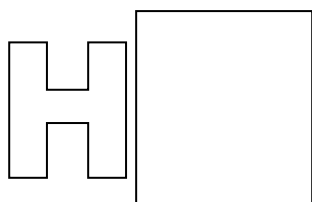


Candidate Name: _____

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2023 Preliminary Examination Pre-University 3

H2 CHEMISTRY

9729/04

Paper 4 Practical

30 August 2023

2 hours 30 minutes

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so.

Write your name, class and admission number in the spaces at the top of this page.

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.

Question	1	2	3	Total
Marks	18	24	13	55

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

1 To determine the effect of concentration changes on the rate of a reaction

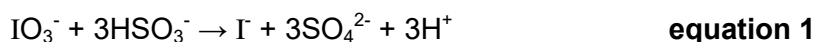
FA 1, 0.0200 mol dm⁻³ aqueous potassium iodate(V), KIO₃

FA 2, 0.0200 mol dm⁻³ aqueous sodium hydrogen sulfite, NaHSO₃

FA 3, 0.0600 mol dm⁻³ aqueous sulfuric acid, H₂SO₄

FA 4 is starch solution

In this experiment, the Landolt-Iodine clock reaction is illustrated by the following equations.



Any I₂ produced in equation 2 while HSO₃⁻ ions still remain in the solution is rapidly reduced to I⁻ in equation 3. Once all the HSO₃⁻ ions have been used up, I₂ will accumulate in the solution. When this happens, the iodine can no longer be converted back to iodide ions. The presence of iodine can be confirmed from the blue-black colour produced upon addition of starch.

Overview of experiment

You will carry out **five** similar experiments, 1 to 5 with varying concentrations of IO₃⁻. In each experiment, you will be required to prepare two solutions – **solution A** and **solution B**.

Note:

- **Solution B** should only be prepared once for all five experiments, while **solution A** must be prepared five times.
- Perform the experiments in order, from experiment 1 to 5.
- The measuring apparatus used to prepare **solutions A** and **B** must be kept separate at all times.

For each experiment, you will record the time taken, *t*, for the solution to turn blue-black.

The rate of the reaction is given to be, $r = \frac{\text{initial } [\text{HSO}_3^-]}{t} \text{ mol dm}^{-3} \text{ s}^{-1}$.

You will record in a table in the space provided on **page 4**, the following values for **each** of the five experiments.

- all volumes of **FA 1** and deionised water used to prepare **solution A**,
- values of *t*, to the **nearest second**,
- calculated values of initial [IO₃⁻] in the reaction mixture to 3 significant figures, and
- calculated values of *r*, to 3 significant figures.

Note: volumes used to prepare solution **B** need not be recorded.

(a) (i) Preparing solution B

1. Using a pipette, transfer 25.0 cm^3 of **FA 2** to the 250 cm^3 volumetric flask.
2. Using an appropriate measuring cylinder, transfer to the same volumetric flask
 - 50.0 cm^3 of **FA 4**, then,
 - 50.0 cm^3 of **FA 3**.
3. Make up the solution to 250 cm^3 with deionised water and **mix thoroughly**.
This is solution **B**.

(ii) Preparing solution A

1. Fill a burette with **FA 1**.
2. Fill another burette with deionised water.
3. Transfer 10.00 cm^3 of **FA 1**, followed by 10.00 cm^3 of deionised water into a 100 cm^3 conical flask. This is solution **A**.

(iii) Experiment 1

1. Using an appropriate measuring cylinder, measure out 10.0 cm^3 of **solution B**.
2. Add **solution B** from the measuring cylinder into the conical flask containing **solution A**. Swirl and start the stopwatch immediately upon mixing.
3. Stop the stopwatch when the end-point is reached.
4. Record this value of t , to the nearest second.

At the end of experiment 1, wash the conical flask and allow it to stand to drain on a paper towel.

(iv) Experiments 2 to 5

1. Repeat step 3 in **(a)(ii)** and the procedures in **(a)(iii)** a further four times to perform experiments 2 to 5.
2. In step 3 in **(a)(ii)**, you are to use different volumes of **FA 1** and deionised water to prepare a different **solution A** for each experiment. You should use a minimum volume of 2.00 cm^3 of **FA 1** and a maximum volume of 10.00 cm^3 of **FA 1**. By adding the appropriate volume of deionised water, ensure that the total volume of **solution A** is always 20.00 cm^3 .

