Question 1

In this experiment, you are required to find the concentration in mol dm⁻³ of sodium thiosulfate, $Na_2S_2O_3$, in solution **FA 1**.

You are provided with:

FA 1 contains sodium thiosulfate, $Na_2S_2O_3$.

FA 2 is potassium manganate (VII) containing 1.83 g dm⁻³ KMnO₄.

FA 3 is 1 mol dm⁻³ sulfuric acid, H_2SO_4 .

FA 4 is 10% potassium iodide containing 4 g dm⁻³ KI.

You are also provided with starch indicator.

Dilution of FA 2

(a) By using a burette measure between 41.00 cm³ and 42.00 cm³ of **FA 2** into the 250 cm³ graduated flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Final burette reading / cm ³	41.50
Initial burette reading / cm ³	0.00
Volume of FA2 used / cm ³	41.50

[2]

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Make up the contents of the flask to the 250 cm³ mark with distilled water. Stopper and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA5**.

Titration

Fill a second burette with **FA 1**, the solution containing sodium thiosulfate.

Use a measuring cylinder to transfer 10 cm³ of **FA 3** and 10 cm³ of **FA 4** into a conical flask. Pipette 25.0 cm³ of **FA 5** into the conical flask containing the mixture of **FA 3** and **FA 4**. The potassium manganate (VII) oxidises potassium iodide to iodine, I_2 .

Titrate the liberated iodine with **FA 1** as follows. Run the solution from the burette into the conical flask until the initial brown colour of the iodine becomes pale yellow. Then add 1 cm³ of the starch indicator and continue to add **FA 1** drop by drop until the blueblack colour of the starch-iodine complex disappears, leaving a colourless solution. This is the end-point of the titration.

Record your titration results in the space below. Make certain that your recorded results show the precision of your working. Repeat your experiment to obtain consistent results.

	1	2
Final burette reading / cm ³	24.20	24.20
Initial burette reading / cm ³	0.00	0.00
Volume of FA1 used / cm ³	24.20	24.20

[6]

(b) From your titration results obtain a suitable volume of FA 1 to be used in your

No. of moles of KMnO₄ added into the graduated flask = $\frac{41.50}{1000}$ X $\frac{1.83}{158.0}$ = 4.81 x 10⁻⁴

(d) Calculate how many moles of KMnO₄ are then pipetted from the 250 cm³ graduated flask into the titration flask.

No. of moles of KMnO₄ pipetted into the titration flask = 4.81 x 10^{-4} x $\frac{25.0}{250}$ = 4.81 x 10^{-5}

(e) Use this answer to calculate how many moles of iodine molecules, I_2 are formed when the manganate (VII) ions react with an excess of iodide ions in the titration flask.

No. of moles of I_2 formed = 4.81 x 10⁻⁵ x 2.5 = 1.20×10^{-4}

For

(f) Use this answer to calculate how many moles of sodium thiosulfate, Na₂S₂O₃ react with the iodine molecules formed. $2S_{2}O_{3}^{2-} \rightarrow S_{4}O_{6}^{2-} + 2e$ $\frac{1}{2} + e \rightarrow \Gamma$ No. of moles of Na₂S₂O₃ reacted = 1.20 x 10⁻⁴ x 2 = 2.40 x 10⁻⁴
No. of moles of thiosulfate ions reacted =[1] (g) Calculate the concentration in mol dm⁻³ of the sodium thiosulfate, Na₂S₂O₃, in **FA 1**.

Concentration of Na₂S₂O₃ in FA1 = 2.40 x 10^{-4} x $\frac{1000}{24.20}$ = 9.93 x 10^{-3} mol dm⁻³

[Total: 14 marks]

[Turn over

Question 2

The derivation of rate equations is an important part of the process of discovering a reaction mechanism.

The experiment detailed in this question is part of an investigation into the mechanism of the iodination of propanone:

 $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$

The reaction is catalysed by hydrogen ions and hence the rate equation can be expressed as

Rate = k $[CH_3COCH_3]^a [H^+]^b [I_2]^c$

where a, b and c are the orders with respect to the species shown in the rate equation.

