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CLASS

NATIONAL JUNIOR COLLEGE SH2 Year-End Practical Examination Higher 2

CANDIDATE NAME SUBJECT REGISTRATION

NUMBER

CHEMISTRY	9729/04
Paper 4 Practical	16 August 2022
Candidates answer on the Question paper	2 hours 30 minutes
Additional Materials: As listed in the Confidential Instructions	

READ THESE INSTRUCTIONS FIRST

Write your identification number and name.

Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in 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 22 and 23.

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	/ 9	
2	/ 21	
3	/ 17	
4	/ 8	
Total	/ 55	

This document consists of **23** printed pages including this cover page.

2

Answer all the questions in the spaces provided.

1 Determination of the enthalpy change of a reaction, ΔH_r

FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃ (to be used for Q3 as well)
FA 2 is 2.00 mol dm⁻³ sodium hydroxide, NaOH
FA 3 is 2.00 mol dm⁻³ sulfuric acid, H₂SO₄

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in **Tables 1.1** and **1.2**.

Experiment A

Reaction between FA 1, NaHCO₃, and FA 2, NaOH.

Reaction 1 NaHCO₃(aq) + NaOH(aq) \rightarrow Na₂CO₃(aq) + H₂O(l) $\Delta H_{\text{reaction1}}$

The molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with NaOH.

- 1 Using a 50 cm³ measuring cylinder, transfer 30.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 1**, *T*_{FA1}.
- **3** Using another 50 cm³ measuring cylinder, measure 20.0 cm³ of **FA 2.**
- 4 Stir and measure the temperature of this **FA 2**, *T*_{FA2}.
- 5 Add **FA 2** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- 6 Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 1** and **FA 2** using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA2} \times T_{FA2})}{(V_{FA1} + V_{FA2})}$$

	Experiment A
<i>Τ</i> _{FA1} /°C	
<i>Т</i> _{FA2} /°С	
T_{average} /°C	
7 _{max} ∕°C	
ΔT_{max} /°C	ΔT_{max}

Table 1.1

Experiment B

Reaction between FA 1, NaHCO₃, and FA 3, H₂SO₄.

3

The molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with H₂SO₄.

- 1 Using a measuring cylinder, transfer 30.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 1**, *T*_{FA1}.
- **3** Using another measuring cylinder, measure 20.0 cm³ of **FA 3.**
- 4 Stir and measure the temperature of this **FA 3**, *T*_{**FA3**}.
- 5 Add **slowly**, the **FA 3** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- **6** Using the thermometer, stir the mixture continuously until a minimum temperature is reached. Read and record this temperature T_{min} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 1** and **FA 3** using the formula given below:

 $T_{\text{average}} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA3} \times T_{FA3})}{(V_{FA1} + V_{FA3})}$

Table 1.2

- (a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm^{-3} and specific heat capacity, *c*, of $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.
 - (i) Use your results from **Table 1.1** to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$. You may show your calculations in terms of ΔT_{max} .

 $\Delta H_{\text{reaction1}} = \dots$ [2]

(ii) Use your results from **Table 1.2** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$. You may show your calculations in terms of ΔT_{min} .

 $\Delta H_{\text{reaction2}} = \dots$ [2]

5

$H^{+}(aq) + OH^{-}(aq) \longrightarrow H_2O(l)$	ΔH_{neu} = -57.1 kJ mol ⁻¹	
HCO₃⁻(aq) + OH⁻(aq)→ CO₃²⁻(aq) + H₂O(<i>l</i>)	$\Delta H_{\text{reaction1}}$	
$HCO_3^-(aq) + H^+(aq) \to H_2O(l) + CO_2(g)$	$\Delta H_{\text{reaction2}}$	

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2HCO_3^{-}(aq) \Delta H_{reaction3}$

Using your calculated answers in (a), together with the given value of enthalpy change of neutralisation, ΔH_{neu} , construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

 $\Delta H_{\text{reaction3}} = \dots$

[3]

[Total: 9]

2 Qualitative analysis of some organic and inorganic compounds

You are provided with liquids FA 4, FA 5, FA 6, FA 7, and FA 8.

You are to perform the tests described in **Tables 2.1** and **2.3** and record your observations.

At each stage of any test, you are to record details of the following:

- colour changes seen
- the formation of any precipitate and its solubility in an excess of the reagent added
- the formation of any gas and its identification by a suitable test
- if there is no observable change, write **no observable change**

You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise. If any solution is warmed, a **boiling tube** must be used. Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

- (a) FA 4, FA 5, FA 6 and FA 7 are organic compounds with the molecular formula shown.
 - **FA 4**: C₃H₆O
 - **FA 5**: C₃H₆O
 - **FA 6**: C₃H₈O
 - **FA 7**: C₃H₆O₂

You will perform some of the tests described in Table 2.1.

Using the observations in **Table 2.1** and the given molecular formula, you will then deduce the identities of **FA 4**, **FA 5**, **FA 6** and **FA 7**.

Perform the tests given in **Table 2.1**. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in **Table 2.1**.

Safety: Organic compounds are flammable. Transfer your organic waste into the waste bottle for disposal after the end of the assessment.