- (b) The concentration of **FA 2** in the reaction mixture remains the same in each experiment.

(i) Calculate the amount of **FA 2**, HSO_3^- , in 250 cm^3 of **solution B**.

Amount of FA2 added into the volumetric flask = $25/1000 \times 0.02 = 0.000500 \text{ mol}$

amount of **FA 2** in $250 \text{ cm}^3 = \dots\dots\dots[1]$

(ii) Calculate the amount of **FA 2**, HSO_3^- , in 10.0 cm^3 of **solution B** that was measured out for reaction.

Amount of HSO_3^- in $10 \text{ cm}^3 = 0.000500 / 25 = 2.00 \times 10^{-5} \text{ mol}$;

amount of **FA 2** in $10.0 \text{ cm}^3 = \dots\dots\dots[1]$

(iii) Hence, determine the concentration of **FA 2**, $[\text{HSO}_3^-]$, in each reaction mixture.

$[\text{FA 2}]$ in each reaction mixture = $(2.00 \times 10^{-5}) / (30/1000) = 6.67 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{FA 2}] = \dots\dots\dots[1]$

(c) Results

	Vol of FA1 / cm^3	Vol of H_2O / cm^3	t / s	initial $[\text{IO}_3^-] /$ mol dm^{-3}	$r / \text{mol dm}^{-3} \text{ s}^{-1}$
1	10.00	10.00	13	0.00667	0.0000513
2	7.00	13.00	19	0.00467	0.0000351
3	5.00	15.00	31	0.00333	0.0000215
4	3.00	17.00	63	0.00200	0.0000106
5	2.00	18.00	110	0.00133	0.00000607

Total volume for each experiment = 30.0 cm^3

Table with correct headers and units – 1m

Correct precision (2dp for volumes, nearest sec for t , 3sf for calculated values) – 1m

