SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Bromine, Br_2, reacts with propanone, CH_3COCH_3, in aqueous solution.

$$Br_2(aq) + CH_3COCH_3(aq) \rightarrow HBr(aq) + CH_3COCH_2Br(aq)$$

(i) If the initial bromine concentration, $[Br_2(aq)]$, was $0.0020\,mol\,dm^{-3}$ and the Br_2 was completely used up in 17 min 30 seconds, calculate the rate of the reaction (including units). [2]

(ii) Outline one method which could be used to determine the rate for this reaction. [2]

(iii) The following results were obtained when propanone and bromine were reacted in acid solution.

Rate of reaction / $mol\,dm^{-3}\,min^{-1}$	$[Br_2(aq)]$ / $mol\,dm^{-3}$	$[CH_3COCH_3(aq)]$ / $mol\,dm^{-3}$
6.80×10^{-5}	0.10	0.40
1.36×10^{-4}	0.10	0.80
1.36×10^{-4}	0.20	0.80

Determine the orders of reaction with respect to $Br_2(aq)$ and with respect to $CH_3COCH_3(aq)$. [2]

(iv) A separate experiment was carried out to determine the effect of pH on the rate of reaction.

Rate of reaction / $mol\,dm^{-3}\,min^{-1}$	$[Br_2(aq)]$ / $mol\,dm^{-3}$	$[CH_3COCH_3(aq)]$ / $mol\,dm^{-3}$	pH
1.36×10^{-3}	0.10	0.80	0
1.36×10^{-4}	0.10	0.80	1
1.36×10^{-5}	0.10	0.80	2

I State how the rate of reaction varies with change in pH. [1]

II Using the table, show that the reaction is first order with respect to H^+ ions. [1]

III State the role of H^+ ions in the reaction. [1]

IV Write the full rate equation for the reaction, giving the units for the rate constant. [2]

(QWC) [1]

3. *Read the passage below and then answer questions (a) to (c) in the spaces provided.*

The oxides of nitrogen

The atmosphere around us consists principally of two elements – nitrogen gas, N_2, and oxygen gas, O_2. The relative stability of this mixture of two elements hides the fact that the elements can combine to form a number of oxides of nitrogen. Their original names are shown below.

Dinitrogen monoxide	N_2O
Nitrogen monoxide	NO
Dinitrogen trioxide	N_2O_3
Nitrogen dioxide	NO_2
Dinitrogen tetroxide	N_2O_4
Dinitrogen pentoxide	N_2O_5
Nitrogen trioxide	NO_3

Many of these oxides are useful but several can also cause environmental problems.

Dinitrogen monoxide, N_2O

This gas was one of the first gaseous compounds to be identified and is probably one of the best known of the oxides of nitrogen. Commonly called 'laughing gas', due to the behaviour of those exposed to the gas, this oxide has since been used as an anaesthetic. It was initially used for the relief of pain during dental treatment and it remained one of the dentist's most useful aids for over a century. It was also commonly used to relieve the pain of childbirth due to the rarity of any adverse reactions to the gas.

Nitrogen dioxide, NO_2

Nitrogen dioxide is a brown gas with a notable sharp odour. It can prove toxic by inhalation. The properties of the pure material are difficult to identify due to the existence of the following equilibrium, which leads to the presence of N_2O_4 in any sample of NO_2.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Nitrogen dioxide is a key intermediate in the production of nitric acid. The nitrogen dioxide is produced by the oxidation of ammonia and this is then combined with water in a disproportionation reaction.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Nitrogen dioxide, NO_2, along with nitrogen monoxide, NO, is considered to be a key air pollutant and these two oxides are grouped together as NO_x when air quality measurements are undertaken. Both gases are produced during combustion using air as a source of oxygen, such as in the combustion of fuel in vehicle engines. They contribute to the production of atmospheric nitric acid, a key component of acid rain.

Dinitrogen pentoxide, N_2O_5

Dinitrogen pentoxide is a colourless solid at temperatures around 0 °C, however when warmed to 32 °C the oxide sublimes to form $N_2O_5(g)$. In the gas phase the dinitrogen pentoxide is unstable and decomposes, producing nitrogen dioxide.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

colourless gas — brown gas — colourless gas

Solutions of dinitrogen pentoxide dissolved in trichloromethane, $CHCl_3$, have been used as nitration agents to introduce the $—NO_2$ grouping into organic compounds. The use of this reagent requires a great deal of care as it is a strong oxidising agent and forms explosive mixtures with a range of organic materials.

