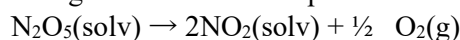


26.1 RATE EQUATIONS, ORDER AND RATE CONSTANTS

<https://subarnam.com.np/>

Introduction

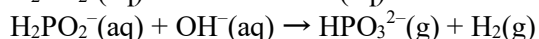
1. Dinitrogen pentoxide, N_2O_5 , is dissolved in an inert solvent (solv), and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.



Suggest what measurements could be used to follow the rate of this reaction from the given information.

.....
 [1]

2. $\text{H}_2\text{PO}_2^-(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$.



The following table shows the results of a series of experiments used to investigate the rate of this reaction.

Experiment	$[\text{H}_2\text{PO}_2^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{OH}^-(\text{aq})] / \text{mol dm}^{-3}$	Volume of H_2 produced in 60 s / cm^3
1	0.40	2.00	6.4
2	0.80	2.00	12.8
3	1.20	1.00	4.8

The volume of H_2 was measured under room conditions.

Use the molar volume of gas, V_m , and the data from experiment 1 to calculate the rate of reaction in $\text{mol dm}^{-3} \text{s}^{-1}$.

rate of reaction = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

3. Explain what is meant by the order of reaction.

.....

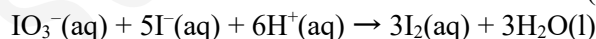
 [1]

4. Explain what is meant by the overall order of reaction.

.....

 [1]

5. The Dushman reaction is the reaction between iodate(V) ions and iodide ions in an acidic solution.



The rate equation for this reaction is shown.

$$\text{rate} = k [\text{IO}_3^-][\text{I}^-]^2[\text{H}^+]^2$$

The rate of this reaction is investigated in a buffer solution.

The initial concentrations are shown.

$$[\text{IO}_3^-] = 0.500 \text{ mol dm}^{-3} \quad [\text{I}^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3} \quad [\text{H}^+] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$$

Under these conditions, the initial rate of the reaction is $2.10 \times 10^{-2} \text{ mol dm}^{-3} \text{s}^{-1}$.

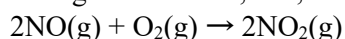
(i) Use the information to calculate the rate constant, k . State its units.

$$k = \dots\dots\dots \text{units} = \dots\dots\dots [2]$$

- (ii) This reaction is repeated at the same temperature and with the same initial values of $[\text{IO}_3^-]$ and $[\text{I}^-]$. The $[\text{H}^+]$ is increased to $3.00 \times 10^{-2} \text{ mol dm}^{-3}$. Calculate the initial rate of this reaction.

$$\text{rate} = \dots\dots\dots \text{mol dm}^{-3} \text{ s}^{-1} [1]$$

6. Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO_2 .



The rate equation for the forward reaction is shown.

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (a) Complete the following table.

[1]

The order of reaction with respect to $[\text{NO}]$	
The order of reaction with respect to $[\text{O}_2]$	
The overall order of reaction	

- (b) Two separate experiments are carried out at 30°C to determine the rate of the forward reaction.

experiment	$[\text{NO}] / \text{mol dm}^{-3}$	$[\text{O}_2] / \text{mol dm}^{-3}$	rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

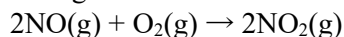
- (i) Use the data for experiment 1 to calculate the value of the rate constant, k . State the units of k .

$$k = \dots\dots\dots \text{units} = \dots\dots\dots [2]$$

- (ii) Calculate the value of $[\text{NO}]$ in experiment 2.

$$[\text{NO}] = \dots\dots\dots \text{mol dm}^{-3} [1]$$

7. Nitrogen monoxide reacts with oxygen.



This reaction is second order with respect to nitrogen monoxide and first order with respect to oxygen.

Under certain conditions the value of the rate constant, k , is $8.60 \times 10^6 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.

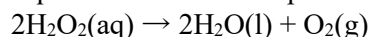
- (i) Construct the rate equation for this reaction.

rate = ... [1]

- (ii) Calculate the initial rate of the reaction under these conditions when the initial concentration of nitrogen monoxide is $7.20 \times 10^{-4} \text{ mol dm}^{-3}$ and the initial concentration of oxygen is $1.90 \times 10^{-3} \text{ mol dm}^{-3}$.

rate of reaction = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

8. The equation for the decomposition of hydrogen peroxide without a catalyst is shown.

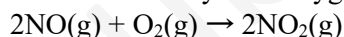


Under certain conditions, this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k , of $2.0 \times 10^{-6} \text{ s}^{-1}$ at 298 K.

Calculate the initial rate of decomposition of a 0.75 mol dm^{-3} hydrogen peroxide solution at 298 K.

initial rate = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

9. NO reacts readily with oxygen.



The table shows how the initial rate of this reaction at 25°C depends on the initial concentrations of the reactants.

initial concentration/ mol dm^{-3}		initial rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$
[NO(g)]	[O ₂ (g)]	
0.100	0.0500	3.50
0.0500	0.100	1.75
0.0500	0.0500	0.875

- (i) Deduce the order of reaction with respect to each reactant. Explain your reasoning.

order with respect to [NO(g)]

.....

order with respect to [O₂(g)]

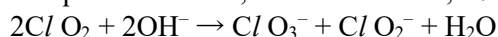
..... [2]

(ii) State the rate equation for this reaction. Use the rate equation to calculate the rate constant. Include the units for the rate constant in your answer.

rate =

rate constant, $k = \dots\dots$ (ans = 7000) $\dots\dots$ units of $k = \dots\dots\dots$ [3]

10. In aqueous solution, chlorine dioxide, ClO_2 , reacts with hydroxide ions as shown.



A series of experiments is carried out using different concentrations of ClO_2 and OH^- . The table shows the results obtained.

Experiment	$[\text{ClO}_2]/\text{mol dm}^{-3}$	$[\text{OH}^-]/\text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{ min}^{-1}$
1	0.020	0.030	7.20×10^{-4}
2	0.020	0.120	2.88×10^{-3}
3	0.050	0.030	4.50×10^{-3}

(i) Use the data in the table to determine the order of reaction with respect to each reactant, ClO_2 and OH^- . Explain your reasoning.

.....

.....

.....

.....

.....

..... [2]

(ii) Use your answer to (i) to construct the rate equation for this reaction.

rate = ... [1]

(iii) Use your rate equation and the data from experiment 1 to calculate the rate constant, k , for this reaction.

Include the units of k .

$k = \dots\dots\dots$ units $\dots\dots\dots$ [2]

11. A student collects some data for the reaction of H_2O_2 with acidified IO_3^- , as shown in the table.

Experiment	$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	$[\text{IO}_3^-]/\text{mol dm}^{-3}$	$[\text{H}^+]/\text{mol dm}^{-3}$	initial rate of reaction/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0500	0.0700	0.025	1.47×10^{-5}
2	0.100	0.0700	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

(i) Use the data to determine the order of reaction with respect to $[\text{H}_2\text{O}_2]$, $[\text{IO}_3^-]$, and $[\text{H}^+]$.
Show your reasoning.

order with respect to $[\text{H}_2\text{O}_2]$ = ...

.....

.....

.....

order with respect to $[\text{IO}_3^-]$ = ...

.....

.....

.....

order with respect to $[\text{H}^+]$ = ...

.....

.....

.....[3]

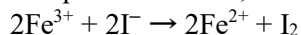
(ii) Use your answer to (b)(i) to write the rate equation for this reaction.

Rate = ...[1]

(iii) Calculate the value of the rate constant, k , using data from experiment 4 and your answer to (ii).
Give the units of k .

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

12. In aqueous solution, iron(III) ions react with iodide ions, as shown.



A series of experiments is carried out using different concentrations of Fe^{3+} and I^- , as shown in the table.

Experiment	$[\text{Fe}^{3+}] / \text{mol dm}^{-3}$	$[\text{I}^-] / \text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0400	0.0200	2.64×10^{-4}
2	0.1200	0.0200	7.92×10^{-4}
3	0.0800	0.0400	2.11×10^{-3}

(i) Use the data in Table 4.1 to deduce the order of reaction with respect to Fe^{3+} and with respect to I^- . Explain your reasoning.

.....

 [2]

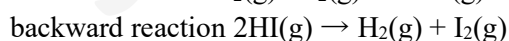
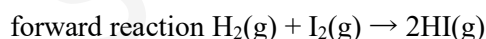
(ii) Use your answer to (i) to construct the rate equation for this reaction.

rate = ... [1]

(iii) Use your answer to (ii) and the data from experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

$k = \dots\dots\dots$ units [2]

13. At 400 K, the rate constant for the forward reaction is approximately 1000 times greater than the rate constant for the backwards reaction. The overall orders of the forward and backwards reactions are the same.



(i) Use this information to explain what will happen if equal concentrations of $\text{HI}(\text{g})$, $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ are mixed at 400 K.

You should comment on:

- the relative initial rates of the forward and backwards reactions
- the position of the equilibrium reached.

.....

 [1]

(ii) At 700 K, the rate constant for the forward reaction is approximately 50 times greater than the rate constant for the backwards reaction.

