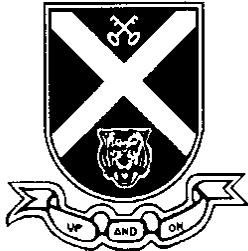


Name:		Shift:	
Class:	21S	Lab:	

ST ANDREW'S JUNIOR COLLEGE



JC2 PRELIMINARY EXAMINATION

CHEMISTRY	9729/04
Paper 4 Practical	18 Aug 2022
	2 hours 30 minutes

Additional Materials: Qualitative Analysis Notes

READ THESE INSTRUCTIONS FIRST.

Write your name and class on all the work you hand in.

Give details of the practical shift and laboratory in the boxes provided above.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

Do not use staples, 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.

The number of marks is given in the brackets [] at the end of each question or part question.

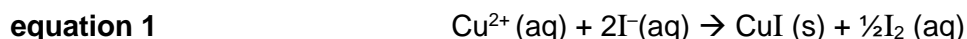
For Examiner's Use	
1	19
2	14
3	14
4	8
Total	55

This document consists of **22** printed pages, including 1 blank page.

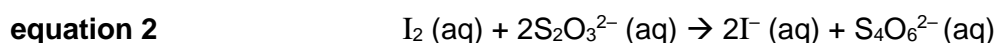
1 Determination of water of crystallisation in a sample of hydrated copper(II) sulfate

The formula of hydrated copper(II) sulfate is $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, where x refers to the number of moles of water of crystallisation. In **1(a)(i)**, you will perform titration to determine the value of x .

Excess aqueous KI is first added to copper(II) sulfate solution. This will produce a white precipitate in a brown solution of I_2 .



The liberated iodine is then titrated against sodium thiosulfate.



You are provided with:

- solid **FA 1**, hydrated copper(II) sulfate
- **FA 2**, $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- **FA 3**, potassium iodide solution, KI
- **Solution S**, starch solution.

Note: **Solution S** will also be used in Question 2.

(a) (i) Procedure

1. Fill a burette with **FA 2**.
2. Weigh accurately about 5 g of **FA 1**. Record the mass on page 3. Transfer all the solids into a 100 cm^3 beaker. Add about 75 cm^3 of deionised water and stir with a glass rod to dissolve them.
3. Transfer the solution into a 250 cm^3 volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.
4. Make up to the 250 cm^3 mark with deionised water. Stopper the volumetric flask and shake well to mix. Label this solution as **FA 4**.
5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and use a measuring cylinder to add 15 cm^3 of **FA 3** into the same conical flask.
6. Titrate this solution with **FA 2** until the mixture becomes pale brown. An off-white precipitate is also present in the conical flask.

7. Add approximately 1 cm³ of **solution S** to the conical flask and continue titration until the blue-black colour just disappears, with the off-white precipitate remaining in the conical flask.
8. Discard the contents and rinse the conical flask with water.
9. Repeat the titration to obtain consistent results. Record your titration results in the space below.

Results

Mass of empty weighing bottle / g	
Mass of FA 1 and weighing bottle / g	
Mass of FA 1 / g	5.030

	1	2
final burette reading / cm ³		
initial burette reading / cm ³		
volume of FA 2 used / cm ³	20.00	19.95

- (ii) 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** = cm³ [1]

- (b) (i) Calculate the amount, in moles, of Cu²⁺ present in 25.0 cm³ of **FA 4**.

Amount of Cu²⁺ = mol [1]

- (ii) Calculate the concentration of Cu²⁺ in **FA 4**.

Concentration of Cu²⁺ = mol dm⁻³ [1]

- (iii) Given that the concentration of CuSO₄•*x*H₂O in **FA 4** is 20.00 g dm⁻³, use your answer in (b)(ii) to determine the value of *x*.

[A_r: H, 1.0 Cu, 63.5 S, 32.1 O, 16.0]

x = [4]

- (iv) In step 5, **FA 3** was added using a 25 cm³ measuring cylinder. Calculate the percentage error in the measurement of the specified volume in step 5.

Percentage error = % [1]

- (c) (i) A student conducted the experiment as mentioned in (a)(i). After carrying out step 5, he left the conical flask containing **FA 3** and **FA 4** to stand for 30 minutes, before continuing with steps 6 to 8. It was noted that his titre volume was less than expected. Suggest a reason for this observation.

.....
 [1]

- (ii) Two other students conducted the same experiment in (a)(i) but with the following modifications to the procedures.

Student 2: In Step 5, add 30 cm³ of **FA 3** instead of 15 cm³.

Student 3: In Step 7, omit the use of **solution S**.

Explain how each of these modifications will affect the accuracy of the results.

Student 2

.....

Student 3

.....
 [2]

(iii) Another student proposed the following modification.

- Filtering the contents in the conical flask after step 5, before carrying out the titration in step 6.

State an advantage and a disadvantage of this modification.

.....

.....

.....

[2]

(d) Table 1.1 shows some standard electrode potential values.

Table 1.1

electrode reaction	E^\ominus / V
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.15
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54

The E^\ominus_{cell} for **equation 1** is -0.39 V . Explain why the reaction occurred in **(a)(i)** despite the negative E^\ominus_{cell} value.

.....

.....

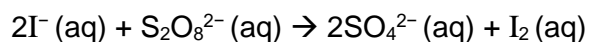
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[2]

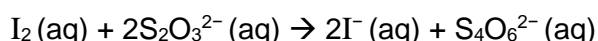
[Total: 19]

2 Determination of the kinetics of the iodide-peroxodisulfate redox reaction

This question seeks to investigate the kinetics of the redox reaction between iodide ions, I^- , and peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$. The redox reaction may be represented by the equation below.



In order to measure the rate of this reaction, a fixed volume of aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to the reaction mixture. Starch is also added to the reaction mixture. When the sodium thiosulfate completely reacts with the iodine produced, the remaining iodine reacts with starch to form a dark blue complex.



The rate of reaction is studied by measuring the time taken for the solution to turn dark blue, t , in a series of five experiments. You will then graphically analyse your results to determine the order of reaction with respect to $[\text{I}^-]$.

FA 5 is $0.100 \text{ mol dm}^{-3}$ potassium iodide, KI.