– End of passage –

Examiner only

Dinitrogen pentoxide, N_2O_5, decomposes in the gas phase according to the equation shown in *line 38*.

(a) Suggest **two** methods of studying the kinetics of this reaction. [2]

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2. .....

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(b) The initial rates of this reaction for different concentrations of N_2O_5 were measured and are given in the table below.

Concentration of N_2O_5 / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
4.00×10^{-3}	3.00×10^{-5}
6.00×10^{-3}	4.50×10^{-5}
8.00×10^{-3}	6.00×10^{-5}

The rate equation for this reaction is:

$$\text{Rate} = k[N_2O_5]^1$$

(i) Show that the rate equation is consistent with the data above. [2]

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(ii) Calculate the value of the rate constant under these conditions. Give your answer to **three** significant figures and state its units. [3]

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Units .....

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(iii) Two possible mechanisms have been suggested for this reaction. These are shown below.

Mechanism A	*Mechanism B*
$N_2O_5 \rightarrow NO_2 + NO_3^{\bullet}$	$2N_2O_5 \rightarrow 2NO_3^{\bullet} + N_2O_4$
$NO_3^{\bullet} \rightarrow NO^{\bullet} + O_2$	$NO_3^{\bullet} + N_2O_4 \rightarrow NO^{\bullet} + 2NO_2 + O_2$
$NO^{\bullet} + N_2O_5 \rightarrow 3NO_2$	$NO^{\bullet} + NO_3^{\bullet} \rightarrow 2NO_2$

Giving your reasons, state which of the mechanisms is compatible with the rate equation. [2]

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(c) The nitrogen dioxide, NO_2, produced in this reaction exists in dynamic equilibrium with dinitrogen tetroxide, N_2O_4. *(line 24)*

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

(i) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) State and explain the effect of increasing the temperature on the value of K_p. [2]

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(iii) At a temperature of 373 K, the partial pressure of a pure sample of NO_2 was 3.00×10^5 Pa. When the mixture was allowed to reach equilibrium, the partial pressure of the remaining NO_2 was 2.81×10^5 Pa.

Calculate the value of K_p, stating its units. [3]

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Units .....

Total [15]

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SECTION A

Answer **all** *questions in the spaces provided.*

1. Potassium peroxodisulfate(VI) (persulfate) is a white crystalline compound of formula $K_2S_2O_8$. It is a powerful oxidising agent and has uses as a food additive, in hair dyes and as a nappy steriliser.

(a) Unusually for potassium compounds, it is not very soluble in water.

Temperature / °C	Solubility / g per 100 g H_2O
0	1.75
20	5.29

1 dm^3 of a saturated solution of potassium persulfate at 20 °C was cooled to 0 °C. Calculate the mass of solid potassium persulfate that crystallised from the solution. [2]

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(b) (i) A hot solution of potassium persulfate slowly decomposes, giving oxygen as one of the products.

$$2K_2S_2O_8(aq) + 2H_2O(l) \longrightarrow 4KHSO_4(aq) + O_2(g)$$

Calculate the maximum volume of oxygen gas that can be produced at 80 °C when a solution containing 0.100 mol of potassium persulfate decomposes as shown above. [2]

[At 80 °C 1 mol of oxygen has a volume of 29.0 dm^3]

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(ii) Suggest a way that the rate of decomposition of the potassium persulfate solution described in (i) could be measured. [1]

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(d) The reaction between persulfate ions and iodide ions in aqueous solution is

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

In an experiment to follow the rate of this reaction, the values below were obtained.

Experiment	Initial rate / mol $dm^{-3}s^{-1}$	Initial concentration of $S_2O_8^{2-}$ / mol dm^{-3}	Initial concentration of I^- / mol dm^{-3}
1	8.64×10^{-6}	0.0400	0.0100
2	3.46×10^{-5}	0.0800	0.0200

(i) The reaction is first order with respect to iodide ions. Use both the initial rate values and the concentrations to show that the order with respect to persulfate ions is also first order. [2]

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(ii) Write the rate equation for this reaction and use it to calculate the value of the rate constant, *k*, giving its units. [3]

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..... *Units* .....