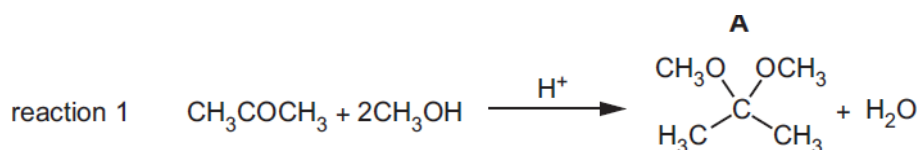
Use this information and the information in (i) to deduce the signs of the ΔH values of the forward and backwards reactions. Explain your answer.

.....

 [2]

14. Propanone, CH_3COCH_3 , is a common organic solvent and reagent.

(a) Propanone reacts with methanol, CH_3OH , under acidic conditions to form compound A, as shown by reaction 1.



The overall order of reaction 1 can be found by studying experimental data.

Table 2.1 shows how the initial rate of reaction changes as $[\text{CH}_3\text{OH}]$ and $[\text{H}^+]$ are varied. In each experiment, a large excess of CH_3COCH_3 is used.

experiment	$[\text{CH}_3\text{OH}] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	Relative initial rate of reaction
1	0.010	0.010	1.00
2	0.015	0.015	2.25
3	0.015	0.020	3.00

(i) Explain why a large excess of CH_3COCH_3 is used in each experiment.

.....

 [1]

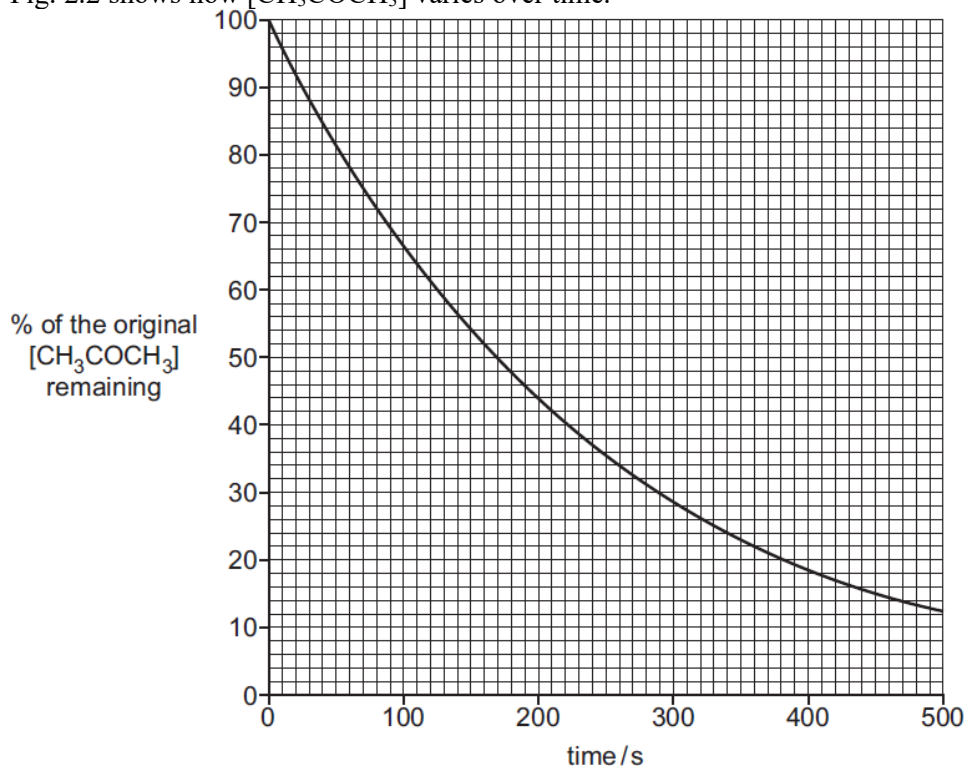
(ii) Use the data in Table 2.1 to determine the order of reaction 1 with respect to CH_3OH and to H^+ ions. Explain your answers.

.....

 [2]

(iii) In a separate experiment, a large excess of CH_3OH and H^+ ions are added to a solution containing a known concentration of CH_3COCH_3 .

Fig. 2.2 shows how $[\text{CH}_3\text{COCH}_3]$ varies over time.



Use Fig. 2.2 to show how, under these conditions, reaction 1 is first order with respect to CH_3COCH_3 .

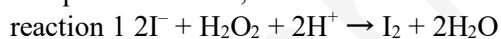
.....

.....

.....

..... [1]

15. In aqueous solution, iodide ions react with acidified hydrogen peroxide, as shown in reaction 1.



The rate equation for reaction 1 is shown.

rate = $k [\text{I}^-][\text{H}_2\text{O}_2]$

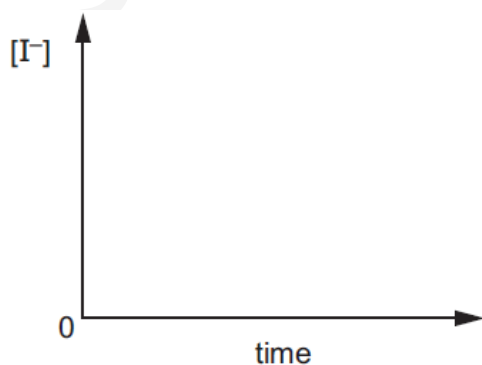
(ii) Complete Table 4.1.

the order of reaction with respect to $[\text{H}^+]$	
the order of reaction with respect to $[\text{I}^-]$	
the order of reaction with respect to $[\text{H}_2\text{O}_2]$	
overall order of the reaction	

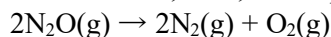
[2]

(iii) Sketch a line on Fig. 4.1 to show the relationship between $[\text{I}^-]$ and time.

[1]

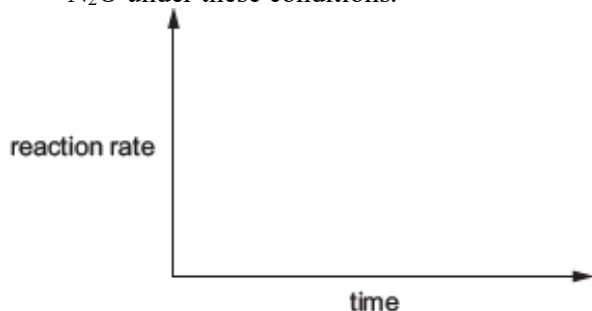


16. Nitrous oxide, N_2O , decomposes into its elements.



At a high temperature, a small amount of platinum wire is added to a large amount of nitrous oxide. The reaction follows zero-order kinetics. The platinum wire behaves as a catalyst.

- (i) Sketch a graph, on the axes below, of reaction rate against time for the catalysed decomposition of N_2O under these conditions. [1]

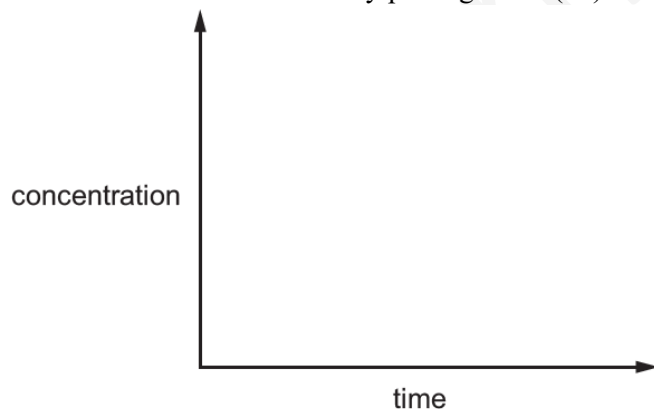


- (iii) Sketch a graph, on the axes below, of $[\text{N}_2\text{O}]$ against time for this reaction. [1]



17. Sketch a concentration–time graph for a **zero-order** reaction.

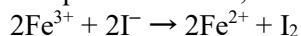
Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (•) in the appropriate box in the table. [2]



successive half-lives decrease	no change in successive half-lives	successive half-lives increase

Effect of temperature change on the rate constant

18. In aqueous solution, iron(III) ions react with iodide ions, as shown.

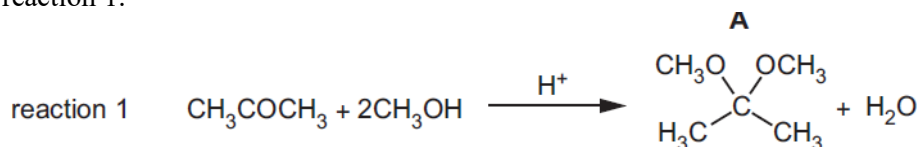


Describe qualitatively the effect of an increase in temperature on the rate constant and on the rate of this reaction.

.....
 [1]

19. Propanone, CH_3COCH_3 , is a common organic solvent and reagent.

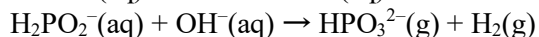
Propanone reacts with methanol, CH_3OH , under acidic conditions to form compound A, as shown by reaction 1.



Describe the effect of an increase in temperature on the rate constant and the rate of reaction 1.

.....
 [1]

20. $\text{H}_2\text{PO}_2^-(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$.



The experiment is repeated using a large excess of $\text{OH}^-(\text{aq})$.

Under these conditions, the rate equation is:

$$\text{rate} = k_1 [\text{H}_2\text{PO}_2^-(\text{aq})]$$

Describe how an increase in temperature affects the value of the rate constant, k_1 .

.....
 [1]

21. Describe the effect of an increase in temperature on the rate of reaction of $\text{CH}_3\text{CHClCOO}^-$ and NH_3 .
 Explain your answer.

