1. 9701/42/F/M/16 Q4

(a) Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

$[CH_3CHO]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate of reaction (relative values)
0.10	0.015	1
0.20	0.015	2
0.40	0.030	8

(i) Deduce the order of the reaction with respect to CH_3CHO.

.... [1]

(ii) Deduce the order of the reaction with respect to OH^-.

.... [1]

(iii) State the overall rate equation for this reaction.

rate = ... [1]

(iv) State the units for the rate constant, *k*.

.... [1]

(v) Calculate the initial rate of reaction (relative value) for a reaction where the $[CH_3CHO]$ is 0.30 mol dm^{-3} and $[OH^-]$ is 0.030 mol dm^{-3}.

[1]

Using your rate equation in **(iii)**, predict which is the rate-determining step.
Explain your answer.

rate-determining step ....

explanation ....

.... [2]

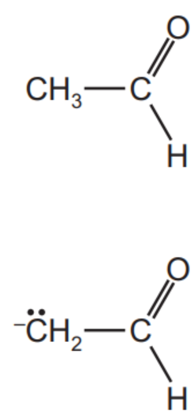
(ii) Describe the chemical behaviour of CH_3CHO in step 1.

.... [1]

(c) Name the mechanism occurring in steps 2 and 3.

.... [1]

(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.



[2]

[Total: 11]

2. 9701/41/O/N/17 Q1

The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

....

....

.... [2]

(b) Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

(c) The rate of the reaction was measured at various concentrations of the two reactants, NO and Br_2, and the following results were obtained.

experiment	[NO] / $mol\,dm^{-3}$	[Br_2] / $mol\,dm^{-3}$	initial rate / $mol\,dm^{-3}\,s^{-1}$
1	0.03	0.02	3.4×10^{-3}
2	0.03	0.04	6.8×10^{-3}
3	0.09	0.04	6.1×10^{-2}
4	0.12	0.06	to be calculated

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[NO]^a[Br_2]^b$$

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

....

.... [1]

(ii) Use the data in the table to deduce the values of *a* and *b* in the rate equation.
Show your reasoning.

....

....

....

.... [2]

(iii) Use the data in the table to calculate the initial rate for experiment 4.

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

(iv) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

rate constant, *k* = ... units .... [2]

(v) By considering the rate equation, explain why the rate decreases with decreasing temperature.

....

.... [1]

(d) The reaction between X and Y was studied.

$$2X + Y \rightarrow Z$$

The following sequence of steps is a proposed mechanism for the reaction.

step 1 $2X \rightarrow V$
step 2 $V + Y \rightarrow Z$

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[X]^m[Y]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of *m* and *n* in the rate equation.

m = ... *n* = ...
[1]

3. 9701/42/O/N/17 Q1

The compound chlorine dioxide, ClO_2, can be prepared by the reaction shown.

$$NaClO_2 + \tfrac{1}{2}Cl_2 \rightarrow ClO_2 + NaCl$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

....

....

.... [2]

(b) The central atom in the molecule of ClO_2 is chlorine.

Draw the 'dot-and-cross' diagram for ClO_2. Show outer electrons only.

[2]

(c) The reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The rate of the reaction was measured at various concentrations of the two reactants and the following results were obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[F_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.010	0.060	2.20×10^{-3}
2	0.025	0.060	to be calculated
3	to be calculated	0.040	7.04×10^{-3}

The rate equation is rate = $k[ClO_2][F_2]$.

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

....

.... [1]

(ii) Use the results of experiment 1 to calculate the rate constant, k, for this reaction. Include the units of k.

rate constant, k = ... units .... [2]

(iii) Use the data in the table to calculate

- the initial rate in experiment 2,

initial rate = ... $mol\,dm^{-3}\,s^{-1}$

- $[ClO_2]$ in experiment 3.

$[ClO_2]$ = ... $mol\,dm^{-3}$

[2]

(d) (i) What is meant by the term *rate-determining step*?

....

.... [1]

(ii) The equation for the reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

$$\text{rate} = k[ClO_2][F_2]$$

The mechanism for this reaction has two steps.

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

step 1 ....

step 2 ....

rate-determining step = ...

[2]

(e) By considering the rate equation, explain why the rate increases with increasing temperature.

....

.... [1]

[Total: 13]

4. 9701/41/M/J/17 Q6

The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, given the following.

- a solution of 0.10 mol dm^{-3} 1-chloro-1-phenylethane, labelled **A**
- a solution of 0.10 mol dm^{-3} sodium hydroxide, labelled **B**
- 0.10 mol dm^{-3} HCl
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

....

....

....

....

....

....

....

.... [4]

(b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[C_6H_5CHClCH_3]$ / $mol\,dm^{-3}$	$[OH^-]$ / $mol\,dm^{-3}$	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

(i) Deduce the order of reaction with respect to each of $[C_6H_5CHClCH_3]$ and $[OH^-]$. Explain your reasoning.

order with respect to $[C_6H_5CHClCH_3]$ ....

....

order with respect to $[OH^-]$ ....

.... [2]

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

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

units of *k* = ...
[1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(c) **(i)** Use your answers in **(b)(i)** to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

....

.... [1]

5. 9701/42/M/J/17 Q 2 c

(c) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[CH_3CH_2CHClCH_3]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

(i) Deduce the order of reaction with respect to each of $[CH_3CH_2CHClCH_3]$ and $[I^-]$. Explain your reasoning.

order with respect to $[CH_3CH_2CHClCH_3]$ ....

....

order with respect to $[I^-]$ ....

.... [2]

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

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

units of *k* = ... [1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(d) **(i)** Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

6. 9701/42/F/M/17 Q4

(a) Chlorine dioxide undergoes the following reaction in aqueous solution.

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

The initial rate of the reaction was measured at different initial concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / $mol\,dm^{-3}$	$[OH^-]$ / $mol\,dm^{-3}$	initial rate / $mol\,dm^{-3}\,s^{-1}$
1	1.25×10^{-2}	1.30×10^{-3}	2.33×10^{-4}
2	2.50×10^{-2}	1.30×10^{-3}	9.34×10^{-4}
3	2.50×10^{-2}	2.60×10^{-3}	1.87×10^{-3}

(i) Use the data in the table to determine the rate equation, showing the order with respect to each reactant. Show your reasoning.

