \therefore \text{1}^{\text{st}} \text{order w.r.t. [R–CH$_2$–Cl]} \quad (1) \]

    Experiments 1 & 3, [R–CH$_2$–Cl] and [OH$^-$] × 2, rate × 4 (1)
    \[ \therefore \text{1}^{\text{st}} \text{order w.r.t. [OH$^-$]} \quad (1) \]

    4

(ii) Rate = k [R–CH$_2$–Cl] [OH$^-$] consequential on (i) 1
(iii) \[ k = \frac{\text{rate}}{[\text{RCH}_2\text{Cl}][\text{OH}^-]} = \frac{4.0 \times 10^{-4} \text{mol dm}^{-3} \text{s}^{-1}}{0.050 \times 0.10 \text{mol dm}^{-3}} = 0.080 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \] (1)

(iv) (S\text{N}2)

![Reaction Mechanism Diagram]

\[ \text{Note S_N1: allow if first order deduced from parts (1) and (ii) for full marks.} \]

11. (a) (i) Working to show first order with respect to [S\text{O}_2\text{S}^2^-] (1)
Working to show first order with respect to [I^-] (1)
overall equation (1)
Consequential

(ii) Sum of power of the concentration terms (for thio and iodide) in rate equation / number of each species involved up to and including or, in, the rate–determining step in the reaction mechanism / Sum of the partial / individual orders / general equation of the form [thio]^m[iodide]^n overall order = m + n (1)

(iii) 36 (1) dm^3 mol^{-1} s^{-1} (1)
Consequential on part (i)

(iv) Rate equation depends on mechanism / rate equation only involves those species in the rate determining step / slowest step (1)

(b) (i) Colorimetry / conductivity / remove samples and titrate with (standard) sodium thiosulphate solution (1)

(ii) Constant temperature (1)

(iii) Colorimeter / conductivity adv that monitoring is continuous / does not need removal of samples or disadv of titration is problems with timing (1)

12. (a) (i) • Rate of reaction - Rate of decrease / change in concentration
of reactants (1)
- Overall order of a reaction - sum of the powers to which concentration terms are raised in the overall rate equation (1)

(ii) (The stoichiometric equation includes all the reactants) the rate equation only includes those species involved in the rate determining step / rate depends on mechanism (1)

\[
\text{H} + \text{C}_2\text{H}_5\text{C}_\text{Br}\text{CH}_3 \rightarrow \text{H} + \text{C}_2\text{H}_5\text{C}_\text{OH}\text{CH}_3 + \text{Br}^-
\]

Intermediate(1) \rightarrow (1)

(b) (i)

\[
\text{C}_2\text{H}_5\text{C}_\text{OH}\text{CH}_3
\]

(ii) • The reaction goes through a planar intermediate and this can be attacked from either side (1)
- producing an equal mixture of the two optical isomers / racemic mixture / 50-50 mixture (1)

(iii) • Double conc. bromo compound rate double \(\propto\) power 1 (1)
- Treble conc of bromo compound and double cone OH rate only up three times thus not dependant on conc of OH (1)

Rate = rate constant [bromoalkane] (1)

Must show use of data

(c) After given time remove sample (1)
neutralise with nitric acid / quench / stop by adding specified reagent (1)
add silver nitrate and observe extent of ppt.
/ as above and titrate solution with silver nitrate / titrate with specified reagent (1)
Allow 1 mark for continuous method based on conductivity or pH

13. (a) (i) \(200 \times 0.05 / 330 = 30.3 \times 10^{-3} = 3.03 \times 10^{-2}\) (1)
(ii) graph linear axes at a sensible scale (1)
    all points correct (1)
    sensible smooth curve (1)
calculate 2 rates correctly (2)
    $1.25 \times 10^{-6}$ (1.0–1.5)
    $2.5 \times 10^{-5}$ (2.0–4.0)  

(b) (i) $0.0300 - 0.0150 = 800$
    $0.0150 - 0.00750 = 900$
    $0.0080 - 0.0040 = 800$
    Any 2 half life correctly calculated (1)
    constant half life = 800 (1)  
    first order (1)  

(ii) • second reaction faster than first at beginning (1)
    • first speeds up when product present (1)  

(c) (i) Presence of potassium (ions) or $K^+$  

(ii) Add NaOH to solution until in excess (1)
    Buff / cream / beige ppt. (turning brown) shows manganese(II) (1)  

14. (a) Measure (volume/ amount of gas) with a gas syringe / inverted burette

OR Loss in mass with (top pan) balance

OR Described titrimetric method (1)

.........at regular time intervals (1)  

(b) (i) Rate is proportional to (hydrogen peroxide) concentration

OR Index of (hydrogen peroxide) concentration in rate equation is 1  

(ii) $\text{Rate} = k[H_2O_2(aq)]$  

(iii) Measure/ calculate/ find several/two hal-lives (1)

(Check) half–lives are constant (1)  

[14]
Number of molecules with kinetic energy, $E$

General shape of $T_1$ graph (1)

General shape of $T_2$ graph: higher temperature peak lower and moved to the right (1)

Check that graphs start at zero – penalise once

Check that graphs do not meet energy axis – penalise once.

