26.1 RATE EQUATIONS, ORDER AND RATE CONSTANTS

Learning outcomes

Candidates should be able to:

1. explain and use the terms rate equation, order of reaction, overall order of reaction, rate constant, half-life, rate-determining step and intermediate
2. (a) understand and use rate equations of the form rate = k [A]^m[B]^n (for which m and n are 0, 1 or 2)
   (b) deduce the order of a reaction from concentration–time graphs or from experimental data relating to the initial rates method and half-life method
   (c) interpret experimental data in graphical form, including concentration–time and rate–concentration graphs
   (d) calculate an initial rate using concentration data
   (e) construct a rate equation
3. (a) show understanding that the half-life of a first-order reaction is independent of concentration
   (b) use the half-life of a first-order reaction in calculations
4. calculate the numerical value of a rate constant, for example, by:
   (a) using the initial rates and the rate equation
   (b) using the half-life, $t_{½}$, and the equation $k = 0.693/t_{½}$
5. for a multi-step reaction:
   (a) suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction
   (b) predict the order that would result from a given reaction mechanism and rate-determining step
   (c) deduce a rate equation using a given reaction mechanism and rate-determining step for a given reaction
   (d) identify an intermediate or catalyst from a given reaction mechanism
   (e) identify the rate determining step from a rate equation and a given reaction mechanism
6. describe qualitatively the effect of temperature change on the rate constant and hence the rate of a reaction

Initial assessment

1. Explain the meaning of the terms: *rate of reaction*, *frequency*, *effective collisions*, and *non-effective collisions*.
2. Write a paragraph using ideas about colliding particles to explain the effect of increasing the concentration of a reactant on the rate of reaction and decreasing the temperature on the rate of reaction.
3. Work with a group of other learners to suggest three different methods of monitoring the rate of a reaction.
4. Write a paragraph about how catalysts increase the rate of a chemical reaction.
5. Sketch a reaction pathway diagram for an endothermic reaction in the presence and absence of a catalyst.
6. Explain how you can find the rate of reaction at any one time from a graph of volume of gas (y-axis) against time (x-axis).
7. Draw and explain the shape of the graph obtained by plotting the loss in mass of the reaction mixture with time for the reaction

   $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

Introduction

rate of reaction

We calculate the *rate of reaction* by measuring a decrease in concentration of a particular reactant or an increase in concentration of a particular product over a period of time.

Rate of reaction = $\frac{change\ in\ concentration}{time\ taken}$

Units of concentration are usually expressed in mol dm^{-3}, and units of time are usually expressed in seconds. Therefore, the units of the rate of reaction are typically mol dm^{-3} s^{-1}.

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.
   $N_2O_5(solv) \rightarrow 2NO_2(solv) + ½\ O_2(g)$
   Suggest what measurements could be used to follow the rate of this reaction from the given information.

   .....

   ..... [1]

2. $H_2PO_2^-(aq)$ reacts with $OH^-(aq)$.
   $H_2PO_2^-(aq) + OH^-(aq) \rightarrow HPO_3^{2-}(g) + H_2(g)$
   The following table shows the results of a series of experiments used to investigate the rate of this reaction.

Experiment	$[H_2PO_2^-(aq)]$ / mol dm^{-3}	$[OH^-(aq)]$ / 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 volume of H_2 was measured under room conditions.
   Use the molar volume of gas, Vm, and the data from experiment 1 to calculate the rate of reaction in mol dm^{-3} s^{-1}.

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

The **rate equation** is an expression showing how the rate of reaction is linked to the concentration of the reactants. The rate is equal to the rate constant (k) multiplied by the concentration of each reactant raised to certain whole-number powers (called orders).

The rate equation for the general reaction P + Q → R + S is:

rate = $k[P]^x [Q]^y$

where x is the **order of reaction** with respect to reactant P, y is the order of reaction with respect to reactant Q, and k is the **rate constant**.

Rate equation: an equation showing the relationship between the rate constant and the concentrations of the species that affect the rate of reaction.

Rate constant: the proportionality constant, k, in a rate equation

The **overall order of the reaction** is the sum of all the orders in the rate equation. For this reaction, the overall order of reaction would be $x + y$.

Rate has units of mol dm^{-3} s^{-1}.

Concentration has units of mol dm^{-3}.

The units of the rate constant, k, depend on the overall order of the reaction, and the units can be calculated.

Order of reaction: the power to which the concentration of the reactant is raised in the rate equation. If a rate is directly proportional to concentration, it is a first-order reaction; if the rate is directly proportional to the square of the concentration, it is a second-order reaction. The overall order of reaction is the sum of these powers.

REMEMBER that the units of rate are usually mol dm^{-3}, but the units of rate constant must be worked out from the rate equation.

Working out order from rate tables Working out order from rate tables (more difficult example)

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 acid solution.

$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

The rate equation for this reaction is shown.

rate = $k [IO_3^-][I^-]^2[H^+]^2$

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

The initial concentrations are shown.

$[IO_3^-] = 0.500$ mol dm^{-3} $[I^-] = 1.00 \times 10^{-3}$ mol dm^{-3} $[H^+] = 1.00 \times 10^{-2}$ mol dm^{-3}

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

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

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

(iii) This reaction is repeated at the same temperature and with the same initial values of $[IO_3^-]$ and $[I^-]$. The $[H^+]$ is increased to 3.00×10^{-2} mol dm^{-3}.

Calculate the initial rate of this reaction.

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

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

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

The rate equation for the forward reaction is shown.

rate = $k[NO]^2[O_2]$

(a) Complete the following table. [1]

The order of reaction with respect to [NO]	
The order of reaction with respect to $[O_2]$	
The overall order of reaction	

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

experiment	[NO] / mol dm^{-3}	$[O_2]$ / mol dm^{-3}	rate / mol dm^{-3} 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 = ... units = ...[2]

(ii) Calculate the value of [NO] in experiment 2.

[NO] = ... mol dm^{-3} [1]

7. Nitrogen monoxide reacts with oxygen.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

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 8.60×10^6 mol^{-2} dm^6 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 7.20×10^{-4} mol dm^{-3} and the initial concentration of oxygen is 1.90×10^{-3} mol dm^{-3}.

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

8. NO reacts readily with oxygen.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

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/ mol dm^{-3} 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 [O_2(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 = ...(ans = 7000) ..... units of k = …….……..... [3]

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

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Under certain conditions, this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k, of 2.0×10^{-6} 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 = ... mol dm^{-3} s^{-1} [1]

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

$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$

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

Experiment	$[ClO_2]$/ mol dm^{-3}	$[OH^-]$/ mol dm^{-3}	initial rate/ mol dm^{-3} 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.

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..... [2]

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

rate = ... [1]

(iv) 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 = ... units ..... [2]

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

Experiment	$[H_2O_2]$/ mol dm^{-3}	$[IO_3^-]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	initial rate of reaction/ mol dm^{-3} 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 $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$.
Show your reasoning.

order with respect to $[H_2O_2]$ = ...

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order with respect to $[IO_3^-]$ = ...

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.....

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order with respect to $[H^+]$ = ...

.....

.....

..... [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]

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

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

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

Experiment	$[Fe^{3+}]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate/mol dm^{-3} 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.

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

14. 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.
forward reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$
backward reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$
(i) Use this information to explain what will happen if equal concentrations of HI(g), $H_2(g)$ and $I_2(g)$ 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.

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..... [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.

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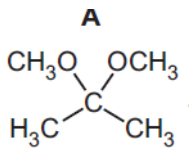
..... [2]

Pseudo first order reaction

15. 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.

reaction 1 $CH_3COCH_3 + 2CH_3OH \xrightarrow{H^+}$ **A** $+ H_2O$



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 $[CH_3OH]$ and $[H^+]$ are varied. In each experiment, a large excess of CH_3COCH_3 is used.

experiment	$[CH_3OH]$/ mol dm^{-3}	$[H+]$/ 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.

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.....

..... [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.

