

EUNOIA JUNIOR COLLEGE JC2 Preliminary Examination 2022 General Certificate of Education Advanced Level Higher 2

CANDIDATE NAME					
CIVICS GROUP	2	1	-		INDEX NUMBER

CHEMISTRY

Paper 4 Practical

9729/04

30 August 2022 2 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.

Give details of the practical shift and laboratory, where appropriate, in the boxes provided. Write in dark blue or black pen.

Volume und an HP papeil for any diagram

You may use an HB pencil for any diagrams or graphs.

Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper. The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use		
1	/18	
2	/18	
3	/11	
4	/ 8	
Total	/55	

This document consists of 17 printed pages and 3 blank pages.

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

1 To determine the percentage by mass of Fe(NO₃)₂ in a salt mixture

FA 1 is a solution containing a salt mixture of two different ionic compounds. One of the compound is $Fe(NO_3)_2$. The other compound, **X**, contains a cation and an anion.

In this question, you will determine the percentage by mass of $Fe(NO_3)_2$ in the mixture by preparing a diluted solution of **FA 1** and carry out a titration using potassium manganate(VII). The iron(II) ions, Fe^{2+} , are oxidised by the manganate(VII) ions, MnO_4^- .

equation 1 $5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

The end-point of the titration occurs when the presence of unreacted MnO_4^- causes the colour of the solution to become pale pink.

The following reagents are provided.

FA 1 is a solution containing 90.0 g dm⁻³ of the salt mixture in sulfuric acid **FA 2** is 0.010 mol dm⁻³ manganate(VII) ions, MnO_4^- **FA 3** is 1 mol dm⁻³ sulfuric acid, H_2SO_4

(a) Determining the percentage by mass of Fe(NO₃)₂

- 1. Fill a burette with **FA 2**.
- 2. Use a pipette to transfer 25.0 cm³ of **FA 1** into a 250 cm³ volumetric flask.
- 3. Make up to the mark with deionised water and label this solution **FA 4**. Shake to obtain a homogeneous solution.
- 4. Pipette 25.0 cm³ of **FA 4** into a 250 cm³ conical flask.
- 5. Use the 25.0 cm³ measuring cylinder to add 25.0 cm³ of **FA 3** into the conical flask.
- 6. Run **FA 2** from the burette into the conical flask. The end-point is reached when the solution changes colour from yellow to pale pink.
- 7. Record your titration results in the space on the next page. Make certain that your recorded results show the precision of your working.
- 8. Repeat steps 4 to 7 as necessary until consistent results are obtained.

Results

final burette reading / cm ³	20.75	20.80
initial burette reading / cm ³	0.00	0.00
volume of FA 2 added / cm ³	20.75	20.80

[3]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** =[3]

(c) (i) Calculate the amount of MnO₄⁻ ions present in the volume of FA 2 calculated in 1(b).

amount of MnO ₄ -	ions =	. [1]	
------------------------------	--------	-------	--

(ii) Calculate the amount of Fe^{2+} ions present in 25.0 cm³ of FA 4.

amount of Fe ²⁺ ions =	1]
	• •

(iii) Calculate the concentration of Fe²⁺ ions present in 25.0 cm³ of FA 1.

concentration of Fe²⁺ ions =.....[2]

(iv) Hence, calculate the percentage by mass of Fe(NO₃)₂ in the salt mixture. [*A*_r: Fe, 55.8; N, 14.0; O, 16.0]

(d) Suggest why a solution containing Fe²⁺ ions readily turns yellow when it comes into contact with air.

.....

.....[1]

(e) A student suggested that **FA 3** can be hydrochloric acid instead of sulfuric acid. Explain why hydrochloric acid cannot be used in the titration and how it would impact the accuracy of the titration result.

(f) Calculate the percentage error for your average titre value in (b).

percentage error =.....[1]

(g) Hydrogen peroxide can act as an oxidising agent and reducing agent as shown by the following half-equations:

 $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$

 $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$

(i) Hydrogen peroxide can also oxidise the Fe^{2+} ions. Write a balanced equation for the reaction of Fe^{2+} with H_2O_2 in an acidic medium.

.....[1]

(ii) Explain why hydrogen peroxide is not a suitable replacement for KMnO₄ in this experiment.

.....[1]

[Total: 18]

2 Determination of the kinetics of the reaction between iron(III) and iodide ions

FA 5 is aqueous potassium iodide, KI. **FA 6** is aqueous iron(III) chloride, FeC l_3 . **FA 7** is 0.0065 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

You are also provided with a starch indicator and deionised water.

