HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		CT GROUP	20S

CHEMISTRY 9729/04

Paper 4 Practical

18 August 2021

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 17 and 18.

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	
2	
3	
4	
Total	

1 Determination of the values for the enthalpy changes associated with several chemical reactions and concentration of aqueous sodium hydroxide

FA 1 is aqueous sodium hydroxide, NaOH
FA 2 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

FA 3 is citric acid crystals, $C_3H_4(OH)(CO_2H)_3 \cdot H_2O$

Sodium hydroxide and sulfuric acid react according to equation 1. The enthalpy change for the reaction is ΔH_1.

equation 1 $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ ΔH_1

Sodium hydroxide and citric acid crystals react according to equation 2. The enthalpy change for the reaction is ΔH_2.

equation 2 $3NaOH(aq) + C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2Na)_3(aq) + 4H_2O(l)$ ΔH_2

In this question, you will perform experiments to determine the values for ΔH_1 and ΔH_2. You will use your values of ΔH_1 and ΔH_2 to calculate a value for the enthalpy change shown in equation 3.

equation 3 $C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2^-)_3(aq) + 3H^+(aq) + H_2O(l)$ ΔH_3

In **1(c)**, you will use data provided to determine the concentration of sodium hydroxide in **FA 1**.

(a) You will follow the instructions to perform experiments 1 and 2. Record your results in the space provided on page 3.

Experiment 1

1. Using a measuring cylinder, transfer 50.0 cm^3 of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
2. Stir and measure the temperature of this **FA 1**, $T_{\mathbf{FA1}}$.
3. Using another measuring cylinder, measure 20.0 cm^3 of **FA 2**.
4. Stir and measure the temperature of this **FA 2**, $T_{\mathbf{FA2}}$.
5. Add the **FA 2** from the measuring cylinder to the **FA 1** in the Styrofoam cup.
6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.

Experiment 2

1. Weigh the capped bottle containing **FA 3**.
2. Using a measuring cylinder, transfer 50.0 cm^3 of **FA 1** into the other clean Styrofoam cup. Place this cup inside the used Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 1**, $T_{\mathbf{FA1}}$.
4. Add all the **solid FA 3** to the **FA 1** in the Styrofoam cup.
5. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.
6. Reweigh the empty bottle and its cap.

In an appropriate format in the space below,
- record all measurements of temperature,
- record all measurements of mass,
- calculate the values for the average of $T_{\mathbf{FA1}}$ and $T_{\mathbf{FA2}}$, T_{ave}, and ΔT_{max} for experiment 1,
- calculate the mass of **FA 3** added and ΔT_{max} for experiment 2.

$$T_{ave} = \frac{(50 \times T_{FA1}) + (20 \times T_{FA2})}{70}$$

[3]

(b) Given that:
- sodium hydroxide is used in excess in experiments 1 and 2;
- M_r of $C_3H_4(OH)(CO_2H)_3 \cdot H_2O$ is 210.0;
- specific heat capacities of the Styrofoam cup, lid and thermometer are negligible;
- specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1};
- density of the mixture is 1.00 g cm^{-3},

(i) calculate the heat change, q_1, for Experiment 1 and hence determine a value for the enthalpy change ΔH_1 shown in equation 1.

q_1 = ...

ΔH_1 = ...

[2]

(ii) calculate the heat change, q_2, for Experiment 2 and hence determine a value for the enthalpy change ΔH_2 shown in equation 2.

q_2 = ...

ΔH_2 = ...
[2]

(iii) Use your values of ΔH_1 and ΔH_2 to determine a value for the enthalpy change ΔH_3 shown in equation 3. Show your working clearly.

equation 3 $C_3H_4(OH)(CO_2H)_3{\cdot}H_2O(s) \rightarrow C_3H_4(OH)(CO_2^-)_3(aq) + 3H^+(aq) + H_2O(l)$ ΔH_3

ΔH_3 = ... [2]

(c) The procedure in experiment 1 can be used to determine the concentration of sodium hydroxide in **FA 1**.

A series of seven experiments were performed using different volumes of **FA 1** and **FA 2**. In each experiment, the total volume of the two solutions was kept at 50 cm^3 and the change in temperature, ΔT, was determined. The results from the experiments are plotted on the grid in Fig. 1.1.