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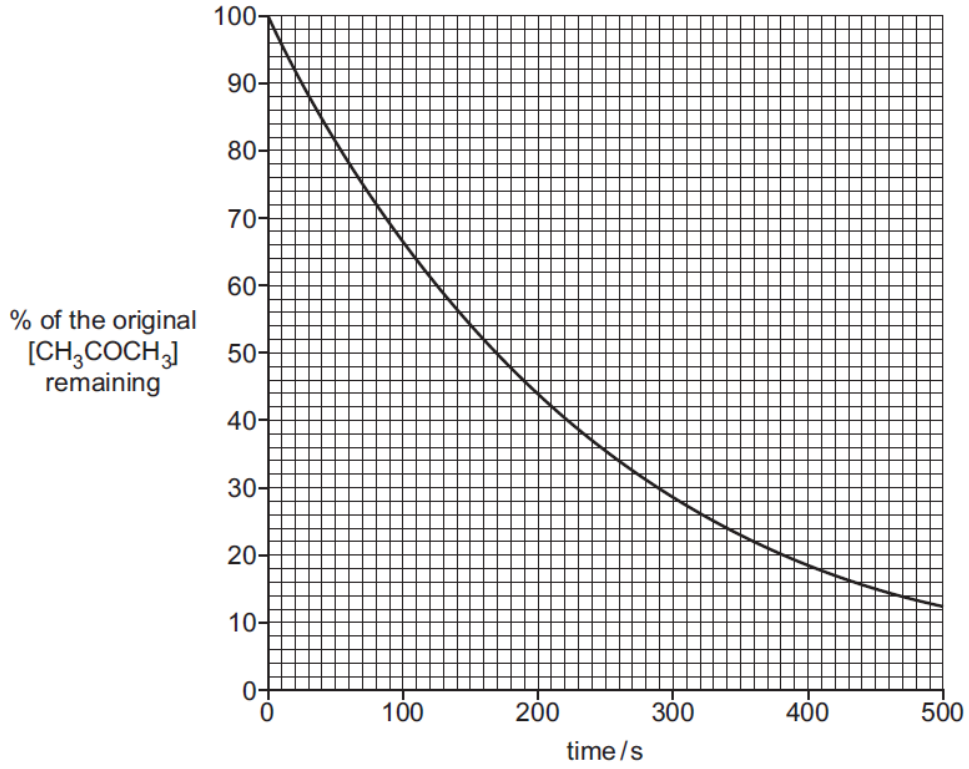
.....

..... [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 $[CH_3COCH_3]$ varies over time.



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

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..... [1]

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

reaction 1 $2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$

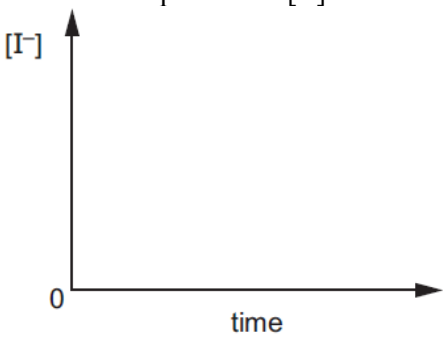
The rate equation for reaction 1 is shown.

rate = $k [I^-][H_2O_2]$

(ii) Complete Table 4.1. [2]

the order of reaction with respect to [H+]	
the order of reaction with respect to [I–]	
the order of reaction with respect to $[H_2O_2]$	
overall order of the reaction	

(iii) Sketch a line on Fig. 4.1 to show the relationship between $[I^-]$ and time. [1]

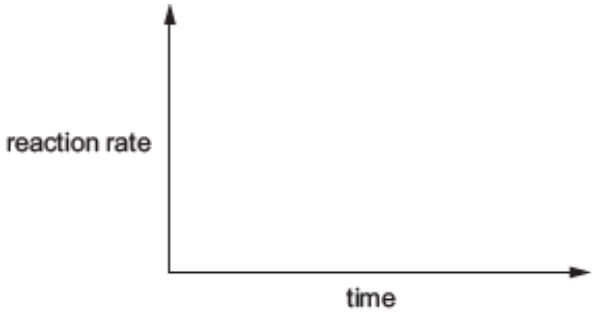


17. Nitrous oxide, N_2O, decomposes into its elements.

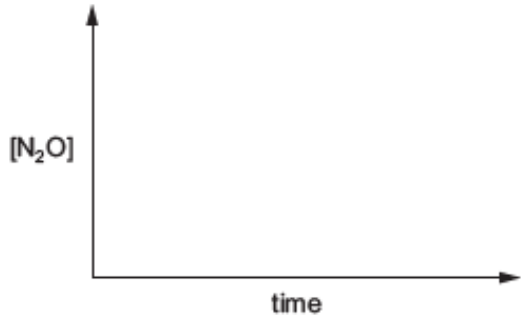
$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

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]

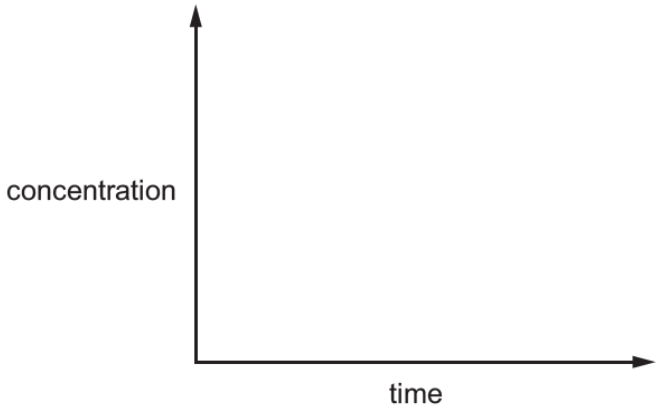


(iii) Sketch a graph, on the axes below, of $[N_2O]$ against time for this reaction. [1]



18. Sketch a concentration-time–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

[326 - K1 Kinetics of Ester Hydrolysis]

Effect of temperature change on the rate constant

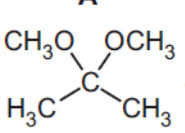
19. In aqueous solution, iron(III) ions react with iodide ions, as shown.
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
Describe qualitatively the effect of an increase in temperature on the rate constant and on the rate of this reaction.

.....

..... [1]

20. 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.

reaction 1 $CH_3COCH_3 + 2CH_3OH \xrightarrow{H^+}$ A + H_2O



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

.....

..... [1]

21. $H_2PO_2^-(aq)$ reacts with $OH^-(aq)$.
$H_2PO_2^-(aq) + OH^-(aq) \rightarrow HPO_3^{2-}(g) + H_2(g)$
The experiment is repeated using a large excess of $OH^-(aq)$.
Under these conditions, the rate equation is:
rate = k_1 $[H_2PO_2^-(aq)]$
Describe how an increase in temperature affects the value of the rate constant, k_1.

.....

..... [1]

22. Describe the effect of an increase in temperature on the rate of reaction of $CH_3CHClCOO^-$ and NH_3.
Explain your answer.

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..... [2]

Half life

Half-life t½: time taken for the amount (or concentration) of the limiting reactant in a reaction to decrease to half its initial value.

First-order reactions have a fixed half-life time, which is given by the following relation:

$$k = 0.693/t_{1/2}$$

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The half-life of a second-order reaction is not constant; it changes with time.

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

    .....

    ..... [1]

24. In aqueous solution, thiosulfate ions, $S_2O_3^{2-}$, react with hydrogen ions, as shown in reaction 2.

    reaction 2 $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$

    The rate of reaction is first order with respect to $[S_2O_3^{2-}]$ and zero order with respect to $[H^+]$ under certain conditions.

    The rate constant, k, for this reaction is 1.58×10^{-2} s^{-1}.

    Calculate the half-life, t½, for reaction 2.

    t½ = ... s [1]

25. $H_2PO_2^-(aq)$ reacts with $OH^-(aq)$.

    $H_2PO_2^-(aq) + OH^-(aq) \rightarrow HPO_3^{2-}(g) + H_2(g)$

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

Experiment	$[H_2PO_2^-(aq)]$ / mol dm^{-3}	$[OH^-(aq)]$ / 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:

    rate = k $[H_2PO_2^-(aq)]$ $[OH^-(aq)]^2$

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

    .....

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    .....

    .....