FA 6 is $0.500 \text{ mol dm}^{-3}$ sodium peroxodisulfate, $\text{Na}_2\text{S}_2\text{O}_8$.

FA 7 is $0.00500 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

You will also need **Solution S** from **Question 1**.

(a) Prepare a table in the space provided on page 9 to record, to an appropriate level of precision:

- volume of **FA 5**, $V_{\text{FA 5}}$
- volume of deionised water,
- all values of t ,
- all calculated values of $1/t$, $\lg(1/t)$ and $\lg(V_{\text{FA 5}})$.

Experiment 1

1. Fill the burette with **FA 5**.
2. Transfer 20.00 cm^3 of **FA 5** into a 250 cm^3 conical flask.
3. Using separate 10 cm^3 measuring cylinders, add 10.0 cm^3 of **FA 7** and 1.0 cm^3 of **Solution S** into the same conical flask.
4. Using a 25 cm^3 measuring cylinder, measure 20.0 cm^3 of **FA 6**.
5. Start the stopwatch upon adding **FA 6** into the conical flask. Swirl the reaction mixture and place the conical flask on a white tile.

6. Stop the stopwatch when the solution first turns dark blue.
7. Record the time taken, t , to the nearest second in your table.
8. Discard the reaction mixture and wash out the conical flask. Stand it upside down on a paper towel to drain.

Experiments 2 to 5

Repeat experiment 1 four times, using 18.00 cm³, 16.00 cm³, 14.00 cm³ and 12.00 cm³ of **FA 5** respectively at step 2.

In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding appropriate volumes of deionised water.

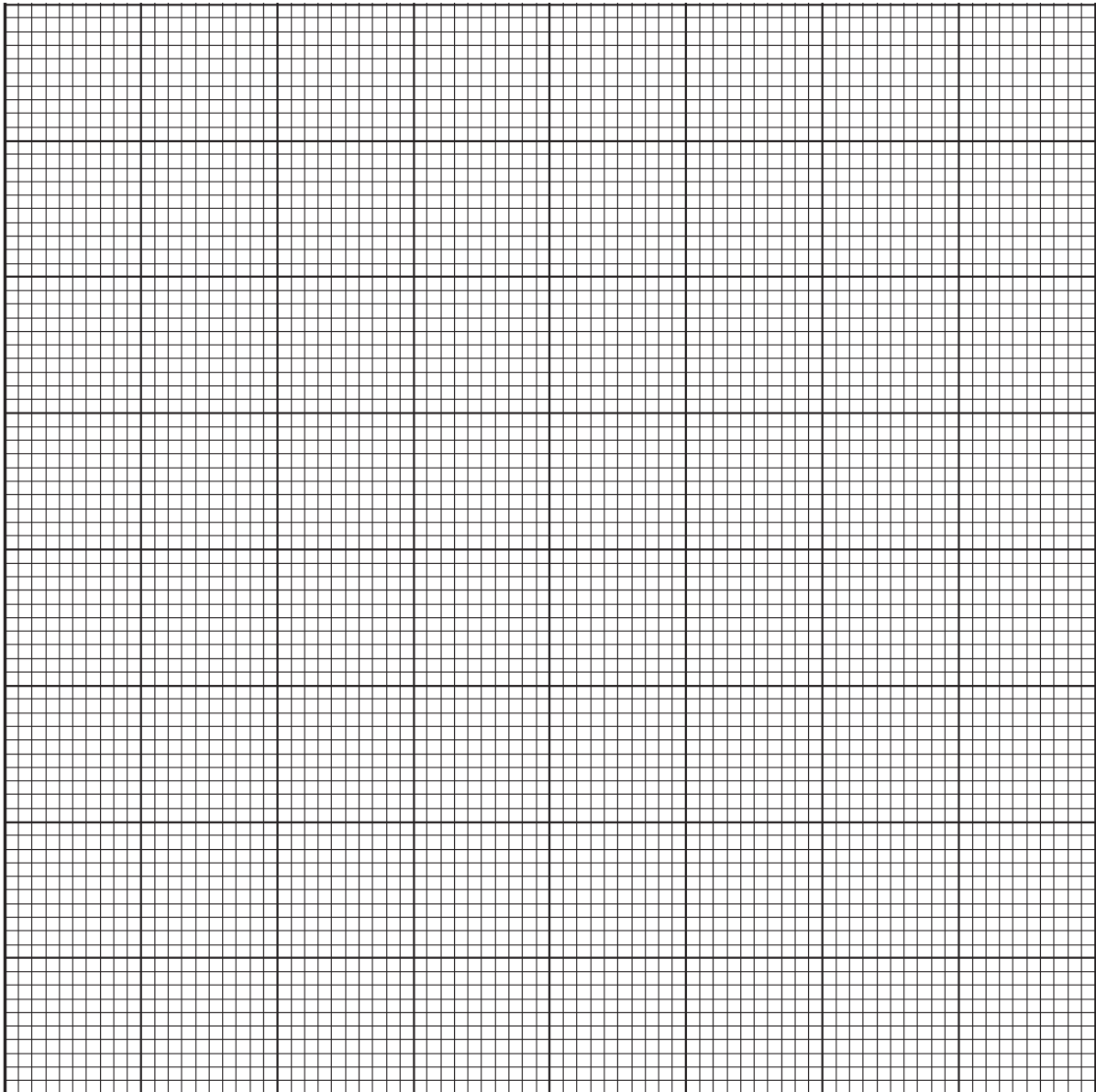
You should alternate the use of the two conical flasks.

Results

Complete the table below.

$V_{\text{FA 5}} / \text{cm}^3$	Vol of deionised water / cm ³	t / s	$1/t / \text{s}^{-1}$	$\lg (1/t)$	$\lg (V_{\text{FA 5}})$
20.00	0.0	24			
18.00	2.0	25			
16.00	4.0	30			
14.00	6.0	36			
12.00	8.0	44			

- (b) (i) Plot a graph of $\lg(1/t)$ on the y-axis against $\lg(V_{FA5})$ on the x-axis.
Draw a best-fit straight line through your plotted points.

[3]

- (ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of reaction with respect to $[I^-]$.

Gradient =

Order of reaction with respect to $[I^-]$ =

[3]

- (iii) Explain why the total volume of the reaction mixture needs to be kept constant in all five experiments in (a).

