NAME DATE STARTED TARGET END DATE

GCE A LEVEL — CHEMISTRY UNIT 3 QUESTION PACK

1095-01 (Legacy CH5) · New spec Unit 3 Topic 4 · A2 unit, first sat 2017, 80 marks, 1h 45min paper

REVISE.wales

CHEMISTRY — UNIT 3 · Chemical Kinetics — Rate Equations & Orders

Topic 3.5 — Kinetics: rate equations from initial-rates data, orders of reaction, rate constant k, half-life and rate-determining step

Determining rate equations from initial-rate experiments, identifying orders of reaction graphically and numerically, computing the rate constant k with units, recognising first-order half-life behaviour, and proposing the rate-determining step in a multi-step mechanism.

Legacy 2008 specification

Estimated time for entire question pack: ~2 h 27 min

Derived from the legacy CH5 paper's pace of ~1.3 min/mark, padded for long-prose and calculation answers (92 marks over 7 questions).

*You are advised to **not** attempt to complete all of this in one sitting.*

ABOUT THIS QUESTION PACK

This is a **comprehensive practice question pack**, not a single mock paper. It contains every question from the legacy WJEC CH5 papers (2008 modular spec, Jun 2010 – Jun 2016) that maps onto the new-spec A2 Unit 3 Topic 3.5.

Questions are ordered by source paper date.

INSTRUCTIONS

Use black ink or black ball-point pen. Show all working — quality of written communication will affect marks. A calculator is allowed. You will need the WJEC Periodic Table / Data Booklet.

For Examiner's use only

Q	Source	Max	Mark
1	Jun 10 Q4	12	
2	Jun 11 Q3	15	
3	Jun 12 Q1	14	
4	Jun 13 Q2	11	
5	Jun 14 Q1	10	
6	Jun 15 Q5	20	
7	Jun 16 Q1	10	
Total		92	

Chemical Kinetics — Rate Equations & Orders — what the new spec asks

WJEC GCE A Level Chemistry (from 2015) · Unit 3: Physical & Inorganic Chemistry · Topic 3.5.

Rate equation basics

- rate = $k[A]^m[B]^n$: experimentally determined orders, never from stoichiometry.
- Overall order = m + n.
- Units of k depend on overall order; first-order ⇒ s^{-1}.
- k increases with T (Arrhenius).

Determining orders

- Initial rates: vary one [reactant] while keeping others constant; ratio of rates gives order.
- Zero: doubling [A] ⇒ rate unchanged.
- First: doubling [A] ⇒ rate × 2.
- Second: doubling [A] ⇒ rate × 4.

Graphical methods

- Concentration-time: zero = linear; first = exponential decay (constant half-life).
- Rate-concentration: zero = horizontal; first = straight line through origin; second = curve.
- Half-life $t_{1/2}$ = ln 2 / k for first-order; independent of $[A]_0$.

Rate-determining step

- The slowest step in a multi-step mechanism — sets overall rate.
- Rate equation matches RDS stoichiometry (orders = coefficients in RDS only).
- Species not in rate equation appear after RDS.
- Rate equation evidence for mechanism (e.g. S_N1 vs S_N2).

Worked examples

- I_2 + propanone (acid catalysed): rate = k[propanone][H^+]; I_2 not in RDS ⇒ zero order in I_2.
- $S_2O_8^{2-} + 2I^-$: rate = $k[S_2O_8^{2-}][I^-]$ ⇒ 2nd order overall.
- $NO_2 + CO \rightarrow NO + CO_2$: rate = $k[NO_2]^2$; CO is zero-order ⇒ $2NO_2$ is the RDS.

Catalysis & activation energy

- Catalyst provides lower-E_a pathway; increases k.
- Doesn't change ΔH, K, or equilibrium position.
- Heterogeneous: surface adsorption (Fe, Pt, V_2O_5).
- Homogeneous: same phase as reactants; intermediate formed.

Chemical Kinetics — Rate Equations & Orders in one page

Quick-reference notes — revisit before each question.

Initial rates method

Hold all [reactant] constant except one; vary that one. Order in X = log(rate ratio) / log([X] ratio). Repeat for all reactants.

Half-life trick

If $t_{1/2}$ constant ⇒ first order in that reactant. $t_{1/2} = 0.693 / k$.

Units of k

- 0th order: mol dm^{-3} s^{-1}
- 1st: s^{-1}
- 2nd: dm^3 mol^{-1} s^{-1}
- 3rd: dm^6 mol^{-2} s^{-1}

RDS spotting

Sum of orders in rate equation = molecularity of RDS. Species not in rate eqn appear in steps after RDS.

