1. Nov/2023/Paper_9701/41/No.1

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 $\rightarrow$

step 2 $\rightarrow$

[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 $2.00 \times 10^{-3}\,mol\,dm^{-3}$.

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.

$$\text{rate} = k_1[F_2]$$

The half-life, $t_{\frac{1}{2}}$, 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.

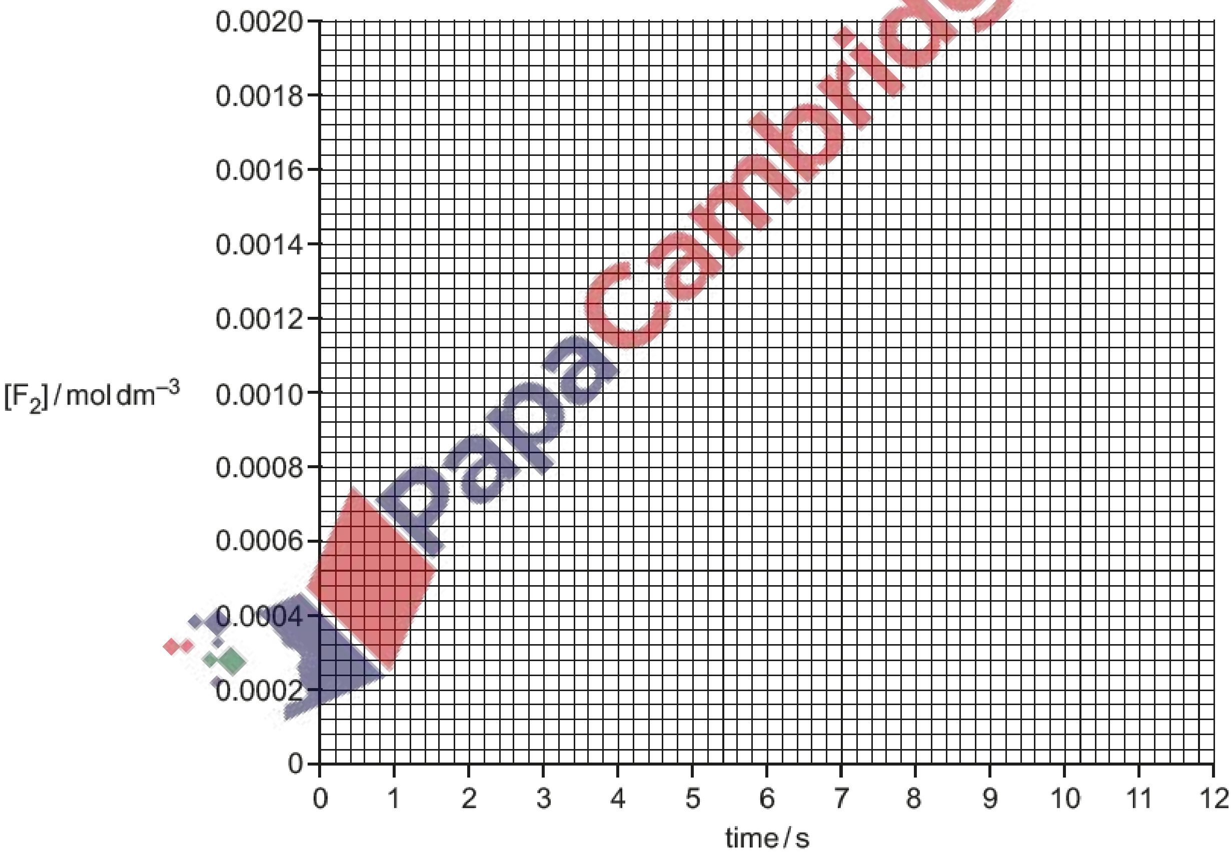


Fig. 1.1

[1]

(iii) 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]

[Total: 9]

2. Nov/2023/Paper_9701/41/No.3(d)

(d) The decomposition of H_2O_2(aq) is catalysed by aqueous iron(III) chloride and by silver metal.

Identify which of these two catalysts is acting as a homogeneous catalyst.

Explain your answer.

homogeneous catalyst ....

explanation ....

[1]

3. Nov/2023/Paper_9701/42/No.1

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.