.....

.....

[1]

- (c) (i) Iron(III) salts are sometimes used as a catalyst for the reaction you performed in (a). Suggest why there is a need for a catalyst.

.....

.....

[1]

- (ii) Using data from **Table 2.1** below, show how iron(III) ions can perform this role and write relevant equation(s).

Table 2.1

electrode reaction	E^\ominus/V
$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$	-0.04
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01

[2]

[Total: 14]

[Turn Over]

3 Investigation of some inorganic reactions

- (a) **FA 8** is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**.

Perform the tests described in **Table 3.1**. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

Tests		Observations for FA 8
1.	Place a spatula of FA 8 in a dry boiling tube and heat.	Blue crystals become/form <u>white powder/solid</u> . ✓ Note: No mark for “blue crystals form white ppt ” as ppt is only used for solids forming in solution. <u>Colourless</u> liquid <u>droplets</u> can be found near the opening of the boiling tube. ✓
2.	Add a spatula of FA 8 in a test-tube. Add 1 cm depth of H_2O_2 , followed by 1 cm depth of aqueous sodium hydroxide.	Blue solid dissolved to form <u>blue solution</u> . ✓ Upon adding sodium hydroxide, a <u>black / brown / greenish-brown / green ppt</u> ✓ is formed. <u>Effervescence</u> ✓ is seen, which <u>relights a glowing splint</u> ✓. Gas is <u>oxygen</u> ✓.
3.	Add half a spatula of FA 8 into a test-tube. Add aqueous ammonia dropwise until it is in excess.	A (pale) <u>blue ppt</u> is formed ✓ Ppt is <u>soluble in excess NH_3</u> , ✓ forming a <u>deep blue/dark blue solution</u> . ✓

4.	<p>Add half a spatula of FA 8 into a test-tube and dissolve with 1 cm depth deionised water. Use a glass rod to stir if necessary.</p> <p>Add aqueous sodium carbonate dropwise to the resultant solution until it is in excess.</p>	<p>Blue solid dissolves to form a <u>blue solution</u> ✓.</p> <p>A (pale) <u>blue ppt</u> ✓ is formed.</p> <p><u>Ppt insoluble in excess.</u> ✓</p>
----	---	--

[4]

(b) Consider your observations in **Table 3.1**.

(i) Based on your observations for test 2, suggest the role of **FA 8**.

..... [1]

(ii) **Table 3.2** shows the K_{sp} values for both copper(II) carbonate and copper(II) hydroxide.

Table 3.2

	K_{sp}
CuCO_3	$1.4 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
Cu(OH)_2	$4.8 \times 10^{-20} \text{ mol}^3 \text{ dm}^{-9}$

Calculate the solubility of each salt. Hence, suggest the identity of the species responsible for the observations seen in test 4.

.....

.....

.....

.....

..... [3]

[Turn Over

(c) To determine the identity of anion in **FA 8**, a student added barium nitrate solution to a solution of **FA 8**. A white ppt is formed.

(i) Based on the observations given, state the possible identities of the anions.

..... [1]

(ii) Suggest a test to confirm the identity of the anion in **FA 8**. **DO NOT** carry out the test.

Test: [1]

(d) **Note: You are NOT given FA 9.**

FA 9 is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**. **Table 3.3** shows a test which is performed on **FA 9** and the corresponding observations.

Table 3.3

Test	Observations for FA 9
To 1 cm depth of a solution of FA 9 , add aqueous ammonia dropwise until it is in excess.	A white ppt is formed. It dissolves in excess aqueous ammonia to give a colourless solution.

(i) Suggest the identity of the cation present in **FA 9**.

..... [1]

(ii) Suggest an explanation for the observations in **Table 3.3** in terms of the species present.

.....

[1]

(iii) **Assuming** you have an aqueous solution of **FA 9**.

There is no observable change when barium nitrate solution is added to **FA 9** solution.

Devise a series of simple tests to identify the anion in **FA 9**. Your tests should be based on the Qualitative Analysis Notes and should use only the bench reagents provided. Record your tests in the space below.

[2]

[Total: 14]

4 Planning

The labels for a bottle of carbonic acid and a bottle of citric acid were mixed up. Both acids have the same concentration of 1.00 mol dm^{-3} . Carbonic acid is dibasic and citric acid is tribasic. In order to identify the correct acids, a series of six experiments will be performed, where different volumes of the acid from one of the bottles and sodium hydroxide are chosen to ensure there are sufficient points before and after the equivalence point. The total volume for each experiment should be kept constant at 60.0 cm^3 .

The temperature change, ΔT , for each neutralisation is calculated using the formula below:

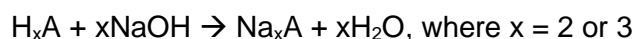
$$\Delta T = T_{\text{final}} - T_{\text{average}},$$

where T_{average} is the weighted average of the initial temperatures of the acid and sodium hydroxide:

$$T_{\text{average}} = \frac{(V_{\text{acid}} \times T_{\text{acid}}) + (V_{\text{NaOH}} \times T_{\text{NaOH}})}{V_{\text{acid}} + V_{\text{NaOH}}}$$

A suitable graph can then be plotted to determine the basicity of the acid.

Let the unknown acid be H_xA . The neutralisation reaction is shown below.



You are provided with:

- 1.00 mol dm^{-3} sodium hydroxide, NaOH
 - 1.00 mol dm^{-3} acid from one of the bottles, H_xA
 - the equipment normally found in a school or college laboratory.
- (a) (i) Calculate the volumes of acid required for complete reaction if the acid is dibasic and tribasic respectively.

(ii) Using your answers in (i), fill in the volumes of acid and NaOH in the table below.