Iodination of propanone

rate = $k[CH_3COCH_3][H^+]$. I_2 is zero-order ⇒ RDS is enolisation, not iodination.

Catalyst

Provides alternative pathway with lower E_a. K and ΔH unchanged. Same effect on forward and reverse rates.

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]

1. ....

....

2. ....

....

(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]

....

....

....

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

....

....

....

Units ....

Examiner only

(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]

....

....

....

(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]

....

....

....

(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]

....

....

....

Units ....

Total [15]

Examiner only

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]

....

....

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

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

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]

....

....

....

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

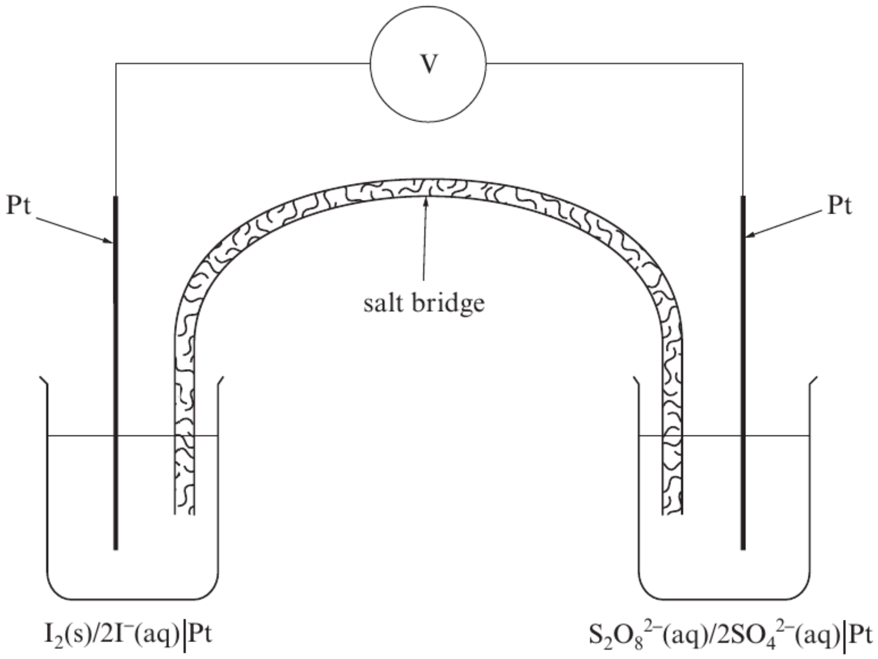
....

....

....

Examiner only

(c) The diagram below shows a cell that uses persulfate ions in aqueous solution.



(i) State the role of the platinum electrodes in this cell. [1]

....

(ii) Use the information given in the equations to state and explain the direction of electron flow in the external circuit. [2]

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^\ominus = +2.01\ V$$

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^\ominus = +0.54\ V$$

....

....

....

1095 010003

Examiner only

(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]

....

....

....

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

....

....

....

.... *Units* ....

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

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

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

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

....

....