.....

 [2]

Half life

22. Explain the term half-life of a reaction.

.....
 [1]

23. In aqueous solution, thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, react with hydrogen ions, as shown in reaction 2.



The rate of reaction is first order with respect to $[\text{S}_2\text{O}_3^{2-}]$ and zero order with respect to $[\text{H}^+]$ under certain conditions.

The rate constant, k , for this reaction is $1.58 \times 10^{-2} \text{ s}^{-1}$.

Calculate the half-life, $t_{1/2}$, for reaction 2.

$$t_{1/2} = \dots\dots\dots \text{ s [1]}$$

24. $\text{H}_2\text{PO}_2^-(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$.

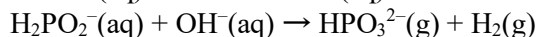


Table 2.1 shows the results of a series of experiments used to investigate the rate of this reaction.

Experiment	$[\text{H}_2\text{PO}_2^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{OH}^-(\text{aq})] / \text{mol dm}^{-3}$	Volume of H_2 produced in 60 s / cm^3
1	0.40	2.00	6.4
2	0.80	2.00	12.8
3	1.20	1.00	4.8

(i) The rate equation was found to be:

$$\text{rate} = k [\text{H}_2\text{PO}_2^-(\text{aq})] [\text{OH}^-(\text{aq})]^2$$

Show that the data in Table 2.1 is consistent with the rate equation.

.....

.....

.....

.....

..... [2]

(iii) State the units of the rate constant, k , for the reaction.

..... [1]

(iv) The experiment is repeated using a large excess of $\text{OH}^-(\text{aq})$.

Under these conditions, the rate equation is:

$$\text{rate} = k_1 [\text{H}_2\text{PO}_2^-(\text{aq})];$$

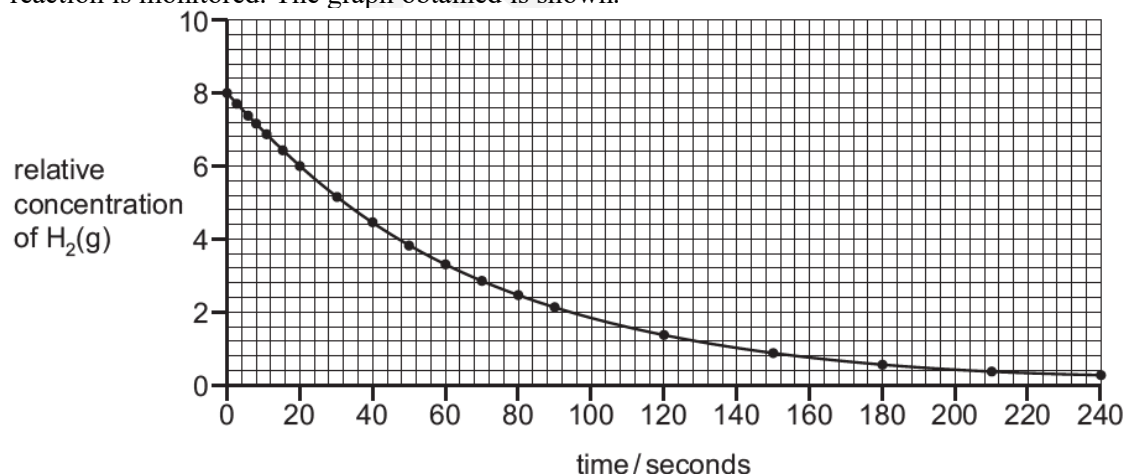
$$k_1 = 8.25 \times 10^{-5} \text{ s}^{-1}$$

Calculate the value of the half-life, $t_{1/2}$, of the reaction.

$$t_{1/2} = \dots\dots\dots \text{ s [1]}$$

25. The rate of the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is studied.

(a) A small amount of $\text{H}_2(\text{g})$ is mixed with a large excess of $\text{I}_2(\text{g})$ at a temperature of 400 K, and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $\text{I}_2(\text{g})$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $\text{H}_2(\text{g})$.

Use data from the graph to confirm this statement.

.....

.....

.....

..... [2]

- (b) Three separate experiments were carried out at 400 K with different starting concentrations of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$. The results are shown in the table.

experiment	$[\text{H}_2(\text{g})] / \text{mol dm}^{-3}$	$[\text{I}_2(\text{g})] / \text{mol dm}^{-3}$	rate of reaction/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-17}
2	1.0×10^{-1}	1.0×10^{-1}	2.0×10^{-15}
3	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-14}

- (i) Use the data and the order of reaction with respect to $\text{H}_2(\text{g})$ given in (a)(ii), to deduce the order of reaction with respect to $\text{I}_2(\text{g})$.

Explain your answer, giving data in support of your explanation.

.....

 [3]

- (ii) Use information from (a)(ii) and your answer to (b)(i) to write the rate equation for the forward reaction.

rate = ... [1]

- (iii) Use your rate equation and data from experiment 1 to calculate the value of the rate constant, k , for the forward reaction at 400 K. Include units for k .

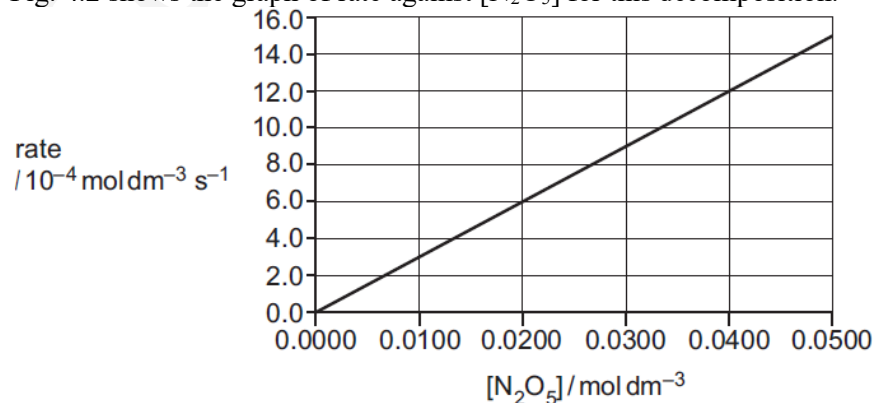
k = ... units = ... [2]

26. Dinitrogen pentoxide, N_2O_5 , can decompose to NO_2 and O_2 .

The rate equation for this decomposition is shown.

$$\text{rate} = k [\text{N}_2\text{O}_5]$$

Fig. 4.2 shows the graph of rate against $[\text{N}_2\text{O}_5]$ for this decomposition.



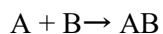
(i) Use Fig. 4.2 to calculate a value for the rate constant, k , for this decomposition.

$k = \dots\dots\dots$ [1]

(ii) Use your answer to (i) to calculate the half-life, $t_{1/2}$, in seconds, for this decomposition.

$t_{1/2} = \dots\dots\dots$ s [1]

27. A and B react together to give product AB.



When the concentrations of A and B are both $0.0100 \text{ mol dm}^{-3}$, the rate of formation of AB is $7.62 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. When the concentrations of A and B are both $0.0200 \text{ mol dm}^{-3}$, the rate of formation of AB is $3.05 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

(i) Complete the three possible rate equations that are consistent with these data.

rate = $\dots\dots\dots$

rate = $\dots\dots\dots$

rate = $\dots\dots\dots$ [2]

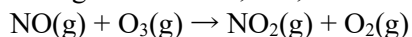
(ii) Choose one of the rate equations you have written in (i), and calculate the value of the rate constant, k . Include the units of k .

$k = \dots\dots\dots$ units $\dots\dots\dots$ [2]

(iii) Explain why it is not possible to calculate a value for the half-life, $t_{1/2}$, of this reaction using the value of the rate constant k calculated in (ii) and the equation $k = 0.693 / t_{1/2}$.

$\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$ [1]

28. Nitrogen monoxide, NO, reacts with ozone, O₃.



This reaction is first order with respect to both NO and O₃.

At 298 K, the rate constant $k = 11\,500 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

(i) Complete the rate equation for this reaction.

rate = ... [1]

(ii) A reaction is carried out in which the initial concentrations of NO and O₃ are both $1.20 \times 10^{-6} \text{ mol dm}^{-3}$. Calculate the initial rate of the reaction. State its units.

rate of reaction = ... units = ... [2]

(iii) The reaction described in (ii) is monitored over a period of time.

Predict whether or not the graph of [NO] against time, under these conditions, shows that the reaction has a constant half-life. Explain your answer.

prediction.....

explanation

..... [1]

29. The drug cisplatin, Pt(NH₃)₂Cl₂, hydrolyses in water.



The rate equation is shown.

$$\text{rate} = k [\text{Pt(NH}_3)_2\text{Cl}_2]$$

The value of k is $2.50 \times 10^{-5} \text{ s}^{-1}$ under certain conditions.

(i) This reaction has a constant half-life.

Explain why this is the case.

.....

..... [1]

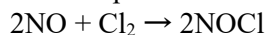
(ii) Use the information in this question to show that the half-life of this reaction is $2.77 \times 10^4 \text{ s}$. [1]

(iii) 8.00×10^{-6} moles of Pt(NH₃)₂Cl₂ are added to 100 cm³ of water.