Test	Procedure	Observations with FA 4, C ₃ H ₆ O	Observations with FA 5, C ₃ H ₆ O	Observations with FA 6, C ₃ H ₈ O	Observations with FA 7, C ₃ H ₆ O ₂
1.	[2,4-DNPH] To 1 cm depth of unknown liquid, add 1cm depth of 2,4-dinitrophenylhydrazine solution.	Orange precipitate observed	Orange precipitate observed	No observable change	No observable change
2.	To 1 cm depth of unknown liquid, add aqueous sodium carbonate. Test for and identify any gas evolved.	No observable change	No observable change	No observable change	Effervescence produced. White precipitate observed when gas is bubbled into limewater
3.	[lodoform Test] To 1 cm depth of unknown liquid, add 8 drops of aqueous sodium hydroxide followed by iodine solution, dropwise, until a permanent orange/red colour is present. Warm the mixture in a beaker of hot water for two minutes.	No observable change	Yellow precipitate observed	Yellow precipitate observed	No observable change

4.	[Tollens' reagent] To 1 cm depth of aqueous silver nitrate, slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate formed dissolves. You may use a clean glass rod to stir the mixture	Yellow precipitate observed	No observable change	No observable change	No observable change
	and help dissolve the precipitate. Add 1 cm depth of unknown liquid to this mixture, shake the tube and let it stand.				

Table 2.1

[4]

Give evidence from the observations in **Table 2.1** to support your conclusions.

	Compound	Evidence
FA 4		
FA 5		
FA 6		
FA 7		

FA 8 is a mixture of two salts and contains two cations.

You will perform a series of test-tube reactions and use the observations to help you identify the two cations.

(c)	Test	Observation
1.	Test the FA 8 solution using Universal indicator paper.	 Universal indicator paper turns orange pH 3 – 4
2.	Prepare about 2 cm ³ of dilute sulfuric acid in a clean test tube.	
	Place about 2 cm ³ of FA 8 into another clean test-tube. Carefully add aqueous sodium hydroxide, dropwise with shaking, until no further change is seen.	 white ppt formed then green ppt, insoluble in excess NaOH (turning brown in contact with air)
	Swirl and filter the mixture, collecting the filtrate in the test tube containing dilute sulfuric acid.	 green residue turns brown in contact with air/ brown residue obtained
	Observe the residue and filtrate until no further change is seen.	 colourless/pale yellow filtrate White ppt observed
3.	To 1cm ³ of FA 8 , carefully add aqueous potassium manganate, dropwise with shaking, until no further change is seen.	 Purple KMnO₄ decolourises Colourless solution turns yellow Orange/ Brown (eventually purple)
	Table	2.3
l) (i)	Identify the cations in FA 8.	[5
	Cation 1:	Cation 2: [2]
(ii)	With the aid of an equation, explain the	e observation for Test 1 in Table 2.3.

 (iii) Identify the metal-containing complex formed when excess sodium hydroxide is added to FA 8.

Write equations to illustrate the formation of this complex.



[Total: 21]

3 To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction

FA 12 is 1.00 mol dm⁻³ propanone, CH_3COCH_3 FA 13 is 1.00 mol dm⁻³ sulfuric acid, H_2SO_4 FA 14 is an aqueous solution of iodine, I_2 FA 15 is 0.0150 mol dm⁻³ sodium thiosulfate, $Na_2S_2O_3$ FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, $NaHCO_3$ (same solution used in Q1)

You are also provided with a starch indicator.

The iodination of propanone, to form iodopropanone, proceeds as shown in the equation below.

Reaction 1: $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This reaction is first order with respect to both CH₃COCH₃ and H⁺ ions.

You are to investigate the order of reaction with respect to I₂.

A reaction mixture containing FA 12, FA 13, and FA 14 is first prepared. At different chosen times, aliquots (fixed volumes) of this reaction mixture is removed and quenched using excess FA 1.

It is necessary that you titrate each aliquot against **FA15** before transferring the next aliquot. I_2 and $S_2O_3^{2-}$ react as shown in **Reaction 2**.

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

The required order of reaction can be obtained by the graphical analysis of your results.

The first aliquot should be removed approximately 4 minutes after the reagents were mixed. You will then remove four further aliquots, at time intervals of your choice, up to a maximum time of 30 minutes.

In an appropriate format in the space provided on **page 14**, 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 $t_d = 4 \text{ min } + 33/60 = 4.6 \text{ min}$,
- the burette readings and the volume of **FA 15** added.
- **Safety:** Propanone is flammable. Transfer your titrated solutions into the waste bottle for later disposal.

Keep the conical flask (reaction mixture) stoppered except when removing aliquots.