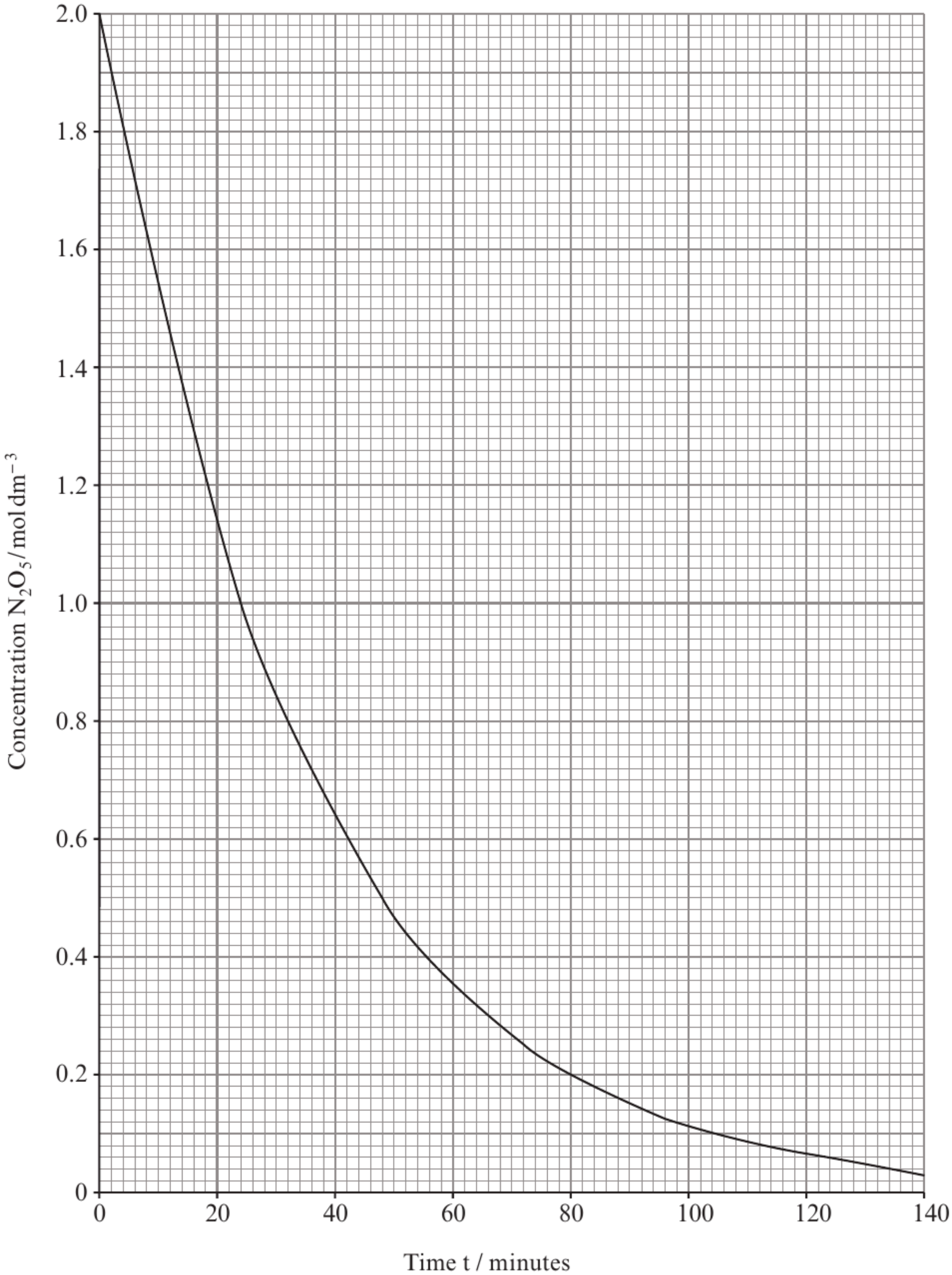
Total [14]

Examiner only

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.



Examiner only

(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]

....

....

....

(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]

....

....

....

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

....

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

Value of k = ...

Units = ...

1095 010005

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

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

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

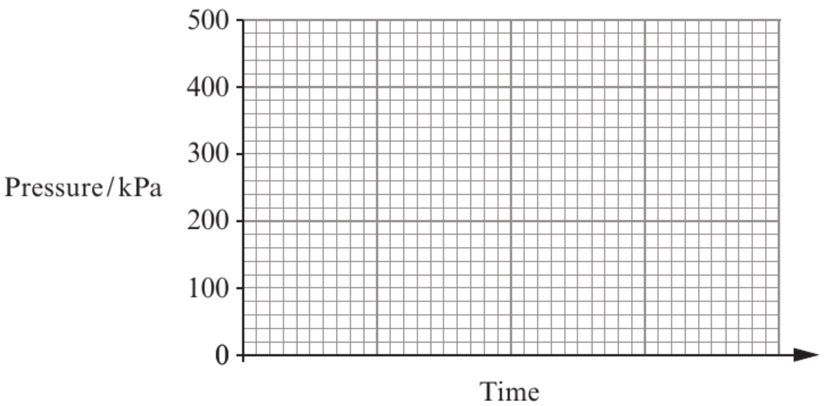
State, with a reason, which student's suggested mechanism is more likely to be correct. [1]

....

....

....

(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]

BLANK PAGE

1095
010007

Examiner only

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]

....

....

(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]

....

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

....

....