A solution containing potassium iodide, sodium thiosulfate and starch is mixed with iron(III) chloride solution. After a few seconds a dark blue colour suddenly appears. This is one of a number of reactions referred to as iodine clock reaction.

equation 2 $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

equation 3 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$

When the above solutions are mixed, iodine is generated according to equation 2. The iodine is being consumed as they are generated, according to equation 3. Therefore, only a small amount of iodine is present in the mixture.

The reaction in equation 3 stops once all the thiosulfate ions have reacted. The concentration of iodine now increases and the dark blue colour of the iodine-starch complex appears.

The reaction in equation 2 is first order with respect to the iodide ion concentration, [I⁻].

You are to perform a series of experiments to determine the rate order for the reaction in equation 2 with respect to the iron(III) chloride concentration, [FeCl₃].

(a) Experiments

You will attempt five experiments.

- In **Experiment 1**, **Solution A** will be prepared as described below.
- In the remaining experiments you will repeat the procedure from **Experiment 1**, but using volumes of **FA 6** of your choice.

For each experiment, you note the time taken, *t*, for the solution to turn dark blue.

(i) Experiment 1

Fill the burette labelled E2 with FA 6.

• Transfer 25.00 cm³ of **FA 6** to a conical flask.

Solution A

- Using a 10 cm³ measuring cylinder, add 10.0 cm³ of **FA 5** to the beaker labelled **Solution A**.
- Using a 25 cm³ measuring cylinder, add 20.0 cm³ of **FA 7** to the same beaker.
- Using a 10 cm³ measuring cylinder, add 5.0 cm³ of starch indicator to the same beaker.
- Mix the contents thoroughly by swirling the beaker.
- 1. Pour **Solution A** rapidly into the conical flask containing **FA 6**. Start the stopwatch when you have added about half of **Solution A**.
- 2. Mix the contents thoroughly by swirling the flask.
- 3. Stop the stopwatch when the dark blue colour first appears.
- 4. Note the time elapsed, *t*, to the nearest second.
- 5. Wash the conical flask and beaker thoroughly with water and allow to drain.

(ii) Remaining Experiments

You are now to perform **four** other experiments in order to determine the rate order with respect to $[FeCl_3]$ for reaction **2**. You should number these experiments **2** to **5**.

In each experiment, the volumes of **FA 5**, **FA 7** and starch indicator are the same as those used in **Experiment 1**.

Select suitable volumes of **FA 6**, *V*_{FA 6}, ensuring that your chosen volumes:

- allow you to obtain sufficient data to determine the order through the plotting of a graph,
- are not larger than the volume used in **Experiment 1**,
- are not less than 15.00 cm³.

In each case, the total volume of the reaction mixture must be kept the same as that used in **Experiment 1**, by adding deionised water as required.

(b) Results

The volumes of **FA 5**, **FA 7** and starch indicator are not changed in these experiments, and do not need to be recorded.

Prepare a table in the space provided below in which to record, for each experiment:

- all volumes apart from those of **FA 5**, **FA 7** and starch indicator,
- the value of *t*,

Record your results in the table.

(i) Table of results

Complete the table below.

experiment	<i>V</i> ға 6 ∕ ст³	volume of deionised water / cm ³	t/s	rate / µmol dm⁻³ s⁻¹
1	25.00		33	
2	15.00		65	
3	23.00		36	
4	20.00		39	
5	18.00		50	

(ii) Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, used in each experiment in 2(a).

(iii) Use your answer to **2(b)(ii)**, and the equations for the reactions involved, to calculate the amount of iron(III) ions, Fe³⁺, that reacted in each experiment in **2(a)**.

(iv) Use your answer to **2(b)(iii)** to calculate the change in concentration of Fe³⁺, [Fe³⁺], that occurred when enough iodine was produced to produce the dark blue colour in each experiment in **2(a)**.

change in [Fe³⁺] =.....[1]

(v) The expression below shows the experimental rate of this reaction as the change in concentration of Fe³⁺ per unit time.

experimental rate = $-\frac{\text{change in } \left[\text{Fe}^{3+}\right]}{\text{time, } t} \times 10^6 \text{ } \mu\text{mol } \text{dm}^{-3} \text{ s}^{-1}$

 $(1 \ \mu mol = 10^{-6} \ mol)$

Complete your table on page 7 by calculating the experimental rates of reaction for all 5 experiments, taking into consideration the units.