    ..... [2]

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

    ..... [1]

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

    Under these conditions, the rate equation is:

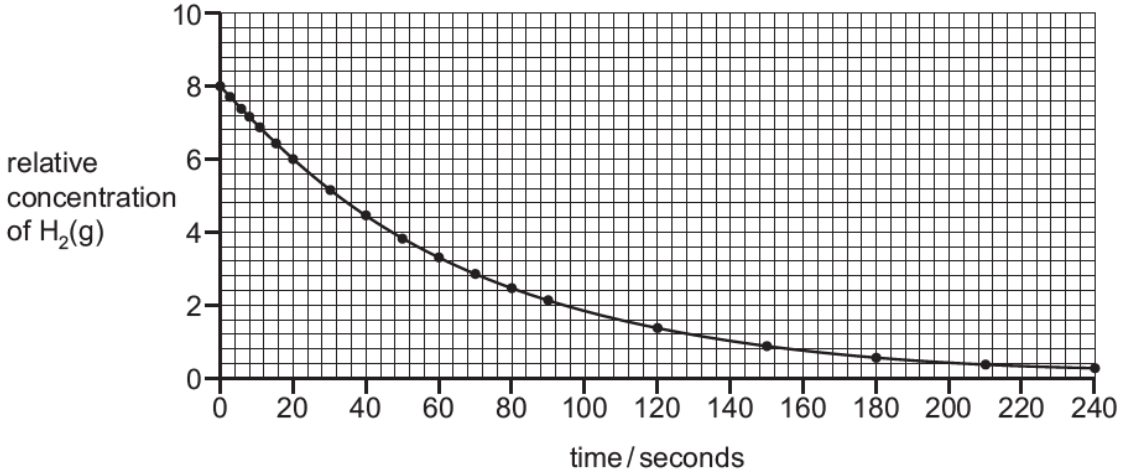
    rate = k_1 $[H_2PO_2^-(aq)]$; $k_1 = 8.25 \times 10^{-5}$ s^{-1}

    Calculate the value of the half-life, t ½, of the reaction.

    t ½ = ... s [1]

26. The rate of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is studied.

(a) A small amount of $H_2(g)$ is mixed with a large excess of $I_2(g)$ at a temperature of 400 K, and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $I_2(g)$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $H_2(g)$.
Use data from the graph to confirm this statement.

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..... [2]

(b) Three separate experiments were carried out at 400 K with different starting concentrations of $H_2(g)$ and $I_2(g)$. The results are shown in the table.

experiment	$[H_2(g)]$ / mol dm^{-3}	$[I_2(g)]$ / mol dm–3	rate of reaction/ mol dm^{-3} 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 $H_2(g)$ given in (a)(ii), to deduce the order of reaction with respect to $I_2(g)$.
Explain your answer, giving data in support of your explanation.

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..... [3]

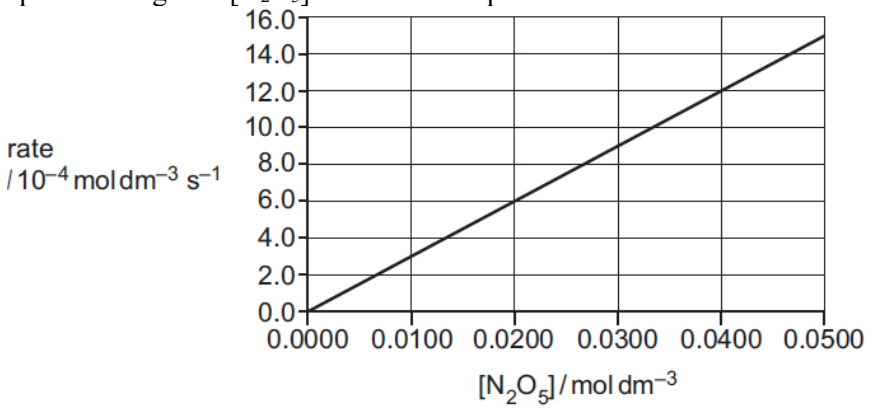
(ii) Use information from (a)(ii) and your answer to (b)(i) to write the rate equation for the forward reaction.

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]

27. Dinitrogen pentoxide, N_2O_5, can decompose to NO_2 and O_2.
The rate equation for this decomposition is shown.
rate = k $[N_2O_5]$
Fig. 4.2 shows the graph of rate against $[N_2O_5]$ for this decomposition.



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

k = ... [1]

(ii) Use your answer to (i) to calculate the half-life, t½, in seconds, for this decomposition.

t ½ = ... s [1]

28. A and B react together to give product AB.
A + B→ AB
When the concentrations of A and B are both 0.0100 mol dm^{-3}, the rate of formation of AB is 7.62×10^{-4} mol dm^{-3} s–1. When the concentrations of A and B are both 0.0200 mol dm^{-3}, the rate of formation of AB is 3.05×10^{-3} mol dm^{-3} 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, t½, of this reaction using the value of the rate constant k calculated in (ii) and the equation k = 0.693 /t½.

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……..... [1]

29. Nitrogen monoxide, NO, reacts with ozone, O_3.

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

This reaction is first order with respect to both NO and O_3.

At 298 K, the rate constant k = 11 500 mol^{-1} dm^3 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 O_3 are both 1.20×10^{-6} 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]

30. The drug cisplatin, $Pt(NH_3)_2Cl_2$, hydrolyses in water.

$Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2Cl\ (H_2O)]^+ + Cl^-$

The rate equation is shown. rate = k $[Pt(NH_3)_2Cl_2]$

The value of k is 2.50×10^{-5} 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 2.77×10^4 s. [1]

(iii) 8.00×10^{-6} moles of $Pt(NH_3)_2Cl_2$ are added to 100 cm^3 of water.
Calculate the time taken for the concentration of $Pt(NH_3)_2Cl_2$ to fall to 2.50×10^{-6} mol dm^{-3}.

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

31. Three experiments are carried out to investigate the reaction of nitrogen oxide, NO, with chlorine.
$2NO + Cl_2 \rightarrow 2NOCl$
The rate equation for this reaction is shown.
rate = k $[NO]^2[Cl_2]$
(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 mol dm^{-3} 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 2.57×10^{-6} mol dm^{-3} 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 = ... mol dm^{-3} s^{-1} [1]

(b) Experiment 3 uses a large excess of NO.
The initial concentration of Cl_2 is 2.00×10^{-4} mol dm^{-3}.
(i) The graph of $[Cl_2]$ against time shows that the reaction has a constant half-life, t ½.
Explain this observation.

.....

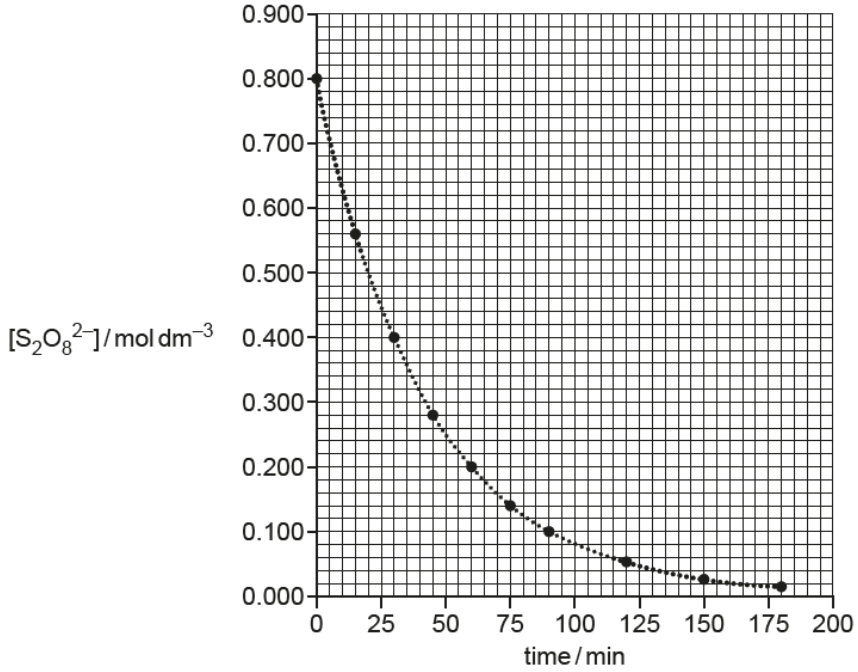
..... [1]

(ii) Under the conditions used in experiment 3, the value of the rate constant is 105.6.
Show that t½ of $[Cl_2]$ is 6.56×10^{-3} s under these conditions. [1]

(iii) Calculate the time taken, in s, for $[Cl_2]$ to fall to 1.25×10^{-5} mol dm^{-3} in experiment 3.

time = ... s [1]

32. In aqueous solution, persulfate ions, $S_2O_8^{2-}$, react with iodide ions, as shown in reaction 1.
reaction 1 $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
The rate of reaction 1 is investigated.
A sample of $S_2O_8^{2-}$ 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) ..... mol dm^{-3} min^{-1} [1]

(ii) The rate equation for reaction 1 is rate = k $[S_2O_8^{2-}]$ $[I^-]$.
Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

.....

