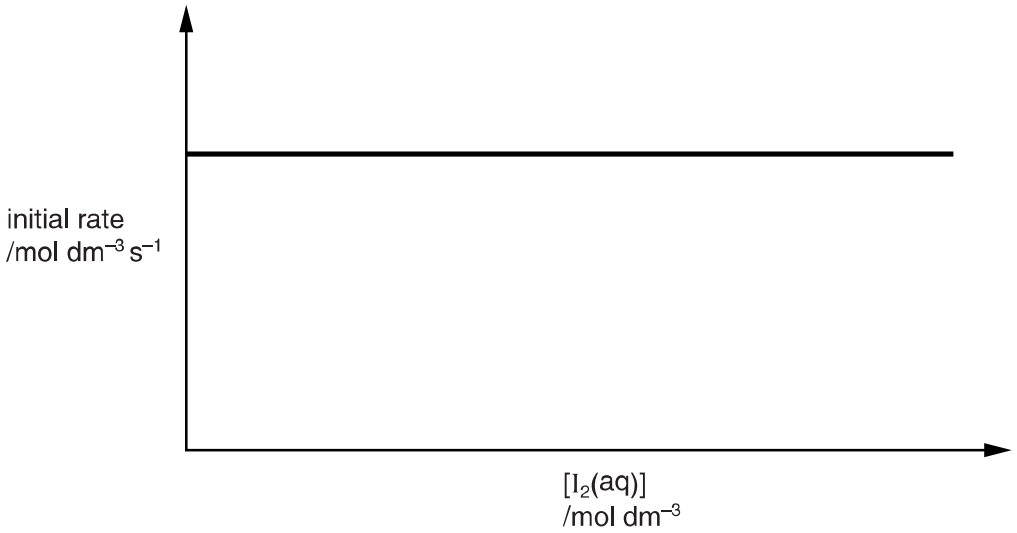
Answer **all** the questions.

1 A student investigates the reaction between iodine, I_2, and propanone, $(CH_3)_2CO$, in the presence of aqueous hydrochloric acid, HC*l*(aq).

The results of the investigation are shown below.

Rate–concentration graph



Results of initial rates experiments

experiment	[$(CH_3)_2CO$(aq)] / mol dm^{-3}	[HC*l*(aq)] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.50×10^{-3}	2.00×10^{-2}	2.10×10^{-9}
2	3.00×10^{-3}	2.00×10^{-2}	4.20×10^{-9}
3	3.00×10^{-3}	5.00×10^{-2}	1.05×10^{-8}

(a) Determine the orders with respect to I_2, $(CH_3)_2CO$ and HC*l*, the rate equation and the rate constant for the reaction.

Explain all of your reasoning.

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(b) The student then investigates the reaction of hydrogen, H_2, and iodine monochloride, IC*l*.

The equation for this reaction is shown below.

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The rate equation for this reaction is shown below.

$$\text{rate} = k[H_2(g)]\,[ICl(g)]$$

Predict a possible two-step mechanism for this reaction. The first step should be the rate-determining step.

step 1 .....