Appropriate volumes of FA 1 chosen and correct volume of water added – 1m

Correct calculation of $[\text{IO}_3^-]$ to 3sf – 1m

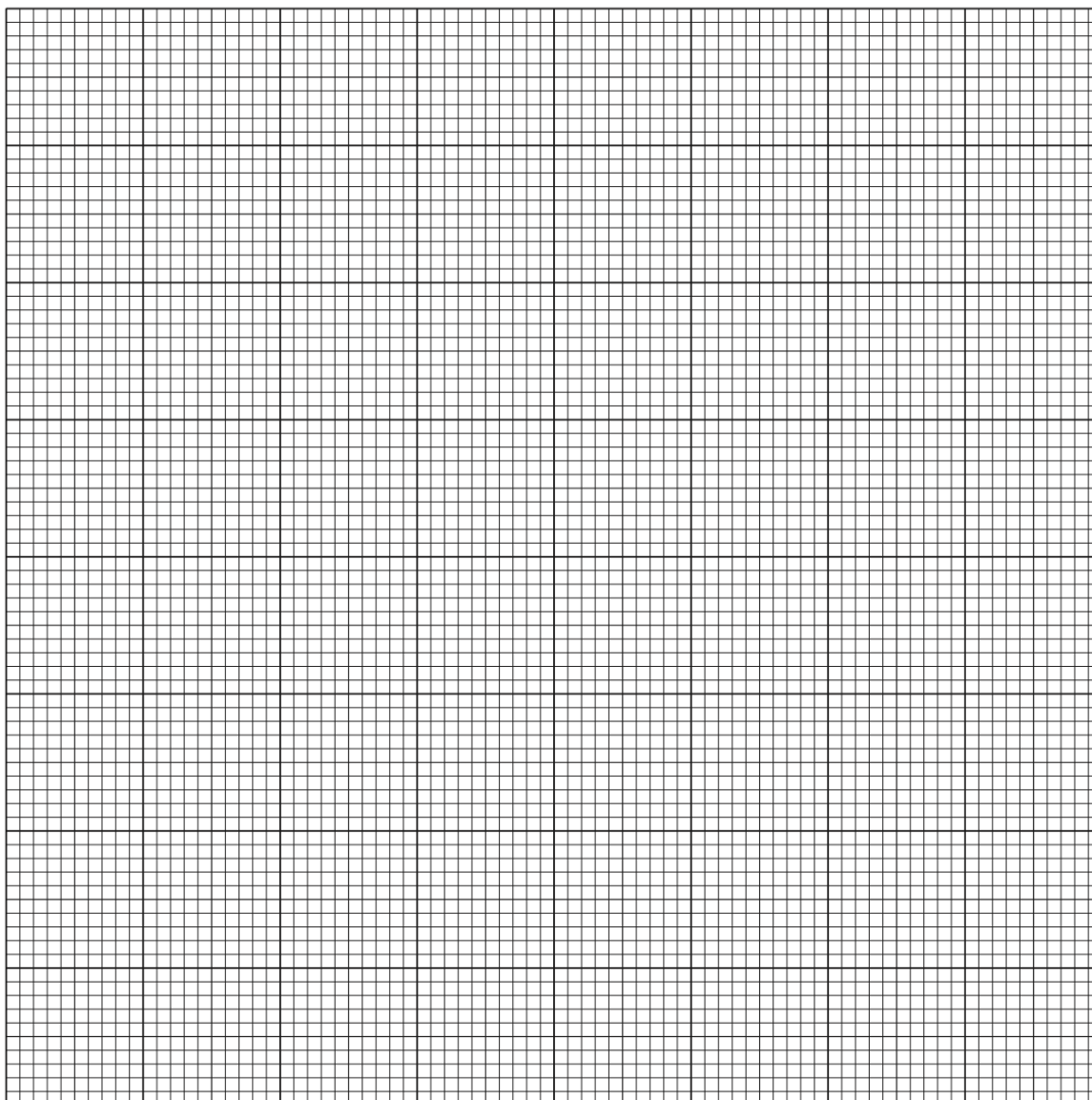
Correct calculation of r to 3sf – 1m

Sample calculation of initial $[\text{IO}_3^-]$ for Expt 1

Amount of FA1 added = $10/1000 \times 0.02 = 0.000200 \text{ mol}$

$[\text{IO}_3^-] = 0.000200 / (30/1000) = 0.00667 \text{ mol dm}^{-3}$

- (d) Plot a graph of rate, r , on the y -axis against initial $[\text{IO}_3^-]$ on the x -axis.
Draw an appropriate line taking into account all of your plotted points.

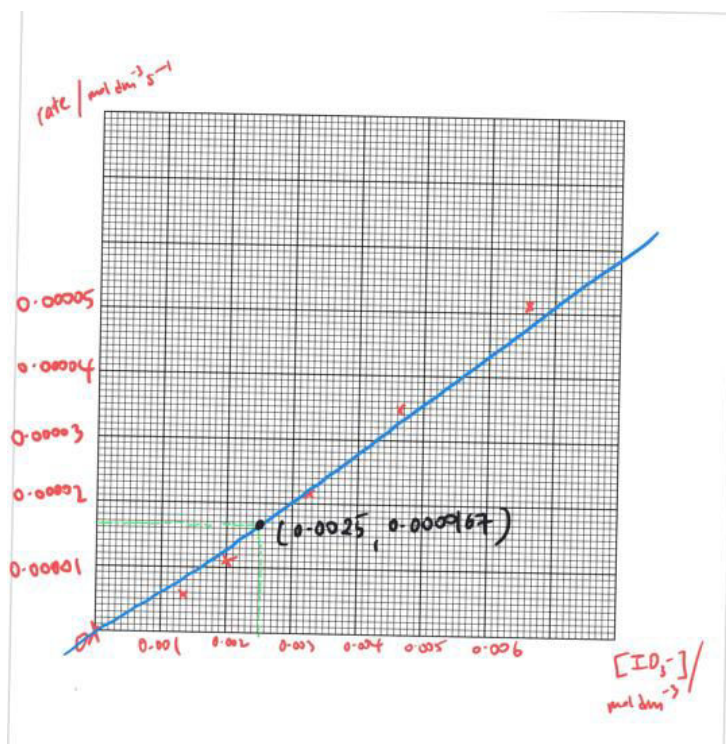


[3]

1m for axes and label

1m for correctly plotted points

1m for best fit (line to take into consideration coordinate 0,0)



- (e) (i) The rate equation for the reaction is shown below.

$$r = k [\text{H}^+][\text{HSO}_3^-][\text{IO}_3^-]^x$$

Use your graph to deduce the order of reaction, x , with respect to the concentration of IO_3^- ions.

order of reaction, x =

explanation

rate order = 1 ;

A straight line graph is obtained which shows that the rate is directly proportional to the change in concentration of IO_3^- . ;

.....[2]

- (ii) Hence, calculate the value of the rate constant, k , given that the $[\text{H}^+]$ in each reaction mixture is $0.00800 \text{ mol dm}^{-3}$. State the units of k clearly.