Experiment	Volume of acid / cm ³	Volume of NaOH / cm ³
1		
2		
3		
4		
5		
6		

[1]

(b) In your plan to determine the basicity of H_xA, 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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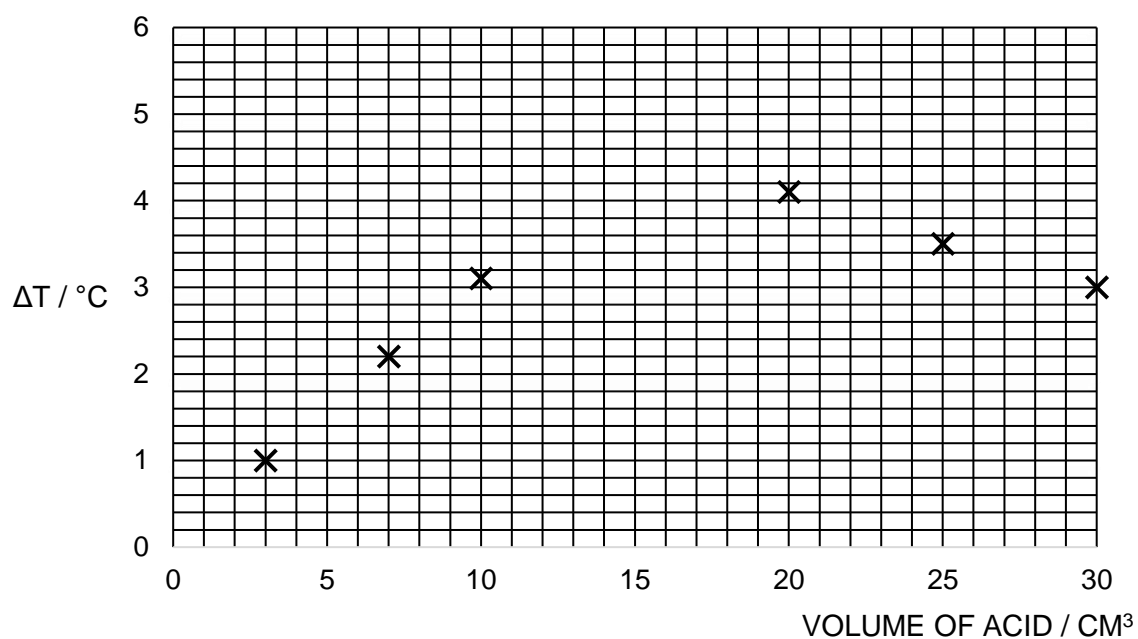
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[Turn Over]

- (b) A student conducted the experiment and obtained the following graph of ΔT against volume of acid.



Draw 2 best-fit straight lines and extrapolate both lines to find volume of acid required to completely react with NaOH.

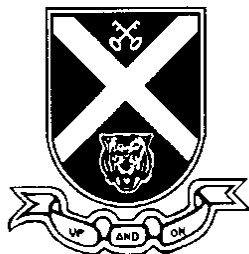
Hence, deduce the identity of the acid.

[2]

[Total: 8]

[Turn Over]

Name:		Shift:	
Class:	21S	Lab:	

ST ANDREW'S JUNIOR COLLEGE**JC2 PRELIMINARY EXAMINATION****CHEMISTRY****9729/04****Paper 4 Practical****18 Aug 2022****2 hours 30 minutes****Additional Materials: Qualitative Analysis Notes****READ THESE INSTRUCTIONS FIRST.**

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Do not use staples, 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.

The number of marks is given in the brackets [] at the end of each question or part question.

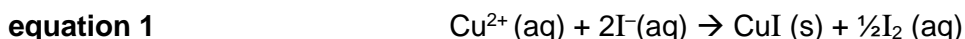
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This document consists of **22** printed pages, including 1 blank page.**[Turn Over**

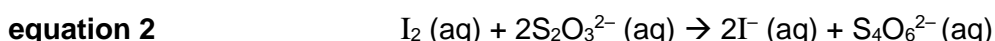
1 Determination of water of crystallisation in a sample of hydrated copper(II) sulfate

The formula of hydrated copper(II) sulfate is $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, where x refers to the number of moles of water of crystallisation. In **1(a)(i)**, you will perform titration to determine the value of x .

Excess aqueous KI is first added to copper(II) sulfate solution. This will produce a white precipitate in a brown solution of I_2 .



The liberated iodine is then titrated against sodium thiosulfate.



You are provided with:

- solid **FA 1**, hydrated copper(II) sulfate
- **FA 2**, $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- **FA 3**, potassium iodide solution, KI
- **Solution S**, starch solution.

Note: **Solution S** will also be used in Question 2.

(a) (i) Procedure

10. Fill a burette with **FA 2**.
11. Weigh accurately about 5 g of **FA 1**. Record the mass on page 3. Transfer all the solids into a 100 cm^3 beaker. Add about 75 cm^3 of deionised water and stir with a glass rod to dissolve them.
12. Transfer the solution into a 250 cm^3 volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.
13. Make up to the 250 cm^3 mark with deionised water. Stopper the volumetric flask and shake well to mix. Label this solution as **FA 4**.
14. Pipette 25.0 cm^3 of **FA 4** into a conical flask and use a measuring cylinder to add 15 cm^3 of **FA 3** into the same conical flask.
15. Titrate this solution with **FA 2** until the mixture becomes pale brown. An off-white precipitate is also present in the conical flask.

16. Add approximately 1 cm^3 of **solution S** to the conical flask and continue titration until the blue-black colour just disappears, with the off-white precipitate remaining in the conical flask.
17. Discard the contents and rinse the conical flask with water.
18. Repeat the titration to obtain consistent results. Record your titration results in the space below.

Results

Mass of empty weighing bottle / g	
Mass of FA 1 and weighing bottle / g	
Mass of emptied weighing bottle / g	
Mass of FA 1 / g	5.030

	1	2
final burette reading / cm^3		
initial burette reading / cm^3		
volume of FA 2 used / cm^3	20.00	19.95

- Mass of FA 1 used should be **5 +/- 0.05 g** [1]
- Tabulates **correct headers and units for both mass and titration** [1]
- All values are recorded to **2 decimal places** and to **nearest 0.05 cm^3** [1]
- **Two** titre volumes **within 0.10 cm^3** [1]

[4]

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

- **Average of 2 consistent titre volumes, recorded to 2 d.p [1]**

Volume of **FA 2** = cm³ [1]

- (b) (i) Calculate the amount, in moles, of Cu²⁺ present in 25.0 cm³ of **FA 4**.

Amount of S₂O₃²⁻ = (average titre volume / 1000) x 0.1

= Amount of Cu²⁺ in 25 cm³ of **FA 4** [1]

Amount of Cu²⁺ = mol

[1]

- (ii) Calculate the concentration of Cu²⁺ in **FA 4**.

