HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		**CT GROUP**	**22S**

CHEMISTRY

9729/04

Paper 4 Practical

24 August 2023

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your name and class on all 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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, 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.
Qualitative Analysis Notes are printed on pages 19 and 20.

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

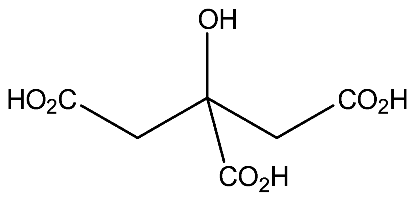
For Examiner's Use	
1	/ 16
2	/ 23
3	/ 16
Total	**55**

This document consists of **19** printed pages and **1** blank page.

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

1 Determination of a molar enthalpy change by an indirect method

Citric acid (M_r = 192) is an organic tribasic acid and its structure is shown below.



citric acid

In this question, the formula for citric acid will be written as $C_3H_5O(CO_2H)_3$.

Citric acid reacts with sodium hydrogencarbonate to produce sodium citrate, carbon dioxide and water as shown in equation 1 and equation 2. The molar enthalpy change of reaction is different depending on whether solid or aqueous citric acid is used.

equation 1

$$C_3H_5O(CO_2H)_3(s) + 3NaHCO_3(aq) \rightarrow C_3H_5O(CO_2^-Na^+)_3(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H_1$$

equation 2

$$C_3H_5O(CO_2H)_3(aq) + 3NaHCO_3(aq) \rightarrow C_3H_5O(CO_2^-Na^+)_3(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H_2$$

You will perform an experiment to determine the molar enthalpy change of reaction, ΔH_1, in **1(a)** and plan a set of experiments to determine the molar enthalpy change of reaction, ΔH_2, in **1(b)**.

FA 1 is solid citric acid, $C_3H_5O(CO_2H)_3$.
FA 2 is 1.00 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$.
(Note: **FA 2** is also used in question 3.)

In the space provided on page 3, prepare tables in which to record for your experiment:

- all weighings to an appropriate level of precision
- all values of temperature to an appropriate level of precision.

(a) Determination of the molar enthalpy change of reaction, ΔH_1

(i) Procedure

1. Weigh the capped container containing **FA 1**. Record the mass in your table on page 3.
2. Place one polystyrene cup inside another polystyrene cup and place both in a 250 cm^3 glass beaker. Transfer 50 cm^3 of **FA 2** into the polystyrene cup using a 50 cm^3 measuring cylinder.
3. Place a lid on the cup and insert the thermometer through the lid. Stir gently the solution of **FA 2** in the cup with the thermometer. Measure and record the initial temperature, T_i, of **FA 2**.
4. Open the lid and empty the container of **FA 1** into the polystyrene cup containing **FA 2**. (You may need to tap the capped container to loosen the **FA 1**

solid before the transfer). Close the lid and use the thermometer to gently stir the mixture. Measure and record the lowest temperature of the mixture, T_f.

5. Reweigh the empty capped container. Record this mass in your table on page 3.

Results

[2]

(ii) Calculate the temperature change, ΔT, produced by the experiment in **1(a)(i)**, and hence calculate the heat change, *q*.

You should assume that the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1} and the density of the solution is 1.00 g cm^{-3}.

ΔT = ………………………………

q = ………………………………
[2]

(iii) Show that citric acid is the limiting reactant in the experiment that you carried out in **1(a)(i)**.
[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

[1]

(iv) Using your answer in **1(a)(ii)** and **1(a)(iii)**, calculate the molar enthalpy change of reaction, ΔH_1, for the experiment in **1(a)(i)**.

ΔH_1 = ………………………………… [1]

(v) Predict and explain how the change in temperature will be affected if the volume of **FA 2** added is doubled.

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…………………………………………………………………………………………….. [1]

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(b) Planning

When aqueous citric acid reacts with aqueous sodium hydrogencarbonate, an endothermic reaction occurs, as shown in equation 2.

equation 2

$C_3H_5O(CO_2H)_3(aq) + 3NaHCO_3(aq)$ d $C_3H_5O(CO_2^-Na^+)_3(aq) + 3CO_2(g) + 3H_2O(l)$ $\Delta H_2 > 0$

The minimum temperature change occurring during this reaction may be determined graphically.