Calculate the time taken for the concentration of Pt(NH₃)₂Cl₂ to fall to $2.50 \times 10^{-6} \text{ mol dm}^{-3}$.

time taken = ... (Ans = 1.39×10^5)..... s [2]

30. Three experiments are carried out to investigate the reaction of nitrogen oxide, NO, with chlorine.



The rate equation for this reaction is shown.

$$\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]$$

(a) Under the conditions used in experiments 1 and 2, the value of k is 26.4.

(i) The rate of the reaction is measured in $\text{mol dm}^{-3} \text{s}^{-1}$. State the units of k .

units of k = ... [1]

(ii) In experiment 1, the initial concentrations of NO and Cl_2 are equal.

The initial rate of the reaction in experiment 1 is $2.57 \times 10^{-6} \text{ mol dm}^{-3} \text{s}^{-1}$.

Calculate the initial concentration of NO.

Show your working.

initial concentration of NO = ... mol dm^{-3} [2]

(iii) In experiment 2, the initial concentrations of NO and Cl_2 are both ten times greater than the initial concentrations used in experiment 1.

Calculate the initial rate of the reaction in experiment 2.

initial rate of reaction in experiment 2 = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

(b) Experiment 3 uses a large excess of NO.

The initial concentration of Cl_2 is $2.00 \times 10^{-4} \text{ mol dm}^{-3}$.

(i) The graph of $[\text{Cl}_2]$ against time shows that the reaction has a constant half-life, $t_{1/2}$.

Explain this observation.

.....

..... [1]

(ii) Under the conditions used in experiment 3, the value of the rate constant is 105.6.

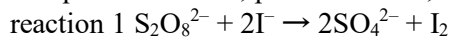
Show that $t_{1/2}$ of $[\text{Cl}_2]$ is $6.56 \times 10^{-3} \text{ s}$ under these conditions.

[1]

(iii) Calculate the time taken, in s, for $[\text{Cl}_2]$ to fall to $1.25 \times 10^{-5} \text{ mol dm}^{-3}$ in experiment 3.

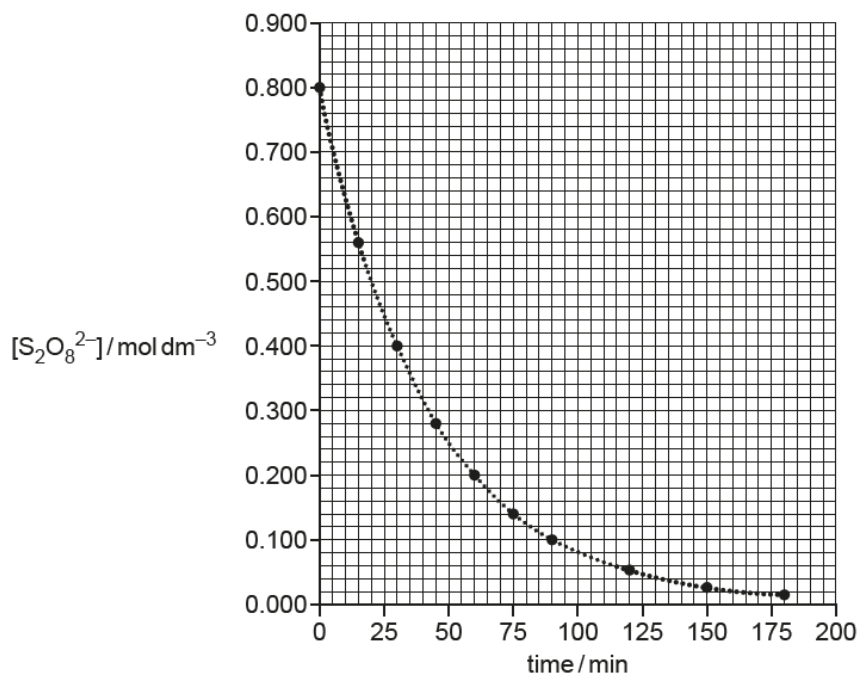
time = ... s [1]

31. In aqueous solution, persulfate ions, $\text{S}_2\text{O}_8^{2-}$, react with iodide ions, as shown in reaction 1.



The rate of reaction 1 is investigated.

A sample of $\text{S}_2\text{O}_8^{2-}$ is mixed with a large excess of iodide ions of known concentration. The graph in Fig. 5.1 shows the results obtained.



Use Fig. 5.1 to determine the initial rate of reaction 1. Show your working.

rate = ... (ans = 0.016 to 0.040) $\text{mol dm}^{-3} \text{ min}^{-1}$ [1]

(ii) The rate equation for reaction 1 is $\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$.

Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

.....

 [1]

32. The equation for reaction 1 is shown.



Reaction 1 is first order with respect to the concentration of X. The half-life of the reaction, $t_{1/2}$, is 900 s at 20 °C.

(i) A solution of X with a concentration of $0.180 \text{ mol dm}^{-3}$ is prepared at 20 °C. Calculate the average rate of reaction 1 over the first 1800 s.

average rate of reaction 1 = ... [2]

(ii) Complete the rate equation for reaction 1.

rate = ... [1]

(iii) Show that the rate constant, k , is $7.70 \times 10^{-4} \text{ s}^{-1}$ at 20°C .

(iv) Calculate the initial rate of reaction 1 when the concentration of X is $0.150 \text{ mol dm}^{-3}$. Include units. [1]

rate = ... units [2]

33. Propanone, CH_3COCH_3 , reacts with iodine, I_2 , in the presence of an acid catalyst.



The rate equation for this reaction is shown.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

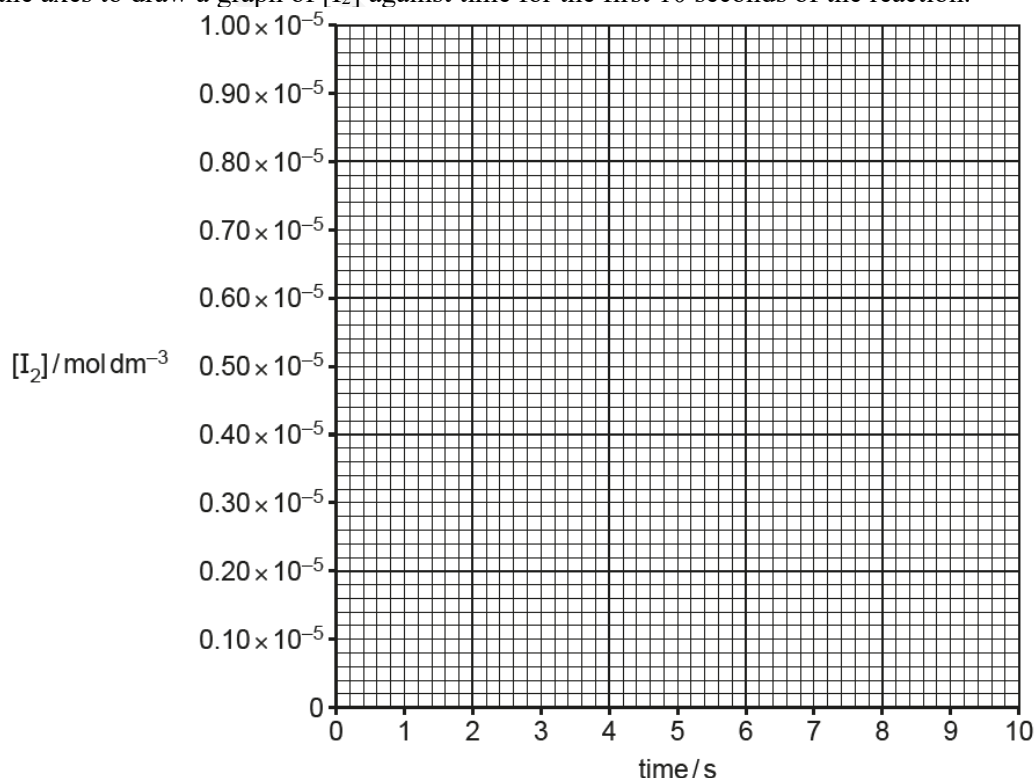
(a) Complete Table 1.1 to describe the order of the reaction. [2]

order of the reaction with respect to $[\text{CH}_3\text{COCH}_3]$	
order of the reaction with respect to $[\text{I}_2]$	
order of the reaction with respect to $[\text{H}^+]$	
overall order of the reaction	

(b) An experiment is performed using a large excess of CH_3COCH_3 and a large excess of $\text{H}^+(\text{aq})$.

The initial concentration of I_2 is $1.00 \times 10^{-5} \text{ mol dm}^{-3}$. The initial rate of decrease in the I_2 concentration is $2.27 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$.

(i) Use the axes to draw a graph of $[\text{I}_2]$ against time for the first 10 seconds of the reaction.



State whether it is possible to calculate the numerical value of the rate constant, k , for this reaction from your graph. Explain your answer.

..... [1]
 (c) The experiment is repeated at a different temperature. The initial concentrations of H^+ ions, I_2 and CH_3COCH_3 are all $0.200 \text{ mol dm}^{-3}$.