Concentration of Cu²⁺ in **FA 4** = Ans from (b)(i) / 0.025 [1]

Concentration of Cu²⁺ = mol dm⁻³

[1]

- (iii) Given that the concentration of CuSO₄•xH₂O in **FA 4** is 20.00 g dm⁻³, use your answer in (b)(ii) to determine the value of **x**.

[Ar: H, 1.0 Cu, 63.5 S, 32.1 O, 16.0]

Molar mass of hydrated CuSO₄

= 20.00 / ans from (b)(ii) = _____ [1] g mol⁻¹

Molar mass = (63.5 + 32.1 + 64 + x18)

x ≈ 5 [1; rounded off to nearest whole number]

[1] for unit and 3 sf for (b)(i) and (b)(ii)

Accuracy mark [1]

x = [4]

- (iv) In step 5, **FA 3** was added using a 25 cm³ measuring cylinder. Calculate the percentage error in the measurement of the specified volume in step 5.

$$\% \text{ error} = \pm (0.25 / 15) \times 100\% = \pm 1.67\% \quad [1]$$

Percentage error = %

[1]

- (c) (i) A student conducted the experiment as mentioned in (a)(i). After carrying out step 5, he left the conical flask containing **FA 3** and **FA 4** to stand for 30 minutes, before continuing with steps 6 to 8. It was noted that his titre volume was less than expected. Suggest a reason for this observation.

.....

.....

[1]

Iodine is volatile and some will escape from the conical flask. [1]

Or words to the effect, e.g. evaporation of iodine.

- (ii) Two other students conducted the same experiment in (a)(i) but with the following modifications to the procedures.

Student 2: In Step 5, add 30 cm³ of **FA 3** instead of 15 cm³.

Student 3: In Step 7, omit the use of **solution S**.

Explain how each of these modifications will affect the accuracy of the results.

Student 2:

Potassium iodide was already added in excess in (a)(i) / The amount of iodine formed will be the same for both 15 cm³ and 30 cm³ of FA 3. / Cu²⁺ is limiting reagent.

Hence, it will not be affected the accuracy of the results / the results will be the same. [1]

Student 3:

The colour change at end-point from yellow / pale brown to colourless will not be sharp / obvious, thus leading to inaccuracy in the titre volumes recorded. [1]

(iii) Another student proposed the following modification.

- Filtering the contents in the conical flask after step 5, before carrying out the titration in step 6.

State an advantage and a disadvantage of this modification.

Advantage: Easier to see the colour change at end-point without the interference of white ppt. [1]

Disadvantage: Some iodine may be lost OR remain on the filter paper, thus reducing the accuracy of titration results. [1]

(d) Table 1.1 shows some standard electrode potential values.

Table 1.1

electrode reaction	E^\ominus / V
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.15
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54

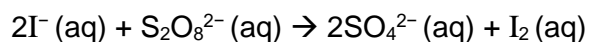
The E^\ominus_{cell} for **equation 1** is -0.39 V . Explain why the reaction occurred in **(a)(i)** despite the negative E^\ominus_{cell} value.

When CuI ppt is formed, $[\text{Cu}^+]$ / amount of Cu^{2+} decreases. By Le Chatelier's Principle, the position of equilibrium for $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$ shifts right [1] to form more Cu^+ , resulting in its E_{cathode} (or words to the effect) to be more positive and hence, E_{cell} will become positive. [1]

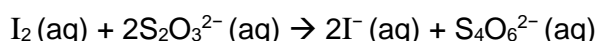
[Total: 19]

2 Determination of the kinetics of the iodide-peroxodisulfate redox reaction

This question seeks to investigate the kinetics of the redox reaction between iodide ions, I^- , and peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$. The redox reaction may be represented by the equation below.



In order to measure the rate of this reaction, a fixed volume of aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to the reaction mixture. Starch is also added to the reaction mixture. When the sodium thiosulfate completely reacts with the iodine produced, the remaining iodine reacts with starch to form a dark blue complex.



The rate of reaction is studied by measuring the time taken for the solution to turn dark blue, t , in a series of five experiments. You will then graphically analyse your results to determine the order of reaction with respect to $[\text{I}^-]$.

FA 5 is $0.100 \text{ mol dm}^{-3}$ potassium iodide, KI.

FA 6 is $0.500 \text{ mol dm}^{-3}$ sodium peroxodisulfate, $\text{Na}_2\text{S}_2\text{O}_8$.

FA 7 is $0.00500 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

You will also need **Solution S** from **Question 1**.

(a) Prepare a table in the space provided on page 9 to record, to an appropriate level of precision:

- volume of **FA 5**, $V_{\text{FA 5}}$
- volume of deionised water,
- all values of t ,
- all calculated values of $1/t$, $\lg(1/t)$ and $\lg(V_{\text{FA 5}})$.

Experiment 1

9. Fill the burette with **FA 5**.
10. Transfer 20.00 cm^3 of **FA 5** into a 250 cm^3 conical flask.
11. Using separate 10 cm^3 measuring cylinders, add 10.0 cm^3 of **FA 7** and 1.0 cm^3 of **Solution S** into the same conical flask.
12. Using a 25 cm^3 measuring cylinder, measure 20.0 cm^3 of **FA 6**.
13. Start the stopwatch upon adding **FA 6** into the conical flask. Swirl the reaction mixture and place the conical flask on a white tile.

14. Stop the stopwatch when the solution first turns dark blue.
15. Record the time taken, t , to the nearest second in your table.
16. Discard the reaction mixture and wash out the conical flask. Stand it upside down on a paper towel to drain.

Experiments 2 to 5

Repeat experiment 1 four times, using 18.00 cm³, 16.00 cm³, 14.00 cm³ and 12.00 cm³ of **FA 5** respectively at step 2.

In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding appropriate volumes of deionised water.

You should alternate the use of the two conical flasks.