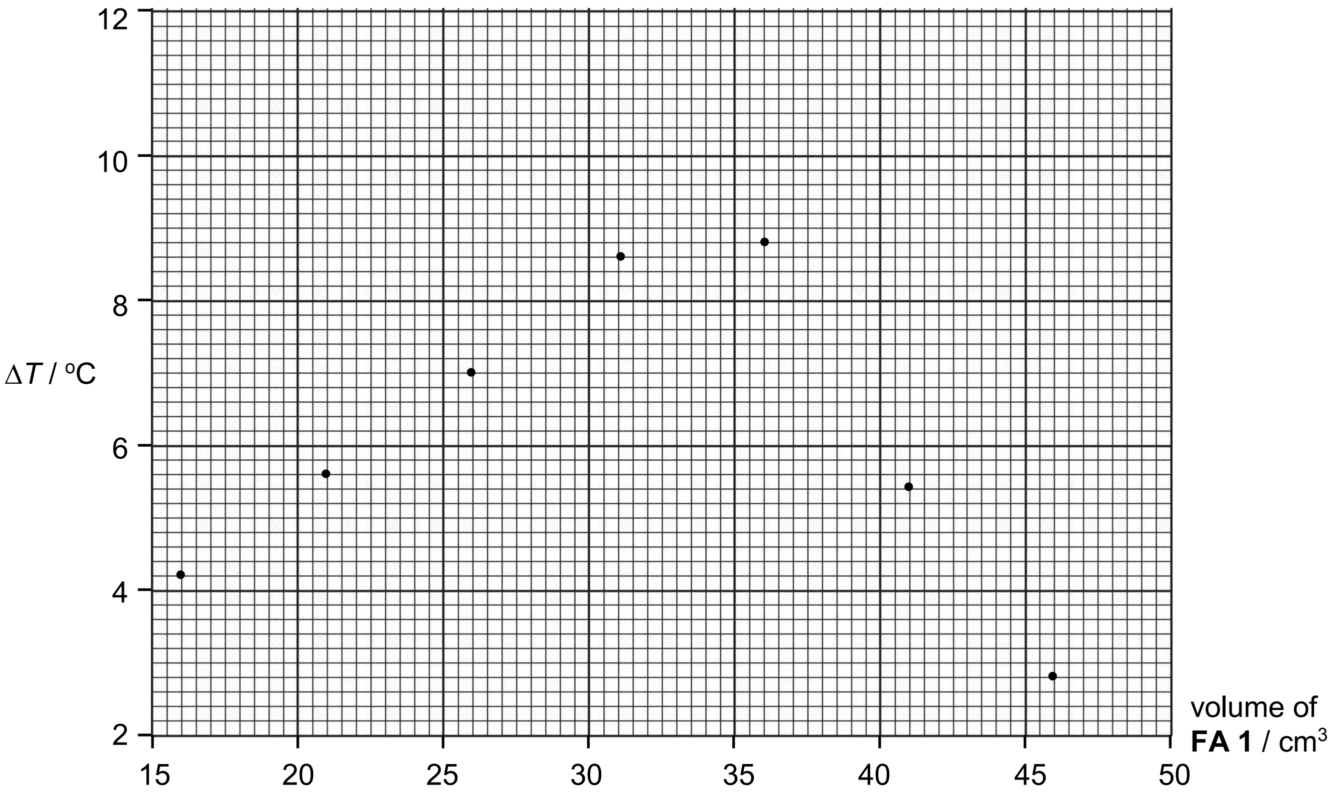

Fig. 1.1

(i) Draw two best-fit straight lines, the first line taking into account the points before the maximum change in temperature and the second line using the remaining data.

Extrapolate (extend) both lines until they cross.

[1]

(ii) Explain, in terms of the chemistry involved, the significance of the point of intersection of the two best-fit lines.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(iii) Using your graph, determine the concentration of sodium hydroxide in **FA 1**.

concentration of sodium hydroxide in **FA 1** = ……………………………….
[2]

[Total: 14]

2 Planning

The hydrolysis of an ester is catalysed by either an acid or alkali. In the presence of an acid catalyst, the reaction is reversible and reaches equilibrium in about 48 hours.

Ethyl ethanoate hydrolyses to give ethanoic acid and ethanol as shown in equation 4.

equation 4 $CH_3CO_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CO_2H(l) + CH_3CH_2OH(l)$ K_c

(a) To determine the equilibrium constant, K_c, it is necessary to determine the amounts of ethyl ethanoate, water, ethanoic acid and ethanol present in the equilibrium mixture. One way of doing this is described below.