The value of k at this temperature is $2.31 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Calculate the initial rate of this reaction.

rate = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

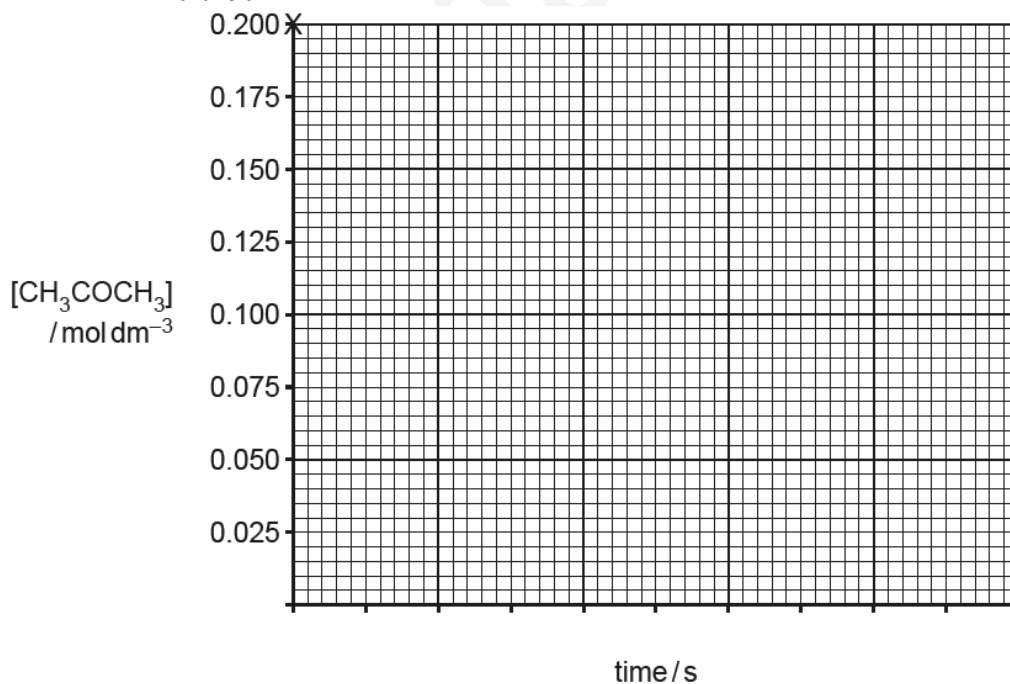
(d) The experiment is repeated using an excess of $\text{H}^+(\text{aq})$. The new rate equation is shown.

rate = $k_1[\text{CH}_3\text{COCH}_3]$

(i) The value of k_1 is $1.1 \times 10^{-3} \text{ s}^{-1}$. Calculate the value of the half-life, $t_{1/2}$.

$t_{1/2}$ = ... s [1]

(ii) Use your answer to (i) to draw a graph of $[\text{CH}_3\text{COCH}_3]$ against time for this reaction. The initial value of $[\text{CH}_3\text{COCH}_3]$ on your graph should be $0.200 \text{ mol dm}^{-3}$. The final value of $[\text{CH}_3\text{COCH}_3]$ on your graph should be $0.0250 \text{ mol dm}^{-3}$.



34. (a) A and B react together to give product AB.

$\text{A} + \text{B} \rightarrow \text{AB}$

When the concentrations of A and B are both $0.0100 \text{ mol dm}^{-3}$, the rate of formation of AB is $7.62 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. When the concentrations of A and B are both $0.0200 \text{ mol dm}^{-3}$, the rate of formation of AB is $3.05 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

(i) Complete the three possible rate equations that are consistent with these data.

rate = ...

rate = ...

rate = ... [2]

(ii) Choose one of the rate equations you have written in (i), and calculate the value of the rate constant, k . Include the units of k .

k = ... units [2]

(iii) Explain why it is not possible to calculate a value for the half-life, $t_{1/2}$, of this reaction using the value of the rate constant k calculated in (ii) and the equation $k = 0.693 / t_{1/2}$.

.....

.....

..... [1]

35. The rate of reaction between 2-chloro-2-methylpropane, $(\text{CH}_3)_3\text{CCl}$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.

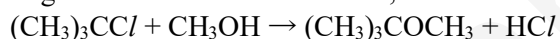
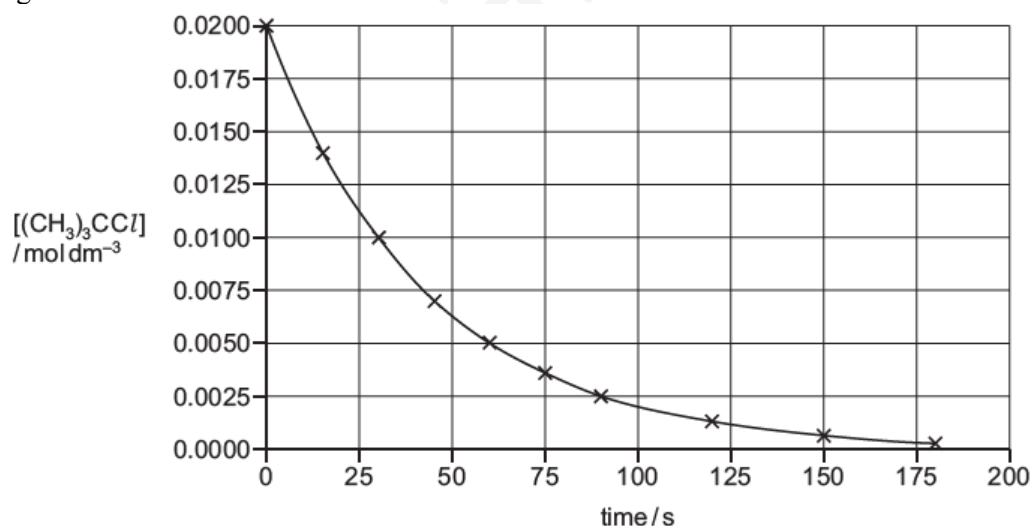


Fig. 3.1 shows the results obtained.



(i) Use the graph to determine the rate of reaction at 40 s. Show all your working.

rate = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

(ii) Use the graph to show that the overall reaction is first order. Explain your answer.

.....

..... [2]

(b) In a different reaction, which is also a first-order reaction, 75% of the reactant is consumed in 320 s. Calculate the rate constant, k , for this reaction. State the units for k .

$k = \dots\dots\dots$ units = $\dots\dots\dots$ [2]

36. Aqueous acidified iodate(V) ions, IO_3^- , react with iodide ions, as shown.



The initial rate of this reaction is investigated. Table 3.1 shows the results obtained.

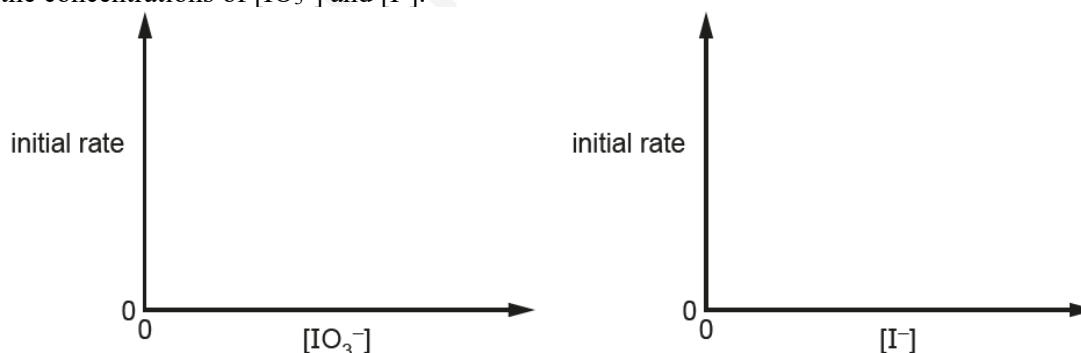
Experiment	$[\text{IO}_3^-] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	$[\text{I}^-] / \text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{ min}^{-1}$
1	0.0400	0.0150	0.0250	4.20×10^{-2}
2	0.120	to be calculated	0.0125	7.09×10^{-2}

The rate equation for this reaction is $\text{rate} = k [\text{IO}_3^-][\text{H}^+]^2[\text{I}^-]^2$.

(i) Complete Table 3.2. [1]

the order of reaction with respect to $[\text{IO}_3^-]$	
the order of reaction with respect to $[\text{H}^+]$	
the order of reaction with respect to $[\text{I}^-]$	
the overall order of reaction	

(ii) Use your answer to (i) to sketch lines in Fig. 3.1 to show the relationship between the initial rates and the concentrations of $[\text{IO}_3^-]$ and $[\text{I}^-]$. [1]



(iii) Use data from Table 3.1 to calculate the rate constant, k , for this reaction. Include the units of k .

$k = \dots\dots\dots$ units $\dots\dots\dots$ [2]

(iv) Use data from Table 3.1 to calculate the concentration of hydrogen ions, $[H^+]$, in experiment 2.

$$[H^+] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

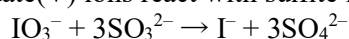
(vi) This reaction is repeated in two separate experiments.

The experiments are carried out at the same temperature and with the same concentrations of I^- and IO_3^- . One experiment takes place at pH 1.0, and the other experiment takes place at pH 2.0.

Calculate the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$

$$\text{value of } \frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}} = \dots\dots\dots [1]$$

37. Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.



The initial rate of reaction was found to be first order with respect to IO_3^- , first order with respect to SO_3^{2-} and first order with respect to H^+ .