Using expt 1,

$$0.0000513 = k (0.008) (6.67 \times 10^{-4}) (0.00667)$$

$$k = 1440 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

1m for answer

1m for units

e.c.f awarded

k =[2]

- (iii) Using your graph, calculate the volume of **FA 1** needed to prepare **solution A** so that the reaction mixture turns blue-black after 40 seconds.

$$r = \frac{\text{initial } [\text{HSO}_3^-]}{t}$$

$$r = (6.67 \times 10^{-4}) / 40 = 0.0000167$$

To read from graph the corresponding value of $[\text{IO}_3^-] = 0.0025 \text{ mol dm}^{-3}$;

$$\text{Amount of FA 1} = 0.0025 \times 30/1000 = 0.0000750 \text{ mol}$$

$$\text{Volume of FA 1} = 0.000075 / 0.02 = 3.75 \text{ cm}^3 ;$$

volume of **FA1** required =[2]

- (f) Student **Z** performed experiment 1 but she accidentally added less water to the conical flask in (a)(ii). State and explain how the value of **t** obtained for student **Z** is likely to differ from another student who prepared the reaction mixture correctly.

When less water was added to the boiling tubes, the concentration of the resulting solution will be larger. A higher concentration will lead to a faster rate of reaction, thus the value of **t** obtained by student **Z** will be smaller. ;

.....[1]

[Total: 18]

2 To determine the percentage composition of Na_2CO_3 in a mixture

FA 5 is a solid mixture of Na_2CO_3 and NaCl

FA 6 is a $0.100 \text{ mol dm}^{-3}$ aqueous solution of sulfuric acid, H_2SO_4

FA 7 is Methyl orange indicator

Sulfuric acid only reacts with Na_2CO_3 but not with NaCl , according to the equation shown.



(a) (i) Preparation of a standard solution, **FA 8**

1. Weigh accurately 5.00 g of **FA 5** into a weighing bottle. Record your readings in an appropriate table on **page 9**.
2. Transfer the weighed **FA 5** to a small beaker. Add deionised water and stir the solution with a glass rod to dissolve all the solid.
3. Transfer the solution into a 250 cm^3 volumetric flask.
4. Rinse the beaker with deionised water and add the rinsing to the volumetric flask to ensure all **FA 5** have been transferred.
5. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
6. Place the stopper in the flask and mix the contents thoroughly.
This solution is **FA 8**.

(ii) Titration

1. Fill a burette with **FA 6**.
2. Pipette 25.0 cm^3 of **FA 8** into a conical flask.
3. Add to the flask 2-3 drops of methyl orange indicator and titrate with **FA 6** until the end point is reached.
4. Repeat the titration as necessary to obtain consistent results.

Record all measurements of mass and your titration results on **page 9**.

(b) Results

Mass of empty weighing bottle / g	
Mass of weighing bottle and FA 5 / g	
Mass of FA 5 used / g	4.96

	1	2
Final burette reading / cm ³	23.10	23.10
Initial burette reading / cm ³	0.00	0.00
Volume of FA 6 used / cm ³	23.10	23.10
	✓	✓

Table has correct headers and units. (1m for mass, 1m for burette readings) ; ;

All burette readings and volumes are correctly recorded to the nearest 0.05 cm³. ;

All mass readings correctly recorded to 2dp (following weighing balance) ;

At least 2 consistent readings within ± 0.10 cm³. ;

Accuracy - if student's value is ± 0.40 cm³ of teacher's value (marker to decide range) ;

[6]

- (c) (i) From your titration results, obtain a **suitable** volume of **FA 6** to be used in your calculations.

$$\text{Average volume of FA 6} = (23.10 + 23.10) / 2 = 23.10 \text{ cm}^3$$

volume of **FA 6** =[1]

- (ii) Calculate the amount of Na₂CO₃ in 25.0 cm³ of **FA 8**.