FA 1 contains sodium thiosulfate, $Na_2S_2O_3$ (from Question 1) **FA 3** is 1 mol dm⁻³ sulfuric acid, H_2SO_4 (from Question 1) **FA 6** is 1 mol dm⁻³ aqueous propanone **FA 7** is 0.02 mol dm⁻³ I₂ in KI solution (5 g of I₂ and 33 g of KI in 1 dm³ solution) **FA 8** is 1 mol dm⁻³ NaHCO₃

Procedure

- 1. Pipette 25.0 cm³ of **FA 3** into a conical flask.
- 2. Using the same pipette deliver 25.0 cm³ of **FA 6** into the same conical flask.
- 3. Using a measuring cylinder, collect 50 cm³ of **FA 7**.
- 4. Transfer the **FA 7** into the conical flask containing the mixture of **FA 3** and **FA 6** as quickly as possible and at the same time start the stop watch. Swirl the mixture in the conical flask to ensure complete mixing.
- 5. When the reaction has been going on for 3 minutes, pipette 10.0 cm³ of the reaction mixture into another conical flask containing 10 cm³ of **FA 8**, noting the exact time at which this was done.
- Mix the solution thoroughly and titrate the mixture against FA 1 from a burette until the solution turns yellow. Using the plastic dropper add 1 cm³ of starch and continue titration until the solution becomes colourless.
- 7. Repeat steps 5 6, at times of 6, 9, 12 and 15 minutes.
- 8. Record yours results in the table below:

Results

Time when reaction mixture was added to NaHCO ₃			
Final Volume / cm ³			
Initial Volume / cm ³			
Vol. of FA1 used / cm ³			

[6]

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(d) Based on your graph, what conclusion can your draw about how the rate of reaction depends on the reactant of interest in this investigation?

Whilst iodine concentration is decreasing with time, the graph is a straight line and hence rate is constant throughout the reaction [1]. Reaction is independent of iodine concentration [1].

[2]

In another similar experiment at the same temperature, the volume of propanone used was halved but the total volume was kept constant by adding water to the reaction mixture. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

(e) Why must water be added to the reaction mixture to keep total volume constant in the second experiment?

To ensure that the concentration of propanone varies directly with its volume

[1]

(f) What conclusion can you draw from the above information?

1st order with respect to propanone as halving the concentration cause the rate of reaction to halve as well.

[1]

Planning

The **method of initial rates** allows the values of these orders to be found by running the reaction multiple times under controlled conditions and measuring the rate of the reaction in each case. All variables are held constant from one run to the next, except for the concentration of one reactant. The order of that reactant concentration in the rate law can be determined by observing how the reaction rate varies as the concentration of that one reactant is varied. This method is repeated for each reactant until all the orders are determined. The initial rate experiment involves measuring the time taken for some easily recognisable event to happen very early on in a reaction. In using the initial rate method, time interval for the reaction to proceed to a given point must be kept short, otherwise the rate will become more of an average rate rather than the initial (instantaneous rate).

For the reaction investigated in Question 2, you are to design a plan that will allow you to determine the rate equation by the **initial rate method**.

In your plan, you should include details of

- Step-wise procedure that must be followed
- Details of type of apparatus used
- Results to be tabulated
- Processing of results
- Interpretation of results

Considerations

Using the initial rate method

- In using the initial rate method, time interval for the reaction to proceed to a given point must be kept reasonably short. Since the time taken for the iodine colour to be discharged is used as a measure of the reaction rate, the amount of iodine used in the reaction must be small.
- Hence, set up reaction mixtures with different amount of the reactant of interest keeping the rest constant, will allow for the concentration of the reactant that we are interested in to be varied and hence understand how the rate varies with it.

Procedure

- Into a clean dry conical flask, place 5 cm³ of sulfuric acid, 4cm³ of iodine solution and 11 cm³ of deionized water. All volumes can be measured using different measuring cylinders of appropriate capacity.
- Instill 3 drops of starch solution into the conical flask.
- Using another measuring cylinder, collect 5 cm³ of the propanone.
- Pour the propanone into the conical flask and start the stop watch immediately.
- Swirl the reaction mixture and place it on a white tile.
- Record the time taken for the dark blue colour of the reaction mixture to disappear.
- Repeat the experiment for the other mixtures as shown in the table below.