Experiment

NOTE READ THE FULL PROCEDURE BEFORE STARTING YOUR EXPERIMENT

- 1. Label each of the boiling tubes **1** to **5**.
- 2. Add approximately 10 cm³ of **FA 1** to each of these boiling tubes.
- 3. Fill a burette with **FA 15**

Preparing the reaction mixture

- 4. Using a 50 cm³ measuring cylinder, transfer 25.0 cm³ of **FA 12** into the 100 cm³ beaker.
- 5. Using the same 50 cm³ measuring cylinder, transfer 25.0 cm³ of **FA 13** into the same 100 cm³ beaker.
- 6. Using another 50 cm³ measuring cylinder, transfer 50.0 cm³ of **FA 14** into the 250 cm³ conical flask, labelled **reaction mixture.**
- 7. Pour the contents of the 100 cm³ beaker into this 250 cm³ conical flask. Start the stopwatch, **insert the stopper** and swirl the mixture thoroughly. Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture and titration

- 8. At approximately 4 minutes, using a 10.0 cm³ pipette, remove a 10.0 cm³ aliquot of the reaction mixture.
- 9. **Immediately** transfer this aliquot into the boiling tube labelled **1** and swirl the mixture. Read and record the transfer time in minutes and seconds, to the nearest second, when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
- 10. Pour all the contents of **boiling tube 1** into a clean 250 cm³ conical flask. Wash out the boiling tube and add the washings to the conical flask.
- 11. Titrate the iodine in this solution with **FA 15**. Add about 1 cm³ of starch indicator when the colour of the solution turns pale yellow. The solution will turn blue–black. The end–point is reached when the dark blue–black colour just disappears. Record your results.
- 12. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
- 13. At approximately 8 minutes, repeat points 8 to 12. Transfer this aliquot into the boiling tube labelled 2.
- 14. Repeat point 8 to 12 for the remaining boiling tubes at about four-minute intervals.

(a) Results

Actual time	t/min	Initial burette	Final burette	Volume of FA 15
		reading/cm ³	reading/cm ³	used/cm ³
4 min 6s	4.1	0.00	15.90	15.90
8 min 3s	8.1	15.90	30.30	14.40
12 min 3s	12.1	0.00	12.90	12.90
15 min 56s	15.9	12.90	24.40	11.50
19 min 59s	20.0	24.40	34.50	10.10

(b) (i) On Fig 3.1, plot a graph of volume of sodium thiosulfate, FA 15, on the y-axis, against decimal time, t_d , on the x-axis. Start the x-axis at $t_d = 0$. You should choose a scale which will allow you to extrapolate your graph back to $t_d = 0$.

7

Draw the most appropriate best-fit line taking into account all of your plotted points.



Fig 3.1

[3]

- - (ii) Calculate the gradient of the line you have drawn in **Fig 3.1**, showing clearly how you did this.

gradient = $cm^3 min^{-1}$ [1]

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

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

(iv) Hence, deduce the rate of disappearance of I_2 in mol min⁻¹.

rate of disappearance of $I_2 = \dots mol min^{-1}$ [1]

8

rate of change of $[I_2]$ in the reaction mixture = mol dm⁻³ min⁻¹ [1]

(vi) Hence, calculate the value of the rate constant for this reaction, giving its units.

rate constant =

[2]

(d) Step 7 requires you to mix each aliquot immediately with an excess of sodium hydrogencarbonate solution, FA 1. Suggest a clear explanation for this requirement.

.....

.....

- [1]
- (e) Explain why the concentration of iodine in FA 14 used is very much lower than the concentrations of propanone in FA 12 and of H⁺ ions in FA 13.

[1]

[Total: 17]

4 Planning – Extension to Q3

You are to plan a series of experiments to verify that the order with respect to propanone in the iodination of propanone is 1.

10

 $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This investigation can be carried out by monitoring the time taken for the colour of a limited amount of iodine to be discharged when reacting with varying concentrations of propanone.

You may assume that it takes approximately 1 minute for the iodine colour to be discharged when a mixture of 20 cm³ of 2.00 mol dm⁻³ of propanone, CH_3COCH_3 and 10 cm³ of 1.00 mol dm⁻³ sulfuric acid, H_2SO_4 is reacted with 10 cm³ of 0.20 mol dm⁻³ iodine, I_2 .

You may assume that you are provided with:

- Only 60 cm³ of 2.00 mol dm⁻³ propanone, CH₃COCH₃
- 1.00 mol dm⁻³ sulfuric acid, H₂SO₄
- 1.00 mol dm⁻³ solution of iodine, I₂
- 100 cm³ volumetric flasks
- starch indicator
- stopwatch
- the equipment normally found in a school or college laboratory.

(a) Serial dilution

Suggest how propanone of concentrations 1.00 mol dm⁻³, 0.50 mol dm⁻³ 0.25 mol dm⁻³ and 0.125 mol dm⁻³ can be prepared from the 2.00 mol dm⁻³ propanone provided.

Clearly outline the procedure for the dilution.

 (b) Plan a procedure to collect sufficient data to allow a graph to be plotted to verify the order of reaction with respect to propanone.

You are to use the 1.00 mol dm⁻³, 0.50 mol dm⁻³, 0.25 mol dm⁻³ and 0.125 mol dm⁻³ propanone solutions you have prepared in **(a)** in your procedure.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantity of the different solutions you would use,
- the procedure you would follow,
- how you would verify that the order with respect to propanone is 1.

.....

.....

[4]

(c) A student suggested that preparing individual solutions of propanone of varying concentrations for use in this analysis is very time consuming and not necessary.

Suggest how the above procedure can be modified to investigate the order with respect to propanone by just using 2.00 mol dm⁻³ propanone.