If you are unable to calculate a value for the change in $[Fe^{3+}]$ in **2(b)(iv)**, use the value -2.50×10^{-3} mol dm⁻³. (Note: this is not the actual value.) [2]

(c) Plot a graph of experimental rate on the y-axis against $V_{FA 6}$ on the x-axis.

The scales of both axes must be chosen to provide an origin.

Draw the best-fit straight line through the origin, taking into account all of your plotted points.



[3]

(d) By considering the shape of the graph in (c), state and explain the order of the reaction with respect to [FeCl₃].

- (e) The order of reaction with respect to [I⁻] is one. With reference to experiment **1**, state and explain the expected time taken for the appearance of the dark blue colour when the experiment is carried out using a mixture comprising the following:
 - 5.0 cm³ of **FA 5**
 - 25.00 cm³ of **FA 6**
 - 10 cm³ of **FA 7**
 - 15.0 cm³ of deionised water
 - 5 cm³ of starch

[2]

(f) A student suggested that a more accurate timing can be obtained when the volume of **FA 5** is measured with a burette rather than a measuring cylinder.

A teacher said that the student's claim is incorrect. Explain why this is so.

[Total: 18]

3 Planning

 MnO_4^- ions oxidises $C_2O_4^{2-}$ ions in acidic medium as shown in equation 4. The Mn^{2+} ions produced in equation 4 act as a catalyst for the reaction. This is an example of 'autocatalysis'.

equation 4 $2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

The change in $[MnO_4^-]$ with time may be followed by preparing a reaction mixture containing sulfuric acid, aqueous potassium manganate(VII) and a large excess of sodium ethanedioate.

Portions of the reaction mixture are

- removed at timed intervals,
- quenched by adding 10 cm³ of aqueous potassium iodide (an *excess*), in which the following reaction takes place:

 $2MnO_4^{-}(aq) + 10I^{-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$

• titrated against a standard solution of sodium thiosulfate, in which the reaction in equation 3 (page 5) takes place.

The volume of sodium thiosulfate solution added in each titration (titre) is proportional to $[MnO_4^-]$.

So, in this experiment, there is no need to calculate [MnO₄-].

You may assume that you are provided with:

- 0.100 mol dm⁻³ potassium iodide, KI
- 0.020 mol dm⁻³ potassium manganate(VII), KMnO₄
- 0.200 mol dm⁻³ sodium ethanedioate, Na₂C₂O₄
- 0.0100 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃
- 1.0 mol dm⁻³ sulfuric acid, H₂SO₄
- starch indicator
- the equipment normally found in a school or college laboratory
- (a) 25 cm³ of KMnO₄(aq) is mixed with x cm³ of Na₂C₂O₄(aq), y cm³ of H₂SO₄(aq) and z cm³ of deionised water such that the total volume of the mixture is 125 cm³.
 - (i) Given that the mole ratio of MnO_4^- : $C_2O_4^{2-}$: H⁺ in the mixture is 1 : 20 : 20 respectively, calculate the amounts of KMnO₄(aq), Na₂C₂O₄(aq) and H₂SO₄(aq).

(ii) Hence, determine the values for x, y and z.

(b) Plan a procedure to collect sufficient data to allow a graph of *volume of sodium thiosulfate* against *time* to be drawn.

[1]

In your plan you should include brief details of

- the apparatus you would use,
- the procedure you would follow,
- the measurements you would make.

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(c) Sketch on Fig. 3.1 the graph you would expect to obtain from your results.

Explain your answer.



[Total: 11]

4 Qualitative analysis of an inorganic compound

Compound **X** is a salt consisting of one cation and one anion, both of which can be found in the Qualitative Analysis Notes on pages 19 and 20.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Details of colour changes should be noted and you should indicate clearly at what stage in a test a change occurs.

Test and identify any gases evolved.

