ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

NAME:_____ ( ) **CLASS:** 19 /____

CHEMISTRY **9729/04**

Paper 4 Practical **27 August 2019**

2 hours 30 minutes

Candidates answer on the Question Paper.
Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number 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 a pencil for any diagrams, graphs or rough working.
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.
Quantitative 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	
2	
3	
Total	

This document consists of **23** printed pages.

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

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

FA 1 is 1.00 mol dm^{-3} propanone, CH_3COCH_3
FA 2 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
FA 3 is an aqueous solution of iodine, I_2
FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
FA 5 is 0.50 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$

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 CH_3COCH_3 and H^+ ions.

You are to investigate the order of reaction with respect to I_2.

A reaction mixture containing **FA 1**, **FA 2**, and **FA 3** is first prepared. At different chosen times, aliquots (fixed volumes) of this reaction mixture is removed and quenched using excess **FA 5.**

The remaining amount of I_2 at different times can then be determined by titration against **FA 4**. Each titration can only be performed once.

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 20 minutes.

Prepare a table in the space provided on **page 4** in which to record, to an appropriate level of precision, your chosen time, the actual time and your titration results for each of your aliquots. All values of actual time should be converted to decimal value, ***t***, in minutes and recorded to one decimal place.

For example if actual time = 4 min 33 s then ***t*** = 4 min + 33/60 min = 4.6 min

Experiment

Safety: Propanone is flammable. Transfer your titrated solutions into the waste bottle for later disposal. Keep this bottle stoppered when not in use.

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

Preparing the boiling tubes

1. Label each of the boiling tubes with one of your chosen times.
2. Add approximately 10 cm^3 of **FA 5** to each of these boiling tubes.

Preparing the reaction mixture

3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the 100 cm^3 beaker.
4. Using a different pipette, transfer 25.0 cm^3 of **FA 2** into the same 100 cm^3 beaker.
5. Using a burette, transfer 50.00 cm^3 of **FA 3** into the 250 cm^3 conical flask, labelled **reaction mixture.**
6. Pour the contents of the 100 cm^3 beaker into this 250 cm^3 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

7. At approximately 4 minutes, using a 10.0 cm^3 pipette, remove a 10.0 cm^3 aliquot of the reaction mixture. **Immediately** transfer this aliquot into the boiling tube labelled **4 minutes** and swirl the mixture. Note the actual time when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
8. At each of your chosen times, repeat **step 7** but transfer each aliquot to its appropriately labelled boiling tube.

Titrations

9. Pour the whole of the contents of a boiling tube into a clean 250 cm^3 conical flask. Wash out the boiling tube and add the washings to the conical flask.
10. Titrate the iodine in this solution with **FA 4**. Add about 1 cm^3 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.
11. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
12. Repeat **steps 9 to 11** for each of your boiling tubes.

(a) Results

[3]

(b) **(i)** On Fig 1.1, plot a graph of **volume of sodium thiosulfate, FA 4**, on the y–axis, against time, ***t***, on the x–axis. Start the x–axis at ***t*** = 0. You should choose a scale which will allow you to extrapolate your graph back to ***t*** = 0.