(iii) It is suggested that this reaction occurs in two steps.

Step 1 $S_2O_8^{2-} + I^- + H_2O \longrightarrow 2SO_4^{2-} + HOI + H^+$

Step 2 $HOI + H^+ + I^- \longrightarrow H_2O + I_2$

State, using your answer to (ii), why Step 1 is the rate-determining step. [1]

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Total [14]

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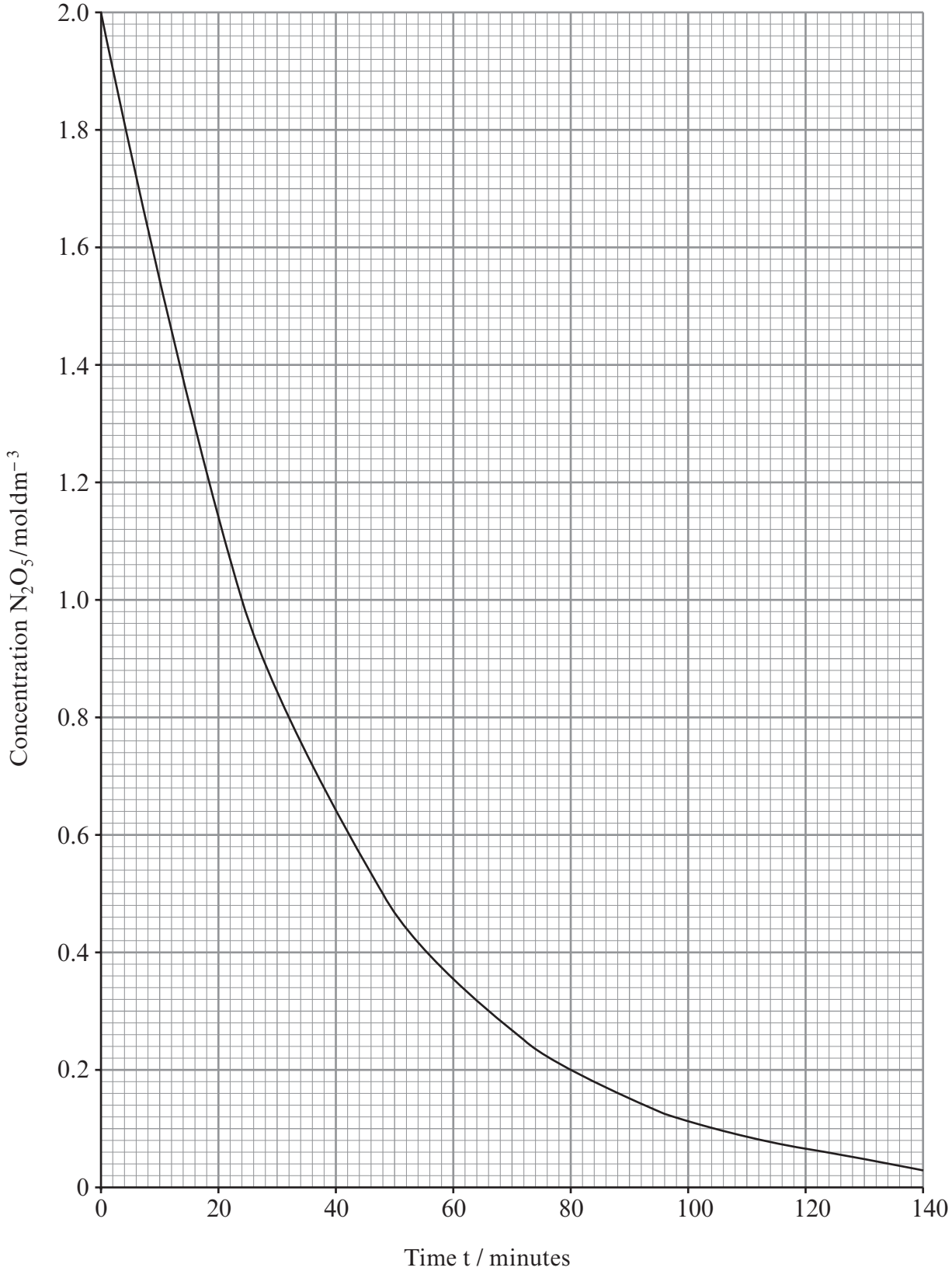
2. Nitrogen forms a variety of oxides including dinitrogen pentoxide, N_2O_5, which can decompose as shown in the equation.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The rate at which this decomposition occurs can be followed by measuring the change in concentration of N_2O_5. A graph of the results of this decomposition is shown below.