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

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

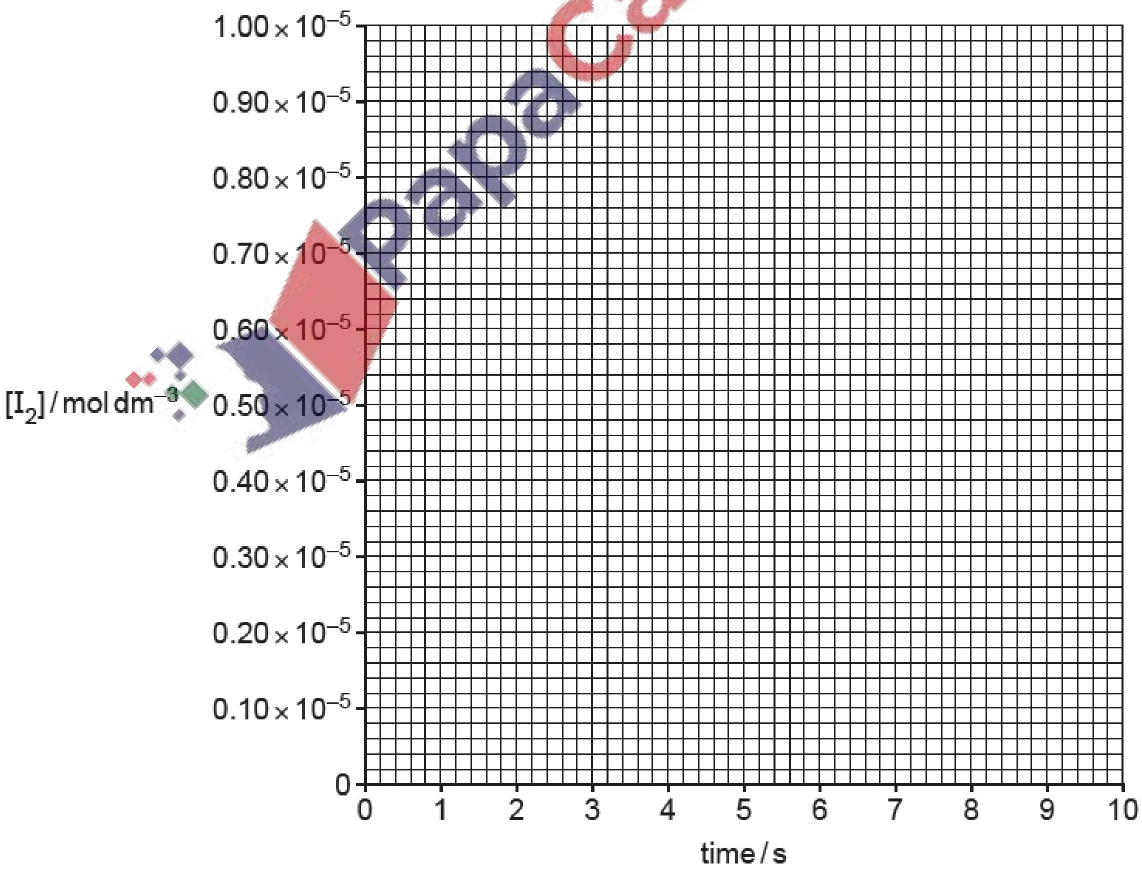
Table 1.1

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	

[2]

(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 $1.00 \times 10^{-5}\,\text{mol dm}^{-3}$. 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 $[I_2]$ against time for the first 10 seconds of the reaction.



[1]

(ii) 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]

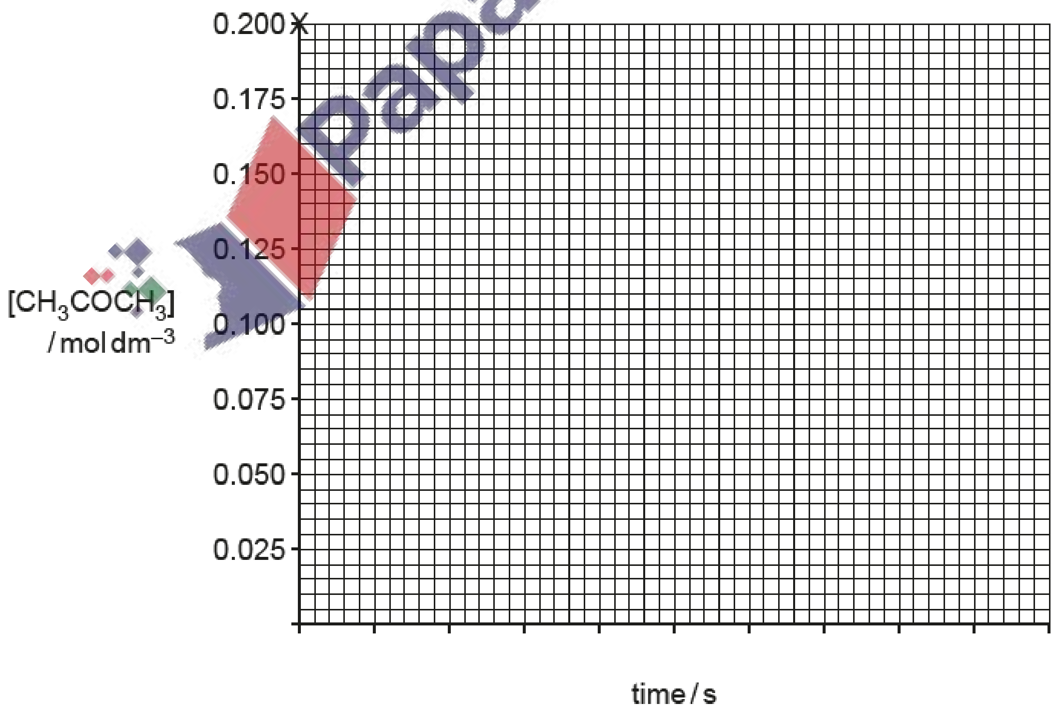
(d) The experiment is repeated using an excess of H^+(aq). The new rate equation is shown.