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

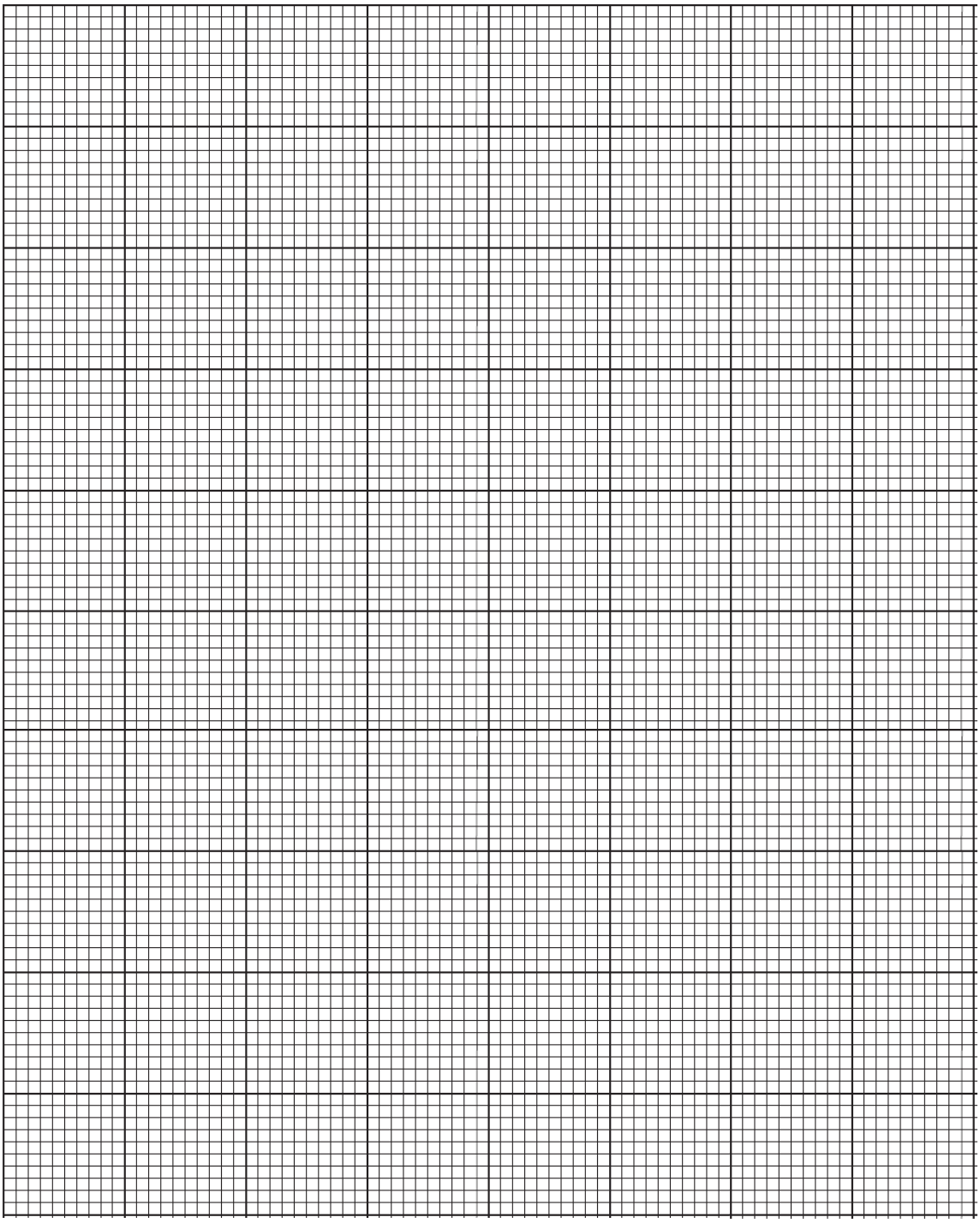

Fig 1.1

[2]

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

order.....

explanation.....

.....

.....
[1]

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

..... [1]

(ii) Calculate the gradient of the line you have drawn in Fig 1.1, showing clearly how you did this.

gradient = ...
[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 = ... 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 = ...
[1]

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

rate constant = ...
[1]

(d) **Step 7** requires you to mix each aliquot immediately with an excess of sodium hydrogencarbonate solution, **FA 5**. Suggest a clear explanation for this requirement.

……

……... [1]

(e) Explain why the concentration of iodine in **FA 3** is very much lower than the concentrations of propanone in **FA 1** and of H^+ ions in **FA 2**.

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……... [1]

(f) Planning

The Finkelstein reaction can be used to synthesise 1–iodopropane, a colourless liquid, from 1–bromopropane and sodium iodide. The reaction is carried out using dry propanone as a solvent.

$$CH_3CH_2CH_2Br + NaI \rightleftharpoons CH_3CH_2CH_2I + NaBr$$

(i) What *type of reaction* is the Finkelstein reaction?

…… [1]

(ii) Explain why it is important for **dry** propanone to be used as a solvent for this reaction.

.....

..... [1]

(iii) Table 1.1 shows the solubilities of sodium bromide and sodium iodide in propanone.

Table 1.1

compound	solubility at 25 °C in g / 100 g of propanone
sodium bromide	0.00841
sodium iodide	39.9

Use this information to explain why, although the reaction between $CH_3CH_2CH_2Br$ and NaI is reversible, the reaction produces a very high yield of $CH_3CH_2CH_2I$.