(Many) more molecules with energy in excess of $E_A/E_{\text{min}}$ / a certain value (1)

Can be shown (as shading) on the diagram

Activation energy shown (1)
Axes correct with correct labels (1)
Sensible Scales – as shown
but can be shifted up/down or right/left (1)
Points correct with best fitting straight line (1)
15. (a) \( \text{rate} = k[A][B] \) (1) or any other where \( m+n = 2 \)
\( \text{rate} = k[A]^2 \) (1)
\( \text{rate} = k[B]^2 \) (1)

(b) (i) Working to show first order with respect to \( \text{H}_2 \) (1)
Working to show second order with respect to \( \text{NO} \) (1)
Overall rate equation (must be consequential)
\( \text{rate} k [\text{H}_2][\text{NO}]^2 \) (1)

(ii) \( 0.02 = k (1.0)^2(1.0) \) or correct use of either of the other two rows of data
\( k = 0.02 / 1.0 = 0.02 \) (1)
\( \text{mol}^{-2}\text{dm}^6\text{s}^{-1} \) (1)

Consequential on (b)(i)

(c) • Molecules move faster/have more kinetic energy (1)
• More molecules / collisions have at least \( \text{E}_{\text{act}} \) (1)
• Greater proportion/fraction of collisions are successful OR more of the collisions are successful (1)

(d) \( k \) increases (1)

(e) • Catalyst provides an alternative route (1)
• With a lower activation energy (consequential on first mark) (1)
• Rate increases because more collisions have enough energy to overcome the lower activation energy (1)
[Accept argument based on Arrhenius equation for third mark] (3)
16. (a) (i) The reaction produces ions (H\(^+\) and Br\(^-\)) / the number of ions increases
(ii) To enable the halogenoalkane to mix with water / to dissolve / to increase solubility
(iii) The rate doubles
(iv) Order 1/first order
(v) Water a possible reactant is present in excess

(b) (i) \[
\frac{0.75}{5} = 0.15 / 0.150 (\times 10^{-3})
\]
\[
\frac{1.5}{9} = 0.17 / 0.167 (\times 10^{-3})
\]
\[
\frac{2.25}{14} = 0.16 / 0.161 (\times 10^{-3})
\]
Method (1)
Answers (1)
(ii) Rate is unaffected / very little affect
(iii) Zero

(c) (i) Rate = \(k_{(1)} [C_5H_{11}Br]\)
(ii) \[
C_5H_{11}Br \quad \text{slow} \to C_5H_{11}^+ + Br^- \quad (1)
\]
\[
C_5H_{11}^+ + OH^- \quad \text{fast} \to C_5H_{11}OH \quad (1)
\]
No speeds (1 \text{ max})
Can be stated in words (2)

17. (a) (i) \(I_2 + 2S_2O_3^{2-} \to 2I^- + S_4O_6^{2-}\)
species (1)
balance (1)
(ii) starch (1)
blue / blue–black to colourless (1)

(b) double [I\(_2\)] no change so zero order (1)
double [Me\(_2\)CO] doubles rate so first order (1)
rate = \(k[Me_2CO][H^+]\) (1)
(c) (i) Power to which concentration raised in rate equation
OR
the number of that species involved up to and including the rate
determining step 1

(ii) Sum of the individual reaction orders OR sum of powers 1

(d) Iodine not involved in the rate determining step (1)
two (1) NOT “more than 1” 2

(e) \[ \text{CH}_3\text{COCH}_3 + 3\text{I}_2 + 4\text{Na OH} \rightarrow \text{CH}_3\text{COONa} + \text{CHI}_3 + 3\text{NaI} + 3\text{H}_2\text{O} \]
\( \text{CHI}_3 \) (1)
other species (1)
balance (1) 3

18. (a) 1

<table>
<thead>
<tr>
<th>Time</th>
<th>Mass urea</th>
<th>( m_{\text{final}} - m_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>19.1</td>
<td>1.2</td>
</tr>
<tr>
<td>300</td>
<td>20</td>
<td>0.3</td>
</tr>
</tbody>
</table>
(b)

Labelled axes including units and sensible scale (1)
Correct plotting of points and smooth curve (1) 2

(c) \([\text{NH}_4\text{CNO}] / \text{ammonium cyanate concentration}\) 1

(d) (i) Half–lives starting at \(t_0 = 17.30\) min (each \(\pm 5\) min), \(60 \pm 10\)
Starting at \(t = 16\), half–lives are \(20, 37\) min (each \(\pm 5\) min), \(73 \pm 10\).
One correct (1)
Second and third correct half–life (1)
Max 1 if no units 2

(ii) Second order (1)
Because half–life is increasing / doubling / not constant (1) 2

(iii) Rate = \(k[\text{NH}_4\text{CNO}]^2\) or rate = \(k[\text{NH}_4\text{CNO}] [\text{H}_2\text{O}]\) 1
(e)  
(i)  $(\text{rds} = \text{slowest step/stage})$ part of the mechanism  

(ii) Order is with respect to ammonium cyanate as water is in excess  
(approximately $55.5 \text{ mol of water: } 0.35 \text{ mol ammonium cyanate}$)  
So only ammonium cyanate concentration is changing / water  
concentration does not change significantly  

[12]