Expt	Vol of propanone / cm ³	Vol of H_2SO_4 / cm ³	Vol of iodine / cm ³	Vol of water / cm ³	Time taken / s
1	5	5	4	11	
2	10	5	4	6	
3	5	10	4	6	
4	5	5	2	13	

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[10]

Processing of Results

- Rate of reaction α (Vol of I₂ used / time taken)
- Compute the rate for each of the four experiments
- Comparing Expt 1 & 2, deduce order w.r.t. propanone
- Comparing Expt 1 & 3, deduce order w.r.t H⁺
- Comparing Expt 1 & 4, deduce order w.r.t I₂

Interpretation of Results

- If rate remains unchanged when the concentration of the reactant under investigation is changed, then reaction is 0 order with respect to that reactant
- If rate is doubled when concentration of reactant of interest is doubled, then reaction is 1st order with respect to that reactant
- If rate is quadruples when concentration of reactant of interest is doubled, then reaction is 2nd order with respect to that reactant

[Total: 24 marks]

Question 3

You are to perform the tests given in the following table on each of **FA 9**, **FA 10** and **FA 11** to identify, where possible, the cation and anion present in each solution.

10

Record details of colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should identified by a test, described in the appropriate place in your table. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Toot	Observations [7]		
Test	FA 9	FA 10	FA11
1 cm depth of ition in a test-tube, aqueous sodium roxide drop-by-drop, I it is in excess.	White precipitate is formed, soluble in excess of NaOH	No precipitate is formed, hence no observable change	White precipitate is formed, soluble in excess of NaOH
1 cm depth of ition in a test-tube, aqueous ammonia p-by-drop, until it is xcess.	White precipitate is formed, soluble in excess of aqueous NH ₃	No precipitate is formed, hence no observable change	White precipitate is formed, insoluble in excess of aqueous NH ₃
1 cm depth of ition in a test-tube, aqueous barium pride,	No precipitate is formed, hence no observable change	<u>No precipitate is</u> <u>formed</u> , hence no observable change	White precipitate is formed
dilute hydrochloric I.			White precipitate is insoluble in dilute HC <i>l</i>
1 cm depth of ution in a test-tube, 2 cm depth of er and 1 cm depth queous silver ate, n divide the resultant ution into 2 parts.	<u>No precipitate is</u> <u>formed</u> , hence no observable change	Yellow precipitate is formed	<u>No precipitate is</u> <u>formed</u> , hence no observable change
	Test I cm depth of tion in a test-tube, aqueous sodium roxide drop-by-drop, I it is in excess. I cm depth of tion in a test-tube, aqueous ammonia b-by-drop, until it is xcess. I cm depth of tion in a test-tube, aqueous barium ride, dilute hydrochloric I cm depth of tion in a test-tube, 2 cm depth of tion in a test-tube, 2 cm depth of er and 1 cm depth queous silver ate, a divide the resultant tion into 2 parts.	TestFA 9I cm depth of tion in a test-tube, aqueous sodium roxide drop-by-drop, lit is in excess.White precipitate is formed, soluble in excess of NaOHI cm depth of tion in a test-tube, aqueous ammonia b-by-drop, until it is xcess.White precipitate is formed, soluble in excess of aqueous NH3I cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, 2 cm depth of er and 1 cm depth queous silver ate,No precipitate is formed, hence no observable changeI cm divide the resultant tion into 2 parts.No precipitate is formed, hence no observable change	TestObservations [7]FA 9FA 10I cm depth of tion in a test-tube, aqueous sodium roxide drop-by-drop, it is in excess.White precipitate is formed, soluble in excess of NaOHNo precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous ammonia o-by-drop, until it is xcess.White precipitate is formed, soluble in excess of aqueous NH3No precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeNo precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeNo precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, aqueous barium ride,No precipitate is formed, hence no observable changeNo precipitate is formed, hence no observable changeI cm depth of tion in a test-tube, 2 cm depth of er and 1 cm depth queous silver ite, n divide the resultant tion into 2 parts.No precipitate is formed, hence no observable changeI cm depth of er and 1 cm depth queous silver ite,No precipitate is formed, hence no observable changeYellow precipitate is formedn divide the resultant tion into 2 parts.No precipitate is formed, hence no observable changeYellow precipitate is formed