(i) Write the rate equation for this reaction, stating the units of the rate constant, k .

$$\text{rate} = \dots\dots\dots \text{mol dm}^{-3} \text{ s}^{-1}$$

$$\text{units of } k = \dots\dots\dots [2]$$

(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x .

$$x = \dots\dots\dots [1]$$

For a multi-step reaction

38. Define the term rate-determining step.

$$\dots\dots\dots [1]$$

39. The exhaust systems of many diesel-fueled cars contain an additional system to reduce vehicle emissions. This uses a liquid that is added to the exhaust system.

This liquid contains urea, $(\text{NH}_2)_2\text{CO}$, which decomposes on heating to isocyanic acid, HNCO , and ammonia.



Isocyanic acid reacts with water vapour to form ammonia and carbon dioxide.



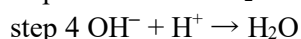
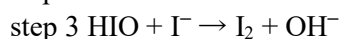
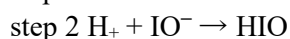
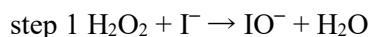
The ammonia formed in reactions 1 and 2 can be used to remove nitrogen dioxide from exhaust emissions, as shown.



Use the equations for reactions 1, 2 and 3 to construct an overall equation for the reduction of NO_2 by $(\text{NH}_2)_2\text{CO}$.

..... [1]

40. A four-step mechanism is suggested for the reaction between hydrogen peroxide and iodide ions in an acidic solution.

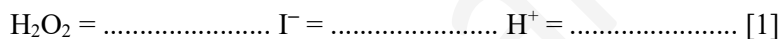


Step 1 is the rate-determining step.

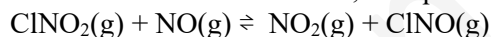
(i) Use this mechanism to construct a balanced equation for this reaction.

..... [1]

(iii) Deduce the order of reaction with respect to each of the following.



41. When ClNO_2 reacts with NO , an equilibrium is established.



In each ClNO_2 molecule, the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

(a) Draw a 'dot-and-cross' diagram for the ClNO_2 molecule.

..... [2]

(b) The reaction between ClNO_2 and NO is first order with respect to each reactant.

(i) Write the rate equation for this reaction.

rate [1]

(ii) Deduce the units of the rate constant, k , when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in $\text{mol dm}^{-3} \text{ s}^{-1}$.

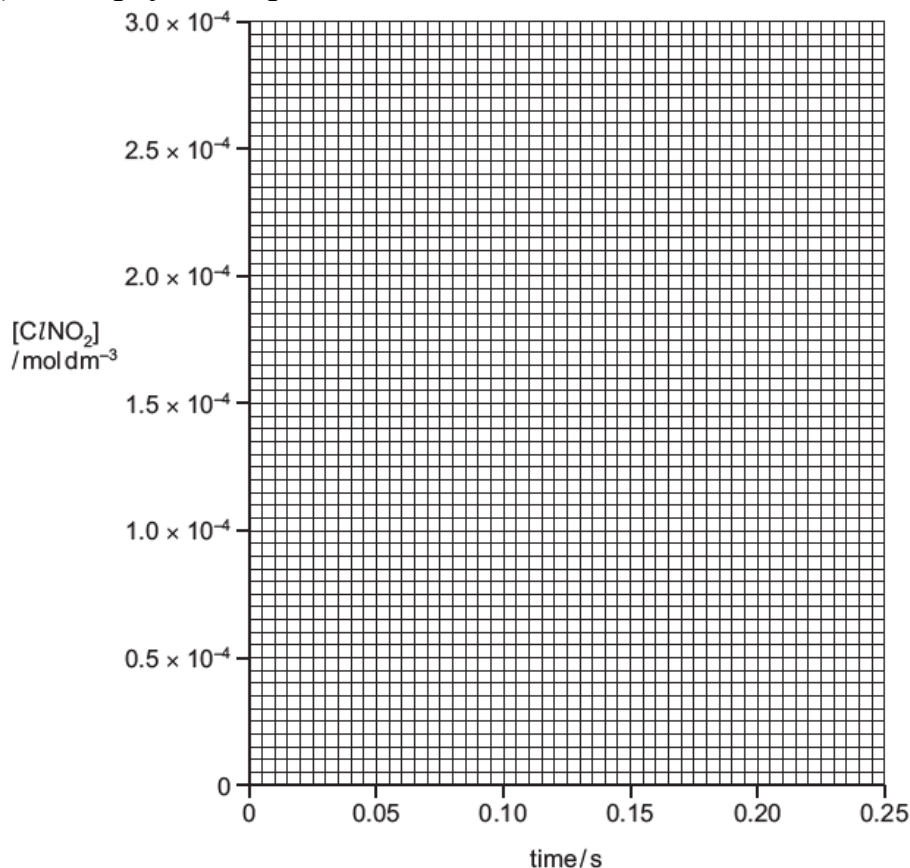
..... [1]

(iii) State and explain whether or not the reaction could take place in a single step.

.....

- [1]
- (c) An experiment is carried out in which the initial $[\text{ClNO}_2]$ is $2.0 \times 10^{-4} \text{ mol dm}^{-3}$. A large excess of NO is used. The initial rate of reaction is $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. The rate of the reaction is assumed to be constant for the first 0.20 seconds.

- (i) Draw a graph on the grid to show how the concentration of ClNO_2 varies for the first 0.20 seconds. [2]



- (ii) Deduce the concentration of the NO_2 product at 0.20 seconds.

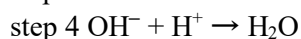
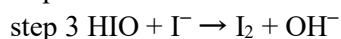
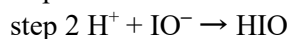
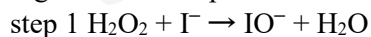
- [1]
- (iii) After 20 seconds, the concentration of ClNO_2 remains constant. Explain this observation.

- [1]
42. In aqueous solution, iodide ions react with acidified hydrogen peroxide, as shown.



The initial rate of reaction is found to be first order with respect to I^- , first order with respect to H_2O_2 and zero order with respect to H^+ .

Fig. 4.1 shows a possible four-step mechanism for this reaction.



- (i) Suggest which of the steps, 1, 2, 3 or 4, in this mechanism is the rate-determining step. Explain your answer.

.....

.....

..... [1]

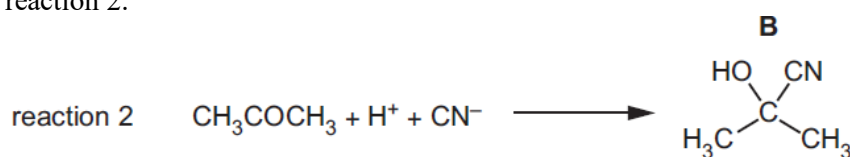
(ii) Identify a step in Fig. 4.1 that involves a redox reaction.
Explain your answer in terms of oxidation numbers.

.....
.....

(iii) Suggest the role of HIO in this mechanism.
Explain your reasoning.

.....
.....

43. Propanone also reacts with acidified cyanide ions to form the hydroxynitrile compound B, as shown by reaction 2. [1]



The following rate equation is determined for reaction 2.

$$\text{rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$$

Four possible mechanisms for reaction 2 are shown in Table 2.2.

proposed reaction mechanism	steps	
1	fast	$\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightarrow [\text{CH}_3\text{C}(\text{OH})\text{CH}_3]^+$
	slow	$[\text{CH}_3\text{C}(\text{OH})\text{CH}_3]^+ + \text{CN}^- \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$
2	fast	$\text{H}^+ + \text{CN}^- \rightarrow \text{HCN}$
	slow	$\text{CH}_3\text{COCH}_3 + \text{HCN} \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$
3	slow	$\text{CH}_3\text{COCH}_3 + \text{CN}^- \rightarrow \text{CH}_3\text{C}(\text{O}^-)(\text{CN})\text{CH}_3$
	fast	$\text{CH}_3\text{C}(\text{O}^-)(\text{CN})\text{CH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$
4	slow	$\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightarrow [\text{CH}_3\text{C}(\text{OH})\text{CH}_3]^+$
	fast	$[\text{CH}_3\text{C}(\text{OH})\text{CH}_3]^+ + \text{CN}^- \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$

Suggest which of these mechanisms is consistent with the rate equation for reaction 2.

Explain your answer.

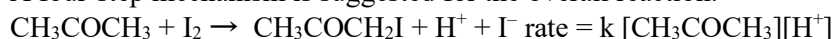
proposed reaction mechanism

explanation

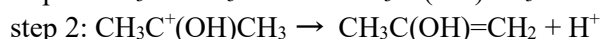
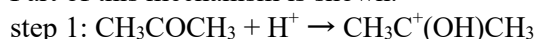
.....
.....

.....[3]

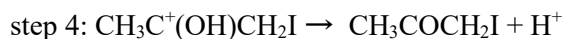
44. A four-step mechanism is suggested for the overall reaction.



Part of this mechanism is shown.



step 3:



(i) Write an equation for step 3.

..... [1]

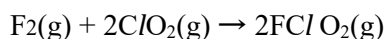
(ii) Suggest the slowest step of the mechanism. Explain your answer.

.....

..... [1]
(iii) Identify one conjugate acid-conjugate base pair in the mechanism.

conjugate acid conjugate base [1]

45. Fluorine reacts with chlorine dioxide, ClO_2 , as shown.



The rate of the reaction is first order with respect to the concentration of F_2 and first order with respect to the concentration of ClO_2 . No catalyst is involved.