Results

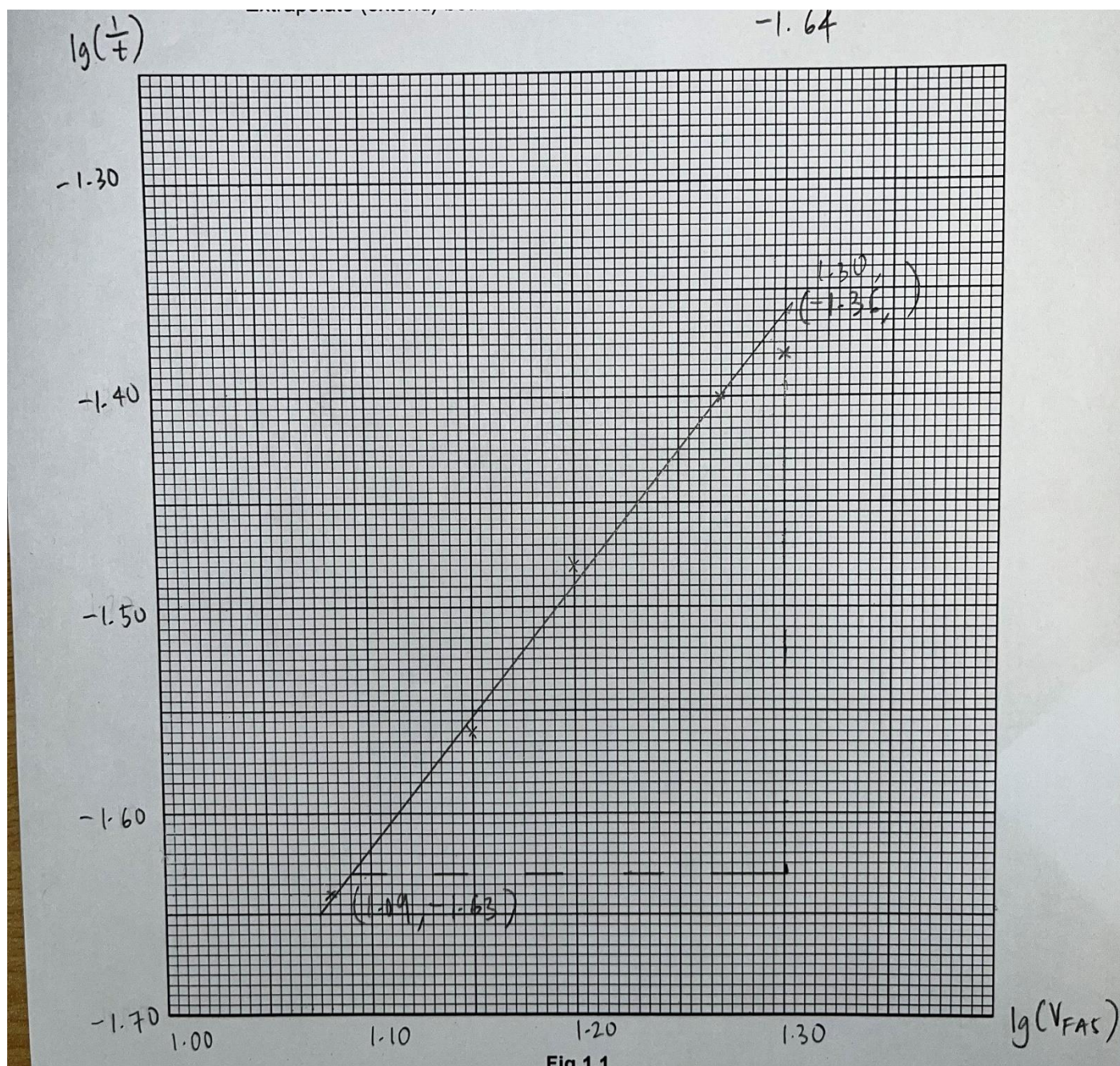
Complete the table below.

$V_{\text{FA 5}} / \text{cm}^3$	Vol of deionised water / cm ³	t / s	$1/t / \text{s}^{-1}$	$\lg (1/t)$	$\lg (V_{\text{FA 5}})$
20.00	0.0	24	0.0417	-1.38	1.30
18.00	2.0	25	0.0400	-1.40	1.26
16.00	4.0	30	0.0333	-1.48	1.20
14.00	6.0	36	0.0278	-1.56	1.15
12.00	8.0	44	0.0227	-1.64	1.08

- All headers with correct units and no units for log [1]
- Correct dp and sf [1]
- Correct calculations [1]
- 5 complete sets of data AND Vol of FA5 + deionised water = 20 cm³ [1]

- (b) (i) Plot a graph of $\lg(1/t)$ on the y-axis against $\lg(V_{FA5})$ on the x-axis.
Draw a best-fit straight line through your plotted points.

[3]



- Labelled axes and suitable scale for plotted points to cover at least half the grid [1]
- Best-fit straight line (not more than 2 anomalous points, allow 2 small squares away from plot) [1]
- Any 2 correctly plotted points [1]

(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of reaction with respect to $[I^-]$.

$$\text{Gradient} = [(-1.36) - (-1.63)] / (1.30 - 1.09) = 1.29 \text{ (3 s.f.)}$$

[1 showing 2 coordinates on the graph or in working]

[1 for correct calculation]

$$\text{Rate} = k[\text{I}^-]^x$$

$$1/t = k(V_{\text{FA5}})^x$$

$$\lg(1/t) = \lg k + x \lg(V_{\text{FA5}})$$

$$x = \text{gradient} \approx 1 \text{ (order of reaction)} \quad [1]$$

[3]

Gradient =

Order of reaction with respect to $[\text{I}^-]$ =

- (iii) Explain why the total volume of the reaction mixture needs to be kept constant in all five experiments in (a).

.....

[1]

By keeping total volume constant, the concentration of each reactant after mixing is directly proportional to the volume used. [1]

- (c) (i) Iron(III) salts are sometimes used as a catalyst for the reaction you performed in (a). Suggest why there is a need for a catalyst.

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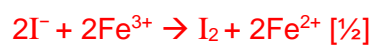
[1]

The negatively charged reactants experience repulsion and hence the rate of reaction is too slow / high activation energy. [1]

- (ii) Using data from **Table 2.1** below, show how iron(III) ions can perform this role and write relevant equation(s).

Table 2.1

electrode reaction	E^\ominus / V
$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$	-0.04
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01



$$E_{\text{cell}} = (+0.77) - (+0.54) = +0.23\text{V} \quad [\frac{1}{2}]$$



$$E_{\text{cell}} = (+2.01) - (+0.77) = +1.24\text{V} \quad [\frac{1}{2}]$$

[2]

[Total: 14]

3 Investigation of some inorganic reactions

- (a) **FA 8** is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**.