You may find it helpful to use of a table to illustrate your answer.

[2]

[Total: 8]



Answer all the questions in the spaces provided.

1 Determination of the enthalpy change of a reaction, ΔH_r

FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃ (to be used for Q3 as well)
FA 2 is 2.00 mol dm⁻³ sodium hydroxide, NaOH
FA 3 is 2.00 mol dm⁻³ sulfuric acid, H₂SO₄

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in **Tables 1.1** and **1.2**.

Experiment A

Reaction between FA 1, NaHCO₃, and FA 2, NaOH.

Reaction 1 NaHCO₃(aq) + NaOH(aq) \rightarrow Na₂CO₃(aq) + H₂O(l) $\Delta H_{\text{reaction1}}$

The molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with NaOH.

- 1 Using a 50 cm³ measuring cylinder, transfer 30.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 1**, *T*_{FA1}.
- **3** Using another 50 cm³ measuring cylinder, measure 20.0 cm³ of **FA 2.**
- 4 Stir and measure the temperature of this **FA 2**, *T*_{FA2}.
- 5 Add **FA 2** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- 6 Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 1** and **FA 2** using the formula given below:

 $T_{\text{average}} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA2} \times T_{FA2})}{(V_{FA1} + V_{FA2})}$

	Experiment A
<i>Т</i> _{FA1} /°С	
<i>Т</i> _{FA2} /°С	
T _{average} /°C	
T _{max} ∕°C	
ΔT_{max} /°C	ΔT_{\max}

Table 1.1

Experiment B

Reaction between FA 1, NaHCO₃, and FA 3, H₂SO₄.

15

The molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with H₂SO₄.

- 1 Using a measuring cylinder, transfer 30.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 1**, *T*_{**FA1**}.
- **3** Using another measuring cylinder, measure 20.0 cm³ of **FA 3.**
- 4 Stir and measure the temperature of this **FA 3**, *T*_{**FA3**}.
- 5 Add **slowly**, the **FA 3** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- **6** Using the thermometer, stir the mixture continuously until a minimum temperature is reached. Read and record this temperature T_{min} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 1** and **FA 3** using the formula given below:

 $T_{\text{average}} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA3} \times T_{FA3})}{(V_{FA1} + V_{FA3})}$

Table 1.2

[2]

For both Tables 1.1 & 1.2: 1m - All temperature readings are recorded to the nearest 0.1 °C. 1m - $\Delta T_{\text{max/min}}$ must be correctly calculated (with sign -ve) i.e. T_{max} – average initial temperature.

- (a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm^{-3} and specific heat capacity, *c*, of $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.
 - (iii) Use your results from **Table 1.1** to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$. You may show your calculations in terms of ΔT_{max} .

```
q = (20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{max}1mn(NaHCO_3) = 1.00 \times 30.0/1000 = 0.03 mol\Delta H_{reaction1} = -(50.0) \times 4.18 \times \Delta T_{max} / n(NaHCO_3)<br/>(this reaction is exothermic)1m (with unit and sign)
```

 $\Delta H_{\text{reaction1}} = \dots$ [2]

(iv) Use your results from **Table 1.2** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$. You may show your calculations in terms of ΔT_{min} .

q = $(20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{min}$ 1m n(NaHCO₃) = $1.00 \times 30.0/1000 = 0.03$ mol $\Delta H_{reaction1} = + (50.0) \times 4.18 \times \Delta T_{min} / n(NaHCO_3)$ (this reaction is endothermic) 1m (with unit and sign)

 $\Delta H_{\text{reaction2}} = \dots$ [2]

$H^{+}(aq) + OH^{-}(aq) \longrightarrow H_2O(l)$	$\Delta H_{\rm neu} = -57.1 \text{ kJ mol}^{-1}$	
HCO₃⁻(aq) + OH⁻(aq)→ CO₃²⁻(aq) + H₂O(<i>l</i>)	$\Delta H_{\text{reaction1}}$	
$HCO_3^{-}(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$	$\Delta H_{\text{reaction2}}$	

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2HCO_3^{-}(aq) \Delta H_{reaction3}$

Using your calculated answers in (a), together with the given value of enthalpy change of neutralisation, ΔH_{neu} , construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

$$\begin{array}{c} \Delta H_{\text{reaction3}}\\ \text{CO}_2(\textbf{g}) + \text{CO}_3^{2-}(\textbf{aq}) + 2\text{H}_2\text{O}(\textbf{I}) \rightarrow 2\text{HCO}_3^{-}(\textbf{aq}) + \text{H}_2\text{O}(\textbf{I})\\ & & & & & \\ \Delta H_{\text{reaction2}} & & & & \\ \text{HCO}_3^{-}(\textbf{aq}) + \text{H}^+(\textbf{aq}) + \text{CO}_3^{2-}(\textbf{aq}) + \text{H}_2\text{O}(\textbf{I}) \leftarrow 2\text{HCO}_3^{-}(\textbf{aq}) + \text{H}^+(\textbf{aq}) + \text{OH}^-(\textbf{aq})\\ & & & & \\ \Delta H_{\text{reaction1}} & & \\ \end{array}$$

 $\Delta H_{\text{reaction3}} = (-\Delta H_{\text{reaction2}}) + (-\Delta H_{\text{reaction1}}) + (-57.1)$

= (- (a)(ii)) + (- (a)(i)) + (-57.1)

1m – cycle 1m – substitute values correctly in eqn 1m – final ans

 $\Delta H_{\text{reaction3}} = \dots$

[3]

[Total: 9]

2 Qualitative analysis of some organic and inorganic compounds

You are provided with liquids FA 4, FA 5, FA 6, FA 7, and FA 8.