....

....

....

....

....

....

rate equation = ...

[3]

(ii) Calculate the value of the rate constant, k, using the data from experiment 2. State its units.

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

(b) (i) Explain the difference between heterogeneous and homogeneous catalysts.

....

....

.... [1]

(ii) Complete the table using ticks (✓) to indicate whether the catalyst used in the reaction is heterogeneous or homogeneous.

catalysed reaction	heterogeneous	homogeneous
manufacture of ammonia in the Haber process		
removal of nitrogen oxides from car exhausts		
oxidation of sulfur dioxide in the atmosphere		

[2]

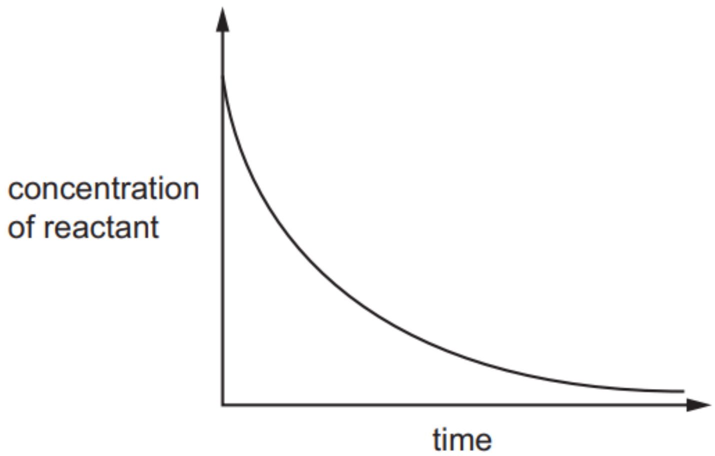
(c) Some reactions are catalysed by one of the products of the reaction. This is called autocatalysis. An example of autocatalysis is the reaction between acidified manganate(VII) ions, MnO_4^-, and ethanedioic acid, $(CO_2H)_2$. Mn^{2+} ions catalyse this reaction. The reaction is slow in the absence of a catalyst.

(i) Balance the equation for this reaction.

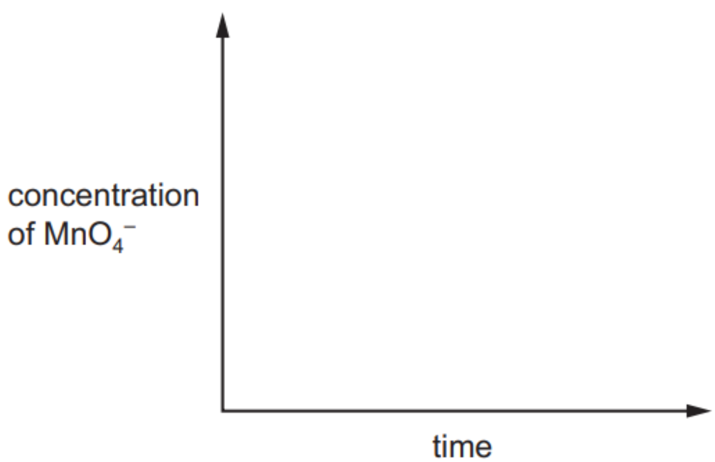
$$......MnO_4^- + ...H^+ + ...(CO_2H)_2 \rightarrow ......Mn^{2+} + ...CO_2 + ...H_2O$$

[2]

(ii) The graph shown is a concentration-time graph for a typical reaction.



On the axes below, sketch the curve you would expect for the autocatalysed reaction in **(i)**.



[2]

(d) (i) Describe, with the aid of a reaction pathway diagram, the effect of a catalyst on a reversible reaction. Suggest why catalysts are used in industrial processes.

....

....

....
[3]

(ii) The reaction for the Haber process to produce ammonia is shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92\,kJ\,mol^{-1}$$

At 500 °C, when pressure is measured in atmospheres, the numerical value of K_p for this equilibrium is 1.45×10^{-5}.

- Write the expression for K_p for this equilibrium.

K_p =

- Calculate the partial pressure of NH_3 at equilibrium at 500 °C, when the partial pressure of N_2 is 20 atm and that of H_2 is 60 atm.

p_{NH_3} = ... atm
[2]

[Total: 17]

7. 9701/41/M/J/18 Q2

Nitrogen monoxide, NO(g), reacts with hydrogen, H_2(g), under certain conditions.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

(a) Define the term *rate of reaction*.

....

.... [1]

(b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

.... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

The result of an experiment in which NO reacted with H_2 is shown in the table.

initial [NO] / mol dm^{-3}	initial [H_2] / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}

(c) Use the data and the rate equation to calculate a value for the rate constant *k*.
Give the units of *k*.

k = ...

units = ...
[2]

(d) A second experiment is performed at the same temperature. The initial concentration of $H_2(g)$ is 4.60×10^{-3} mol dm^{-3}. The initial rate of the reaction is 2.31×10^{-3} mol dm^{-3} s^{-1}.

Calculate the initial concentration of NO(g).

initial concentration of NO(g) = ... mol dm^{-3} [1]

(e) State the order of the reaction with respect to NO(g) and with respect to $H_2(g)$, and the overall order of the reaction.

[NO]	
$[H_2]$	
overall order	

[1]

(f) The reaction is believed to proceed in three steps.

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

(i) Deduce which of the three steps is the rate-determining step.

.... [1]

(ii) Explain your answer to **(i)**.

....

....

