1 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

....

....

....

$Br^-(aq)$

....

(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

....

....

....

(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

....

....

....

....

(Total for Question = 12 marks)

2 This question is about the kinetics of the reaction between bromoethane and aqueous hydroxide ions.

(a) The results of an experiment to find the initial rate of the reaction are shown in the table below.

$[CH_3CH_2Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
0.100	0.150	1.54×10^{-6}

The rate equation for the reaction is

$$\text{rate} \quad k[CH_3CH_2Br][OH^-]$$

(i) Calculate the value of k. Give your answer to three significant figures and include units.

(3)

(ii) Calculate the initial rate if the concentrations of both reactants were changed to 0.020 mol dm^{-3}.

(1)

(b) (i) State the order of the reaction.

(1)

....

(ii) The mechanism for this reaction can be inferred from the rate equation. Draw the transition state formed in the reaction between bromoethane and hydroxide ions.

(2)

(c) The rate constant for the reaction between bromoethane and hydroxide ions was determined at five different temperatures. The results are shown in the table below.

Temperature (T) / K	1/Temperature (1/T) / K^{-1}	Rate constant, k	ln k
293	3.41×10^{-3}	5.83×10^{-5}	9.75
303	3.30×10^{-3}	1.67×10^{-4}	8.70
313	3.19×10^{-3}	5.26×10^{-4}	7.55
323	3.10×10^{-3}	1.36×10^{-3}	6.60
333		3.77×10^{-3}	

(i) Complete the missing values in the table.

(2)

(ii) Plot a graph of ln k against 1/T. Calculate the gradient of your graph and use this to calculate the activation energy, E_A. The Arrhenius equation can be expressed as

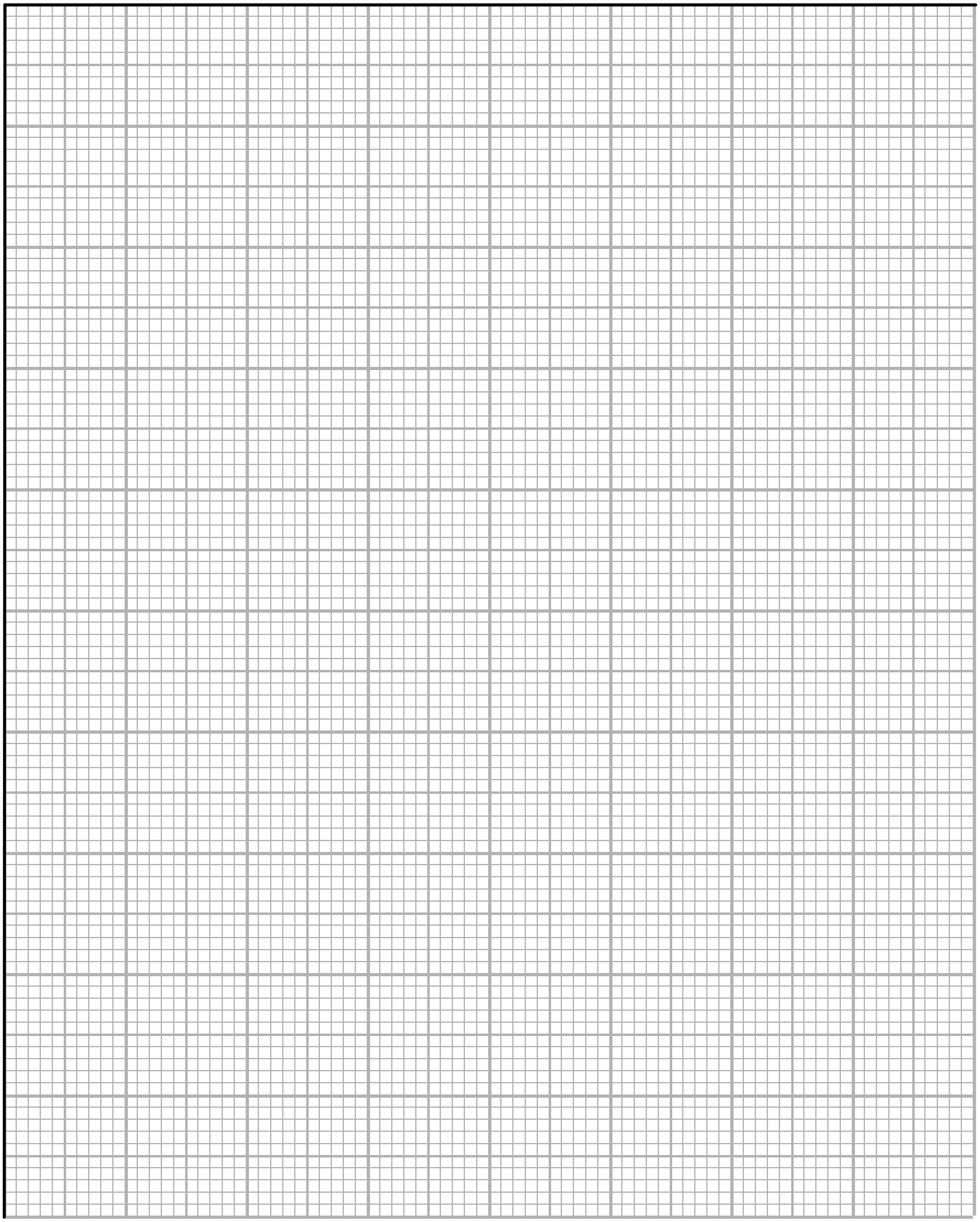
$$\ln k \quad \frac{-E_A}{R} \times \left(\frac{1}{T}\right) + \text{a constant}$$

[Gas constant, R   8.31 J K^{-1} mol^{-1}]

(5)

1/T / K^{-1}

ln k



(Total for Question 14 marks)

3 Iodine and propanone react in the presence of an aqueous acid catalyst as follows

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

To determine the rate equation for the reaction, propanone is reacted with iodine in the presence of aqueous hydrochloric acid at constant temperature. Samples are withdrawn at known times, quenched with sodium hydrogencarbonate solution, and the iodine remaining titrated with a standard solution of sodium thiosulfate.

The rate equation for the reaction is

$$\text{rate} = k[CH_3COCH_3]^1\,[H^+]^1\,[I_2]^0$$

(a) The graph of $[I_2]$ against time is a straight line, showing that the order of reaction with respect to iodine is zero.

(i) Explain why the propanone and the hydrogen ions must be in large excess in this experiment in order to give this straight line.

(2)

(ii) What further experiment could be done to show that the order of reaction with respect to propanone is one? State the effect of this change on the graph.

(2)

(iii) Explain why the minimum number of steps in the mechanism for this reaction is two.

(2)

(b) Sodium hydrogencarbonate stops the reaction by neutralizing the acid catalyst.

(i) Give the ionic equation for the reaction between sodium hydrogencarbonate and acid.

(1)

(ii) Sodium hydroxide cannot be used for neutralization because under very alkaline conditions a reaction occurs between propanone and iodine.

Write the equation for this reaction. State symbols are **not** required.

(3)

(Total for Question = 10 marks)