You are to perform the tests described in **Tables 2.1** and **2.3** and record your observations.

At each stage of any test, you are to record details of the following:

- colour changes seen
- the formation of any precipitate and its solubility in an excess of the reagent added
- the formation of any gas and its identification by a suitable test
- if there is no observable change, write **no observable change**

You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise. If any solution is warmed, a **boiling tube** must be used. Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

(a) FA 4, FA 5, FA 6 and FA 7 are organic compounds with the molecular formula shown.

- **FA 4**: C₃H₆O
- **FA 5**: C₃H₆O
- **FA 6**: C₃H₈O
- **FA 7**: C₃H₆O₂

You will perform some of the tests described in Table 2.1.

Using the observations in **Table 2.1** and the given molecular formula, you will then deduce the identities of **FA 4**, **FA 5**, **FA 6** and **FA 7**.

Perform the tests given in **Table 2.1**. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in **Table 2.1**.

Safety: Organic compounds are flammable. Transfer your organic waste into the waste bottle for disposal after the end of the assessment.

Test	Procedure	Observations with FA 4, C ₃ H ₆ O Propanal	Observations with FA 5, C ₃ H ₆ O Propanone	Observations with FA 6, C ₃ H ₈ O Propan-2-ol	Observations with FA 7, C ₃ H ₆ O ₂ Propanoic acid
1.	[2,4-DNPH] To 1 cm depth of unknown liquid, add 1cm depth of 2,4-dinitrophenylhydrazine solution.	Orange precipitate observed	Orange precipitate observed	No observable change	No observable change
2.	To 1 cm depth of unknown liquid, add aqueous sodium carbonate. Test for and identify any gas evolved.	No observable change	No observable change	No observable change	Effervescence produced. White precipitate observed when gas is bubbled into limewater
3.	[lodoform Test] To 1 cm depth of unknown liquid, add 8 drops of aqueous sodium hydroxide followed by iodine solution, dropwise, until a permanent orange/red colour is present. Warm the mixture in a beaker of hot water for two minutes.	No observable change	Yellow precipitate observed	Yellow precipitate observed	No observable change

4. [Tolle To 1 o nitrate aqueo	ens' reagent] cm depth of aqueous silver e, slowly add 1 cm depth of ous sodium hydroxide.				
Add a with s forme clean and h	aqueous ammonia slowly, shaking, until the precipitate ed dissolves. You may use a glass rod to stir the mixture help dissolve the precipitate.	Yellow precipitate observed	No observable change	No observable change	No observable change
Add 1 to thi and le	cm depth of unknown liquid is mixture, shake the tube et it stand.				

Table 2.1

[4]

Give evidence from the observations in **Table 2.1** to support your conclusions.

	Compound	Evidence
FA 4	Propanal	Positive Tollens' test suggest it is an aldehyde. Hence, propanal.
FA 5	Propanone	Positive 2,4 DNPH test and negative Tollens' suggests it's a ketone. Positive triiodomethane test suggests it's a methyl ketone. Hence, propanone.
FA 6	Propan-2-ol	Positive triiodomethane test but negative 2,4 DNPH test suggests it's a methyl alcohol. Hence propan-2-ol.
FA 7	Propanoic acid	Effervescence with Na ₂ CO ₃ suggests it's a carboxylic acid. Hence propanoic acid.

Table 2.2

1m for each correct compound + required evidence in red

[4]

FA 8 is a mixture of two salts and contains two cations.

You will perform a series of test-tube reactions and use the observations to help you identify the two cations.

(c)	Test	Observation
4.	Test the FA 8 solution using Universal indicator paper.	 Universal indicator paper turns orange pH 3 – 4
5.	Prepare about 2 cm ³ of dilute sulfuric acid in a clean test tube.	
	Place about 2 cm ³ of FA 8 into another clean test-tube. Carefully add aqueous sodium hydroxide, dropwise with shaking, until no further change is seen.	 grey-green <u>ppt</u> formed then <u>green ppt</u>, <u>insoluble</u> in excess NaOH (turning brown in contact with air)
	Swirl and filter the mixture, collecting the filtrate in the test tube containing dilute sulfuric acid.	
	Observe the residue and filtrate until no further change is seen.	 green residue turns <u>brown</u> in contact with air/ brown residue obtained colourless/pale yellow filtrate White ppt observed
6.	To 1 cm ³ of FA 8 , carefully add aqueous potassium manganate, dropwise with shaking, until no further change is seen.	 Purple KMnO₄ decolourises Colourless solution turns yellow Orange/ Brown (eventually purple)

Table 2.3

(d) (i) Identify the cations in FA 8.