.... [1]

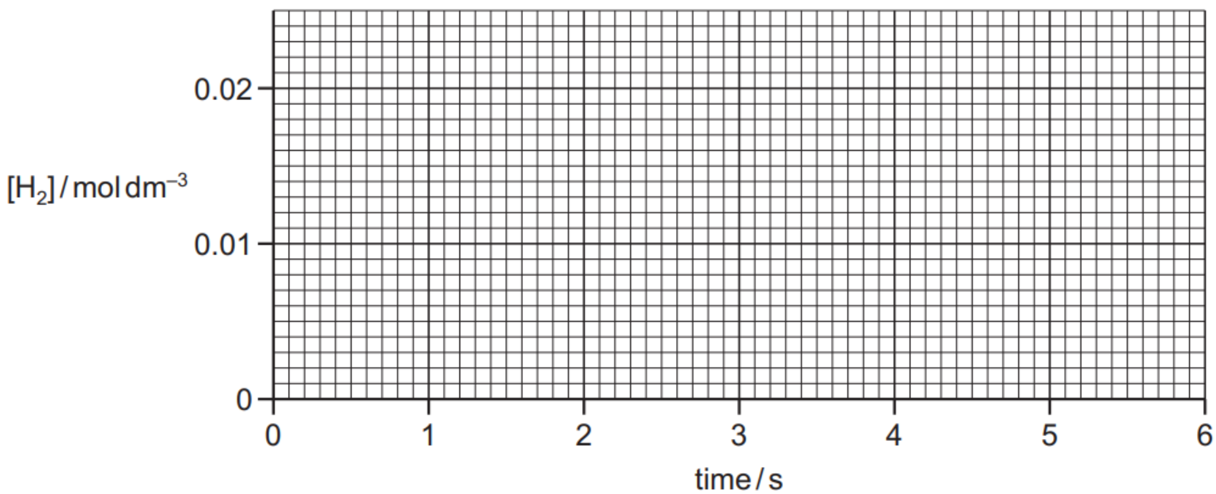
(g) A third experiment is performed under different conditions. A small amount of $H_2(g)$ of concentration 0.0200 mol dm^{-3} is mixed with a large excess of NO(g). The concentration of $H_2(g)$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

....

.... [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $H_2(g)$ during the first 6 seconds under the conditions used.



[2]

(h) NO(g) acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how NO(g) acts as a catalyst in this process.

equation 1 ....

equation 2 ....

[1]

(ii) Explain why NO(g) can be described as a catalyst in this reaction.

....

.... [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

....

.... [1]

[Total: 14]

8. 9701/42/M/J/18 Q2

Iodine monochloride, ICl, is a yellow-brown gas. It reacts with hydrogen gas under certain conditions as shown.

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

Experiments are performed using different starting concentrations of ICl and H_2. The initial rate of each reaction is measured. The following results are obtained.

experiment	$[ICl]$ / mol dm^{-3}	$[H_2]$ / mol dm^{-3}	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

(a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

.... [1]

(b) Use the data in the table to show that the reaction is first order with respect to $H_2(g)$.

....

....

....

.... [1]

(c) Use the data in the table to show that the reaction is first order with respect to $ICl(g)$.

....

....

....

.... [1]

(d) Complete the rate equation for the reaction between $ICl(g)$ and $H_2(g)$.

rate = ... [1]

(e) Use experiment 3 to calculate a numerical value for the rate constant, *k*.

k = ... [1]

(f) The reaction $2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$ is first order with respect to $ICl(g)$ and first order with respect to $H_2(g)$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step .... $\rightarrow$ ....

second step .... $\rightarrow$ ....

[2]

(g) An alternative method is used to show that the reaction is first order with respect to $H_2(g)$. This method uses a large excess of $ICl(g)$ and measures how the concentration of $H_2(g)$ varies with time.

(i) Describe two ways of using these results to show the reaction is first order with respect to $H_2(g)$ concentration.

....

....

....

....

....

.... [3]

(ii) Explain the reason for using a large excess of $ICl(g)$.

....

.... [1]

(h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

....

.... [1]

9. 9701/43/M/J/18 Q2

Nitrogen monoxide, $NO(g)$, reacts with hydrogen, $H_2(g)$, under certain conditions.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

(a) Define the term *rate of reaction*.

....

.... [1]

(b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

.... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

The result of an experiment in which NO reacted with H_2 is shown in the table.

initial [NO] / $mol\,dm^{-3}$	initial [H_2] / $mol\,dm^{-3}$	initial rate of reaction / $mol\,dm^{-3}\,s^{-1}$
2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}

(c) Use the data and the rate equation to calculate a value for the rate constant *k*.
Give the units of *k*.

k = ...

units = ...
[2]

(d) A second experiment is performed at the same temperature. The initial concentration of $H_2(g)$ is 4.60×10^{-3} mol dm^{-3}. The initial rate of the reaction is 2.31×10^{-3} mol dm^{-3} s^{-1}.

Calculate the initial concentration of NO(g).

initial concentration of NO(g) = ... mol dm^{-3} [1]

(e) State the order of the reaction with respect to NO(g) and with respect to $H_2(g)$, and the overall order of the reaction.

[NO]	
[H_2]	
overall order	

[1]

(f) The reaction is believed to proceed in three steps.

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

(i) Deduce which of the three steps is the rate-determining step.

.... [1]

(ii) Explain your answer to **(i)**.

....

....

.... [1]

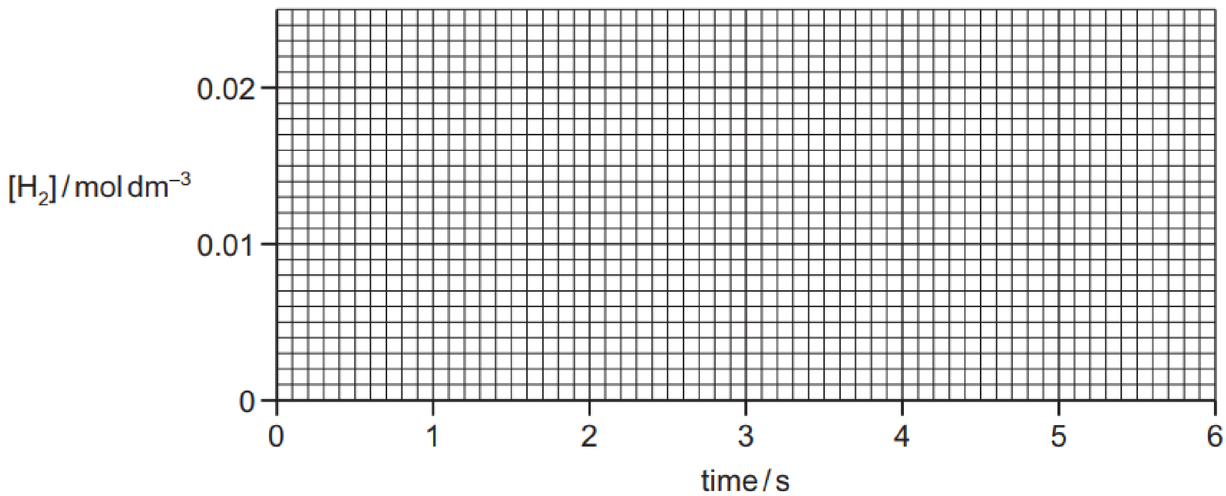
(g) A third experiment is performed under different conditions. A small amount of H_2(g) of concentration 0.0200 mol dm^{-3} is mixed with a large excess of NO(g). The concentration of H_2(g) is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

....

