Q1. 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	$3.78 \times 10_{-3}$

(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

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

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

k = ... Units = ...

(3)

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

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

(1)

(d) The rate equation for a reaction is

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

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

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

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

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

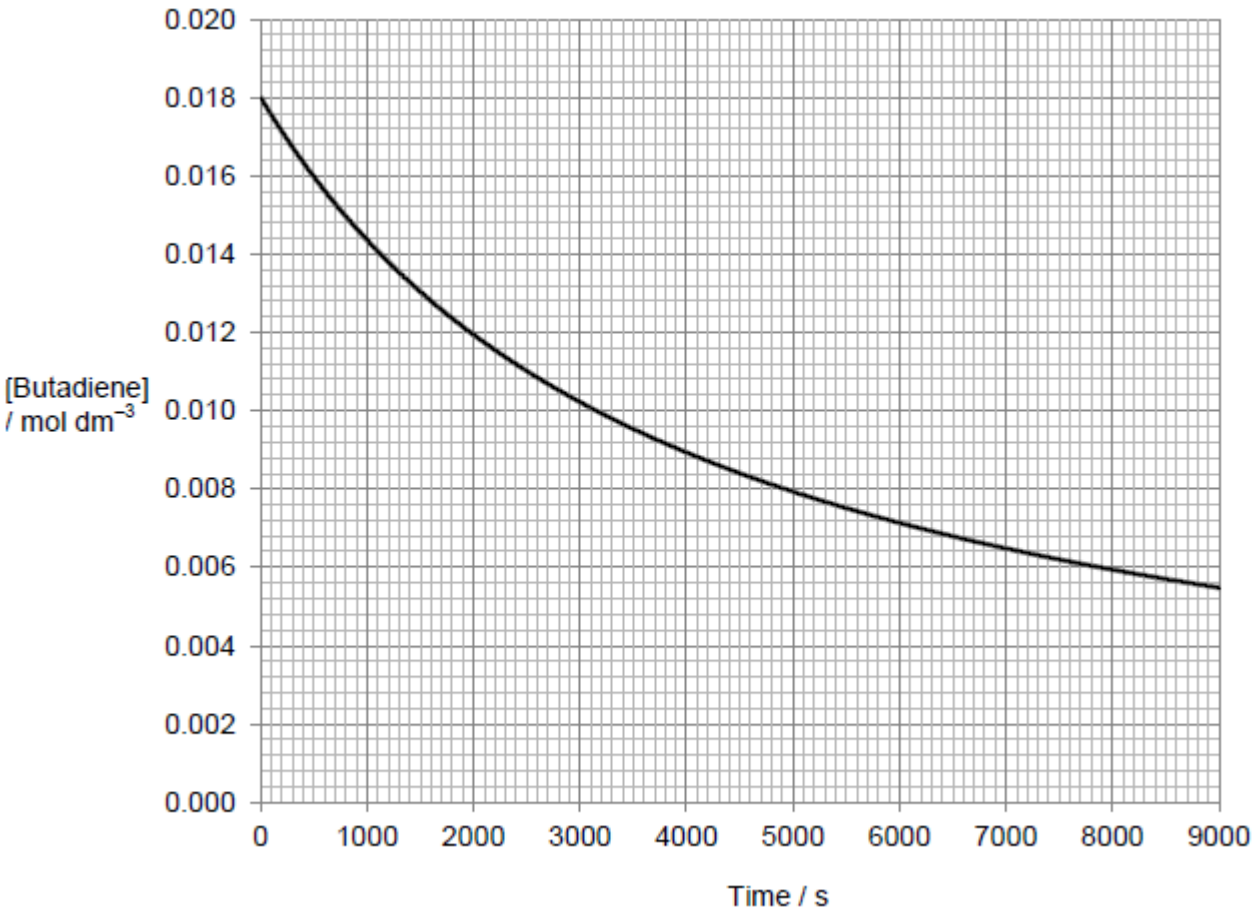
Activation energy = ...

(2)
(Total 12 marks)

Q2. Butadiene dimerises according to the equation

$$2C_4H_6 \longrightarrow C_8H_{12}$$

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 4.57×10^{-6} mol dm^{-3} 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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(5)
(Total 6 marks)

Q3. The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) 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 mol dm^{-3} and the initial concentration of hydroxide ions was 0.035 mol dm^{-3}, the initial rate of the reaction was
8.5×10^{-5} mol dm^{-3} 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

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

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

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

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)

Q4. (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

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

$$\text{rate} = k[NO]^2[H_2]$$

The initial rate of reaction was 6.2×10^{-6} mol dm^{-3} s^{-1} when the initial concentration of NO was 2.9×10^{-2} mol dm^{-3} and the initial concentration of H_2 was 2.3×10^{-2} 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 H_2 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.

Step **1** $NO + NO \longrightarrow X$

Step **2** $X + H_2 \longrightarrow Y$

Step **3** $Y + H_2 \longrightarrow N_2 + 2H_2O$

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

Explain your answer.

Rate-determining step.....

Explanation .....

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(2)
(Total 6 marks)

Q5. 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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(Space for working) .....

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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

$$rate = \mathbf{k}[\mathbf{G}]^2[\mathbf{H}]$$

(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)

Q6.(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

rate = k[**B**]^2[**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 $(CH_3)_3CBr$ reacts with aqueous sodium hydroxide as shown in the folfollowing equation.

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

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

The following two-step process was suggested.

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

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

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

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(1)

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

(1)
(Total 8 marks)

Q7. 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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Units .....

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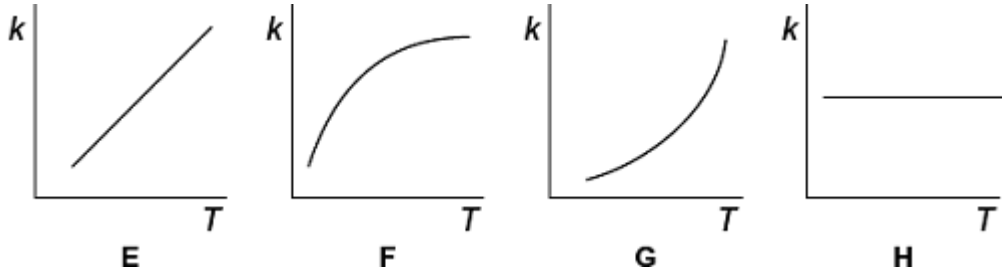
(3)

(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)