Fe²⁺ Cation 1:

- [2]
- (ii) With the aid of an equation, explain the observation for **Test 1** in **Table 2.3**.

 $[Al(H_2O)_6]^{3+} + H_2O \implies [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+$

1m

- From test 1, colour of Universal Indicator paper is orange which shows that the solution is acidic (pH = 3). Al^{3+} has high charge density, polarises and weakens the O-H bond of H₂O, causing one of the six H₂O to undergo hydrolysis to give $[Al (H_2O)_5(OH)]^{2+}$ and H₃O⁺, resulting in an acidic solution. 1m
- [2]

. .

. . .

(iii) Identify the metal-containing complex formed when excess sodium hydroxide is added to FA 8.

Write equations to illustrate the formation of this complex.

```
 \begin{bmatrix} A/(OH)_4 \end{bmatrix}^{-}(aq) & 1m \\ A/(aq)^{3+} + & 4OH^{-} \rightleftharpoons [A/(OH)_4]^{-}(aq) & 1m \\ \begin{bmatrix} A/(H_2O)_6 \end{bmatrix}^{3+} + & 4OH^{-} \rightleftharpoons [A/(OH)_4]^{-}(aq) + & 6H_2O \\ \begin{bmatrix} A/(H_2O)_6 \end{bmatrix}^{3+} + & 4OH^{-} \rightleftharpoons [A/(OH)_4 (H_2O)_2]^{-}(aq) + & 4H_2O \end{bmatrix}  any of these eqns
```

(iv) FA 8 contains either the sulfate ion or a halide anion.

Describe two tests, using only the bench reagents provided, which will allow you to identify the anion present.

In each case, state how you will decide if the test result is positive.

[You **DO NOT** need to carry out these tests.]

```
Test 1: Add AgNO<sub>3</sub> 1m

No ppt – SO<sub>4</sub><sup>2-</sup>

Ppt – halide

Test 2: Add NH<sub>3</sub>(aq) to determine solubility of ppt formed in test 1 1m

White ppt, soluble – Cl<sup>-</sup>

Cream ppt, partially soluble – Br<sup>-</sup>

Yellow ppt, insoluble – I<sup>-</sup>
```

.....

[2]

[2]

[Total: 21]

3 To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction

FA 12 is 1.00 mol dm⁻³ propanone, CH_3COCH_3 FA 13 is 1.00 mol dm⁻³ sulfuric acid, H_2SO_4 FA 14 is an aqueous solution of iodine, I_2 FA 15 is 0.0150 mol dm⁻³ sodium thiosulfate, $Na_2S_2O_3$ FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, $NaHCO_3$ (same solution used in Q1)

You are also provided with a starch indicator.

The iodination of propanone, to form iodopropanone, proceeds as shown in the equation below.

Reaction 1: $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This reaction is first order with respect to both CH₃COCH₃ and H⁺ ions.

You are to investigate the order of reaction with respect to I₂.

A reaction mixture containing FA 12, FA 13, and FA 14 is first prepared. At different chosen times, aliquots (fixed volumes) of this reaction mixture is removed and quenched using excess FA 1.

It is necessary that you titrate each aliquot against **FA15** before transferring the next aliquot. I_2 and $S_2O_3^{2-}$ react as shown in **Reaction 2**.

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

The required order of reaction can be obtained by the graphical analysis of your results.

The first aliquot should be removed approximately 4 minutes after the reagents were mixed. You will then remove four further aliquots, at time intervals of your choice, up to a maximum time of 30 minutes.

In an appropriate format in the space provided on **page 14**, 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 $t_d = 4 \text{ min } + 33/60 = 4.6 \text{ min}$,
- the burette readings and the volume of **FA 15** added.
- **Safety:** Propanone is flammable. Transfer your titrated solutions into the waste bottle for later disposal.

Keep the conical flask (reaction mixture) stoppered except when removing aliquots.

Experiment

NOTE READ THE FULL PROCEDURE BEFORE STARTING YOUR EXPERIMENT

- 15. Label each of the boiling tubes 1 to 5.
- 16. Add approximately 10 cm^3 of **FA 1** to each of these boiling tubes.
- 17. Fill a burette with **FA 15**

Preparing the reaction mixture

- 18. Using a 50 cm³ measuring cylinder, transfer 25.0 cm³ of **FA 12** into the 100 cm³ beaker.
- 19. Using the same 50 cm³ measuring cylinder, transfer 25.0 cm³ of **FA 13** into the same 100 cm³ beaker.
- 20. Using another 50 cm³ measuring cylinder, transfer 50.0 cm³ of **FA 14** into the 250 cm³ conical flask, labelled **reaction mixture.**
- 21. Pour the contents of the 100 cm³ beaker into this 250 cm³ conical flask. Start the stopwatch, **insert the stopper** and swirl the mixture thoroughly. Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture and titration

- 22. At approximately 4 minutes, using a 10.0 cm³ pipette, remove a 10.0 cm³ aliquot of the reaction mixture.
- 23. **Immediately** transfer this aliquot into the boiling tube labelled **1** and swirl the mixture. Read and record the transfer time in minutes and seconds, to the nearest second, when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
- 24. Pour all the contents of **boiling tube 1** into a clean 250 cm³ conical flask. Wash out the boiling tube and add the washings to the conical flask.
- 25. Titrate the iodine in this solution with **FA 15**. Add about 1 cm³ of starch indicator when the colour of the solution turns pale yellow. The solution will turn blue–black. The end–point is reached when the dark blue–black colour just disappears. Record your results.
- 26. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
- 27. At approximately 8 minutes, repeat points 8 to 12. Transfer this aliquot into the boiling tube labelled 2.
- 28. Repeat point 8 to 12 for the remaining boiling tubes at about four-minute intervals.