.... [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of H_2(g) during the first 6 seconds under the conditions used.



[2]

(h) NO(g) acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how NO(g) acts as a catalyst in this process.

equation 1 ....

equation 2 ....

[1]

(ii) Explain why NO(g) can be described as a catalyst in this reaction.

....

.... [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

....

.... [1]

[Total: 14]

10. 9701/41/O/N/19 Q2

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.

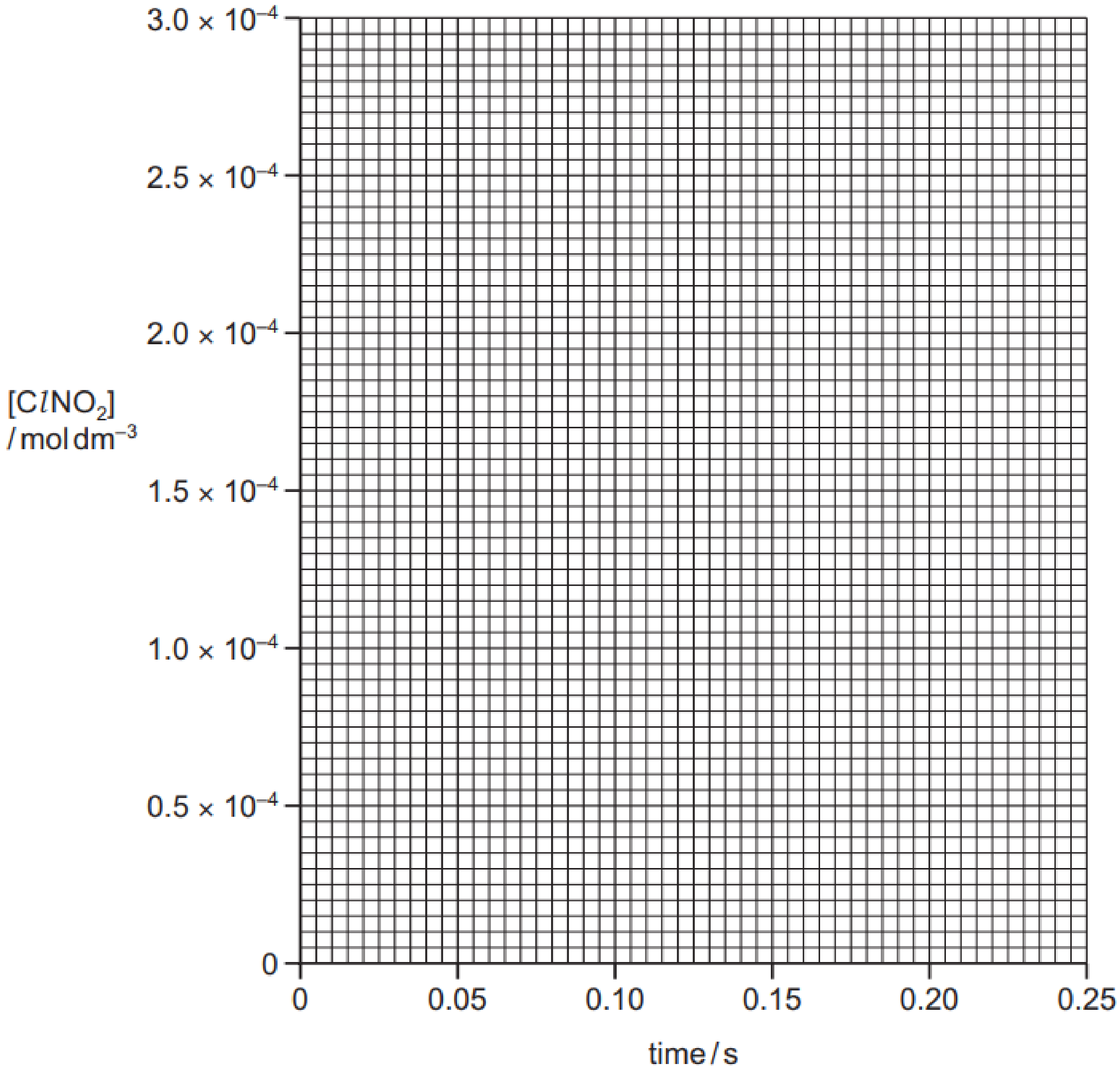
....

....

.... [1]

(c) An experiment is carried out in which the initial [ClNO$_2$] 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]

[Total: 9]

11. 9701/42/O/N/19 Q2

(a) Explain what is meant by the following terms.

half-life of a reaction ....

....

rate-determining step ....

....
[2]

(b) The reaction between hydroxide ions and bromomethane is first order with respect to $[OH^-]$ and first order with respect to $[CH_3Br]$.

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

Suggest a practical method that would confirm that the reaction is first order with respect to $[OH^-]$.

- Your method should include details of measurements that would be taken in order to calculate the rate of the reaction.
- You should include a method of presenting the results to show that the reaction is first order with respect to $[OH^-]$.

....

....

....

....

....

....

....

....

....

....

....

.... [4]

(c) The hydrolysis of methyl ethanoate, $CH_3CO_2CH_3$, by hydroxide ions, OH^-, is first order with respect to $[CH_3CO_2CH_3]$ and also first order with respect to $[OH^-]$.