Perform the tests described in **Table 3.1**. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

Tests		Observations for FA 8
1.	Place a spatula of FA 8 in a dry boiling tube and heat.	Blue crystals become/form <u>white powder/solid</u> . ✓ Note: No mark for “blue crystals form white ppt ” as ppt is only used for solids forming in solution. <u>Colourless</u> liquid <u>droplets</u> can be found near the opening of the boiling tube. ✓
2.	Add a spatula of FA 8 in a test-tube. Add 1 cm depth of H_2O_2 , followed by 1 cm depth of aqueous sodium hydroxide.	Blue solid dissolved to form <u>blue solution</u> . ✓ Upon adding sodium hydroxide, a <u>black / brown / greenish-brown / green ppt</u> ✓ is formed. <u>Effervescence</u> ✓ is seen, which <u>relights a glowing splint</u> ✓. Gas is <u>oxygen</u> ✓.
3.	Add half a spatula of FA 8 into a test-tube. Add aqueous ammonia dropwise until it is in excess.	A (pale) <u>blue ppt</u> is formed ✓ Ppt is <u>soluble in excess NH_3</u> , ✓ forming a <u>deep blue/dark blue solution</u> . ✓

4.	<p>Add half a spatula of FA 8 into a test-tube and dissolve with 1 cm depth deionised water. Use a glass rod to stir if necessary.</p> <p>Add aqueous sodium carbonate dropwise to the resultant solution until it is in excess.</p>	<p>Blue solid dissolves to form a <u>blue solution</u> ✓.</p> <p>A (pale) <u>blue ppt</u> ✓ is formed.</p> <p><u>Ppt insoluble in excess.</u> ✓</p>
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[4]

(b) Consider your observations in **Table 3.1**.

(i) Based on your observations for test 2, suggest the role of **FA 8**.

.....

[1]

Oxidising agent [1]

(ii) **Table 3.2** shows the K_{sp} values for both copper(II) carbonate and copper(II) hydroxide.

Table 3.2

	K_{sp}
CuCO_3	$1.4 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
Cu(OH)_2	$4.8 \times 10^{-20} \text{ mol}^3 \text{ dm}^{-9}$

Calculate the solubility of each salt. Hence, suggest the identity of the species responsible for the observations seen in test 4.

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.....

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.....

.....

[3]

[Turn Over

Let the solubility of CuCO_3 be $x \text{ mol dm}^{-3}$

$$1.4 \times 10^{-10} = x^2 \rightarrow x = \underline{1.18 \times 10^{-5} \text{ mol dm}^{-3}} \text{ [1]}$$

Let the solubility of Cu(OH)_2 be $y \text{ mol dm}^{-3}$

$$4.8 \times 10^{-20} = 4y^3 \rightarrow y = 2.289 \times 10^{-7} \approx \underline{2.29 \times 10^{-7} \text{ mol dm}^{-3}} \text{ (to 3 sf) [1]}$$

Since Cu(OH)_2 [1] has a lower solubility, it is precipitated first and seen in test 4.

- (c) To determine the identity of anion in **FA 8**, a student added barium nitrate solution to a solution of **FA 8**. A white ppt is formed.

- (i) Based on the observations given, state the possible identities of the anions.

..... [1]

CO_3^{2-} , SO_3^{2-} , SO_4^{2-}

[1] for all 3 anions

- (ii) Suggest a test to confirm the identity of the anion in **FA 8**. **DO NOT** carry out the test.

Test: [1]

Add HCl(aq) or $\text{HNO}_3\text{(aq)}$ to the white ppt. [1]

- (d) Note: You are NOT given **FA 9**.

FA 9 is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**. **Table 3.3** shows a test which is performed on **FA 9** and the corresponding observations.

Table 3.3

Test	Observations for FA 9
To 1 cm depth of a solution of FA 9 , add aqueous ammonia dropwise until it is in excess.	A white ppt is formed. It dissolves in excess aqueous ammonia to give a colourless solution.

- (i) Suggest the identity of the cation present in **FA 9**.

..... [1]

Zn^{2+} [1]

- (ii) Suggest an explanation for the observations in **Table 3.3** in terms of the species present.

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.....

[1]

Award 1 mark if students give the identities of white solid is **Zn(OH)₂** and it dissolves to form **[Zn(NH₃)₄]²⁺**.

- (iii) **Assuming** you have an aqueous solution of **FA 9**.

There is no observable change when barium nitrate solution is added to **FA 9** solution.

Devise a series of simple tests to identify the anion in **FA 9**. Your tests should be based on the Qualitative Analysis Notes and should use only the bench reagents provided. Record your tests in the space below.

Test
<u>Add 1 cm depth of NaOH(aq) to 1 cm depth of FA 9 solution and a piece of Al foil. Heat the mixture. [1]</u>
<u>Add 1 cm depth of AgNO₃(aq) to 1 cm depth of FA 9 solution. Add NH₃(aq) to the resulting mixture. [1]</u>

[2]

[Total: 14]

4 Planning

The labels for a bottle of carbonic acid and a bottle of citric acid were mixed up. Both acids have the same concentration of 1.00 mol dm^{-3} . Carbonic acid is dibasic and citric acid is tribasic. In order to identify the correct acids, a series of six experiments will be performed, where different volumes of the acid from one of the bottles and sodium hydroxide are chosen to ensure there are sufficient points before and after the equivalence point. The total volume for each experiment should be kept constant at 60.0 cm^3 .

The temperature change, ΔT , for each neutralisation is calculated using the formula below:

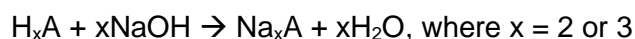
$$\Delta T = T_{\text{final}} - T_{\text{average}},$$

where T_{average} is the weighted average of the initial temperatures of the acid and sodium hydroxide:

$$T_{\text{average}} = \frac{(V_{\text{acid}} \times T_{\text{acid}}) + (V_{\text{NaOH}} \times T_{\text{NaOH}})}{V_{\text{acid}} + V_{\text{NaOH}}}$$

A suitable graph can then be plotted to determine the basicity of the acid.

