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 $CuSO_4 \cdot \boldsymbol{x}H_2O$, 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.

equation 1 $Cu^{2+}(aq) + 2I^{-}(aq) \rightarrow CuI(s) + \frac{1}{2}I_2(aq)$

The liberated iodine is then titrated against sodium thiosulfate.

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

You are provided with:

- solid **FA 1**, hydrated copper(II) sulfate
- **FA 2**, 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
- **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 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.

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

[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.

Volume of **FA 2** = ………………………. cm^3 **[1]**

(b) **(i)** Calculate the amount, in moles, of Cu^{2+} present in 25.0 cm^3 of **FA 4**.

Amount of Cu^{2+} = ………………………. mol **[1]**

(ii) Calculate the concentration of Cu^{2+} in **FA 4**.

Concentration of Cu^{2+} = ……………………… mol dm^{-3} **[1]**

(iii) Given that the concentration of $CuSO_4 \bullet \boldsymbol{x}H_2O$ 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 cm^3 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 cm^3 of **FA 3** instead of 15 cm^3.

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	$\boldsymbol{E^{\ominus}}$ **/ V**
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$I_2 + 2e^- \rightleftharpoons 2I^-$	+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.

....

....

.... **[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, $S_2O_8^{2-}$. The redox reaction may be represented by the equation below.

$$2I^- (aq) + S_2O_8^{2-} (aq) \rightarrow 2SO_4^{2-} (aq) + I_2 (aq)$$

In order to measure the rate of this reaction, a fixed volume of aqueous sodium thiosulfate, $Na_2S_2O_3$, 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.

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

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 $[I^-]$.

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

FA 6 is 0.500 mol dm^{-3} sodium peroxodisulfate, $Na_2S_2O_8$.

FA 7 is 0.00500 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

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

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 cm^3, 16.00 cm^3, 14.00 cm^3 and 12.00 cm^3 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

[4]

(b) **(i)** Plot a graph of lg(1/*t*) on the y-axis against lg($V_{\textbf{FA5}}$) 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**
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	−0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

[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.	
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.	
3.	Add half a spatula of **FA 8** into a test-tube. Add aqueous ammonia dropwise until it is in excess.	

4.	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. Add aqueous sodium carbonate dropwise to the resultant solution until it is in excess.	

[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}
$CuCO_3$	1.4×10^{-10} mol^2 dm^{-6}
$Cu(OH)_2$	4.8×10^{-20} mol^3 dm^{-9}

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

....

....

....

....

.... **[3]**

(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:

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

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

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

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.

$$H_xA + xNaOH \rightarrow Na_xA + xH_2O, \text{ where } x = 2 \text{ or } 3$$

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]

(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.

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

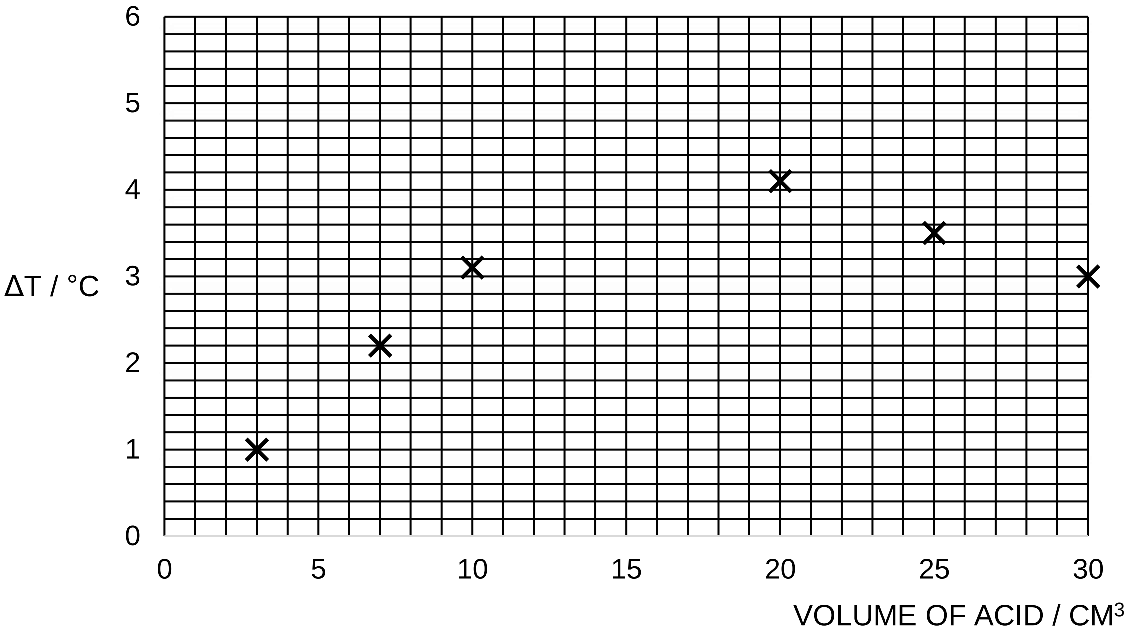
....

....

....

.... **[4]**

(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]

[BLANK]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

Cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off–white ppt. rapidly turning brown on contact with air insoluble in excess	off–white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

Halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange–red
iodine, I_2	black solid / purple gas	brown	purple