In this question, you are to plan a series of experiments to determine the concentration of a solution of aqueous citric acid, named **solution A**, and the molar enthalpy change of reaction, ΔH_2.

You may assume that you are provided with:

- **solution A**, a solution of citric acid of unknown concentration
- **FA 2**, 1.00 mol dm^{-3} sodium hydrogencarbonate ($NaHCO_3$)
- apparatus commonly found in a school laboratory

Your plan should include reacting different volumes of **FA 2** and **solution A** together while keeping the total volume at 50 cm^3, and measuring the temperature change, ΔT, for each experiment. In your plan, ΔT for each experiment should be taken as $T_{\text{final}} - T_{\text{weighted initial}}$, where:

$$T_{\text{weighted initial}} = \frac{(V_{FA\,2} \times T_{FA\,2}) + (V_{solution\,A} \times T_{solution\,A})}{V_{FA\,2} + V_{solution\,A}}$$

A suitable graph is then drawn to obtain the volume of **FA 2**, V_{min}, required to completely react with **solution A**. V_{min} can then be used to determine the concentration of **solution A**.

The minimum temperature change, ΔT_{min}, obtained from the graph can be used to calculate the heat change, q, for this experiment, and hence the molar enthalpy change of reaction, ΔH_2.

(i) Your plan should include brief details of:

- the apparatus you would use,
- the volumes of **FA 2** and **solution A** you would use in the form of a table,
- the procedure you would follow,
- the measurements you would make to allow a suitable graph to be drawn.

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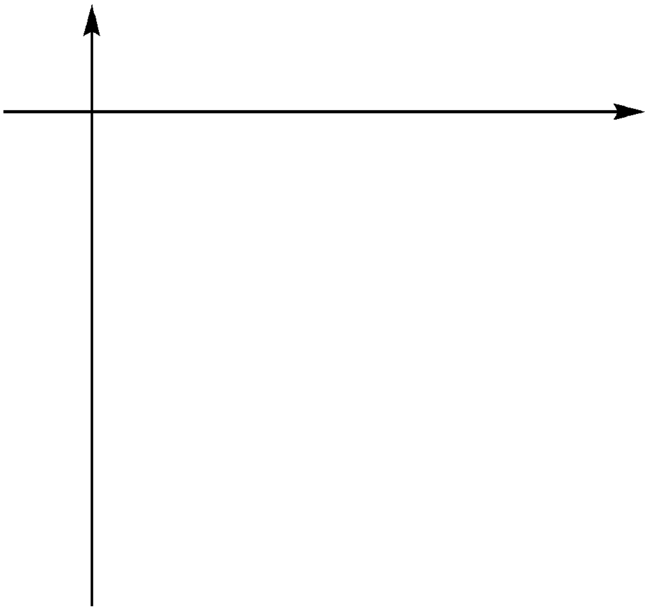
(ii) On the axes given below, sketch the graph you would expect to obtain, and show on your sketch how you would use the graph to obtain the V_{min} and ΔT_{min} of the reaction. Label the axes clearly.



[1]

(iii) Show how you may use the results of your graph in **1(b)(ii)** to derive an expression for the concentration of **solution A**.

[1]

(iv) Show how you may use the results of your graph in **1(b)(ii)** to derive an expression for the molar enthalpy change of reaction, ΔH_2.

[1]

(c) The two molar enthalpy changes of reaction, ΔH_1 and ΔH_2, may be used to find the value of the molar enthalpy change ΔH_3, where $\Delta H_3 = \Delta H_1 - \Delta H_2$.

$$C_3H_5O(CO_2H)_3(s) + 3NaHCO_3(aq) \rightarrow C_3H_5O(CO_2^-Na^+)_3(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H_1$$

$$C_3H_5O(CO_2H)_3(aq) + 3NaHCO_3(aq) \rightarrow C_3H_5O(CO_2^-Na^+)_3(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H_2$$

What is the thermochemical process that ΔH_3 represent?