$$\text{Amount of Na}_2\text{CO}_3 \text{ in } 25.0 \text{ cm}^3 = \text{amount of FA 6} = 23.10/1000 \times 0.1 = 0.00231 \text{ mol} ;$$

amount of Na₂CO₃ in 25.0 cm³ of **FA 8** =[1]

- (iii) Calculate the amount of Na₂CO₃ in 250.0 cm³ of **FA 8**.

$$\text{Amount of Na}_2\text{CO}_3 \text{ in } 250.0 \text{ cm}^3 = 0.00231 \times 10 = 0.0231 \text{ mol}$$

[Turn over

amount of Na_2CO_3 in 250.0 cm^3 of **FA 8** =[1]

(iv) Calculate the percentage by mass of Na_2CO_3 in **FA 5**.

Mass of Na_2CO_3 in 250.0 cm^3 = $0.0231 \times (23 + 23 + 12 + 16 + 16 + 16) = 2.449 \text{ g}$;

% by mass = $(2.449 / 4.96) \times 100\% = 49.4\%$;

% by mass =[2]

(d) When preparing standard solutions, it is incorrect to use a dropper to remove some solution should the mark on the volumetric flask be exceeded.

Explain the effect of this incorrect method of preparation on the volume of **FA 6** used for titration and the percentage by mass of Na_2CO_3 calculated.

The standard solution will have a smaller than expected concentration, leading to a decrease in the amount of **FA 5** (Na_2CO_3). ;

This would lead to a decrease in the volume of **FA 6** needed for complete titration. This will cause the calculated percentage by mass to be smaller. ;

.....[2]

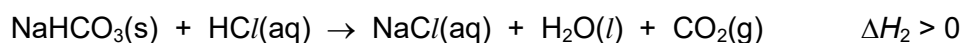
(e) Planning

When sodium hydrogencarbonate, NaHCO_3 , is heated, it decomposes to form sodium carbonate, Na_2CO_3 .



The enthalpy change of reaction, ΔH_r , for the thermal decomposition of NaHCO_3 cannot be determined directly and so an indirect method is used.

By determining the enthalpy change of reaction between $\text{Na}_2\text{CO}_3(\text{s})$ and hydrochloric acid, ΔH_1 , and that between $\text{NaHCO}_3(\text{s})$ and hydrochloric acid, ΔH_2 , a value for ΔH_r for the thermal decomposition of NaHCO_3 can be obtained.

Reaction between $\text{NaHCO}_3(\text{s})$ and hydrochloric acid, ΔH_2 

The reaction between $\text{NaHCO}_3(\text{s})$ and $\text{HCl}(\text{aq})$ is an endothermic process.

The maximum temperature change occurring during this reaction may be determined graphically. The maximum temperature change, ΔT , obtained from the graph can be used to calculate the heat change, q , for this experiment. Using q , a value for ΔH_2 may be determined.

- (i) Outline how you would carry out an experiment to determine the maximum temperature change, ΔT , **graphically** for the reaction between $\text{NaHCO}_3(\text{s})$ and $\text{HCl}(\text{aq})$ in order to determine a value for ΔH_2 .

Your answer should include details of:

- the apparatus used,
- calculations to determine the appropriate quantities of reagents used,
- the experimental procedure,
- the measurements taken to allow a suitable temperature-time graph to be drawn.

Assume that you are provided with:

- 150 cm^3 of 2.00 mol dm^{-3} hydrochloric acid, $\text{HCl}(\text{aq})$,
- 10.0 g of solid sodium hydrogencarbonate, $\text{NaHCO}_3(\text{s})$,
- the equipment normally found in a school laboratory.

1. Weigh an empty weighing bottle using an electronic weighing balance.
2. Weigh accurately 6.00 g of solid NaHCO_3 into the weighing bottle and record the mass.
3. Using a 50 cm^3 measuring cylinder, add 50.0 cm^3 of HCl(aq) into the styrofoam cup supported in a big beaker.
4. Stir the HCl(aq) in the cup using the 0.2°C interval thermometer and record the initial temperature of the solution
5. Start the stopwatch. Record the temperature of the solution in the styrofoam cup at 30 s intervals until 2.5 min.
6. At exactly 3 min, tip the weighed NaHCO_3 into the styrofoam cup and cover the cup with a lid.
7. Stir the contents in the styrofoam cup with the thermometer and record the temperature of the solution at 3.5 min. Continue to stir the contents in the styrofoam cup and record the temperature of the solution at 30 s intervals until 10.0 min.
8. Re-weigh the weighing bottle to find out the actual mass NaHCO_3 added to the styrofoam cup.