$$\text{rate} = k_1[CH_3COCH_3]$$

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

$t_{\frac{1}{2}}$ = ... 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}.



[1]

(e) 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: $\rightarrow$

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]

[Total: 10]

4. June/2023/Paper_9701/41/No.5(a)

(a) The exhaust systems of most modern gasoline-fuelled cars contain a catalytic converter with three metal catalysts.

These metals act as heterogeneous catalysts.

(i) Name **three** metal catalysts used in catalytic converters.

1 .... 2 .... 3 .... [1]

(ii) Explain what is meant by a heterogeneous catalyst.

....

.... [1]

5. June/2023/Paper_9701/41/No.3

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

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

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

Table 3.1

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

(i) Explain what is meant by order of reaction.

....

....

.... [1]

(ii) Complete Table 3.2.

Table 3.2

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	

[1]

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

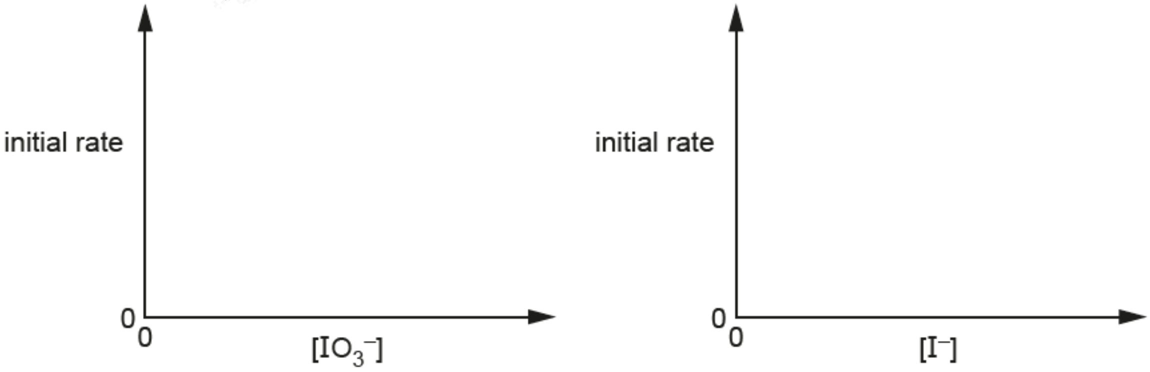


Fig. 3.1

[1]

(iv) 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 $\dfrac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$.

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

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

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

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]

[Total: 10]

6. June/2023/Paper_9701/42/No.4

(a) 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 Table 4.1.

Table 4.1

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) Explain what is meant by overall order of reaction.

....

....

.... [1]

(ii) 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]

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

rate = [1]

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

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

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

....

.... [1]

(b) 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	$OH^- + H^+ \rightarrow H_2O$

Fig. 4.1

(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]

[Total: 10]

7. March/2023/Paper_9701/42/No.2(c, d)

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

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

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

Table 2.1

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, V_m, 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]

(ii) The rate equation was found to be:

$$\text{rate} = k\,[H_2PO_2^-(aq)]\,[OH^-(aq)]^2$$

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 $OH^-(aq)$.

Under these conditions, the rate equation is:

$$\text{rate} = k_1\,[H_2PO_2^-(aq)]$$

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

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

$t_{\frac{1}{2}}$ = ... s [1]

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

....

.... [1]

(d) A student suggests that the reaction between $H_2PO_2^-(aq)$ and $OH^-(aq)$ might happen more quickly in the presence of a heterogeneous catalyst.

Describe the mode of action of a heterogeneous catalyst.

....

....

....

.... [2]