Carry out the following tests and record your observations in Table 4.1 below.

		test	observations
(a)	(i)	Add 1 spatula of X into a test-tube. Add 2 cm depth of aqueous sulfuric acid into the same test-tube. Filter the mixture, if necessary, and	 <u>Effervescence</u> of <u>CO₂</u> gas gave white ppt with Ca(OH)₂(aq). <u>Pale pink filtrate with dark brown residue obtained</u>.
		collect the filtrate for subsequent tests.	
	(ii)	To 1 cm depth of the filtrate in a test-tube, add aqueous sodium hydroxide, slowly with shaking until no further change is seen.	 <u>Off-white / beige / pale or light</u> <u>brown/cream ppt</u> insoluble in <u>excess NaOH(aq)</u>. Ppt rapidly <u>turns brown on</u> <u>contact with air / darkens on</u> <u>standing</u>.
	(iii)	To 1 cm depth of the mixture from (ii), carefully add 1 cm depth of aqueous hydrogen peroxide.	 Ppt / solid turns <u>brown / darker</u> <u>brown / brown-black</u>. <u>Effervescence of O₂ gas relit</u> <u>glowing splint</u>.

Table 4.1

(b) Identify the cation and anion present in X. Use evidence from your observations in (a) to support your deduction.

(c) In test 4(a)(ii), when NaOH(aq) is replaced with NH₃(aq), similar observations were made since ammonia behaved as an Arrhenius base:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

But when an equal volume of aqueous ammonium chloride, NH_4Cl , was added to a portion of the filtrate that was used in **4(a)(ii)** followed by the addition of $NH_3(aq)$, no precipitate formed.

Explain why no precipitate was formed with the addition of $NH_4Cl(aq)$ followed by $NH_3(aq)$.

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

1 To determine the percentage by mass of Fe(NO₃)₂ in a salt mixture

FA 1 is a solution containing a salt mixture of two different ionic compounds. One of the compound is $Fe(NO_3)_2$. The other compound, **X**, contains a cation and an anion.

In this question, you will determine the percentage by mass of $Fe(NO_3)_2$ in the mixture by preparing a diluted solution of **FA 1** and carry out a titration using potassium manganate(VII). The iron(II) ions, Fe^{2+} , are oxidised by the manganate(VII) ions, MnO_4^- .

equation 1 $5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

The end-point of the titration occurs when the presence of unreacted MnO_4^- causes the colour of the solution to become pale pink.

The following reagents are provided.

FA 1 is a solution containing 90.0 g dm⁻³ of the salt mixture in sulfuric acid **FA 2** is 0.010 mol dm⁻³ manganate(VII) ions, MnO_4^- **FA 3** is 1 mol dm⁻³ sulfuric acid, H_2SO_4

(b) Determining the percentage by mass of Fe(NO₃)₂

- 1. Fill a burette with **FA 2**.
- 2. Use a pipette to transfer 25.0 cm³ of **FA 1** into a 250 cm³ volumetric flask.
- 3. Make up to the mark with deionised water and label this solution **FA 4**. Shake to obtain a homogeneous solution.
- 4. Pipette 25.0 cm³ of **FA 4** into a 250 cm³ conical flask.
- 5. Use the 25.0 cm³ measuring cylinder to add 25.0 cm³ of **FA 3** into the conical flask.
- 6. Run **FA 2** from the burette into the conical flask. The end-point is reached when the solution changes colour from yellow to pale pink.
- 7. Record your titration results in the space on the next page. Make certain that your recorded results show the precision of your working.
- 8. Repeat steps 4 to 7 as necessary until consistent results are obtained.

Results

final burette reading / cm ³	20.75	20.80
initial burette reading / cm ³	0.00	0.00
volume of FA 2 added / cm ³	20.75	20.80

[3]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** used = $\frac{20.75 + 20.80}{2} = 20.78 \text{ cm}^3$

volume of **FA 2** =[3]

(c) (i) Calculate the amount of MnO₄⁻ ions present in the volume of FA 2 calculated in 1(b).

amount of MnO₄⁻ present = $\frac{20.78}{1000} \times 0.010 = 2.078 \times 10^{-4} \approx 2.08 \times 10^{-4}$ mol

(ii) Calculate the amount of Fe^{2+} ions present in 25.0 cm³ of FA 4.