Pre-calculations:

Points 2 and 3

For 50.0 cm^3 of HCl(aq) = $50/1000 \times 2 = 0.1 \text{ mol}$ (acid in excess)

For 50.0 cm^3 of HCl(aq) , mass of NaHCO_3 needed = 8.4 g

Suggested marking points:

M1: NaHCO_3

- Use of weighing balance, takes appropriate measurements of mass including reweighing, transfer of solid into cup

M2: HCl

- Use of appropriate measuring cylinder to measure HCl

M3: Use of glass beaker to support cup + mention of insulation (either using two cups or use of a lid) + use of stopwatch

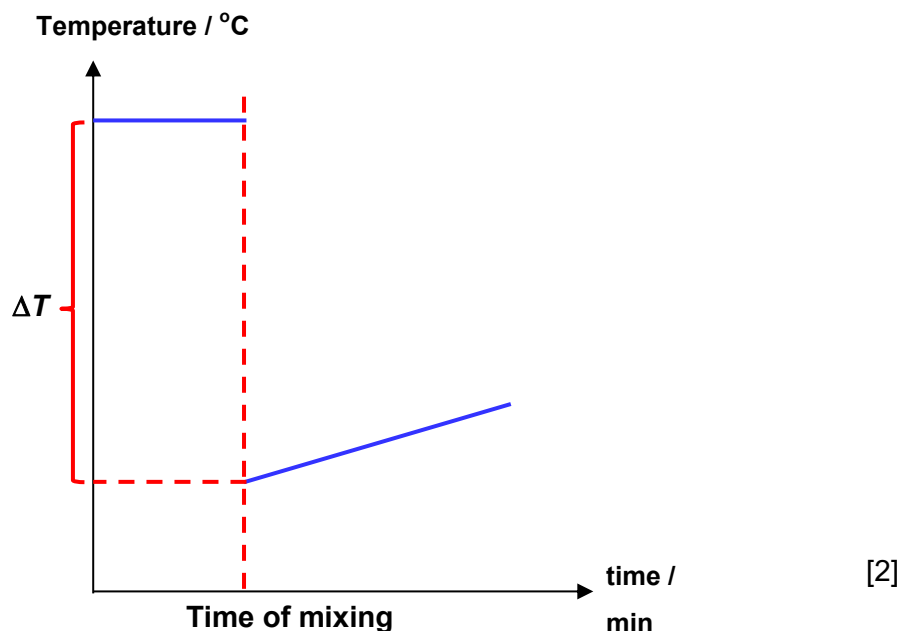
M4: Use of appropriate thermometer and measuring initial temperature from 0 – 2.5 min every 30s.

M5: Add reactant at the 3rd min and measure temperature from the 3.5 min for every 30s until the 10 min mark.

M6: Pre-calculations to determine the quantity of both reactants to use, showing LR clearly

- (ii) Sketch the graph you would expect to obtain in (e)(i).

Indicate how the maximum temperature change, ΔT , can be determined on the graph.



1m for two best lines (including extrapolation)

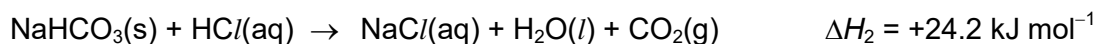
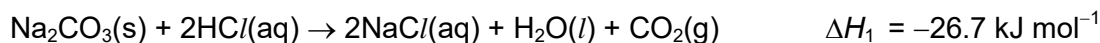
1m for showing ΔT and correct axes

- (iii) Suggest one reason why the graphical method gives an accurate and reliable value for determining a value of ΔT .

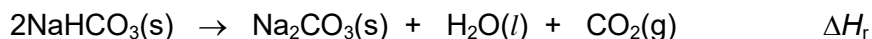
The extrapolation of the graph to the 'time of mixing' has accounted for the heat gained by the surroundings.