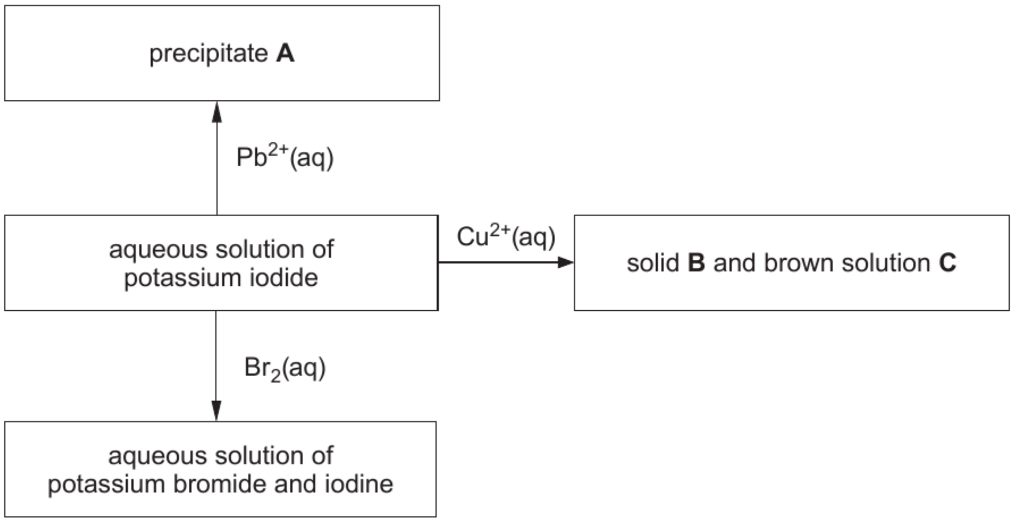
....

Total [10]

10

1095 010003

5. The diagram below shows some of the reactions of potassium iodide solution.



(a) Identify precipitate **A** and give its colour. [2]

(b) Write an equation for the reaction of Cu^{2+}(aq) and I^-(aq), clearly identifying the precipitate. [2]

(c) Bromine reacts with aqueous potassium iodide as shown above, however bromine does not react with aqueous sodium chloride. Use the standard electrode potentials below to explain these observations. [3]
QWC [1]

Half-equation	E^θ/V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

(d) Solid potassium iodide reacts with concentrated sulfuric acid in the same way as sodium iodide.

Describe the observations made during this reaction and identify the products formed. [3]

(e) Hydrogen peroxide reacts with acidified potassium iodide according to the equation below.

$$2H^{+} + 2I^{-} + H_2O_2 \longrightarrow I_2 + 2H_2O$$

(i) This reaction was studied using an iodine clock reaction. Describe the principles of how the rate of a clock reaction is determined. Experimental details are not required. [2]

(ii) The rate of this reaction was studied by a different method for a range of concentrations of H_2O_2(aq) and I^-(aq) and pH values. These are listed in the table below.

Experiment number	Initial concentration of H_2O_2(aq) / mol dm^{-3}	Initial concentration of I^-(aq) / mol dm^{-3}	pH	Initial rate / mol dm^{-3} s^{-1}
1	0.0010	0.10	1	2.8×10^{-6}
2	0.0020	0.10	1	5.6×10^{-6}
3	0.0020	0.10	2	5.6×10^{-6}
4	0.0010	0.40	1	11.2×10^{-6}

I. Some experiments were undertaken at pH 1 and some at pH 2. Give the difference in the concentrations of H^+ ions in these two solutions. [1]

II. Use the data in the table to deduce the rate equation for this reaction, giving your reasoning. [3]

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

IV. The reaction is repeated at a higher temperature. State how the increase in temperature affects the rate equation and rate constant. [1]

Total [20]

Total Section B [40]