.....

..... [1]

33. The equation for reaction 1 is shown.

reaction 1 $X \rightarrow 2Y$

Reaction 1 is first order with respect to the concentration of X. The half-life of the reaction, t½, is 900 s at 20 °C.

(i) A solution of X with a concentration of 0.180 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 7.70×10^{-4} s^{-1} at 20 °C.

[1]

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

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

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

$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$

The rate equation for this reaction is shown.

rate = $k[CH_3COCH_3][H^+]$

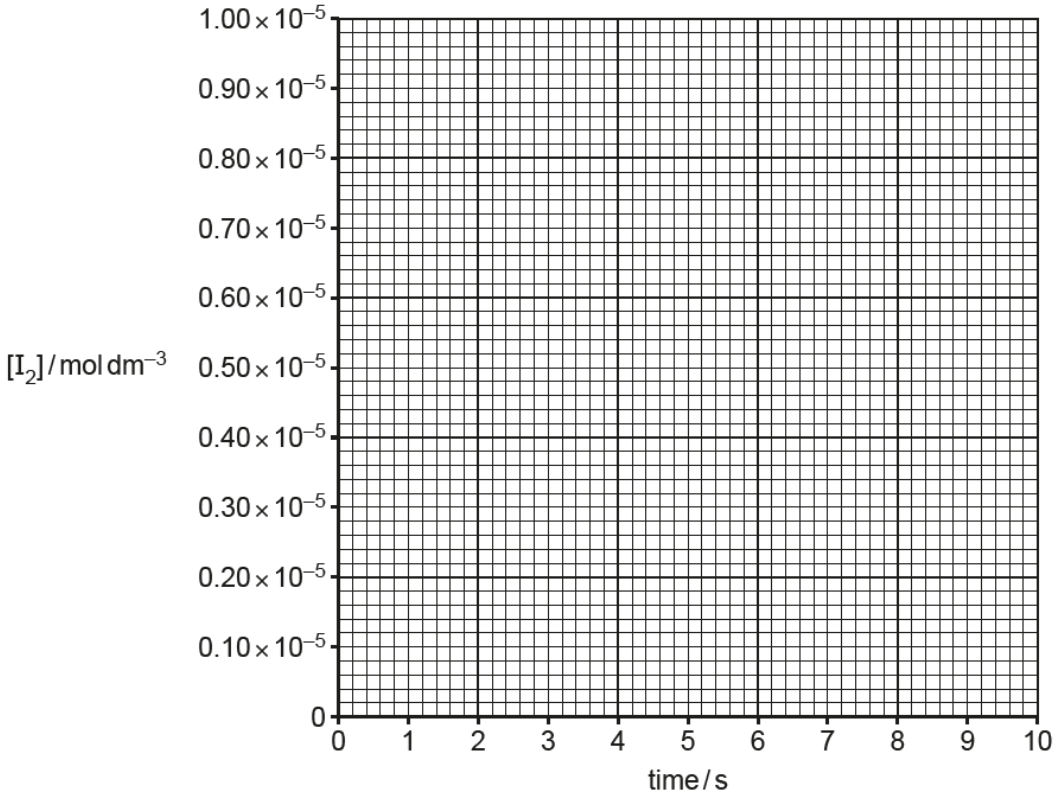
(a) Complete Table 1.1 to describe the order of the reaction. [2]

order of the reaction with respect to $[CH_3COCH_3]$	
order of the reaction with respect to $[I_2]$	
order of the reaction with respect to $[H^+]$	
overall order of the reaction	

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

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

(i) Use the axes to draw a graph of $[I_2]$ 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 mol dm^{-3}.

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

Calculate the initial rate of this reaction.

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

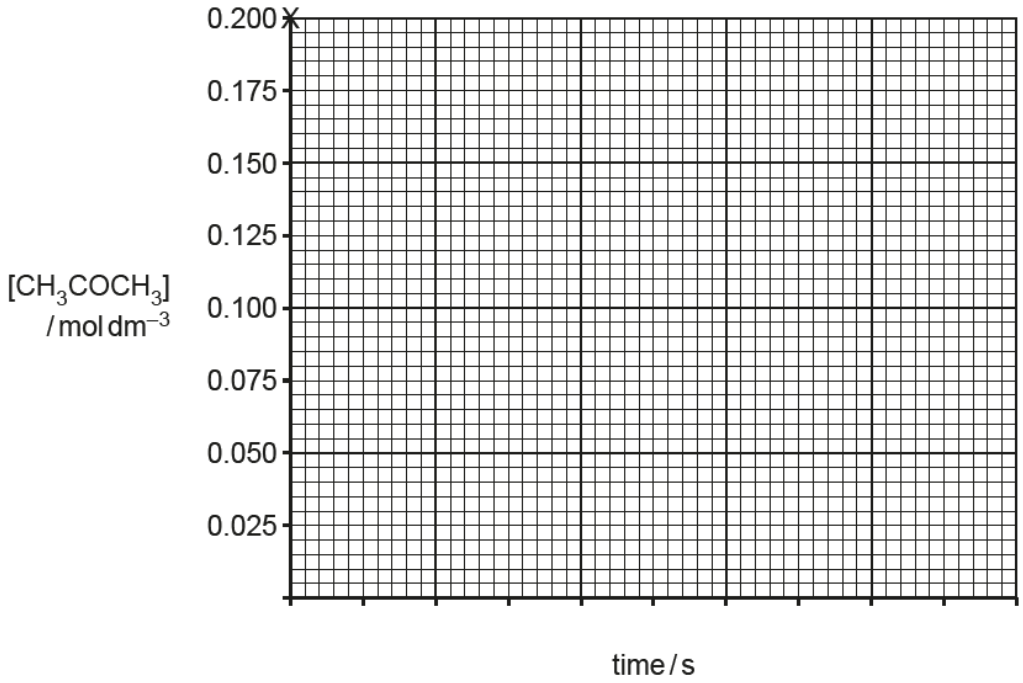
(d) The experiment is repeated using an excess of H^+(aq). The new rate equation is shown.

rate = k1[CH_3COCH_3]

(i) The value of k1 is 1.1×10^{-3} s^{-1}. Calculate the value of the half-life, t½.

t½ = ... s [1]

(ii) Use your answer to (i) to draw a graph of [CH_3COCH_3] against time for this reaction. The initial value of [CH_3COCH_3] on your graph should be 0.200 mol dm^{-3}. The final value of [CH_3COCH_3] on your graph should be 0.0250 mol dm^{-3}.



35. (a) A and B react together to give product AB.
A + B→ AB
When the concentrations of A and B are both 0.0100 mol dm^{-3}, the rate of formation of AB is 7.62×10^{-4} mol dm^{-3} s^{-1}. When the concentrations of A and B are both 0.0200 mol dm^{-3}, the rate of formation of AB is 3.05×10^{-3} mol dm^{-3} 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.