 $5Fe^{2+} \equiv MnO_4^{-1}$

amount of Fe²⁺ present in 25.0 cm³ of FA 4 = $2.078 \times 10^{-4} \times 5$ = $1.039 \times 10^{-3} \approx 1.04 \times 10^{-3}$ mol

amount of Fe^{2+} ions =...... **1.04 × 10⁻³ mol** [1]

(iii) Calculate the concentration of Fe²⁺ ions present in 25.0 cm³ of FA 1.

amount of Fe²⁺ present in 250 cm³ of FA 4 = $1.039 \times 10^{-3} \times \frac{250}{25.0} = 1.039 \times 10^{-2}$ mol

$$\left[\text{Fe}^{2+} \right]$$
 in 25.0 cm³ of **FA 1** = $\frac{1.039 \times 10^{-2}}{\frac{25.0}{1000}}$ = 0.4156 \approx 0.416 mol dm⁻³

(iv) Hence, calculate the percentage by mass of Fe(NO₃)₂ in the salt mixture. [A_r: Fe, 55.8; N, 14.0; O, 16.0] molar mass of Fe(NO₃)₂ = 55.8 + 2(14.0 + 3(16.0)) = 179.8 g mol⁻¹ concentration of Fe(NO₃)₂ in FA 1, in g dm⁻³ = 0.4156 × 179.8 = 74.72 g dm⁻³ percentage by mass of Fe(NO₃)₂ in salt mixture = $\frac{74.72}{90.0} \times 100 = 83.0\%$

(d) Suggest why a solution containing Fe²⁺ ions readily turns yellow when it comes into contact with air.

Fe²⁺ ions can be easily **oxidised by oxygen** in air to form yellow **Fe³⁺**.

.....[1]

(e) A student suggested that **FA 3** can be hydrochloric acid instead of sulfuric acid. Explain why hydrochloric acid cannot be used in the titration and how it would impact the accuracy of the titration result.

 MnO_4^- ion **can oxidise C**t. Additional MnO_4^- will be consumed in the titration upon

reacting with Ct besides reacting with Fe2+. Hence, the titre will be higher than the

actual titre.

(f) Calculate the percentage error for your average titre value in (b).

percentage error = $\frac{2 \times 0.05}{20.78} \times 100 = 0.481\%$ %

percentage error =......[1]

(g) Hydrogen peroxide can act as an oxidising agent and reducing agent as shown by the following half-equations:

 $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$

 $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$

(i) Hydrogen peroxide can also oxidise the Fe^{2+} ions. Write a balanced equation for the reaction of Fe^{2+} with H_2O_2 in an acidic medium.

 $2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$ [1]

(ii) Explain why hydrogen peroxide is not a suitable replacement for KMnO₄ in this experiment.

There is no distinct colour (visual) change at the end-point. Hence, it would

be impossible to know when the reaction has completed.

.....[1]

[Total: 18]

2 Determination of the kinetics of the reaction between iron(III) and iodide ions

FA 5 is aqueous potassium iodide, KI. **FA 6** is aqueous iron(III) chloride, FeC l_3 . **FA 7** is 0.0065 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

You are also provided with a starch indicator and deionised water.

A solution containing potassium iodide, sodium thiosulfate and starch is mixed with iron(III) chloride solution. After a few seconds a dark blue colour suddenly appears. This is one of a number of reactions referred to as iodine clock reaction.

equation 2 $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

equation 3 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$

When the above solutions are mixed, iodine is generated according to equation 2. The iodine is being consumed as they are generated, according to equation 3. Therefore, only a small amount of iodine is present in the mixture.

The reaction in equation 3 stops once all the thiosulfate ions have reacted. The concentration of iodine now increases and the dark blue colour of the iodine-starch complex appears.

The reaction in equation 2 is first order with respect to the iodide ion concentration, [I⁻].

You are to perform a series of experiments to determine the rate order for the reaction in equation 2 with respect to the iron(III) chloride concentration, [FeC l_3].

(a) Experiments

You will attempt five experiments.

- In **Experiment 1**, **Solution A** will be prepared as described below.
- In the remaining experiments you will repeat the procedure from **Experiment 1**, but using volumes of **FA 6** of your choice.

For each experiment, you note the time taken, *t*, for the solution to turn dark blue.

(ii) Experiment 1

Fill the burette labelled E2 with FA 6.

• Transfer 25.00 cm³ of **FA 6** to a conical flask.

Solution A

- Using a 10 cm³ measuring cylinder, add 10.0 cm³ of **FA 5** to the beaker labelled **Solution A**.
- Using a 25 cm³ measuring cylinder, add 20.0 cm³ of **FA 7** to the same beaker.
- Using a 10 cm³ measuring cylinder, add 5.0 cm³ of starch indicator to the same beaker.
- Mix the contents thoroughly by swirling the beaker.
- 1. Pour **Solution A** rapidly into the conical flask containing **FA 6**. Start the stopwatch when you have added about half of **Solution A**.
- 2. Mix the contents thoroughly by swirling the flask.
- 3. Stop the stopwatch when the dark blue colour first appears.
- 4. Note the time elapsed, *t*, to the nearest second.
- 5. Wash the conical flask and beaker thoroughly with water and allow to drain.