Known amounts of ethyl ethanoate and an acid catalyst are mixed in a sealed reagent bottle. After sufficient time, the whole equilibrium mixture is diluted with deionised water. Titration with a standard solution of sodium hydroxide determines the total amount of acid in the mixture: both ethanoic acid and the acid catalyst.

Since the amount of acid catalyst does not change, it is possible to deduce the amount of ethanoic acid and hence the amounts of each of the other components in the equilibrium mixture.

Using these data, a value for K_c may then be determined.

Plan a procedure to collect sufficient data to allow you to determine a value for K_c in equation 4 at 40 °C.

You should plan to make an initial reaction mixture containing
- 5.00 g of ethyl ethanoate,
- 5.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

You may assume that you are also provided with:
- 1.50 mol dm^{-3} sodium hydroxide,
- the equipment and materials normally found in a school or college laboratory.

In your plan you should include brief details of:
- the apparatus you would use,
- the procedure you would use to prepare the equilibrium mixture,
- the procedure you would use to determine the total amount of acid in the equilibrium mixture,
- the measurements you would make.

In your plan, you will titrate the **whole** equilibrium mixture so only **one** titration can be carried out.

[6]

(b) Describe how you would use your results obtained in **2(a)** to calculate the amounts in moles of

- all the components in your initial reaction mixture,
- ethanoic acid present in this mixture at equilibrium,
- all the other components in this mixture at equilibrium.

You may assume that 1.00 cm^3 of hydrochloric acid contains 1.00 cm^3 of water and that the density of water is 1.00 g cm^{-3}.

M_r $CH_3CO_2CH_2CH_3$, 88.0; H_2O, 18.0.

You do **not** need to show how a K_c value is calculated.

[4]

(c) Explain how diluting the equilibrium mixture before titrating it with sodium hydroxide ensures the accuracy of the amount of ethanoic acid present at equilibrium.

……

……

…….. [1]

[Total: 11]

3 Investigation of the kinetics of an acid-catalysed reaction between propanone and iodine

The reaction between propanone and iodine in aqueous solution is catalysed by hydrogen ions:

equation 5 $$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$$

In this experiment you are to investigate how the rate of the reaction is affected by changes in the concentration of iodine.

You are provided with the following chemicals:
FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
FA 5 is aqueous iodine, I_2
FA 6 is hydrochloric acid, HC*l*
FA 7 is propanone, CH_3COCH_3
FA 8 is sodium hydrogen carbonate, $NaHCO_3$

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

Notes:
- Please cap **FA 5** and **FA 7** after use.
- You should **keep the reaction mixture stoppered** except when removing aliquots.
- 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 three minutes of starting the reaction.
- You should aim **not** to exceed a maximum reaction time of **20 minutes** for this experiment.

In Table 3.1 provided on page 11, 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 = 3 min 22 s then t_d = 3 min + 22/60 min = 3.4 min,
- the burette readings and the volume of **FA 4** added.

1. Fill a burette with **FA 4**.
2. Using measuring cylinders, add 50.0 cm^3 of **FA 5** and 25.0 cm^3 of **FA 6** to the conical flask labelled **reaction mixture**.
3. Using a measuring cylinder, add 25.0 cm^3 of **FA 7** to the same conical flask. Start the stopwatch. **Insert the stopper** and swirl the mixture thoroughly to mix its contents.
4. Using a measuring cylinder, add 20.0 cm^3 of **FA 8** 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 conical flask containing **FA 8** 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 I_2 in the conical flask with **FA 4** until the solution is pale yellow. Add 1 cm^3 of starch indicator into this solution and continue titrating until the point when the solution just turns colourless. Record your titration results.
8. Wash out the conical flask with water.
9. Repeat steps **4** to **8** until a total of **five** aliquots have been titrated and their results recorded.

Table 3.1

aliquot	*t*		t_d / min	final burette reading / cm^3	initial burette reading / cm^3	volume of **FA 4** / cm^3
	min	s				
1						
2						
3						
4						
5						

[3]

(ii) Plot a graph of the volume of **FA 4** added, on the y-axis, against decimal time, t_d, on the x-axis on the grid in Fig. 3.1.

Draw the most appropriate best-fit graph taking into account all of your plotted points. Extrapolate (extend) your graph to t_d = 0.0 min.

Fig. 3.1

[3]

(b) The initial rate of change of the concentration of iodine, **FA 5**, $[I_2]$, can be determined from the gradient of the graph in Fig. 3.1 at time t_d = 0.0 min.