In a particular experiment,

- $[CH_3CO_2CH_3] = 0.100\,mol\,dm^{-3}$
- $[OH^-] = 0.100\,mol\,dm^{-3}$
- rate of reaction = $2.06 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$.

Write a rate equation for this reaction and calculate the value of the rate constant, *k*, under these conditions. State the units of *k*.

rate = ...

k = ... units = ...

[3]

[Total: 9]

12. 9701/41/M/J/19 Q5

(a) Chlorate(I) ions undergo the following reaction under aqueous conditions.

$$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$$

A series of experiments was carried out at different concentrations of ClO^- and NH_3.

The table shows the results obtained.

experiment	$[ClO^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

(i) Use the data in the table to determine the order with respect to each reactant, ClO^- and NH_3.

Show your reasoning.

....

....

....

....

....

.... [2]

(ii) Write the rate equation for this reaction.

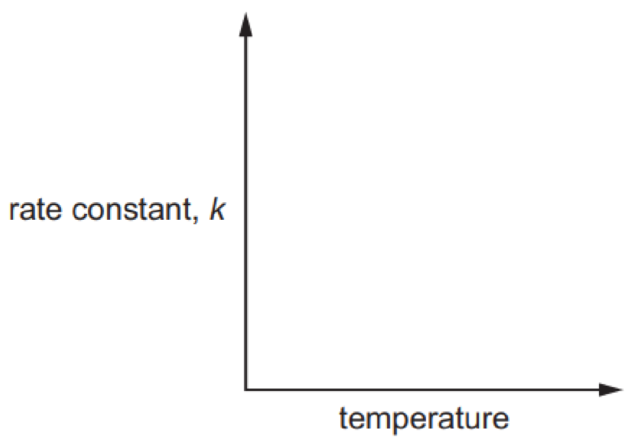
rate = ... [1]

(iii) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ...

units = ...
[2]

(iv) On the axes sketch a graph to show how the value of *k* changes as temperature is increased.



[1]

(b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

(i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

....

....

.... [2]

A three-step mechanism for this reaction is shown.

step 1 $ClO^- + H_2O \rightarrow HClO + OH^-$

step 2 $I^- + HClO \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(ii) Use this mechanism to deduce the overall equation for this reaction.

.... [1]

(iii) Identify a step that involves a redox reaction. Explain your answer.

....

.... [1]

[Total: 10]

13. 9701/42/M/J/19 Q4

The initial rate of reaction for propanone and iodine in acid solution is measured in a series of experiments at a constant temperature.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+ \text{ catalyst}} CH_3COCH_2I + HI$$

The rate equation was determined experimentally to be as shown.

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

(a) State the order of reaction with respect to

- CH_3COCH_3 ....
- I_2 ....
- H^+ ....

and state the overall order of this reaction. ....
[2]

(b) The rate of this reaction is $5.40 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$ when

- the concentration of CH_3COCH_3 is $1.50 \times 10^{-2}\,mol\,dm^{-3}$
- the concentration of I_2 is $1.25 \times 10^{-2}\,mol\,dm^{-3}$
- the concentration of H^+ is $7.75 \times 10^{-1}\,mol\,dm^{-3}$.

(i) Calculate the rate constant, k, for this reaction. State the units of k.

k = ...

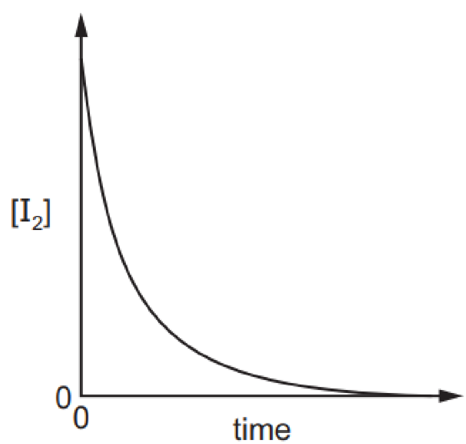
units = ... [2]

(ii) Complete the table by placing **one** tick (✓) in each row to describe the effect of **decreasing** the temperature on the rate constant and on the rate of reaction.

	decreases	no change	increases
rate constant			
rate of reaction			

[1]

(c) From the results, a graph is produced which shows how the concentration of I_2 changes during the reaction.



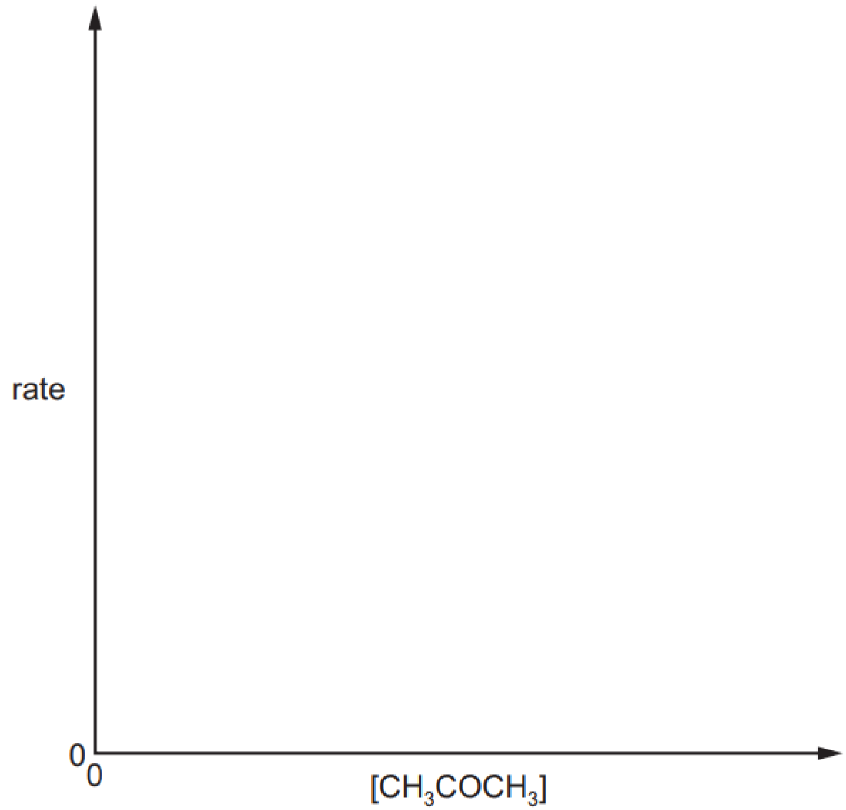
Describe how this graph could be used to determine the initial rate of the reaction.