(ii) Remaining Experiments

You are now to perform **four** other experiments in order to determine the rate order with respect to $[FeCl_3]$ for reaction **2**. You should number these experiments **2** to **5**.

In each experiment, the volumes of **FA 5**, **FA 7** and starch indicator are the same as those used in **Experiment 1**.

Select suitable volumes of **FA 6**, *V*_{FA 6}, ensuring that your chosen volumes:

- allow you to obtain sufficient data to determine the order through the plotting of a graph,
- are not larger than the volume used in **Experiment 1**,
- are not less than 15.00 cm³.

In each case, the total volume of the reaction mixture must be kept the same as that used in **Experiment 1**, by adding deionised water as required.

(b) Results

The volumes of **FA 5**, **FA 7** and starch indicator are not changed in these experiments, and do not need to be recorded.

Prepare a table in the space provided below in which to record, for each experiment:

- all volumes apart from those of **FA 5**, **FA 7** and starch indicator,
- the value of *t*,

Record your results in the table.

(i) Table of results

Complete the table below.

experiment	V _{FA 6} / cm ³	volume of deionised water / cm ³	t/s	rate / µmol dm⁻³ s⁻¹
1	25.00	0.0	33	65.8
2	15.00	10.0	65	33.4
3	23.00	2.0	36	60.3
4	20.00	5.0	39	55.6
5	18.00	7.0	50	43.4

(ii) Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, used in each experiment in 2(a).

amount of S₂O₃²⁻ used in each experiment =
$$\frac{20.0}{1000} \times 0.0065$$

= 1.30×10^{-4} mol

(iii) Use your answer to **2(b)(ii)**, and the equations for the reactions involved, to calculate the amount of iron(III) ions, Fe³⁺, that reacted in each experiment in **2(a)**.

$$\begin{split} 2S_2O_3^{2-} &\equiv I_2 \equiv 2Fe^{3+} \\ \text{amount of } Fe^{3+} \text{ reacted in each experiment} \\ &= \text{amount of } S_2O_3^{2-} \text{ used in each experiment} \\ &= 1.30 \times 10^{-4} \text{ mol} \end{split}$$

(iv) Use your answer to **2(b)(iii)** to calculate the change in concentration of Fe³⁺, [Fe³⁺], that occurred when enough iodine was produced to produce the dark blue colour in each experiment in **2(a)**.

change in $\left[\text{Fe}^{3+} \right] = \frac{-1.30 \times 10^{-4}}{\frac{60.0}{1000}} = -2.167 \times 10^{-3} \approx -2.17 \times 10^{-3} \text{ mol dm}^{-3}$

change in $[Fe^{3+}] = -2.17 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

(v) The expression below shows the experimental rate of this reaction as the change in concentration of Fe³⁺ per unit time.

experimental rate = $-\frac{\text{change in } \left[\text{Fe}^{3+}\right]}{\text{time, } t} \times 10^6 \text{ } \mu\text{mol } \text{dm}^{-3} \text{ s}^{-1}$

 $(1 \ \mu mol = 10^{-6} \ mol)$

Complete your table on page 7 by calculating the experimental rates of reaction for all 5 experiments, taking into consideration the units.

If you are unable to calculate a value for the change in [Fe³⁺] in **2(b)(iv)**, use the value -2.50×10^{-3} mol dm⁻³. (Note: this is not the actual value.) [2]

(c) Plot a graph of experimental rate on the y-axis against $V_{FA 6}$ on the x-axis.

The scales of both axes must be chosen to provide an origin.

Draw the best-fit straight line through the origin, taking into account all of your plotted points.



[3]

(d) By considering the shape of the graph in (c), state and explain the order of the reaction with respect to [FeC l₃].

A straight-line graph through the origin is obtained, hence rate \propto volume of FA 6.

Since total volume is constant, volume of FA 6 \propto [FeCl₃]. Thus rate \propto [FeCl₃], the

order of reaction with respect to [FeCl₃] is 1.