(a) Results

Actual time	t/min	Initial burette	Final burette	Volume of FA 15
		reading/cm ³	reading/cm ³	used/cm ³
4 min 6s	4.1	0.00	15.90	15.90
8 min 3s	8.1	15.90	30.30	14.40
12 min 3s	12.1	0.00	12.90	12.90
15 min 56s	15.9	12.90	24.40	11.50
19 min 59s	20.0	24.40	34.50	10.10

(b) (i) On Fig 3.1, plot a graph of volume of sodium thiosulfate, FA 15, on the y-axis, against decimal time, t_d , on the x-axis. Start the x-axis at $t_d = 0$. You should choose a scale which will allow you to extrapolate your graph back to $t_d = 0$.

Draw the most appropriate best-fit line taking into account all of your plotted points.



Fig 3.1

[3]

[1]: Both axes are correctly labelled + Scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions (taking into consideration the extrapolation) + no odd scale

- [1]: One plotted point is within $\pm \frac{1}{2}$ small square
- [1]: Drawing best fit straight line Data points must reflect a straight line

(ii) Deduce the order of reaction with respect to the I_2 in reaction 1. Explain your answer.

Order of reaction is <u>zero</u> with respect to I ₂ Graph is a <u>straight line with constant gradient</u> / <u>rate of reaction is</u> <u>independent of [I₂] / [I₂] decreases linearly with time</u> / <u>[I₂] decreases at a</u> <u>constant rate</u> . 1 or 0	
	[1]

(c) (i) Write the rate equation for the iodination of propanone.

$$Rate = k [CH_3COCH_3][H^+]$$
 1m with ecf [1]

(ii) Calculate the gradient of the line you have drawn in **Fig 3.1**, showing clearly how you did this.

Gradient =
$$\frac{y_2 - y_1}{x_2 - x_1} = \frac{9 - 14.8}{18.75} = -0.309 \text{ cm}^3 \text{ min}^{-1}$$
 (3 s.f) 1m
Show construction lines on graph + coordinates on the graph or in the working

- gradient = $cm^3 min^{-1}$ [1]
- (iii) Use your answer from (c)(ii) to determine the rate of change of amount of S₂O₃²⁻ ions required in mol min⁻¹.

rate of change = (c)(ii) x 0.0150/1000
= 0.309 x 0.0150/1000
= 4.635 x 10⁻⁶
=
$$\frac{4.64 \times 10^{-6}}{100}$$
 mol min⁻¹ (3 s.f.) 1m

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

(iv) Hence, deduce the rate of disappearance of I_2 in mol min⁻¹.

 $I_{2} \equiv 2S_{2}O_{3}^{2-}$ rate of disappearance of $I_{2} = \frac{1}{2} \times (c)(iii)$ $= \frac{1}{2} \times 4.64 \times 10^{-6}$ $= 2.318 \times 10^{-6}$ $= 2.32 \times 10^{-6} \text{ mol min}^{-1} (3 \text{ s.f.}) \qquad 1\text{m}$

rate of disappearance of $I_2 = \dots mol min^{-1}$ [1]

(v) Use your answer from (c)(iv) to calculate the rate of change of $[I_2]$ in the reaction mixture.



rate of change of $[I_2]$ in the reaction mixture = mol dm⁻³ min⁻¹ [1]

(vi) Hence, calculate the value of the rate constant for this reaction, giving its units.

```
(c)(v) = k[CH<sub>3</sub>COCH<sub>3</sub>][H<sup>+</sup>]

2.32 x 10<sup>-4</sup> = k [CH<sub>3</sub>COCH<sub>3</sub>][H<sup>+</sup>]

2.32 x 10<sup>-4</sup> = k (1.00 x \frac{1}{4})(1.00 x 2 x \frac{1}{4})

k = 1.86 \times 10^{-3} mol<sup>-1</sup> dm<sup>3</sup> min<sup>-1</sup> (3 s.f with units) 1m for ans 1m for units
```

rate constant =[2]

(d) Step 7 requires you to mix each aliquot immediately with an excess of sodium hydrogencarbonate solution, FA 1. Suggest a clear explanation for this requirement.

It is added to <u>react with acid catalyst $\frac{1}{2}$ m</u> so that the <u>reaction will stop $\frac{1}{2}$ m</u> / It is to <u>quench the reaction</u> by <u>reacting with the acid catalyst</u>.

[1]

(e) Explain why the concentration of iodine in FA 14 used is very much lower than the concentrations of propanone in FA 12 and of H⁺ ions in FA 13.