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(d) Using your understanding of the theory of acid-base equilibria, explain why the concentration of the citric acid solution cannot be obtained via a direct titration with the sodium hydrogencarbonate solution provided.

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[Total: 16]

2 **Investigation of the kinetics of the reaction between iodide ions and peroxodisulfate ions**

Iodide ions, I^-, react with peroxodisulfate ions, $S_2O_8^{2-}$, as shown in equation 3.

equation 3 $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

If the concentration of iodide ions is very much higher than that of peroxodisulfate ions, a simplified rate equation can be used.

rate = $k'[S_2O_8^{2-}]^a$ where k' is $k[I^-]$

FA 3 is 0.400 mol dm^{-3} aqueous potassium iodide, KI
FA 4 is 0.010 mol dm^{-3} aqueous peroxodisulfate ions, $S_2O_8^{2-}$
FA 5 is 0.003 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$

You are also provided with starch indicator.

You will add a measured volume of **FA 3** to a measured volume of **FA 4** and, at timed intervals, you will transfer aliquots (portions) of the reaction mixture.

It is necessary that you titrate each aliquot against **FA 5** before transferring the next aliquot.

Iodine and sodium thiosulfate react as shown in equation 4.

equation 4 $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Read the entire procedure before you start the experiment.

(a) **Preparation and titration of the reaction mixture**

Notes: You will perform each titration **once** only. Great care must be taken that you do not overshoot the end-point.

Once you have started the stopwatch, it must continue running for the duration of the experiment. You must **not** stop it until you have finished this experiment.

You should aim to transfer your first aliquot within the first two minutes of starting the reaction.

You should aim **not** to exceed a maximum reaction time of 16 minutes for this experiment.

In an appropriate format in the space provided, prepare a table in which to record for each aliquot

- the time of transfer, t, in minutes and seconds,
- the decimal time, t_d, in minutes, to 0.1 min, for example, if t = 4 min 33 s then t_d = 4 min + 33/60 min = 4.6 min,
- the burette readings and the volume of **FA 5** added, $V_{\text{FA 5}}$, and
- $V_t = V_{max} – V_{\text{FA 5}}$, where V_{max} = 20.00 cm^3, to 2 decimal places.

1 Fill a burette with **FA 5**.

2 Using a 50 cm^3 measuring cylinder, add 30.0 cm^3 of **FA 4** into a conical flask labelled **reaction mixture**.

3 Using a 100 cm^3 measuring cylinder, add 70.0 cm^3 of **FA 3** to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its contents.

4 Using a beaker, add about 100 cm^3 of deionised water to a second conical flask.

5 Transfer a 10.0 cm^3 aliquot (portion) of the reaction mixture to a 10 cm^3 measuring cylinder, using a dropping pipette.

6 **Immediately** transfer this aliquot into the second conical flask and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.

7 **Immediately** titrate the iodine in the second conical flask with **FA 5**. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator and continue titrating until the point when the solution just turns colourless. Record your titration results.

8 Wash out the second conical flask with water.

9 Repeat steps **4** to **8** until a **total** of **five** aliquots have been titrated and their results recorded.

Results

[4]

(b) **(i)** Plot a graph of V_t, on the y-axis, against decimal time, t_d, on the x-axis on the grid in Fig. 2.1.

Draw the most appropriate best-fit curve taking into account all of your plotted points. Extrapolate (extend) this curve to $t_d = 0.0$ min, where the $V_t = V_{max} = 20.00$ cm^3.

Fig. 2.1

[4]

(ii) V_{max} represents the volume of **FA 5** required to react with the iodine produced when the reaction as shown by equation 3 has **completed**, in a 10.0 cm^3 aliquot of the reaction mixture.

Show that V_{max} is 20.00 cm^3.

[2]

(iii) The simplified rate equation for the reaction shown in equation 1 is

rate = $k'[S_2O_8^{2-}]^a$ where k' is $k[I^-]$

Use your graph in Fig. 2.1 to show that a = 1. Explain your answer.

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Hence, complete the expression for the simplified rate equation.

rate = k'…………………………………………………………………………………... [3]

(iv) Using your answer in **2(b)(iii)**, calculate a value for the rate constant, k'.