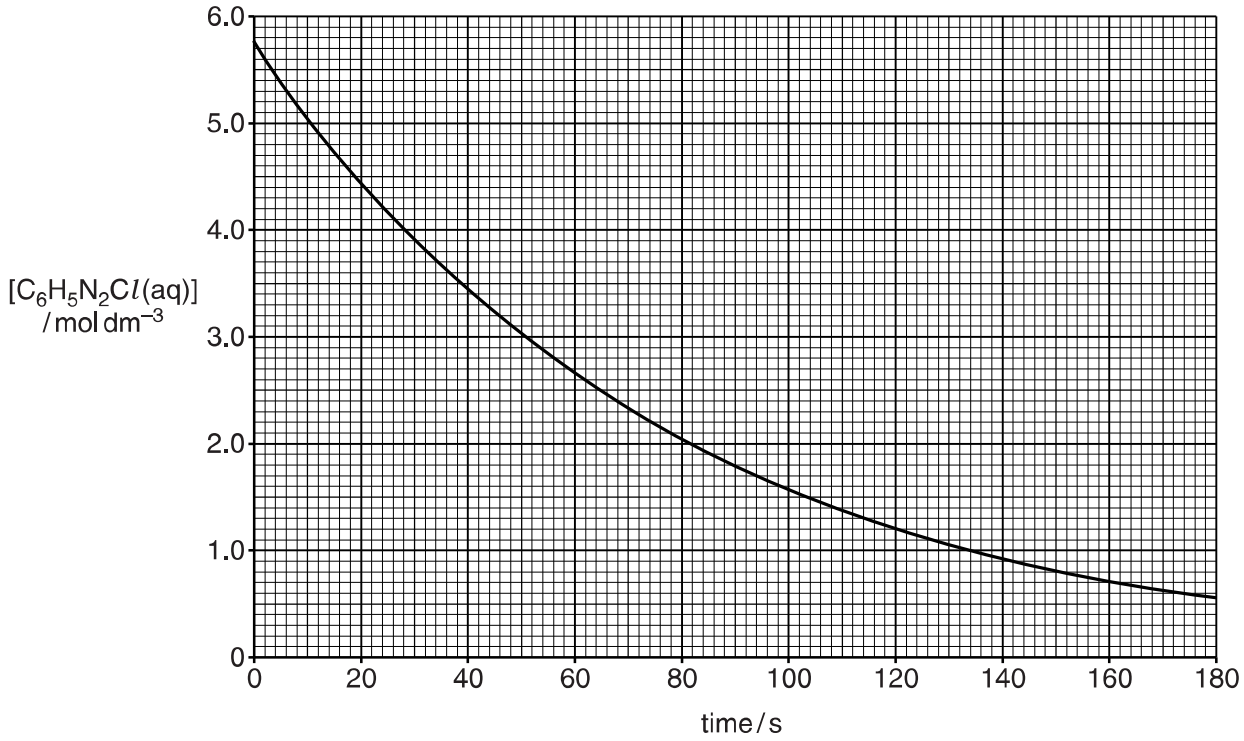
step 2 ..... **[2]**

[Total: 11]

2 In aqueous solution, benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes above 10 °C.

$$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

A student investigates the rate of this reaction using an excess of water at 50 °C. The student takes measurements at intervals during the reaction and then plots his experimental results to give the graph shown below.



(a) The student uses half-life to suggest the order of reaction with respect to $C_6H_5N_2Cl$.

(i) What is meant by the *half-life* of a reaction?

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(ii) Confirm the order of reaction with respect to $C_6H_5N_2Cl$.

Show your working on the graph.

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(iii) What would be the effect, if any, on the half-life of this reaction of doubling the initial concentration of $C_6H_5N_2Cl$?

..... **[1]**

(b) The student predicts that the rate equation is: rate = $k[C_6H_5N_2Cl]$.

(i) Using the graph and this rate equation, determine the rate of reaction after 40 s.

Show your working on the graph.

rate = ...units ..... **[3]**

(ii) Calculate the rate constant, *k*, for this reaction and give its units.

k = ... units ..... **[2]**

(c) The order of this reaction with respect to H_2O is effectively zero.

Explain why.

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[Total: 10]

4 Nitrogen dioxide reacts with ozone as shown below.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$

(a) The kinetics of the reaction between NO_2 and O_3 was investigated and the following experimental results were obtained.

experiment	$[NO_2(g)]$ / mol dm^{-3}	$[O_3(g)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.00150	0.00250	4.80×10^{-8}
2	0.00225	0.00250	7.20×10^{-8}
3	0.00225	0.00500	1.44×10^{-7}

(i) Determine the rate equation and rate constant for the reaction of $NO_2(g)$ and $O_3(g)$.

In your answer you should make clear how your conclusions fit with the experimental results.

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(ii) Suggest a possible two-step mechanism for this reaction.

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(b) The feasibility of the reaction between NO_2 and O_3 is influenced by the enthalpy change and entropy change of the reaction and the temperature.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g) \qquad \Delta H = -198\,kJ\,mol^{-1}, \quad \Delta S = -168\,J\,K^{-1}\,mol^{-1}$$

(i) Explain why this reaction has a negative entropy change.

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(ii) Calculate the value of ΔG, in $kJ\,mol^{-1}$, at 25 °C for the reaction of NO_2 with O_3.

$\Delta G =$ ..... $kJ\,mol^{-1}$ **[3]**

(iii) State and explain how the feasibility of this reaction will change with increasing temperature.

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[Total: 17]

4 Iodide ions, I^-, react with $S_2O_8^{2-}$ ions as shown in the equation below.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

A student investigates the rate of this reaction using the initial rates method.

The student measures the time taken for a certain amount of iodine to be produced.

(a) Outline a series of experiments that the student could have carried out using the initial rates method.

How could the results be used to show that the reaction is first-order with respect to both I^- and $S_2O_8^{2-}$?

In your answer you should make clear how the results are related to the initial rates.

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(b) In one of the experiments, the student reacts together:

- 8.0×10^{-2} mol dm^{-3} $I^-(aq)$
- 4.0×10^{-3} mol dm^{-3} $S_2O_8^{2-}(aq)$.

The initial rate of this reaction is 1.2×10^{-3} mol dm^{-3} s^{-1}.

The reaction is first-order with respect to I^- and first-order with respect to $S_2O_8^{2-}$.

Calculate the rate constant, *k*, for this reaction.
State the units, if any.

k = ... units ..... **[3]**