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..... [1]

Sodium iodide is a white crystalline solid.
1–bromopropane is a colourless liquid which has a density of 1.35 g cm^{-3}.

Table 1.2 gives the boiling points of 1–bromopropane, 1–iodopropane and propanone.

Table 1.2

compound	boiling point / ^{o}C
1–bromopropane	71.0
1–iodopropane	102.6
propanone	56.0

A 100% yield of pure 1–iodopropane is assumed to be obtained using the procedure described below:

1–bromopropane, an excess of sodium iodide and propanone solvent are mixed and then heated under reflux conditions for around thirty minutes.

The crude 1–iodopropane product is distilled to produce the pure 1–iodopropane.

[A_r: C, 12.0; H, 1.0; O, 16.0; Br, 79.9; I, 126.9; Na, 23.0]

(iv) Calculate the minimum volume of 1–bromopropane you would use to prepare 10 g of pure 1–iodopropane, showing your working.

[1]

(v) Write a plan for the preparation of about 10 g of pure 1–iodopropane.

In your plan you should:

- give a full description of the procedures you would use to prepare the crude 1–iodopropane;
- draw a labelled diagram of the assembled apparatus you would use to obtain the pure 1–iodopropane.

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..... [5]

[Total: 23]

2 Investigation of the dissolution of potassium iodide and lithium chloride in water

Both KI and LiCl can dissolve in water to give aqueous solutions.

$$KI(s) \rightarrow K^+(aq) + I^-(aq) \qquad \Delta H > 0$$

$$LiCl(s) \rightarrow Li^+(aq) + Cl^-(aq) \qquad \Delta H < 0$$

The temperature change when a mixture containing KI and LiCl dissolves in water is due to the summation of the temperature change when KI and LiCl dissolve separately in water.

FA 6 is a mixture containing **equal** masses of potassium iodide, KI, and lithium chloride, LiCl.

The ΔT per gram of LiCl dissolved in water may be found by first determining the relationship between mass of KI dissolved in water and the change in temperature of the water due to its dissolution. The temperature change when **FA 6** dissolves completely in water is then determined.

(a) Determination of the value of the decrease in temperature, ΔT_{KI}, for the dissolution of KI in water

(i) You will follow the instructions to perform the following experiment.

1. Weigh accurately about 2.0 g of KI using a weighing bottle.
2. Using a measuring cylinder, transfer 25 cm^3 of deionised water into a Styrofoam cup. Place the cup inside a second Styrofoam cup, which is placed in a 250 cm^3 beaker.
3. Stir and measure the initial temperature of the water in the Styrofoam cup.
4. Add the KI in the weighing bottle into the water in the Styrofoam cup.
5. Stir the mixture continuously until it reaches its **minimum** temperature. Record this temperature.
6. Reweigh the weighing bottle.
7. In an appropriate format in the space below, record all measurements of mass and temperature.
8. Calculate the value of the decrease in temperature, ΔT_{KI}, for this experiment.

Results

[4]

(ii) Using the mass of KI and ΔT_{KI} obtained in **(a)(i)**, together with the data in Table 2.1, plot a graph of ΔT_{KI} against the mass of KI used on the grid in Fig 2.1.
Draw the most appropriate line, taking into account all of the plotted points.