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

step 1

step 2 [2]

(ii) Identify the rate-determining step in this mechanism. Explain your answer. [1]

(b) When the rate of the reaction is measured in $\text{mol dm}^{-3} \text{s}^{-1}$ the numerical value of the rate constant, k , is 1.22 under certain conditions.

(i) Complete the rate equation for this reaction, stating the overall order of the reaction.

rate =

overall order of reaction = [1]

(ii) Use your rate equation in (i) to calculate the rate of the reaction when the concentrations of F_2 and ClO_2 are both $2.00 \times 10^{-3} \text{ mol dm}^{-3}$.

rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

(c) Under different conditions, and in the presence of a large excess of ClO_2 , the rate equation is as shown.

$$\text{rate} = k_1[\text{F}_2]$$

The half-life, $t_{1/2}$, of the concentration of F_2 is 4.00 s under these conditions.

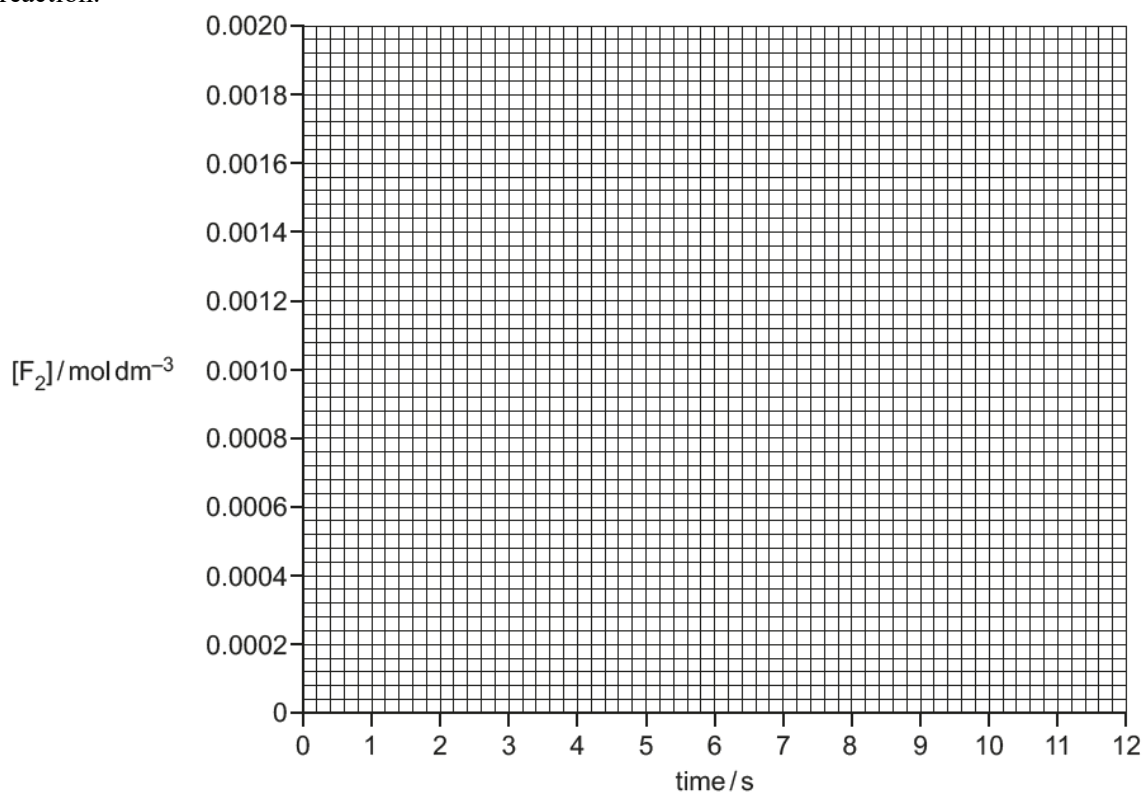
(i) Calculate the numerical value of k_1 , giving its units.

Give your answer to **three** significant figures.

$k_1 = \dots\dots\dots$ units $\dots\dots\dots$ [2]

(ii) An experiment is performed under these conditions in which the starting concentration of F_2 is $0.00200 \text{ mol dm}^{-3}$.

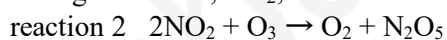
Draw a graph on the grid in Fig. 1.1 to show how the concentration of F_2 changes over the first 12 s of the reaction.



Use your graph in Fig. 1.1 to find the rate of the reaction when the concentration of F_2 is $0.00100 \text{ mol dm}^{-3}$. Show your working on the graph.

rate = $\dots\dots\dots$ $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

46. Nitrogen dioxide, NO_2 , reacts with ozone, O_3 , as shown in reaction 2.



The rate equation for reaction 2 is shown.

rate = $k [\text{NO}_2][\text{O}_3]$

(i) Two experiments are carried out to measure the rate of reaction 2.

In the first experiment, the initial rate is measured starting with known concentrations of NO_2 and O_3 . In the second experiment, the concentrations of NO_2 and O_3 are both increased by a factor of four.

Predict how the initial rate for reaction 2 would change.

$\dots\dots\dots$ [1]

(ii) The reaction mechanism for reaction 2 has two steps.

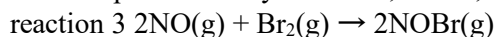
Suggest equations for the two steps of the reaction mechanism for reaction 2.

step 1 $\dots\dots\dots$

step 2 $\dots\dots\dots$

[2]

47. The compound nitrosyl bromide, NOBr, can be formed as shown in reaction 3.



The rate is first-order with respect to [NO] and first-order with respect to [Br₂].

The reaction mechanism has two steps.

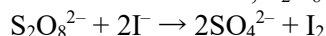
Suggest equations for the **two** steps of this mechanism. State which is the rate-determining step.

step 1

step 2

rate-determining step = ...[2]

48. Peroxodisulfate ions, S₂O₈²⁻, react with iodide ions, I⁻.



The rate equation for the reaction in the absence of any catalyst is shown.

rate = $k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$

(i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1

step 2

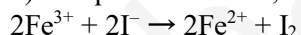
rate-determining step = ...[2]

(ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, [I⁻] = 0.00780 mol dm⁻³. Under the conditions used, the half-life of [I⁻] is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... mol dm⁻³ [1]

b) In aqueous solution, iron(III) ions react with iodide ions, as shown.



The initial rate of reaction is first order with respect to Fe³⁺ and second order with respect to I⁻.

The mechanism for this reaction has three steps.

Each step involves only **two** ions reacting together.

Suggest equations for the **three** steps of this mechanism. Identify the rate-determining step.

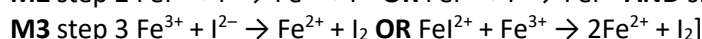
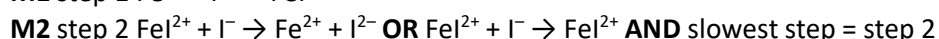
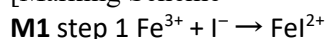
step 1

step 2

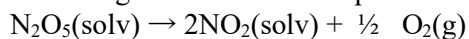
step 3

rate-determining step = ... [3]

[Marking Scheme

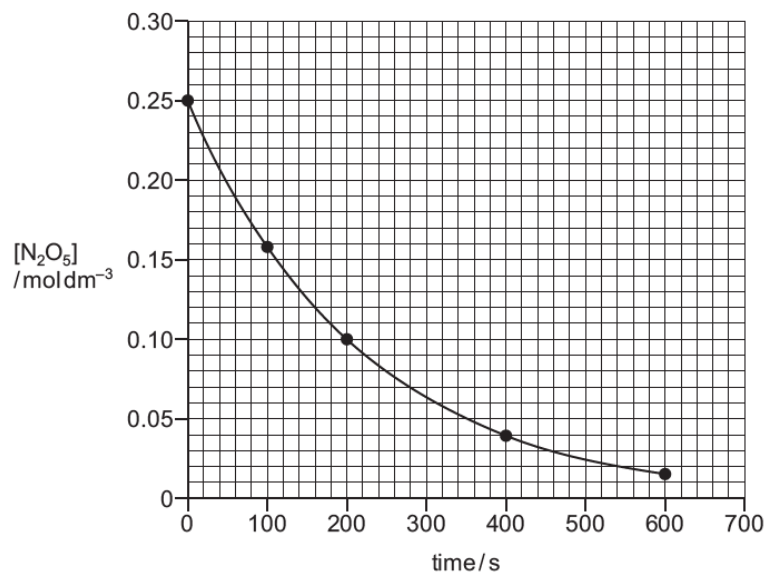


49. Dinitrogen pentoxide, N_2O_5 , is dissolved in an inert solvent (solv) and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.



In an experiment, the rate of the decomposition of $\text{N}_2\text{O}_5(\text{g})$ is investigated.

The graph shows the results obtained.



The reaction is first order with respect to N_2O_5 . This can be confirmed from the graph using half-lives.

- (ii) Determine the half-life of this reaction. Show your working on the graph.

half-life = ... s [1]

- (iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

..... [1]

- (c) (i) Use the graph in 5(b) to determine the rate of reaction at 200 s. Show your working.

rate = ... units = ... [2]

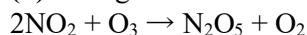
The rate equation for this reaction is shown.

$$\text{rate} = k [\text{N}_2\text{O}_5]$$

- (ii) Use your answer to (c)(i) to calculate the value of the rate constant, k , for this reaction and state its units.