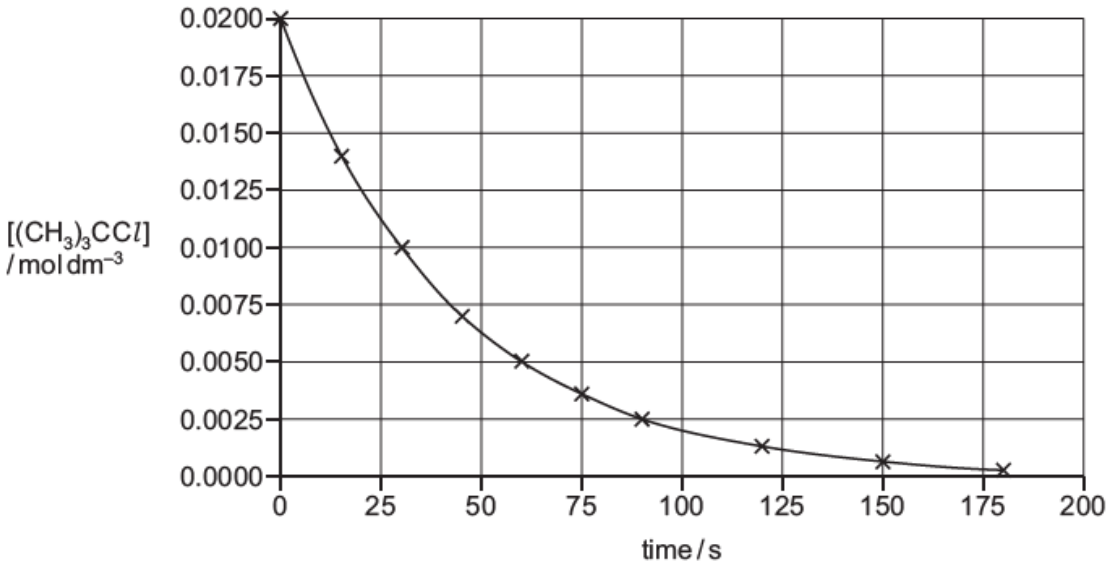
k = ... units ..... [2]
(iii) Explain why it is not possible to calculate a value for the half-life, t½, of this reaction using the value of the rate constant k calculated in (ii) and the equation k = 0.693 / t½.

.....

.....

..... [1]

36. The rate of reaction between 2-chloro-2-methylpropane, $(CH_3)_3CCl$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.
$(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + HCl$
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 = ... mol dm^{-3} 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 = ... units = ... [2]

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

$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$

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

Experiment	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} 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}

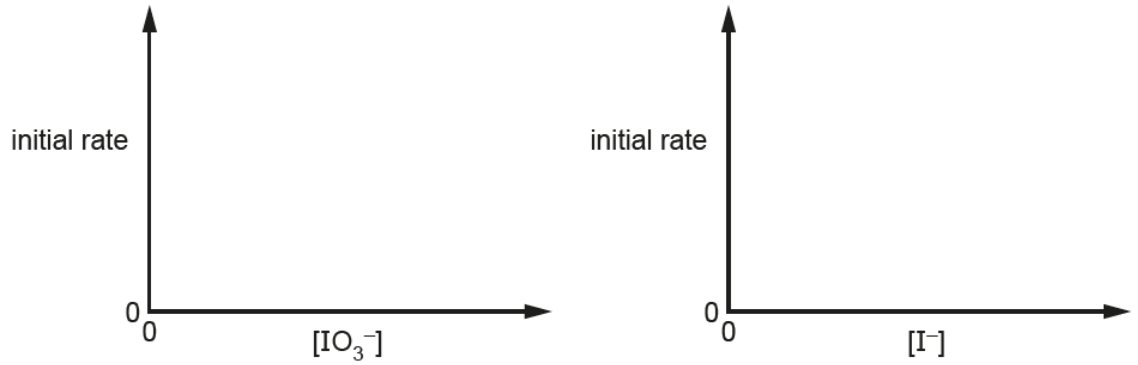
The rate equation for this reaction is rate = $k\,[IO_3^-][H+]^2[I^-]^2$.

Complete Table 3.2. [1]

the order of reaction with respect to $[IO_3^-]$	
the order of reaction with respect to $[H^+]$	

the order of reaction with respect to [I^-]	
the overall order of reaction	

(iii) Use your answer to **(ii)** to sketch lines in Fig. 3.1 to show the relationship between the initial rates and the concentrations of [IO_3^-] and [I^-]. [1]



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

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

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

[H^+] = ... mol dm^{-3} [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 $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$

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

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

$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$

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*.

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

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

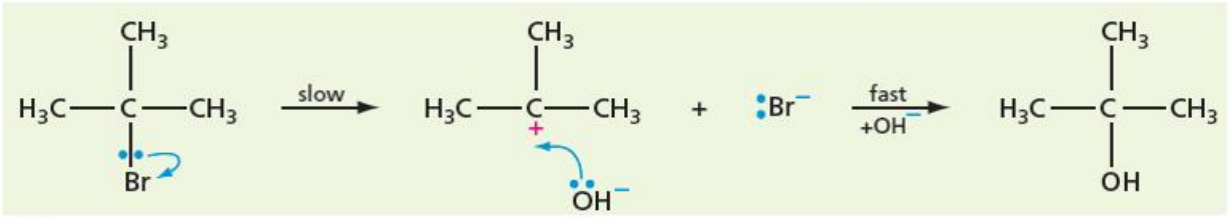
(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.
Use the expression x = $\frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x.

x = ... [1]

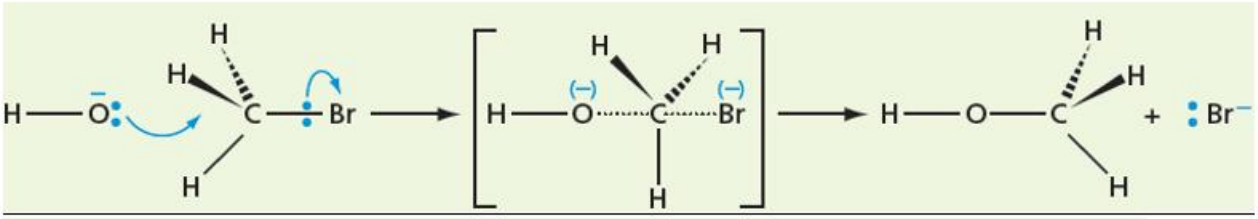
For a multi-step reaction

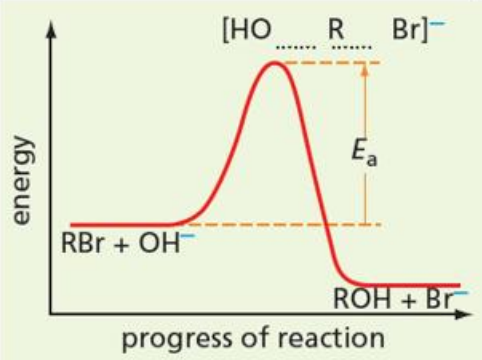
Rate-determining step: the slowest step in a reaction mechanism
Chem Demo: Reaction Mechanism and Rate - YouTube

SN1

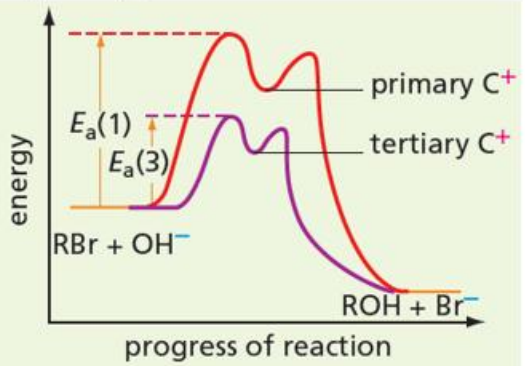


SN2





▲ Figure 16.10 Reaction profile for the S_N2 hydrolysis of bromomethane



▲ Figure 16.11 Reaction profiles for the S_N1 hydrolysis of primary and tertiary bromoalkanes

Predicting the reaction mechanism

The **overall reaction equation** and **rate equation** can be used to predict a possible reaction mechanism of a reaction

For example, nitrogen dioxide (NO_2) and carbon monoxide (CO) react to form nitrogen monoxide (NO) and carbon dioxide (CO_2)

The overall reaction equation is:

NO_2 (g) + CO (g) → NO (g) + CO_2 (g)

The rate equation is:

Rate = k [NO_2]