....

....

.... [2]

(d) On the axes below, sketch a graph to show how the initial rate changes with different initial concentrations of CH_3COCH_3 in this reaction.



[1]

(e) The rate of a reaction between metal ions was studied. The following three-step mechanism has been suggested for this reaction. Step 1 is the rate-determining step.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

step 3 $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

(i) Explain the meaning of the term *rate-determining step*.

....

.... [1]

(ii) Use this mechanism to

- determine the overall equation for this reaction

....

- suggest the role of Mn^{2+} ions in this mechanism. Explain your answer.

....

....

....

[2]

[Total: 11]

14. 9701/42/F/M/19 Q1(d)

(d) 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* = ...

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

15. 9701/41/O/N/20 Q1

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

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

The rate equation for the forward reaction is shown.

$$\text{rate} = k[NO]^2[O_2]$$

(a) Complete the following table.

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

[1]

(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]

(c) Define the term *rate-determining step*.

.... [1]

(d) 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.

$$\text{rate} = k[S_2O_8^{2-}][I^-]$$

(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.

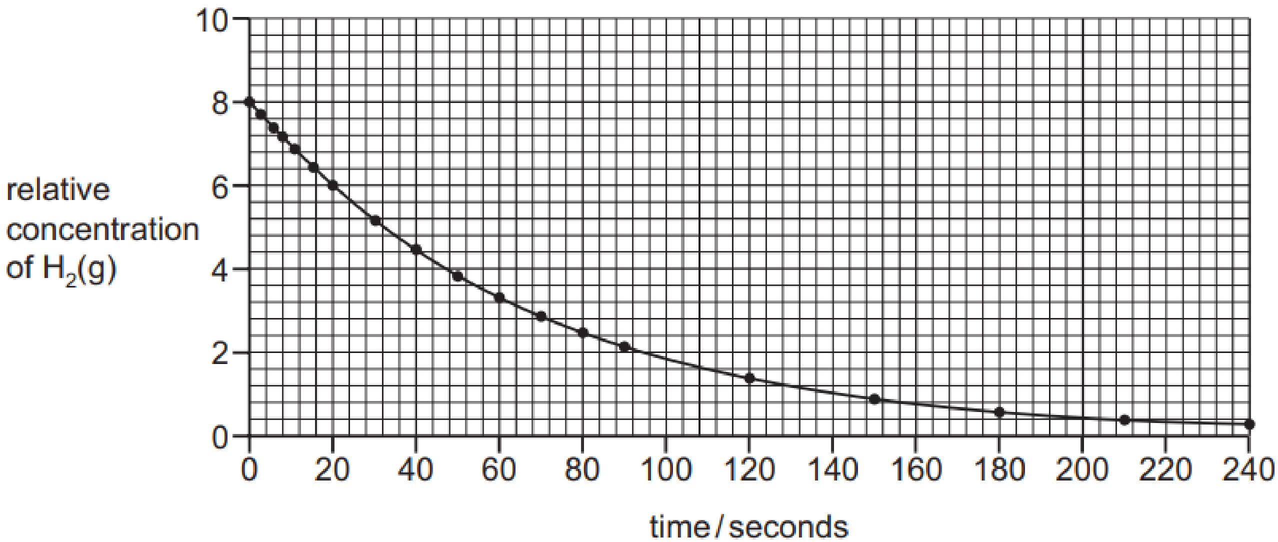
iodide ion concentration = ... $mol\,dm^{-3}$ [1]

[Total: 8]

16. 9701/42/O/N/20 Q1

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.

....

....

....

.... [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.

....

....

....

.... [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]

(c) At 400 K the rate constant for the forward reaction is approximately 1000 times greater than the rate constant for the backward reaction. The overall orders of the forward and backward 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 backward 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 backward reaction.

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

....

....

....

.... [2]

[Total: 12]

17. 9701/41/M/J/20 Q9c

(c) 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) State what is meant by the term *rate-determining step*.

....

.... [1]

(ii) 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]

18. 9701/42/F/M/20 Q3(b)

(b) Aqueous gold(III) chloride, $AuCl_3$, reacts with aqueous hydrogen peroxide, H_2O_2, under certain conditions, forming Au, O_2 and HCl.

A student carries out separate experiments using different initial concentrations of $AuCl_3$ and H_2O_2. The initial rate of each reaction is measured.

The table shows the results that are obtained.

experiment	$[AuCl_3]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}	rate of production of O_2(g) / dm^3 minute^{-1}
1	0.05	0.50	7.66×10^{-2}
2	0.10	0.50	1.53×10^{-1}
3	0.15	1.00	4.60×10^{-1}

(i) Write an equation for the reaction of $AuCl_3$ with H_2O_2.

.... [1]

(ii) Determine the rate equation of the reaction.

Show your reasoning, quoting data from the table.

....

....

....

....

.... [3]

(iii) Use the results of experiment 2 to calculate the value of the rate constant, k, for this reaction.

Include the units of k.

rate constant, k = ...

units = ...
[2]

19. 9701/41/M/J/21 Q5

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.