END OF PAPER

BLANK PAGE

BLANK PAGE

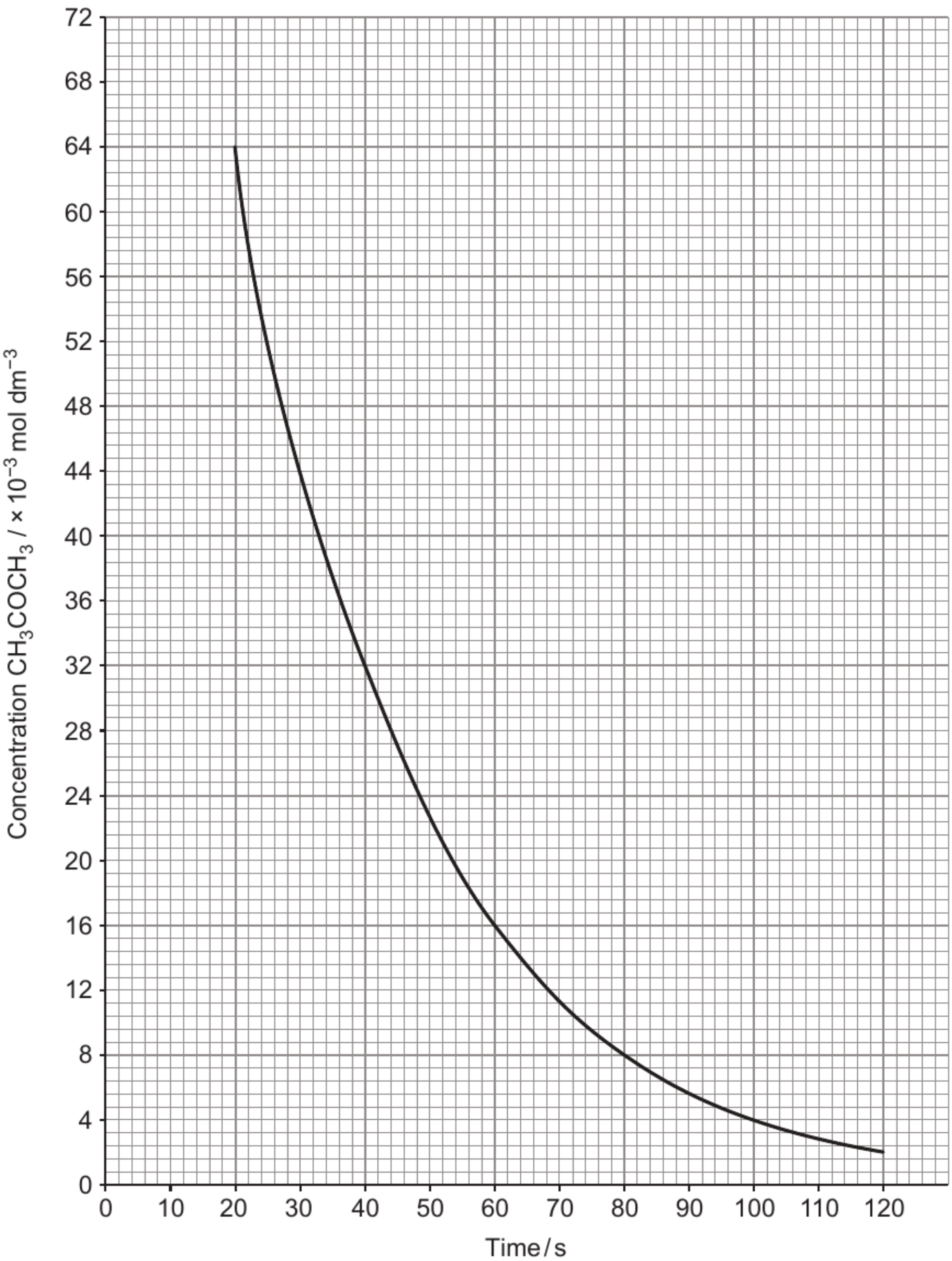
SECTION A

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

1. *(a)* Elen carried out an investigation into the rate of reaction between propanone and iodine in an acidic solution. This is a multi-step reaction but the overall equation for the reaction is:

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

(i) In the first part of the investigation she measured how the concentration of propanone changed with time. Her results are shown in the graph below.



Examiner only

Explain how the graph shows that the reaction is first order with respect to propanone. Use values from the graph to justify your answer. [2]

....

....

....

....

(ii) In the second part of the investigation Elen investigated how different initial concentrations of iodine and acid affected the rate of reaction. The following results were obtained.

$[CH_3COCH_3]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1.5×10^{-3}	0.030	0.020	2.1×10^{-9}
1.5×10^{-3}	0.060	0.040	4.2×10^{-9}
1.5×10^{-3}	0.030	0.040	4.2×10^{-9}

1095 010003

I. Determine the orders of reaction with respect to I_2 and H^+. [2]

I_2 ....

....

H^+ ....

....

II. Write the rate equation for the reaction. [1]

....

III. Calculate the value of the rate constant in the rate equation and state its unit. [2]

k = ...

Unit ....

Examiner only

(b) Another multi-step reaction is the one between nitrogen dioxide and carbon monoxide. The overall equation for the reaction is:

$$NO_2 + CO \longrightarrow NO + CO_2$$

The rate equation for this reaction is as follows.

rate = $k[NO_2]^2$

The first step is the rate-determining step.

(i) Explain what is meant by the *rate-determining step*. [1]

....

....

(ii) Write equations to show a possible two-step mechanism for this reaction. [2]

....

....

Total [10]

10

BLANK PAGE

1095
010005

END OF QUESTION PACK

7 questions · 92 marks · ~2 h 27 min
Source: WJEC CH5 (2008 modular spec, Jun 2010 – Jun 2016)
Curated for WJEC Chemistry 2015 spec A2 Unit 3 — Topic 4 (3.5)