Let the unknown acid be H_xA . The neutralisation reaction is shown below.



You are provided with:

- 1.00 mol dm^{-3} sodium hydroxide, NaOH
- 1.00 mol dm^{-3} acid from one of the bottles, H_xA
- the equipment normally found in a school or college laboratory.

- (a) (i) Calculate the volumes of acid required for complete reaction if the acid is dibasic and tribasic respectively.

[1]

If acid is dibasic, mole ratio of acid : NaOH = 1 : 2

Since $[\text{acid}] = [\text{NaOH}]$, volume of acid : volume of NaOH = 1 : 2.

For complete reaction within a total volume of 60 cm^3 , volume of acid = 20 cm^3

If acid is tribasic, mole ratio of acid : NaOH = 1 : 3

Since $[\text{acid}] = [\text{NaOH}]$, volume of acid : volume of NaOH = 1 : 3.

For complete reaction within a total volume of 60 cm^3 , volume of acid = 15 cm^3

- (ii) Using your answers in (i), fill in the volumes of acid and NaOH in the table below.

Experiment	Volume of acid / cm ³	Volume of NaOH / cm ³
1	5.0	55.0
2	10.0	50.0
3	15.0	45.0
4	20.0	40.0
5	25.0	35.0
6	30.0	30.0

(ignore d.p., Total volume in each experiment must be 60 cm³)

There should be 3 volumes less than/equal to 15 cm³ and 3 volumes larger than/equal 20 cm³. (ecf based on student's answer in (i)).

[1]

- (b) In your plan to determine the basicity of H_xA, you should include brief details of:

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

[4]

1. Place a clean and dry Styrofoam cup inside another Styrofoam cup placed in a 250cm³ beaker.
2. Using a measuring cylinder, measure 5.0 cm³ of acid, H_xA, into the Styrofoam cup.
3. Using another measuring cylinder, measure 55.0 cm³ of NaOH.
4. Record the initial temperatures of each solution with a thermometer.
5. Pour the NaOH into the Styrofoam cup with H_xA and stir the mixture with the thermometer.
6. Record the highest temperature reached with the thermometer.
7. Wash the Styrofoam cup and dry with a paper towel.
8. Repeat Steps 1 to 6 with the volumes in the table in (a)(iii).

Apparatus [3A = 1 mark]:

- Styrofoam cup,

- measuring cylinder of suitable capacity/burette (volume must have corresponding d.p.)
- thermometer

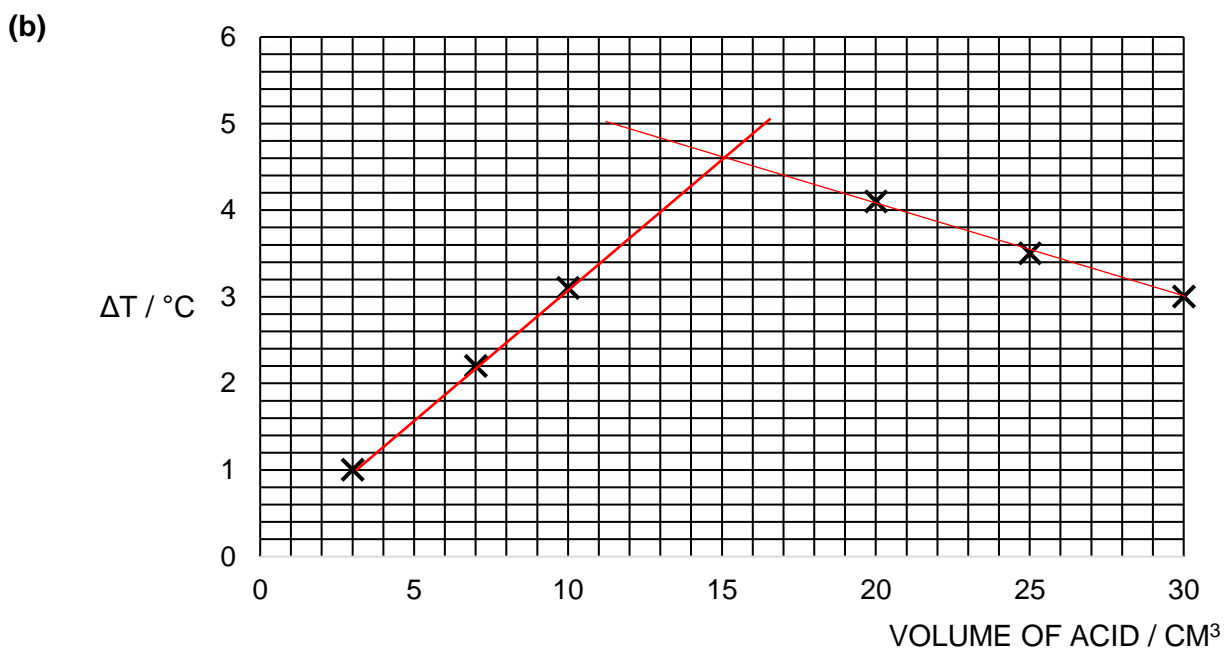
Procedure [3P = 1 mark; 0-2P = 0 marks]:

- Pour one of the solutions into a Styrofoam cup,
- Pour the other solution into same Styrofoam cup,
- Stir (with the thermometer)

Measurements [3M = 2 marks; 1-2M = 1 mark; 0M = 0 marks]

- Initial temperature of acid
- Initial temperature of NaOH
- Highest temperature reached after mixing

- (b) A student conducted the experiment and obtained the following graph of ΔT against volume of acid.



Draw 2 best-fit straight lines and extrapolate both lines to find volume of acid required to completely react with NaOH.

Hence, deduce the identity of the acid.

[2]

[1 for 2 best-fit straight lines that intersect]

[Turn Over

Volume of acid used to completely react with NaOH = 0.015 dm^3 [$\frac{1}{2}$]

Based on calculation in (a)(i), acid is tribasic and the acid is citric acid. [$\frac{1}{2}$]

FYI:

Volume of NaOH used = $0.060 - 0.015 = 0.045 \text{ dm}^3$

Amount of unknown acid used = 0.015 mol

Amount of NaOH used = 0.045 mol

The ratio of NaOH : acid = 3 : 1

[Total: 8]