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

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

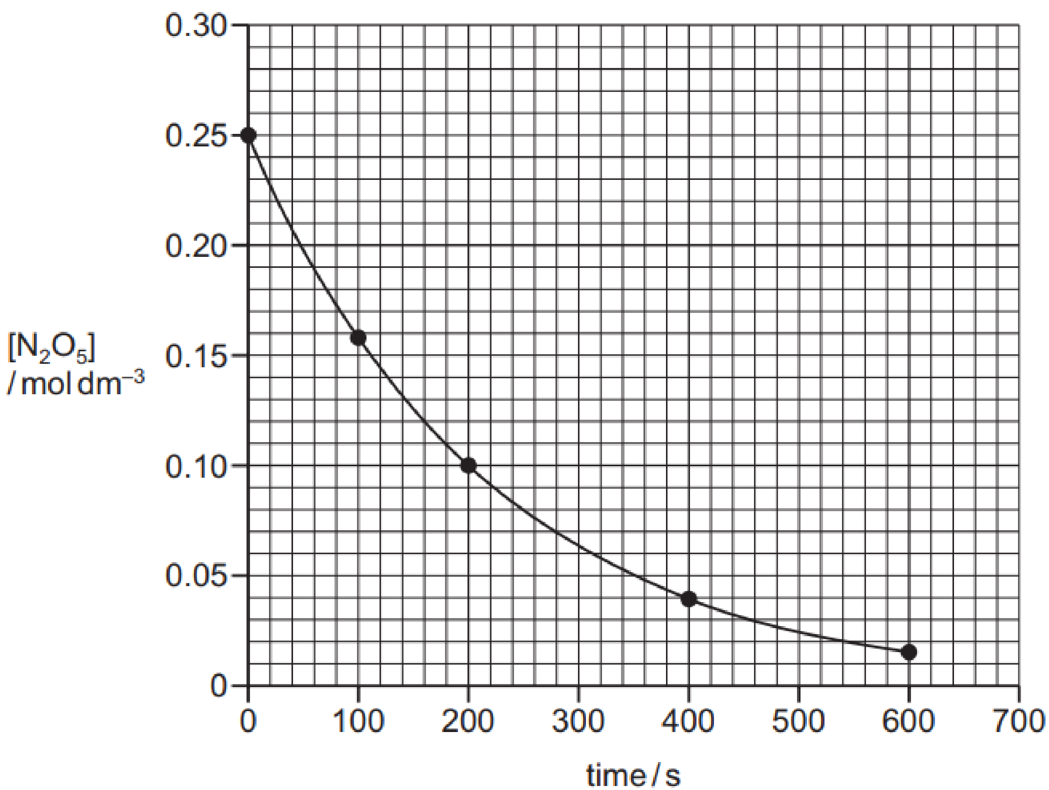
....

.... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

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

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.

(i) Explain the term *half-life of a reaction*.

....

.... [1]

(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.

$$\text{rate} = k[N_2O_5]$$

(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]

[Total: 9]

20. 9701/42/M/J/21 Q7

(a) 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) Explain the term *order of reaction*.

....

.... [1]

(ii) 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]

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

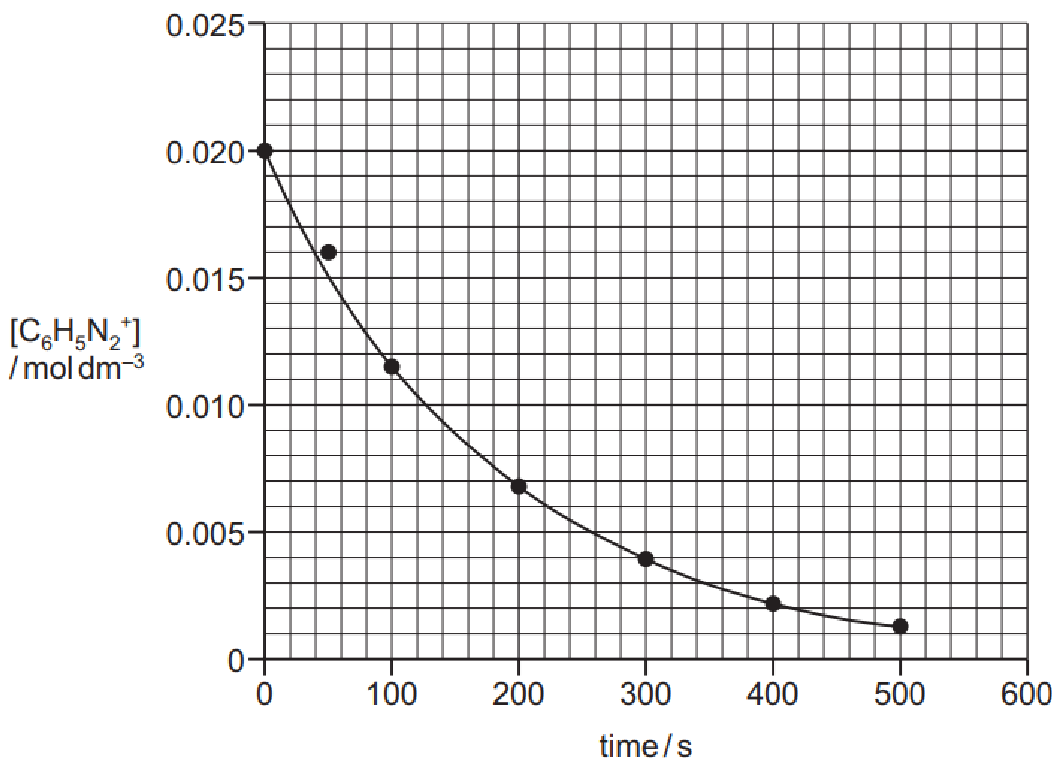
rate = ... [1]

(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]

(b) 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.

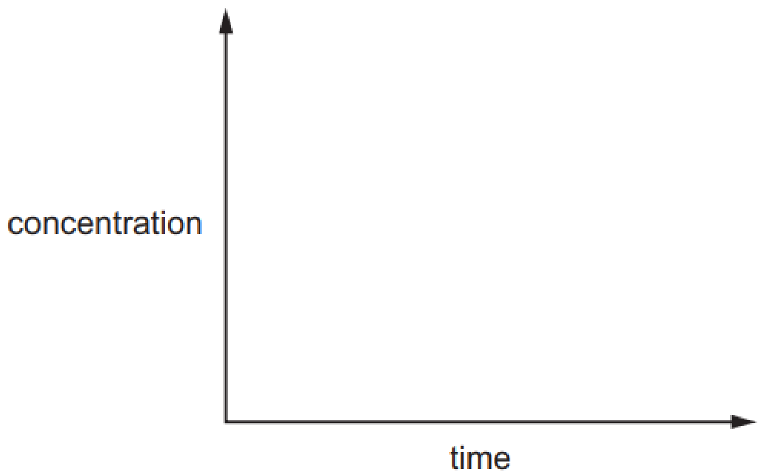
[1]

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

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

(c) 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.