.....[2]

- (e) The order of reaction with respect to [I[−]] is one. With reference to experiment 1, state and explain the expected time taken for the appearance of the dark blue colour when the experiment is carried out using a mixture comprising the following:
 - 5.0 cm³ of **FA 5**
 - 25.00 cm³ of **FA 6**
 - 10 cm³ of **FA 7**
 - 15.0 cm³ of deionised water

• 5 cm³ of starch

The expected measured time should same as in experiment 1, *i.e.* 30 s. When [I⁻] is halved, the time measured should be doubled (volume of FA 5 is halved) as the reaction is first-order with respect to I⁻. When [S₂O₃²⁻] is also halved (volume of S₂O₃²⁻ is halved), the time measured should be halved as there is less S₂O₃²⁻ to react. Hence, the overall measured time is the <u>same</u>. [2] (f) A student suggested that a more accurate timing can be obtained when the volume of FA 5 is measured with a burette rather than a measuring cylinder.

A teacher said that the student's claim is incorrect. Explain why this is so.

Since the measurement is taken to the **nearest second** and **FA 5** is **not added directly** to the reaction mixture after being measured from the burette, the **precision of the measured volume is not important** here.

.....[2]

[Total: 18]

3 Planning

 MnO_4^- ions oxidises $C_2O_4^{2-}$ ions in acidic medium as shown in equation 4. The Mn^{2+} ions produced in equation 4 act as a catalyst for the reaction. This is an example of 'autocatalysis'.

equation 4 $2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

The change in $[MnO_4^-]$ with time may be followed by preparing a reaction mixture containing sulfuric acid, aqueous potassium manganate(VII) and a large excess of sodium ethanedioate.

Portions of the reaction mixture are

- removed at timed intervals,
- quenched by adding 10 cm³ of aqueous potassium iodide (an *excess*), in which the following reaction takes place:

 $2MnO_4^{-}(aq) + 10I^{-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$

• titrated against a standard solution of sodium thiosulfate, in which the reaction in equation 3 (page 5) takes place.

The volume of sodium thiosulfate solution added in each titration (titre) is proportional to $[MnO_4^-]$.

So, in this experiment, there is no need to calculate [MnO₄-].

You may assume that you are provided with:

- 0.100 mol dm⁻³ potassium iodide, KI
- 0.020 mol dm⁻³ potassium manganate(VII), KMnO₄
- 0.200 mol dm⁻³ sodium ethanedioate, Na₂C₂O₄
- 0.0100 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃
- 1.0 mol dm⁻³ sulfuric acid, H₂SO₄
- starch indicator
- the equipment normally found in a school or college laboratory
- (a) 25 cm³ of KMnO₄(aq) is mixed with x cm³ of Na₂C₂O₄(aq), y cm³ of H₂SO₄(aq) and z cm³ of deionised water such that the total volume of the mixture is 125 cm³.
 - (i) Given that the mole ratio of MnO₄⁻ : C₂O₄²⁻ : H⁺ in the mixture is 1 : 20 : 20 respectively, calculate the amounts of KMnO₄(aq), Na₂C₂O₄(aq) and H₂SO₄(aq).

mole ratio of MnO_4^- : $C_2O_4^{2-}$: $H^+ = 1$: 20: 20 amount of MnO_4^- in 25 cm³ = $\frac{25}{1000} \times 0.020 = 5.00 \times 10^{-4}$ mol amount of $C_2O_4^{2-}$ needed = $5.00 \times 10^{-4} \times 20 = 0.0100$ mol amount of H_2SO_4 needed = $\frac{1}{2} \times 5.00 \times 10^{-4} \times 20 = 0.00500$ mol

[2]

(ii) Hence, determine the values for x, y and z. volume of $C_2O_4^{2-}$ needed = 0.0100 ÷ 0.200 = 0.0500 dm³ = 50 cm³ x = 50 volume of H₂SO₄ needed = 0.000500 ÷ 1.0 = 0.00500 dm³ = 5 cm³ y = 5 Therefore, z = 125 - (25 + 50 + 5) = 45

[1]

(b) Plan a procedure to collect sufficient data to allow a graph of *volume of sodium thiosulfate* against *time* to be drawn.

In your plan you should include brief details of

- the apparatus you would use,
- the procedure you would follow,
- the measurements you would make.

1. Fill up a 50 cm³ burette with 0.0100 mol dm⁻³ Na₂S₂O₃(aq).

2. Use a 50 cm³ measuring cylinder to add 50.0 cm³ of 0.200 mol dm⁻³ Na₂C₂O₄(aq),

into a **250 cm³ conical flask** labelled "reaction mixture".