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(a) (i) Use the graph to determine the rate of reaction, in $mol\,dm^{-3}\,min^{-1}$, after 40 minutes. Show clearly on the graph, how you determined your answer. [2]

Rate after 40 minutes = ... $mol\,dm^{-3}\,min^{-1}$

(ii) Explain why the rate of reaction is lower at t = 60 minutes than it was at t = 40 minutes. [1]

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(b) (i) Use the graph to show that the reaction is first order with respect to N_2O_5. Explain how you reached your conclusion. [2]

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(ii) Write the rate equation for the reaction. [1]

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(iii) Find the value of k in the rate equation and state its units. [2]

Value of k = ...

Units = ...

Examiner only

(iv) Two students suggested possible mechanisms for the decomposition of N_2O_5.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Student A

$$N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO + O_2$$

$$NO + O_2 \xrightarrow{\text{fast}} NO_2 + \tfrac{1}{2}O_2$$

Student B

$$2N_2O_5 \xrightarrow{\text{slow}} 4NO + 3O_2$$

$$4NO + 2O_2 \xrightarrow{\text{fast}} 4NO_2$$

State, with a reason, which student's suggested mechanism is more likely to be correct. [1]

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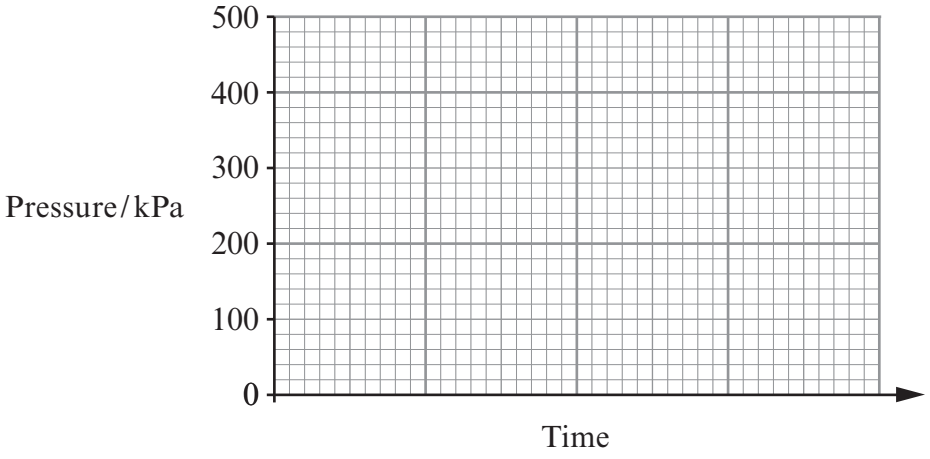
(c) The progress of the reaction could have been followed by monitoring changes in pressure. On the axes below sketch the results expected if the initial pressure of the N_2O_5 was 100 kPa and the reaction reached completion. [2]



Total [11]

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SECTION A

Answer **all** *questions in the spaces provided.*

1. Ammonium salts are very important chemicals as they are used as a nitrogen source in fertilisers.

(a) When cold aqueous sodium hydroxide is added to an ammonium salt, the following equilibrium exists.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

Identify the **two** acid-base conjugate pairs in the equilibrium. [2]

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(b) Ammonium chloride and sodium nitrite react together in aqueous solution to produce nitrogen gas. This can be represented by the ionic equation:

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$

The rate equation for the reaction is given below.

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

(i) Complete the table of data for the above reaction. All experiments were carried out at the same temperature. [3]

	$[NH_4^+(aq)]$ / mol dm^{-3}	$[NO_2^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.200	0.010	4.00×10^{-7}
2		0.010	2.00×10^{-7}
3	0.200		1.20×10^{-6}
4	0.100	0.020	

(ii) Calculate the value of the rate constant, *k*, giving its units. [2]

Value of k = ...

Units .....

Examiner only

(iii) State how the value of *k* will alter, if at all, if the concentration of NH_4^+ ions is increased. [1]

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(iv) State, giving a reason, how the value of *k* will alter, if at all, if the temperature is increased. [2]

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Total [10]

10