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

[1]

[Total: 9]

21. 9701/42/F/M/21 3d

(d) 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 $[H_2O_2]$ = ...

....

....

....

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

....

....

....

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

....

....

....
[3]

(ii) Use your answer to **(d)(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 **(d)(ii)**.

Give the units of k.

k = ...

units = ...
[2]

22. 9701/41/O/N/22 Q2

(a) (i) Explain what is meant by the following terms:

homogeneous catalyst ....

....

heterogeneous catalyst ....

....
[1]

(ii) Iodide ions react with peroxydisulfate ions.

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

This reaction is slow, but it is catalysed by Fe^{2+} ions.

Write two equations to explain how this reaction is catalysed by Fe^{2+} ions.

1 ....

2 ....
[2]

(iii) Suggest why the alternative route in the presence of Fe^{2+} ions has a lower activation energy than the route in the absence of a catalyst.

....

.... [1]

(b) 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 $8.60 \times 10^6\,mol^{-2}\,dm^6\,s^{-1}$.

(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 $7.20 \times 10^{-4}\,mol\,dm^{-3}$ and the initial concentration of oxygen is $1.90 \times 10^{-3}\,mol\,dm^{-3}$.

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

(c) 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.

$$\text{rate} = k[Pt(NH_3)_2Cl_2]$$

The value of k is $2.50 \times 10^{-5}\,s^{-1}$ 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 $2.77 \times 10^4\,s$.

[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 $2.50 \times 10^{-6}\,mol\,dm^{-3}$.

time taken = ... s [2]

23. 9701/42/O/N/22 Q2

(a) 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 $k = 11\,500\ \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$.

(i) Complete the rate equation for this reaction.

rate = ...

[1]

(ii) A reaction is carried out in which the initial concentrations of NO and O_3 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 **(a)(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 ....

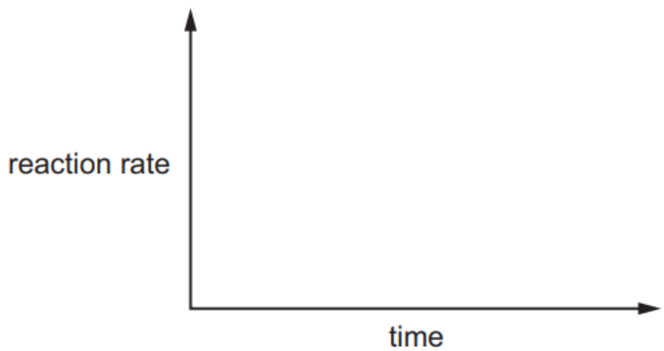
.... [1]

(b) Nitrous oxide, N_2O, decomposes into its elements.

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

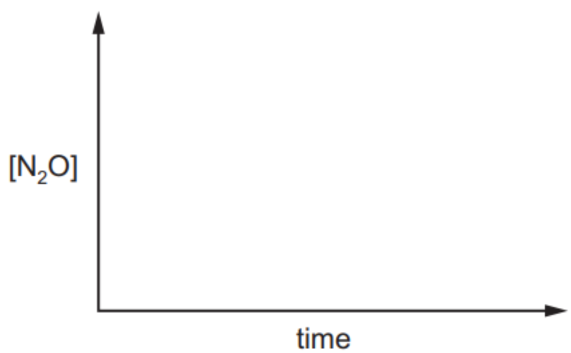
At a high temperature, a small amount of platinum wire is added to a large amount of nitrous oxide. The reaction follows zero order kinetics. The platinum wire behaves as a catalyst.

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



[1]

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



[1]

(iii) Platinum behaves as a heterogeneous catalyst in this reaction.

Describe the mode of action of a heterogeneous catalyst.

....

....

....

.... [3]

(iv) Suggest a reason why this reaction has zero order kinetics when the amount of nitrous oxide is large and the amount of platinum is small.

....

.... [1]

24. 9701/43/M/J/22 Q3

(a) 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.

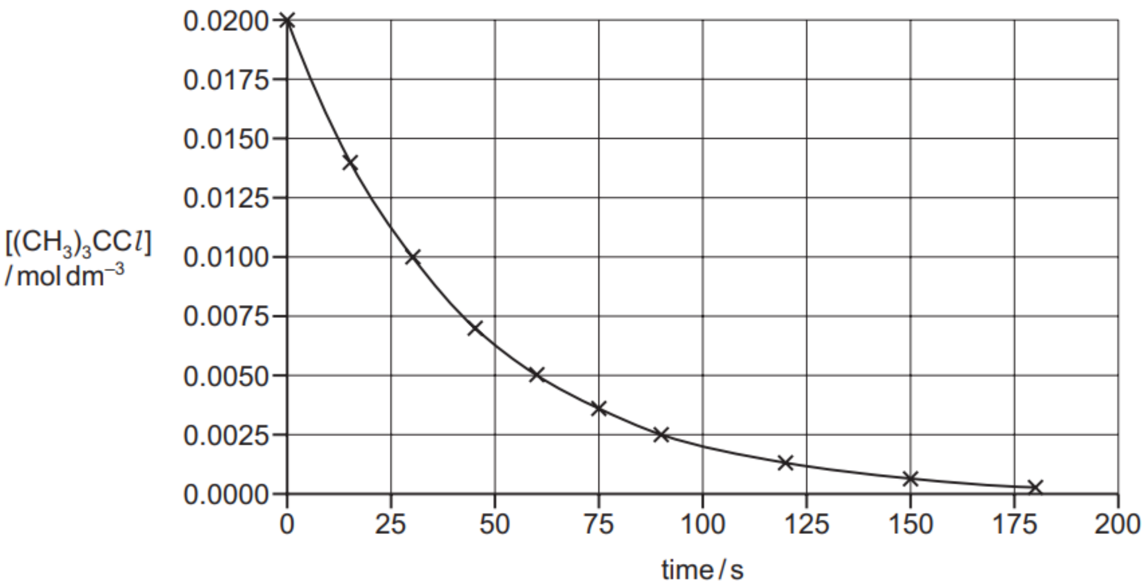


Fig. 3.1

(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]