- 3. Use a 10 cm³ measuring cylinder to add 5.0 cm³ of 1.0 mol dm⁻³ H₂SO₄(aq) into
- the same 250 cm³ conical flask.
- 4. Use a 50 cm³ measuring cylinder to add 45.0 cm³ of deionised water into the

same 250 cm³ conical flask.

3. Using a 25 cm³ measuring cylinder, add 25.0 cm³ of 0.020 mol dm⁻³

KMnO₄(aq) into the same 250 cm³ conical flask. Start the stopwatch and swirl

- the mixture thoroughly to mix its contents.
- 4. Immediately use a 10 cm³ pipette to pipette 10.0 cm³ aliquot of the reaction

mixture into another 250 cm³ conical flask.

5. At the 1st minute, use a 10 cm³ measuring cylinder to add 10 cm³ of 0.100 mol

<u>dm⁻³ KI(aq)</u>.

.....

- Immediately titrate with Na₂S₂O₃(aq). When the colour of the solution turns pale yellow, add about 1 cm³ of starch indicator.
 Continue the titration; the end-point is reached when the dark blue colour just disappears. Record your results.
 Wash out the second conical flask with water.
 Repeat step 4 to 7 another 5 times, quenching at the 4th, 7th, 10th, 13th and 16th minute. [5]
- (c) Sketch on Fig. 3.1 the graph you would expect to obtain from your results.

Explain your answer.





explanation The magnitude of the gradient increases because the Mn²⁺ produced speeds up the rate of reaction. The magnitude of the gradient decreases because the concentration of reactant decrease. [3]

[Total: 11]

4 Qualitative analysis of an inorganic compound

Compound **X** is a salt consisting of one cation and one anion, both of which can be found in the Qualitative Analysis Notes on pages 19 and 20.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Details of colour changes should be noted and you should indicate clearly at what stage in a test a change occurs.

Test and identify any gases evolved.

Carry out the following tests and record your observations in Table 4.1 below.

		test	observations		
(a)	(i)	Add 1 spatula of X into a test-tube. Add 2 cm depth of aqueous sulfuric acid into the same test-tube.	 <u>Effervescence</u> of <u>CO₂</u> gas gave white ppt with Ca(OH)₂(aq). 		
		Filter the mixture, if necessary, and collect the filtrate for subsequent tests.	Pale pink filtrate with dark brown residue obtained.		
	(ii)	To 1 cm depth of the filtrate in a test-tube, add aqueous sodium hydroxide, slowly with shaking until no further change is seen.	 Off-white / beige / pale or light brown/cream ppt insoluble in excess NaOH(aq). Ppt rapidly <u>turns brown on</u> contact with air / darkens on standing. 		
	(iii)	To 1 cm depth of the mixture from (ii), carefully add 1 cm depth of aqueous hydrogen peroxide.	 Ppt / solid turns <u>brown / darker</u> <u>brown / brown-black</u>. <u>Effervescence of O₂ gas relit</u> <u>glowing splint</u>. 		

Table 4.1

(b) Identify the cation and anion present in X. Use evidence from your observations in (a) to support your deduction.

cation present Mn²⁺

evidence Addition of NaOH formed off-white ppt insoluble in excess NaOH(aq).

Ppt rapidly turned brown upon contact with air, indicating presence of Mn²⁺.

.....

anion present CO32-

evidence Addition of an acid, H2SO4, results in effervescence of CO2 gas which

gave a white ppt with Ca(OH)2, indicating presence of CO32=.

.....[2]

(c) In test 4(a)(ii), when NaOH(aq) is replaced with NH₃(aq), similar observations were made since ammonia behaved as an Arrhenius base:

$$\mathsf{NH}_3+\mathsf{H}_2\mathsf{O}\rightleftharpoons\mathsf{NH}_4^++\mathsf{OH}^-$$

But when an equal volume of aqueous ammonium chloride, NH_4Cl , was added to a portion of the filtrate that was used in **4(a)(ii)** followed by the addition of $NH_3(aq)$, no precipitate formed.

Explain why no precipitate was formed with the addition of $NH_4Cl(aq)$ followed by $NH_3(aq)$.

Addition of aqueous ammonium chloride increased [NH4+] and shifted position of

equilibrium $NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$ to the left, decreasing [OH⁻].

[OH⁻] is insufficient to cause precipitation as ionic product $< K_{sp}$ of the Mn(OH)₂.

......[2]

[Total: 8]