From the rate equation, it can be concluded that the reaction is **zero order** with respect to CO (g) and **second order** with respect to NO_2 (g)

This means that there are **two molecules** of NO_2 (g) involved in the **rate-determining step**

A possible reaction mechanism could therefore be:

Step 1:

$2NO_2$ (g) → NO (g) + NO_3 (g)slow (rate-determining step)

Step 2:

NO_3 (g) + CO (g) → NO_2 (g) + CO_2 (g)fast

Overall:

$2NO_2$ (g) + NO_3 (g) + CO (g) → NO_3 (g) + NO (g) + NO_2 (g) + CO_2 (g)

Which simplifies to **NO_2 (g) + CO (g) → NO (g) + CO_2 (g)**

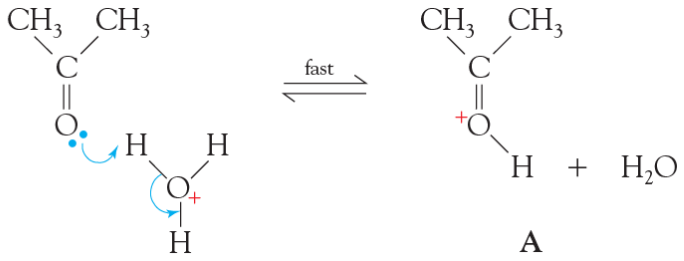
Proposing a mechanism

The rate equation is often used as a basis for suggesting a likely mechanism for the reaction. Most reactions can be broken down into a number of steps, one of which has a high activation energy that determines the overall rate of the reaction. This step is called the **rate-determining step**. An analogy is a group of people buying a paper at the local newsagent. If one person arrives, it takes them 1 second to pick up the paper, 10 seconds to pay for it and 1 second to leave the shop. If ten people arrive at the same time, it takes 10 seconds for them all to pick up their paper and 100 seconds for them all to pay, but they still take only 1 second each to leave the shop. There will be a queue to pick up the paper and at the checkout, but not on the way out of the shop. Any step that takes place after the rate-determining step has no effect on the overall rate. In the rate equation for the iodination of propanone,

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

iodine does not appear in the rate equation, so any step involving iodine must come after the rate-determining step. It is also reasonable to conclude that the first step is the reaction of a proton with propanone, as both H^+ and CH_3COCH_3 appear as first-order terms in the rate equation. This reaction is an acid–base reaction. Such reactions are usually fast and reversible (H^+ exists as H_3O^+ in aqueous solution). So we write:

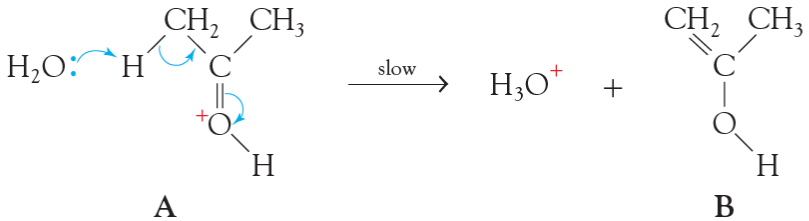
Reaction 1



A

The second step, involving the breaking of a C—H bond, probably controls the rate of the reaction: C—H bond breaking is known to be much slower than O—H bond breaking. In this step, a water molecule could act as a base, taking a proton off the protonated propanone and re-forming H_3O^+. A possible second step is therefore:

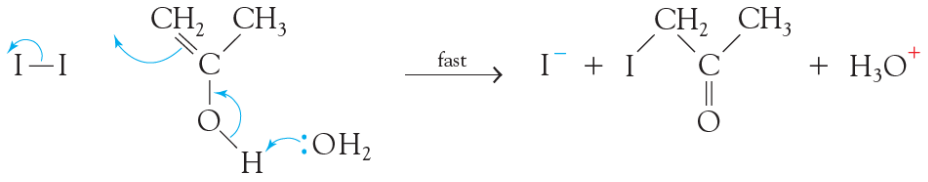
Reaction 2



A B

Iodine reacts rapidly with compounds containing the C═C group, so a fast step follows:

Reaction 3

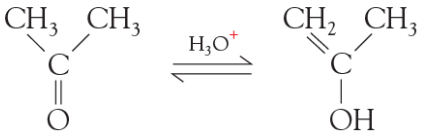


B

Adding up all the individual steps in the mechanism, we arrive at the overall stoichiometric equation:

$$I_2(aq) + CH_3COCH_3(aq) \rightarrow CH_2ICOCH_3(aq) + H^+(aq) + I^-(aq)$$

Mechanistically we can define a **homogeneous catalyst** as a substance that appears in the rate equation but not in the stoichiometric equation. If we consider just the first two steps, of which the second is the rate-determining step, H_3O^+ is a homogeneous catalyst.



Note, however, that the last of the three steps described above produces $H^+(aq)$, which, as we have seen, is the catalyst for the first two steps. A reaction which produces its own catalyst like this is called an **autocatalytic reaction**.

Substances such as:

are known as **intermediates**, because they are produced during the reaction but are not part of the final products.

[orders of reaction and mechanisms]

[Is it a Catalyst or an Intermediate? (Given Mechanism) - YouTube]

39. Define the term rate-determining step.

..... [1]

40. 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, $(NH_2)_2CO$, which decomposes on heating to isocyanic acid, HNCO, and ammonia.
reaction 1 $(NH_2)_2CO \rightarrow HNCO + NH_3$
Isocyanic acid reacts with water vapour to form ammonia and carbon dioxide.
reaction 2 $HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g)$
The ammonia formed in reactions 1 and 2 can be used to remove nitrogen dioxide from exhaust emissions, as shown.
reaction 3 $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$
Use the equations for reactions 1, 2 and 3 to construct an overall equation for the reduction of NO_2 by $(NH_2)_2CO$.

..... [1]

41. A four-step mechanism is suggested for the reaction between hydrogen peroxide and iodide ions in an acidic solution.
step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$
step 2 $H_+ + IO^- \rightarrow HIO$
step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

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.

H_2O_2 = ... I^- = ... H^+ = ... [1]

42. When $ClNO_2$ reacts with NO, an equilibrium is established.

$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$

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 mol dm^{-3} s^{-1}.

..... [1]

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

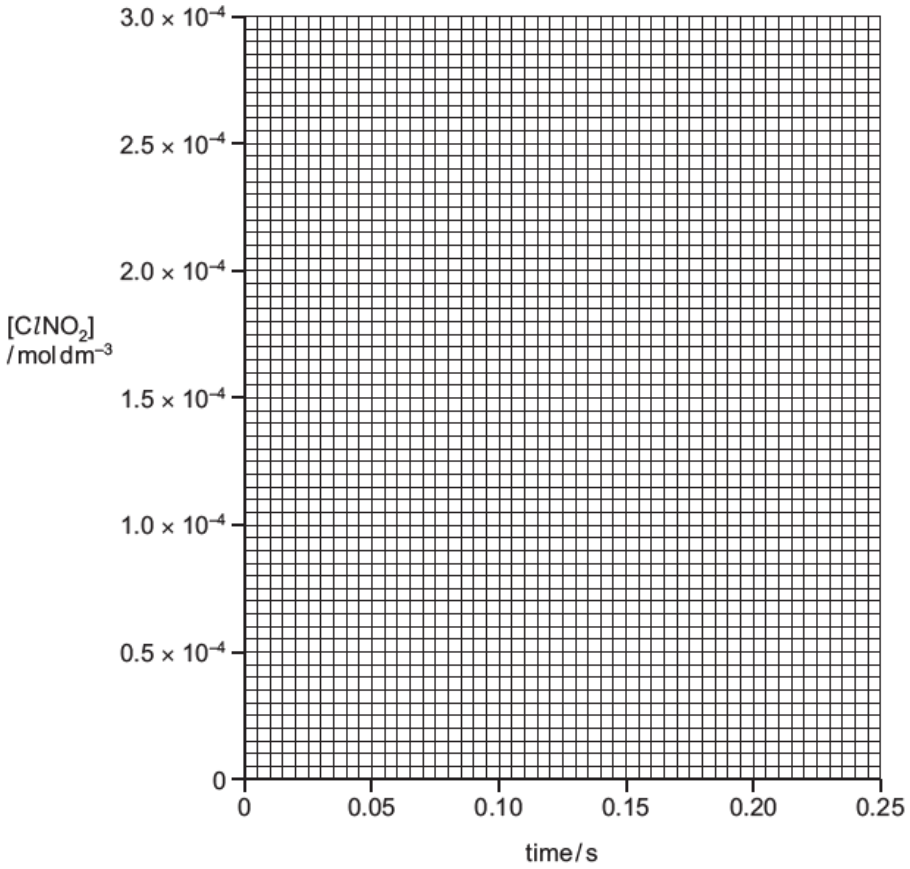
.....