(i) Determine the gradient of graph at time t_d = 0.0 min, showing clearly how you did this.

gradient = ………………………………. $cm^3\ min^{-1}$ [2]

(ii) Use your gradient to determine the rate of change of the amount of $S_2O_3^{2-}$ ions required in mol min^{-1}.

rate of change of the amount of $S_2O_3^{2-}$ required = ……………………… mol min^{-1} [1]

(iii) Sodium thiosulfate and iodine react as shown in equation 6.

equation 6 $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Determine the change in amount of I_2 per minute and hence deduce the rate of change of $[I_2]$ at t_d = 0.0 min, in mol $dm^{-3}\ min^{-1}$.

rate of change of $[I_2]$ at t_d = 0.0 min = ………………………………. mol $dm^{-3}\ min^{-1}$ [4]

(iv) What is the order of reaction with respect to $[I_2]$? Use evidence from your graph in Fig. 3.1 to support your answer.

…………………………………………………………………………………………………….

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

(c) Suggest a modification to the chemicals used in the procedure to investigate the order with respect to [propanone]. Explain briefly how you will use your results from this new experiment, **together** with your previous results, to confirm that it is first order with respect to [propanone].

………

………

………

………

………

……… [2]

[Total: 16]

4 Identification and investigations of some reactions of FA 9

Solid FA 9 is a hydrated salt containing one cation and one anion from the Qualitative Analysis Notes on pages 17 – 18.

You are provided with solid **FA 9** in a capped bottle, and with solution **Y**, which you are not required to identify.

In addition to having access to the usual bench reagents, you are also provided with aqueous potassium iodide, KI.

You will also need access to the **FA 8** solution you used earlier.

(a) Place four spatulas full of solid **FA 9** into a small beaker, and add approximately 40 cm^3 of deionised water. Stir the solution thoroughly to ensure all the solid has dissolved. This is **FA 9 solution**.

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

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. You only need to carry out tests for gases when instructed to do so.

Table 4.1

tests			observations
1.		Test the **FA 9** solution you prepared using Universal Indicator paper.	
2.		To 1 cm depth of **FA 9** solution in a test-tube, add aqueous sodium hydroxide slowly, with shaking, until no further change is seen.	
3.		To 1 cm depth of **FA 9** solution in a test-tube, add aqueous ammonia slowly, with shaking, until no further change is seen.	
4.	**(i)**	To 1 cm depth of **FA 9** solution in a test-tube, add a further 2 cm depth of **FA 8** dropwise, with shaking.	
	(ii)	Transfer 1 cm depth of the resultant mixture to a clean test-tube. Add aqueous sodium hydroxide slowly, with shaking, until no further change is seen. Then, add dilute nitric acid dropwise until no further change is seen.	

tests			observations
5.		Add 1 cm depth of **FA 9** solution to a test-tube. Add an equal volume of aqueous silver nitrate.	
6.	**(i)**	Using a graduated plastic dropper, add 3 cm^3 of **FA 9** solution to a **boiling tube**. Add 9 drops of solution **Y** to the tube. A precipitate is formed. Do not add too much solution **Y** as the precipitate will dissolve. Carefully warm the contents of the boiling tube and test any gas produced with moist litmus paper. **Be careful not to let any liquid be propelled out of the tube.** Allow the boiling tube and its contents to cool, note its appearance and label this solution as **FA 10**, to be used in test **6(ii)**.	
	(ii)	Add 1 cm depth of aqueous potassium iodide to a test-tube. Using a plastic dropper, add **FA 10** dropwise, with shaking, until no further change is seen.	

[7]

(b) **(i)** Identify the cation in **FA 9**.

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

(ii) Suggest an identity for the anion in **FA 9**.

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

(iii) A further test has to be carried out after adding aqueous silver nitrate in test **5** to confirm the identity of the anion in **FA 9**.

State the reagent you would use and the observation you will expect in this test.

reagent: ……………………..………………………………………………………..

observation: ……………………..………………………………………………….

[1]

(c) Account for the chemistry behind the observations in test **4(i).**

....

....

....

....

....

.... [2]

(d) Using your answer to **(b)(ii)** and by considering your observations in test **6**,

(i) state the *role* of solution **Y** in the reaction between **FA 9** solution and solution **Y**.

role of solution **Y** .... [1]

(ii) explain, in terms of the chemistry involved, how one of the observations in test **6** supports your answer to **(d)(i)**. You are not required to identify solution **Y**.

....

....

.... [1]

[Total: 14]

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 $\rightarrow$ (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