To 1 part of solution, add dilute nitric acid.	Yellow precipitate is insoluble in dilute HNO ₃	<u>No precipitate is</u> <u>formed</u> , hence no observable change
To 1 part of solution, add aqueous ammonia.	Yellow precipitate is insoluble in aqueous NH ₃	White precipitate is formed, insoluble in excess of aqueous NH ₃

(e)	For each of the solutions FA 9 , FA 10 and FA 11 , summarise the evidence from the tests performed to identify the cations and/or anions present.	For Examiner's Use
	FA 9 contains Zn ²⁺	l
	Supporting evidence	l
	White precipitate is formed when FA 9 is added to NaOH & aqueous NH_3 . White precipitate is observed to be soluble in excess of both NaOH & aqueous NH_3 .	l
	FA 10 contains I	1
	Supporting evidence	l
	Yellow precipitate of AgI is formed when FA 10 is added to a solution of AgNO ₃ . AgI remains insoluble in dilute HNO_3 & aqueous NH_3 .	l
	FA 11 contains Al ³⁺ and SO ₄ ²⁻	l
	Supporting evidence	l
	When NaOH & aqueous NH_3 are added to sample of FA 11 , a white precipitate is formed, but white precipitate is soluble in excess NaOH & but insoluble in excess aqueous NH_3 .	
	White precipitate of BaSO ₄ is formed when $BaCl_2$ is added to sample of FA 11 , and white precipitate is insoluble in dilute HC <i>l</i> .	
	[4]	l
(f)	Do not perform the tests for the following ions.	l
	It is believed that when testing a solution containing both NH_4^+ ions and NO_3^- ions, students should identify the NH_4^+ ion before attempting to identify the NO_3^- ion. Suggest a reason for the experimental procedure to be as such.	
	To test for the presence of NO_3^- , NaOH, A <i>l</i> strip/foil and heat are required for the liberation of NH ₃ gas. Similarly, NaOH & heat are required to test for the presence of NH_4^+ .	
	Hence it is necessary for students to identify the NH_4^+ ion before identifying NO_3^- , since test for NO_3^- will also yield similar experimental observations.	l

test for NO_3^- will also yield similar experimental observations. Deic

[1]

Planning

You are given aqueous solutions of the following acids:

CH₃CH₂COCOOH; CH₃COCH₂COOH; CH₃CH(OH)CH₂COOH and CH₃CH₂CH(OH)COOH

Outline a sequence of simple chemical tests, by which you could identify each of the above acids.

[5]

EITHER

- Iodoform reaction on all four
 - Positive for CH₃COCH₂COOH and CH₃CH(OH)CH₂COOH
- Oxidation with H⁺/MnO₄⁻ or H⁺/Cr₂O₇²⁻
 - Positive for CH₃CH(OH)CH₂COOH and CH₃CH₂CH(OH)COOH

	lodoform	Oxidation
CH ₃ CH ₂ COCOOH	-	-
CH ₃ COCH ₂ COOH	+	-
CH ₃ CH(OH)CH ₂ COOH	+	+
CH ₃ CH ₂ CH(OH)COOH	-	+

OR

- Brady's test on all four
 - Positive for CH₃COCH₂COOH and CH₃CH₂COCOOH
- lodoform reaction on all four
 - Positive for CH₃CH(OH)CH₂COOH and CH₃COCH₂COOH

	Brady's test	lodoform
CH ₃ CH ₂ COCOOH	+	-
CH ₃ COCH ₂ COOH	+	+
CH ₃ CH(OH)CH ₂ COOH	-	+
CH ₃ CH ₂ CH(OH)COOH	-	-

Procedure

To each of the 4 acids in a test tube, add a few drops of 2,4 dinitrophenylhydrazine.

• The ones that give a yellow ppt contain carbonyl functional groups whilst those that do not probably contain the alcohol functional groups

To a second sample of the 4 acids in separate test tubes add a mixture of iodine in aqueous sodium hydroxide and warm.

 The one that gives a pale yellow ppt will be CH₃COCH₂COOH or CH₃CH(OH)CH₂COOH

Tabulate the results to deduce their identity:

	TEST 1	TEST 2
Α		
В		
С		
D		

[Total: 17 marks]

~ END OF PAPER~

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