[1]

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(v) Calculate the initial concentration of I^- in the reaction mixture. Hence, determine a value for the rate constant, k.

[5]

(c) Explain how half-life will change if $[I^-]$ is halved.

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…………………………………………………………………………………………………… [1]

(d) If a small amount of aqueous iron(II) ions is added to the reaction mixture, the rate of reaction between iodide ions and peroxodisulfate ions increases.

State the property, typical of transition metals, which allows iron(II) ions to behave as a catalyst in this reaction.

Write equations to show how Fe^{2+} can act as a catalyst in this reaction.

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…………………………………………………………………………………………………… [3]

[Total: 23]

3 Qualitative Analysis

(a) Investigation of the chemistry of manganese compounds

FA 3 0.400 mol dm^{-3} aqueous potassium iodide, KI
FA 6 solid manganese dioxide, MnO_2

Perform the tests described in Table 3.1 and record your observations in the table.

Test and identify any gases produced.

Table 3.1

tests		observations
1	Place about 1 cm depth of dilute sulfuric acid into a test-tube. Add a spatula of **FA 6** to this test tube, followed by another 2 cm depth of **FA 3**. Filter the mixture into a clean test-tube and retain the filtrate. To the filtrate, add aqueous sodium thiosulfate dropwise, with shaking, until the solution first becomes colourless. Retain this solution for use in test 2.	
2	To the solution from test 1, add aqueous sodium hydroxide dropwise until no further change is seen.	
3	Place 1 cm depth of hydrogen peroxide into a test-tube. Add, using the tip of a spatula, a small portion of **FA 6** to this test-tube.	

[4]

(i) Explain the reaction between **FA 6** and **FA 3** in test 1. Support your answer using two pieces of evidence from Table 3.1.

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…………………………………………………………………………………………….. [2]

(ii) On its own, hydrogen peroxide decomposes very slowly to produce a gas.

Suggest the role of **FA 6** in test 3 and give an evidence from your observations in Table 3.1 to justify your answer.

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……………………………………………………………………………………………………

……………………………………………………………………………………………...[2]

(b) Organic Analysis

In this question, you will deduce the identities of three organic compounds.

FA 7, FA 8 and **FA 9** have the following molecular formulae (not necessarily in the same order):

$C_2H_2O_4$
C_2H_6O
C_2H_5NO

Each compound only has **one type** of functional group. One of the compounds is a primary amide.

You are provided with aqueous solutions of **FA 7**, **FA 8** and **FA 9**. You will perform tests to identify their functional groups and hence deduce the identities of **FA 7**, **FA 8** and **FA 9**.

Test and identify any gases evolved. If there is no observable change, write **no observable change.**

Use a fresh sample of each solution in each test.

Before starting this analysis, ensure your Bunsen burner is turned off.

All heating or warming in this question should be done using a hot water bath. To prepare a hot water bath, use a 250 cm^3 beaker to collect hot water from the boiler located at the side of the lab.

(i) Carry out the following test on **FA 7**, **FA 8** and **FA 9**. Record your observations in the table below.

test	observations		
	FA 7	**FA 8**	**FA 9**
Add about 1 cm depth of **FA 7** to a test tube. Add about 1 cm depth of **FA 2,** sodium hydrogencarbonate, to this test tube. **Repeat using FA 8 and then using FA 9 instead of FA 7.**			

[1]

(ii) State the solution that can be identified from your observations above and draw the structure of the compound present.

FA …………..

structure:

[1]

(iii) Using only the bench reagents provided, suggest **two** additional chemical tests to identify the remaining two compounds. Each compound should be identified by one positive test result. It is not sufficient to identify a compound simply by eliminating the other.

Perform the two tests you have suggested and record your observations in Table 3.2.

Table 3.2

tests	observations	
	FA ………	**FA** ………

[4]

(iv) Hence, draw the structures of the two remaining compounds by completing Table 3.3.

Table 3.3

	structure
FA ………	

FA ………	

[2]

[Total: 16]

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 aqueous anions

anion	***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 Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al 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 with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test 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