.....

..... [1]

(c) An experiment is carried out in which the initial [Cl NO_2] is 2.0×10^{-4} mol dm^{-3}. A large excess of NO is used. The initial rate of reaction is 1.0×10^{-4} mol dm^{-3} 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]

43. In aqueous solution, iodide ions react with acidified hydrogen peroxide, as shown.

$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$

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.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step 2 $H^+ + IO^- \rightarrow HIO$

step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

(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.

.....

.....

..... [1]

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

.....

.....

..... [1]

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

$F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$

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 mol dm^{-3} 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 2.00×10^{-3} mol dm^{-3}.

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

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

rate = $k_1[F_2]$

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

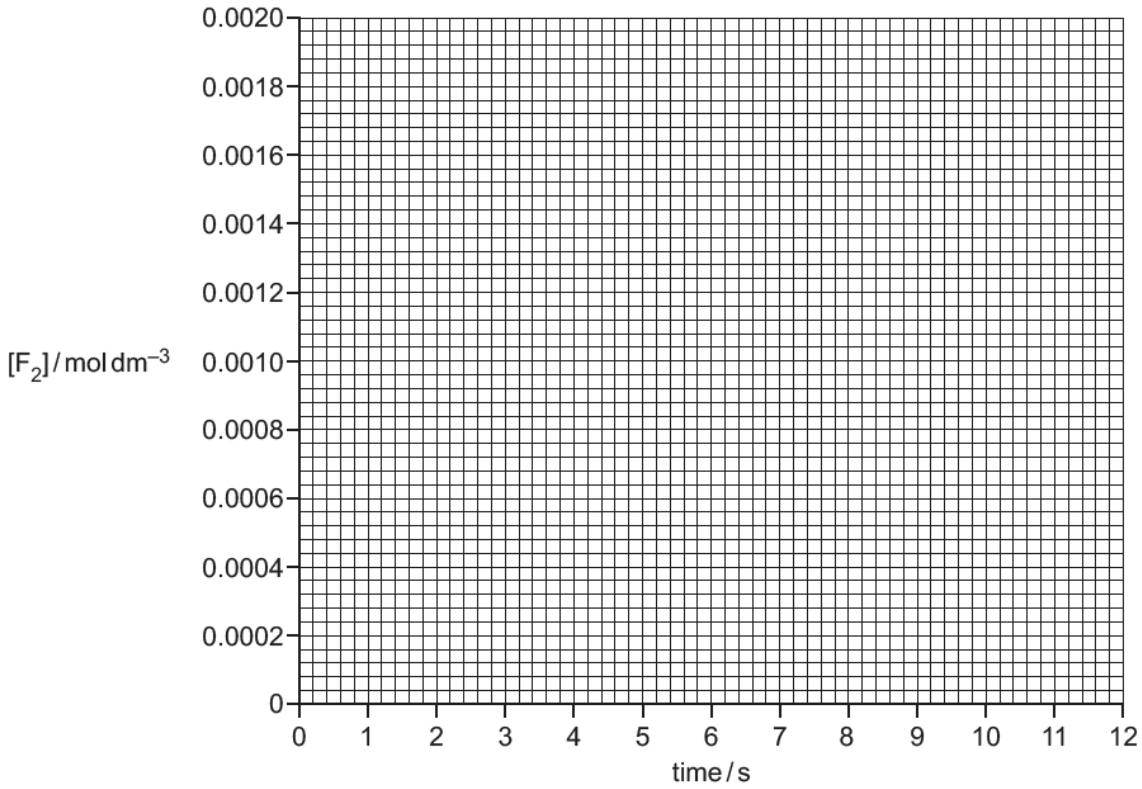
(i) Calculate the numerical value of k_1, giving its units.

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

k_1 = ... units .....[2]

(ii) An experiment is performed under these conditions in which the starting concentration of F_2 is 0.00200 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 mol dm^{-3}. Show your working on the graph.

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

45. A four-step mechanism is suggested for the overall reaction.
$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$ rate = k $[CH_3COCH_3][H^+]$
Part of this mechanism is shown.
step 1: $CH_3COCH_3 + H^+ \rightarrow CH_3C^+(OH)CH_3$
step 2: $CH_3C^+(OH)CH_3 \rightarrow CH_3C(OH)=CH_2 + H^+$
step 3:
step 4: $CH_3C^+(OH)CH_2I \rightarrow CH_3COCH_2I + H^+$
(i) Write an equation for step 3.

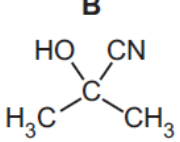
..... [1]
(ii) Suggest the slowest step of the mechanism. Explain your answer.

.....

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

conjugate acid ..... conjugate base ..... [1]

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

reaction 2 $CH_3COCH_3 + H^+ + CN^- \rightarrow$ **B** 

The following rate equation is determined for reaction 2.
rate = k $[CH_3COCH_3]$ [H+]

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

proposed reaction mechanism	steps	
1	fast	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	slow	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$
2	fast	$H^+ + CN^- \rightarrow HCN$
	slow	$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$
3	slow	$CH_3COCH_3 + CN^- \rightarrow CH_3C(O^-)(CN)CH_3$
	fast	$CH_3C(O^-)(CN)CH_3 + H^+ \rightarrow CH_3C(OH)(CN)CH_3$
4	slow	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	fast	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$

Suggest which of these mechanisms is consistent with the rate equation for reaction 2.
Explain your answer.
proposed reaction mechanism .....

explanation .....

.....

.....

..... [3]

47. Nitrogen dioxide, NO_2, reacts with ozone, O_2, as shown in reaction 2.
reaction 2 $2NO_2 + O_3 \rightarrow O_2 + N_2O_5$
The rate equation for reaction 2 is shown.
rate = k $[NO_2][O_3]$
(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.

..... [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 .....

step 2 ..... [2]

48. The compound nitrosyl bromide, NOBr, can be formed as shown in reaction 3.
reaction 3 $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$
The rate is first-order with respect to [NO] and first-order with respect to $[Br_2]$.
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]

49. Peroxodisulfate ions, $S_2O_8^{2-}$, react with iodide ions, I^-.
$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
The rate equation for the reaction in the absence of any catalyst is shown.
rate = k$[S_2O_8^{2-}][I^-]$
(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.

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

The initial rate of reaction is first order with respect to Fe^{3+} 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 .....

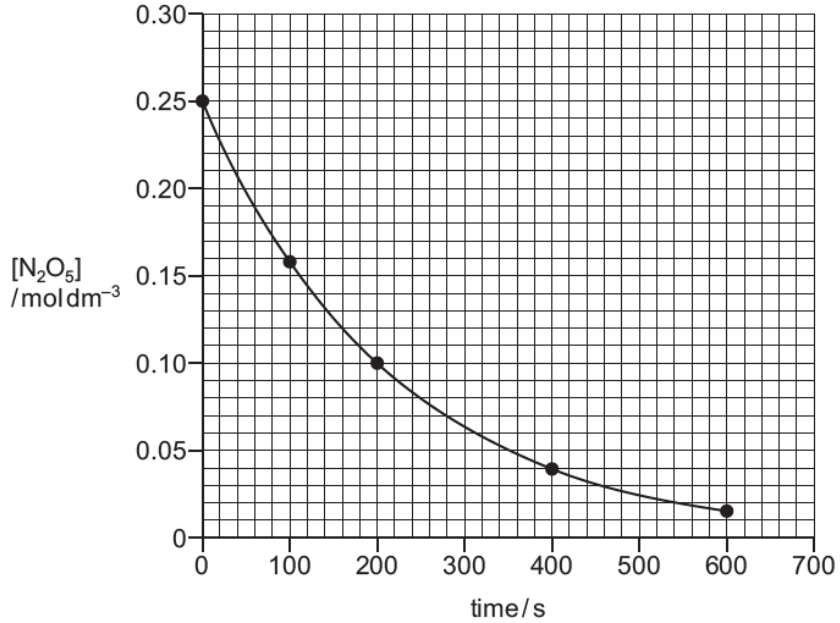
rate-determining step = ... [3]

50. 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.