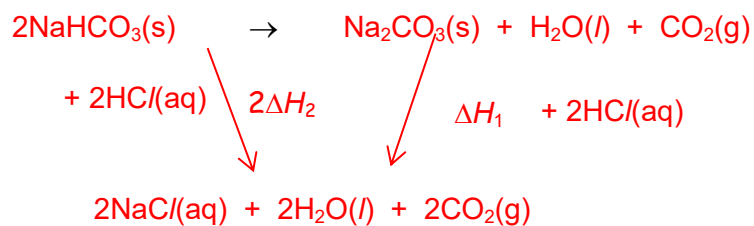
.....[1]

- (iv) Student Z carried out two separate experiments and obtained the following values for ΔH_1 and ΔH_2 .



Using these values of ΔH_1 and ΔH_2 , construct an energy cycle to determine a value for the enthalpy change of reaction, ΔH_r , for the decomposition of $\text{NaHCO}_3(\text{s})$.





$$\begin{aligned}
 \Delta H_r &= 2\Delta H_2 - \Delta H_1 \\
 &= 2(+24.2) - (-26.7) \\
 &= +75.1 \text{ kJ mol}^{-1}
 \end{aligned}$$

1m for energy cycle

1m for hess law and final answer with sign and units

$$\Delta H_r = \dots\dots\dots[2]$$

[Total: 24]

3 Organic Qualitative Analysis

FA 9 is a solution containing an organic compound with the formula $C_4H_8O_2$.

FA 10 is a solution containing an organic compound with **two** functional groups.

Perform the tests described in the table below and record your observations clearly. Some observations have been recorded for you.

Do not use Bunsen burner for heating. Use the hot water provided from the boiler.

(a)	tests	observations for FA 9	observations for FA 10
(i)	Place about 2 cm depth of aqueous sulfuric acid in a test-tube. To this test-tube, add 10 drops of FA , followed by 1 drop of aqueous potassium manganate(VII). Warm the mixture in the hot water bath for five minutes.	Purple $KMnO_4$ decolourised ;	Purple $KMnO_4$ decolourised ;
(ii)	Place about 2 cm depth of aqueous silver nitrate in a test-tube. To this test-tube, add 10 drops of aqueous sodium hydroxide, followed by aqueous ammonia until a clear solution is formed. To this test-tube, add 10 drops of FA . Warm the mixture in the water bath for two minutes.	No silver mirror / no silver ppt observed ;	Silver mirror / silver ppt observed ;
(iii)	Place about 1 cm depth of deionised water in a test-tube. To this test-tube, add 10 drops of FA and add 10 drops of aqueous sodium hydroxide. Now add iodine solution dropwise, until a permanent yellow/ orange colour is obtained. Warm the mixture in the water bath for two minutes.	Yellow ppt obtained ;	No yellow ppt obtained ;

[6]

[Turn over

- (b) In addition to the tests in (a), a student carried out a further test and obtained the following observations.

test	observations for FA 9	observations for FA 10
To 1 cm depth of FA in a test-tube, add 2,4-dinitrophenylhydrazine dropwise.	orange ppt formed	a small quantity of orange ppt formed

Using all the observations in (a) and (b), identify two functional groups present in **FA 9** and **FA 10**. Give evidence(s) to support your answer and state the type of reaction that took place.

FA 9	1 st functional group Primary or Secondary alcohol ;	evidence & type of reaction It undergoes <u>oxidation</u> with acidified KMnO ₄ and <u>decolourises purple</u> KMnO ₄ . ;
	2 nd functional group Ketone ;	evidence & type of reaction It undergoes <u>condensation</u> with 2,4-DNPH to give an orange ppt. but it does not undergo oxidation/react with Tollens' reagent to give a silver mirror. ;
FA 10	1 st functional group Primary or Secondary alcohol	evidence & type of reaction It undergoes oxidation with acidified KMnO ₄ and decolourises purple KMnO ₄ . <u>(no marks awarded for this as same as above)</u>
	2 nd functional group Aldehyde ;	evidence & type of reaction It undergoes <u>oxidation</u> and react with Tollens' reagent to give a silver mirror. ;

[6]

- (c) Suggest and draw one possible structure of **FA 9**.



OR



[1]

[Total: 13]

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

<i>anion</i>	<i>reaction</i>
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$)
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$)
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$)
nitrate, $\text{NO}_3^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown NO_2 in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	SO_2 liberated with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

(c) Tests for gases

<i>gas</i>	<i>test and test result</i>
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 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

<i>halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
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