$k = \dots\dots\dots$ units [1]

(d) Nitrogen dioxide reacts with ozone, O_3 , as shown.



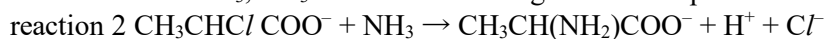
The rate equation for this reaction is $\text{rate} = k [NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

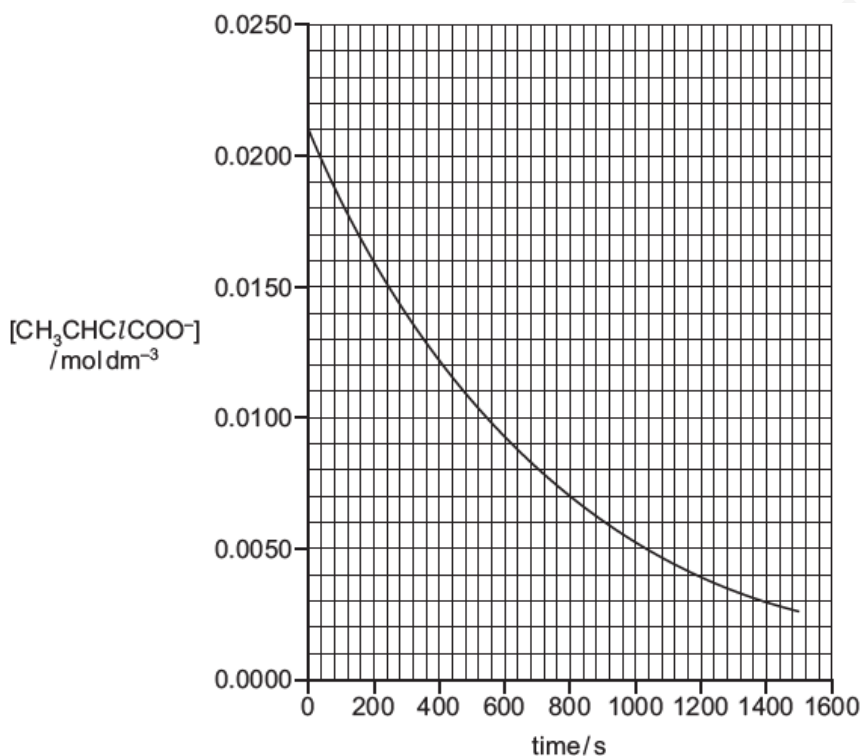
.....

..... [2]

50. In an excess of NH_3 , $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.



A student investigates the rate of reaction 2. The student mixes $CH_3CHClCOO^-$ with a large excess of NH_3 . The graph in Fig. 5.3 shows the results obtained.



(ii) Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to $[CH_3CHClCOO^-]$.

.....

.....

.....

..... [2]

(iii) Explain why a **large** excess of NH_3 needs to be used in order to obtain the results in Fig. 5.3.

.....

..... [1]

(iv) The student measures the effect of changing the concentration of NH_3 on the rate of reaction 2. Table 5.1 shows the results obtained.

experiment	$[\text{CH}_3\text{CHClCOO}^-]/\text{mol dm}^{-3}$	$[\text{NH}_3]/\text{mol dm}^{-3}$	initial rate of reaction/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

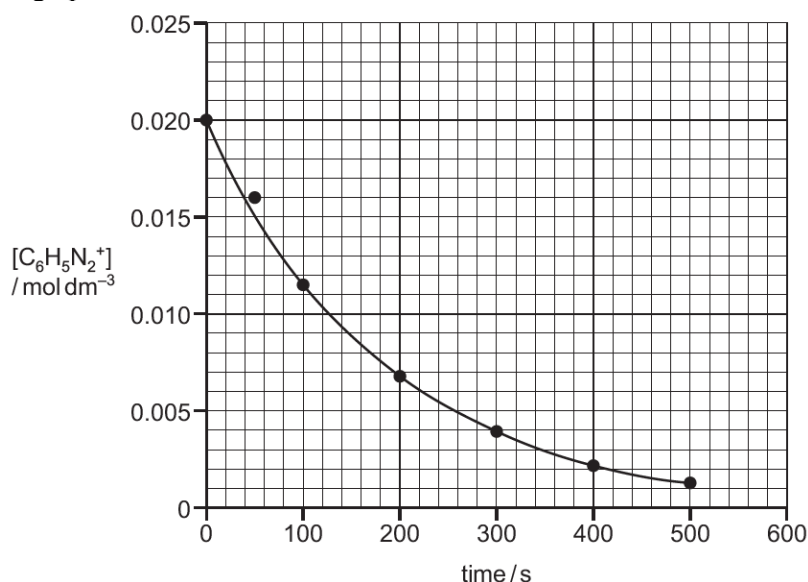
Use the information in Table 5.1 and in (c)(ii) to determine whether the nucleophilic substitution reaction proceeds via an S_N^1 or an S_N^2 mechanism.

Explain your answer.

.....

51. The decomposition of benzenediazonium ions, $\text{C}_6\text{H}_5\text{N}_2^+$, using a large excess of water, is a first-order reaction. [2]

The graph shows the results obtained.



- (i) Draw the structure of the organic product formed in this reaction. [1]

- (ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

rate = ... $\text{mol dm}^{-3} \text{ s}^{-1}$ [1]

52. A student studies the reaction of $\text{CH}_3\text{CHClCOOH}$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $\text{CH}_3\text{CHClCOOH}$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.



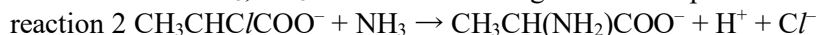
(i) Identify the conjugate acid–base pairs in reaction 1.

conjugate acid–base pair I and

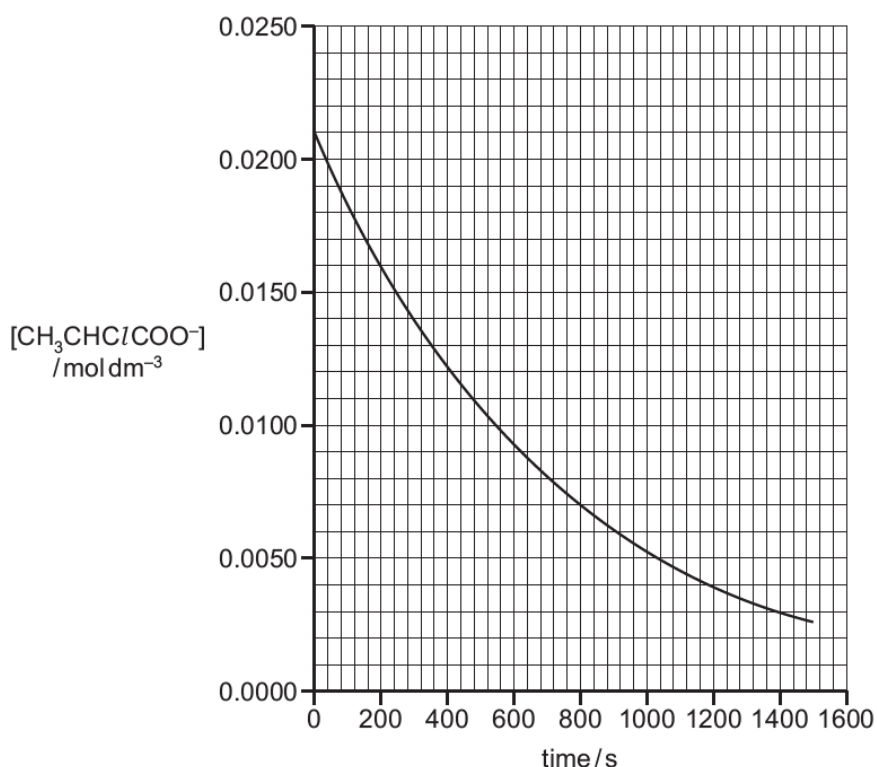
conjugate acid–base pair II and

[1]

In an excess of NH_3 , $\text{CH}_3\text{CHClCOO}^-$ undergoes a nucleophilic substitution reaction.



A student investigates the rate of reaction 2. The student mixes $\text{CH}_3\text{CHClCOO}^-$ with a large excess of NH_3 . The graph in Fig. 5.3 shows the results obtained.



53. Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to $[\text{CH}_3\text{CHClCOO}^-]$.

.....

 [2]

(i) Explain why a **large** excess of NH_3 needs to be used in order to obtain the results in Fig. 5.3.

.....
 [1]

(iv) The student measures the effect of changing the concentration of NH_3 on the rate of reaction 2. Table 5.1 shows the results obtained.

experiment	$[\text{CH}_3\text{CHCl COO}^-]/\text{mol dm}^{-3}$	$[\text{NH}_3]/\text{mol dm}^{-3}$	initial rate of reaction/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

Use the information in Table 5.1 and in (c)(ii) to determine whether the nucleophilic substitution reaction proceeds via an $\text{S}_{\text{N}}1$ or an $\text{S}_{\text{N}}2$ mechanism.

Explain your answer.

.....

 [2]

(vi) When an excess of $\text{CH}_3\text{CHCl COO}^-$ is used, further substitution reactions occur. One product has the formula $\text{C}_6\text{H}_9\text{NO}_4^{2-}$.

Suggest the structure of $\text{C}_6\text{H}_9\text{NO}_4^{2-}$. [1]

.....

<https://subarnam.com.np/>