The low concentration of iodine means that <u>very little propanone and acid are</u> <u>reacted</u> away from the reaction mixture and hence the <u>concentration</u> of propanone and acid remain <u>effectively constant</u>. Hence, the <u>order of reaction with respect to</u> <u>iodine can be determined</u> because any change in the rate is due to the change in concentration of iodine. 1m

[1]

[Total: 17]

4 Planning – Extension to Q3

You are to plan a series of experiments to verify that the order with respect to propanone in the iodination of propanone is 1.

18

 $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This investigation can be carried out by monitoring the time taken for the colour of a limited amount of iodine to be discharged when reacting with varying concentrations of propanone.

You may assume that it takes approximately 1 minute for the iodine colour to be discharged when a mixture of 20 cm³ of 2.00 mol dm⁻³ of propanone, CH_3COCH_3 and 10 cm³ of 1.00 mol dm⁻³ sulfuric acid, H_2SO_4 is reacted with 10 cm³ of 0.20 mol dm⁻³ iodine, I_2 and 1 cm³ of starch.

You may assume that you are provided with:

- Only 60 cm³ of 2.00 mol dm⁻³ propanone, CH₃COCH₃
- 1.00 mol dm⁻³ sulfuric acid, H₂SO₄
- 1.00 mol dm⁻³ solution of iodine, I₂
- 100 cm³ volumetric flasks
- starch indicator
- stopwatch
- the equipment normally found in a school or college laboratory.

To obtain 1.00 mol dm⁻³ propanone:

- 1) Using a burette, transfer 50 cm³ of 2.00 mol dm⁻³ propanone to a 100 cm³ volumetric flask.
- 2) Top up to the mark with deionised water.
- 3) Shake to ensure homogeneous solution.

Repeat steps 1 to 3 with 1.00 mol dm⁻³ propanone to obtain 0.50 mol dm⁻³ propanone. Repeat steps 1 to 3 with 0.50 mol dm⁻³ propanone to obtain 0.25 mol dm⁻³ propanone. Repeat steps 1 to 3 with 0.25 mol dm⁻³ propanone to obtain 0.125 mol dm⁻³ propanone.

[1] Serial dilution concept

[1] Correct dilution procedure

- top up to mark
- shake to ensure homogenous
- apparatus

.....

[2]

(b) Plan a procedure to collect sufficient data to allow a graph to be plotted to determine the order of reaction with respect to propanone.

You are to use the 1.00 mol dm⁻³, 0.50 mol dm⁻³, 0.25 mol dm⁻³ and 0.125 mol dm⁻³ propanone solutions you have prepared in **(a)** in your procedure.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantity you would use,
- the procedure you would follow,
- a table detailing the data you would collect,
- how you would verify that the order with respect to propanone is 1.
- 1) Using a 50 cm³ measuring cylinder, add 20.0 cm³ of 1.00 mol dm⁻³ of propanone to a 250 cm³ conical flask.
- 2) Using a 10 cm³ measuring cylinder, add 10.0 cm³ of 1.00 mol dm⁻³ sulfuric acid, H_2SO_4 into the same flask.
- 3) Using a 10 cm³ measuring cylinder, add 1.0 cm³ of starch into the same conical flask.
- 4) Using another 10 cm³ measuring cylinder, measure out 10.0 cm³ of $1.00 \text{ mol } \text{dm}^{-3}$ iodine, I₂ into the measuring cylinder.
- 5) Add the contents of the measuring cylinder in step 4 into the flask and start the stopwatch when half the volume is added.
- 6) Swirl the flask once.
- 7) Stop the stopwatch when the blue-black colour is discharged. Record the time taken.
- 8) Repeat the experiment with propanone of concentrations 0.50 mol dm⁻³ 0.25 mol dm⁻³ and 0.125 mol dm⁻³.

Calculate the rate for each experiment by taking 1/time and plot the graph of rate against $[CH_3COCH_3]$.

Table

Expt	[CH ₃ COCH ₃]	Time/s	Rate/s ⁻¹
1	1.00		
2	0.50		
3	0.25		
4	0.125		



Since it is 1st order with respect to propanone, a straight line graph passing through the origin will be obtained.

Marking

[1] - Sound general flow

[1] – specifying apparatus – burette not necessary

- [1] correct volumes to be used
- [1] suggesting appropriate graph to be plot and interpretation

[4]

(c) A student suggested that preparing individual solutions of propanone of varying concentrations for use in this analysis is very time consuming and not necessary.

Suggest how the above procedure can be modified to investigate the order with respect to propanone by just using 2.00 mol dm⁻³ propanone.

You may find it helpful to use of a table to illustrate your answer.

Change the concentration of propanone by adding varying volumes of 2.00 mol dm⁻³ propanone and topping up the solution with water to ensure total volume is constant.

Expt	Vol of 2.00 mol dm ⁻³ CH ₃ COCH ₃ added/ cm ³	Volume of H ₂ O added / cm ³	Total Volume of reaction mixture/ cm ³	Time/s	Rate/s ⁻¹
1	20	0			
2	15	5			

Plot graph of Rate vs Vol of CH₃COCH₃ added

[1] – Using water to vary concentration by keeping total volume constant

[1] – Suggestion of volume of propanone replacing concentration in graph plotting.

.....

[2]

[Total: 8]