$N_2O_5(solv) \rightarrow 2NO_2(solv) + \frac{1}{2} O_2(g)$

In an experiment, the rate of the decomposition of $N_5O_5(g)$ is investigated.

The graph shows the results obtained.



The reaction is first order with respect to N_5O_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_2O5 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.

rate = k $[N_2O_5]$

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

k = ... units ..... [1]

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

$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$

The rate equation for this reaction is rate = k $[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

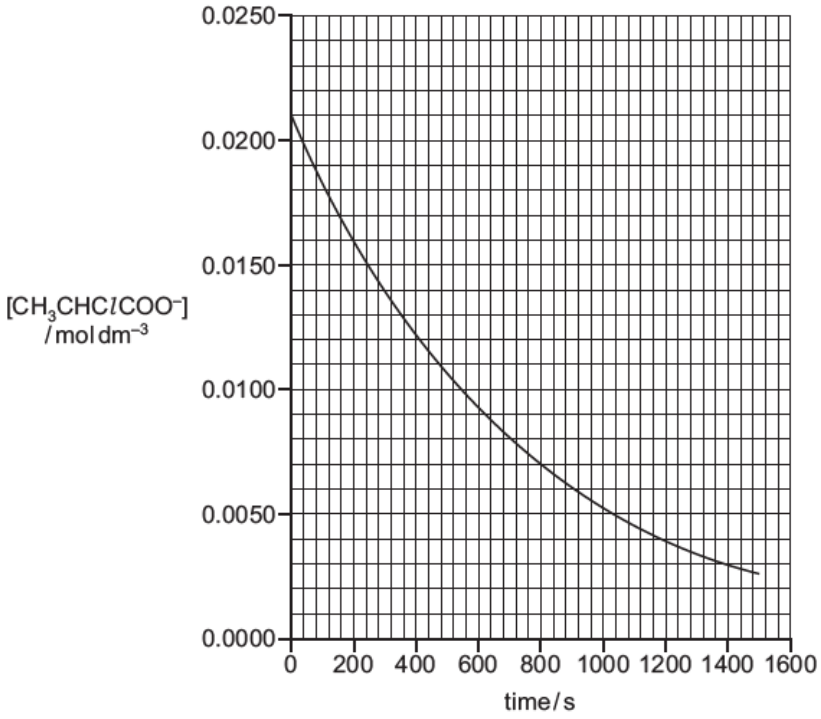
.....

..... [2]

51. In an excess of NH_3, $CH_3CHCl\ COO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $CH_3CHCl\ COO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

A student investigates the rate of reaction 2. The student mixes $CH_3CHCl\ COO^-$ 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 [$CH_3CHCl\ COO^-$].

….....

.....

.....

..... [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	[$CH_3CHCl\ COO^-$]/ mol dm^{-3}	[NH_3]/ mol dm^{-3}	initial rate of reaction/ mol dm^{-3} 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 SN^1 or an SN^2 mechanism.
Explain your answer.

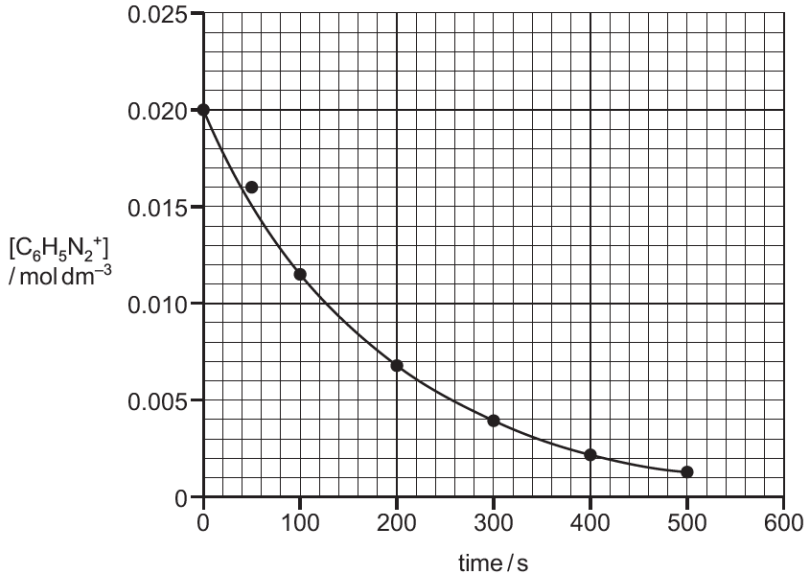
…….....

.....

.....

……..... [2]

52. The decomposition of benzenediazonium ions, $C_6H_5N_2^+$, using a large excess of water, is a first-order reaction. 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.

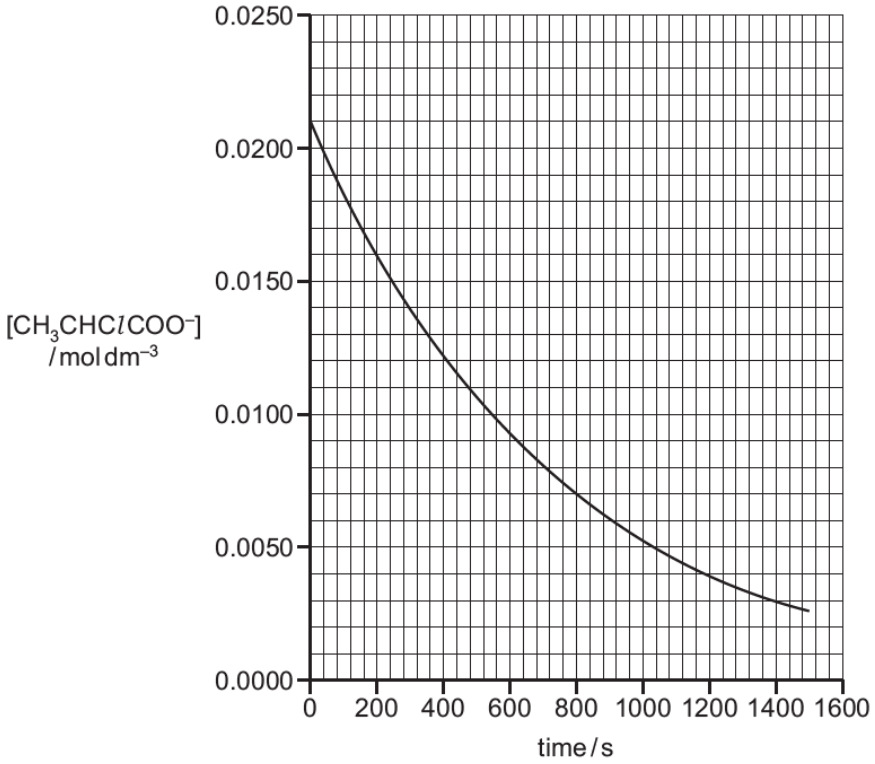
rate = ... mol dm^{-3} s^{-1} [1]

53. A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism.
The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.
reaction 1 $CH_3CHClCOOH + NH_3 \rightarrow CH_3CHClCOO^- + NH4+$
(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, $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.
reaction 2 $CH_3CHClCOO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$
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.



54. Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to [CH_3CHCl COO–].

.....

.....

.....

..... [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	[CH_3CHCl COO–]/ mol dm–3	[NH_3]/ mol dm–3	initial rate of reaction/ mol dm–3 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 SN1 or an SN2 mechanism.
Explain your answer.

.....

.....

.....

..... [2]

(vi) When an excess of CH_3CHCl COO– is used, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$.
Suggest the structure of $C_6H_9NO_4^{2-}$.[1]