Table 2.1

mass of KI / g	decrease in temperature, ΔT_{KI} / °C
4.00	4.1
6.00	6.2
8.00	7.8

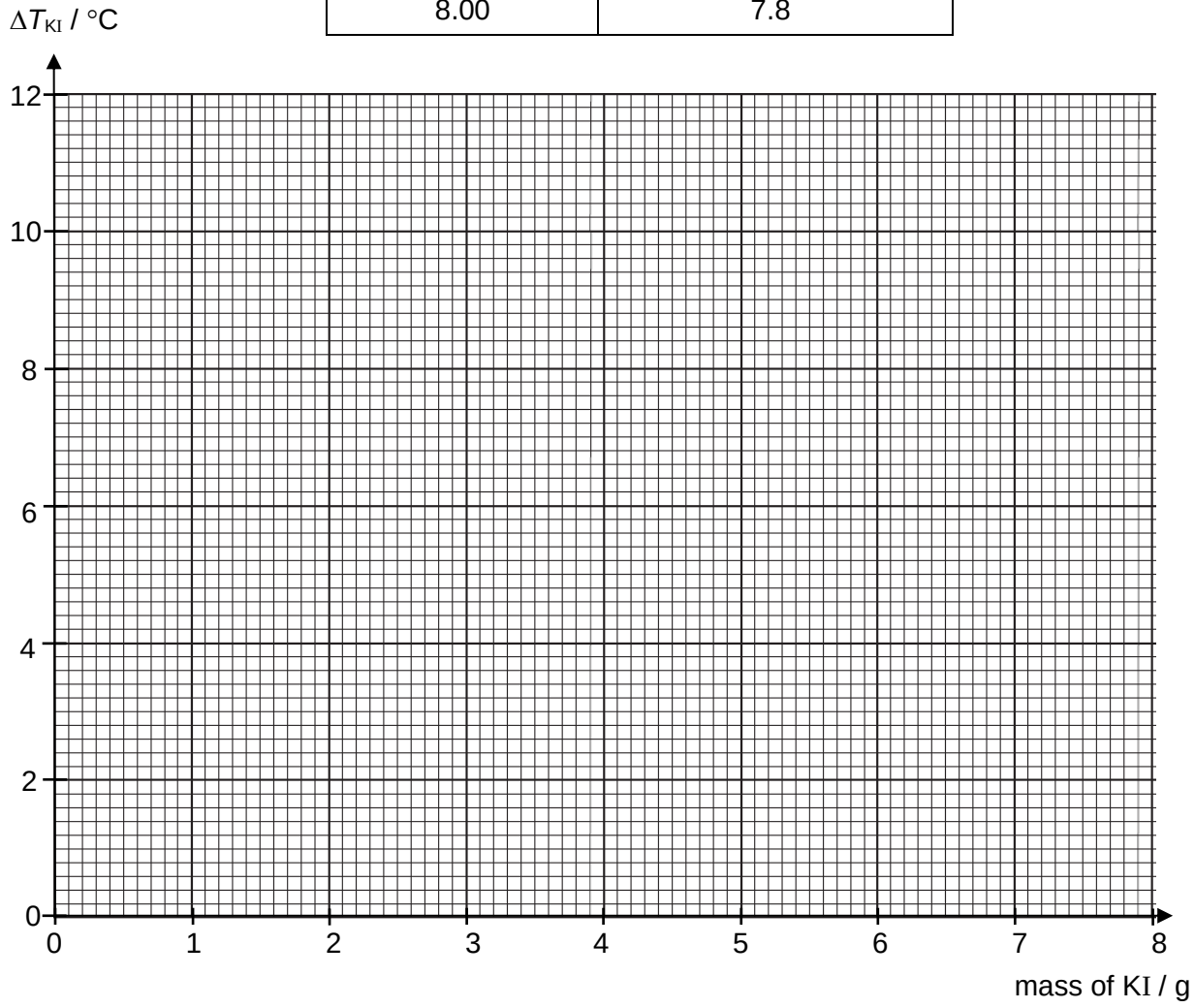


Fig 2.1

[1]

(b) Determination of the maximum temperature change, ΔT_m, for the dissolution of FA 6 in water

The maximum temperature change, ΔT_m, when **FA 6** dissolves completely in water was determined by measuring the temperature at timed intervals. The mass of **FA 6** used in the experiment was 6.020 g.

The results from this experiment are plotted on the grid in Fig 2.2 on Page 16.

Draw two best–fit lines, the first taking into account the points before the **FA 6** was added and the second taking into account the points after the reaction had finished.

Extrapolate both lines to four minutes.

Determine a value for the maximum temperature change, ΔT_m, at t = 4.0 min using the graph.

ΔT_m = ……°C
[2]

(c) (i) Using the graph in **(a)(ii)**, determine the change in temperature due to the dissolution of potassium iodide in **FA 6**.

ΔT_{KI} = ……°C
[1]

(ii) Using your results in **(b)** and **(c)(i)**, determine the change in temperature due to the dissolution of lithium chloride in **FA 6**.

ΔT_{LiCl}= ……°C
[1]

(iii) Hence, show clearly how the ΔT per gram of LiC*l* dissolved in water can be determined.

ΔT per gram of LiC*l* = ……°C g^{-1}
[3]

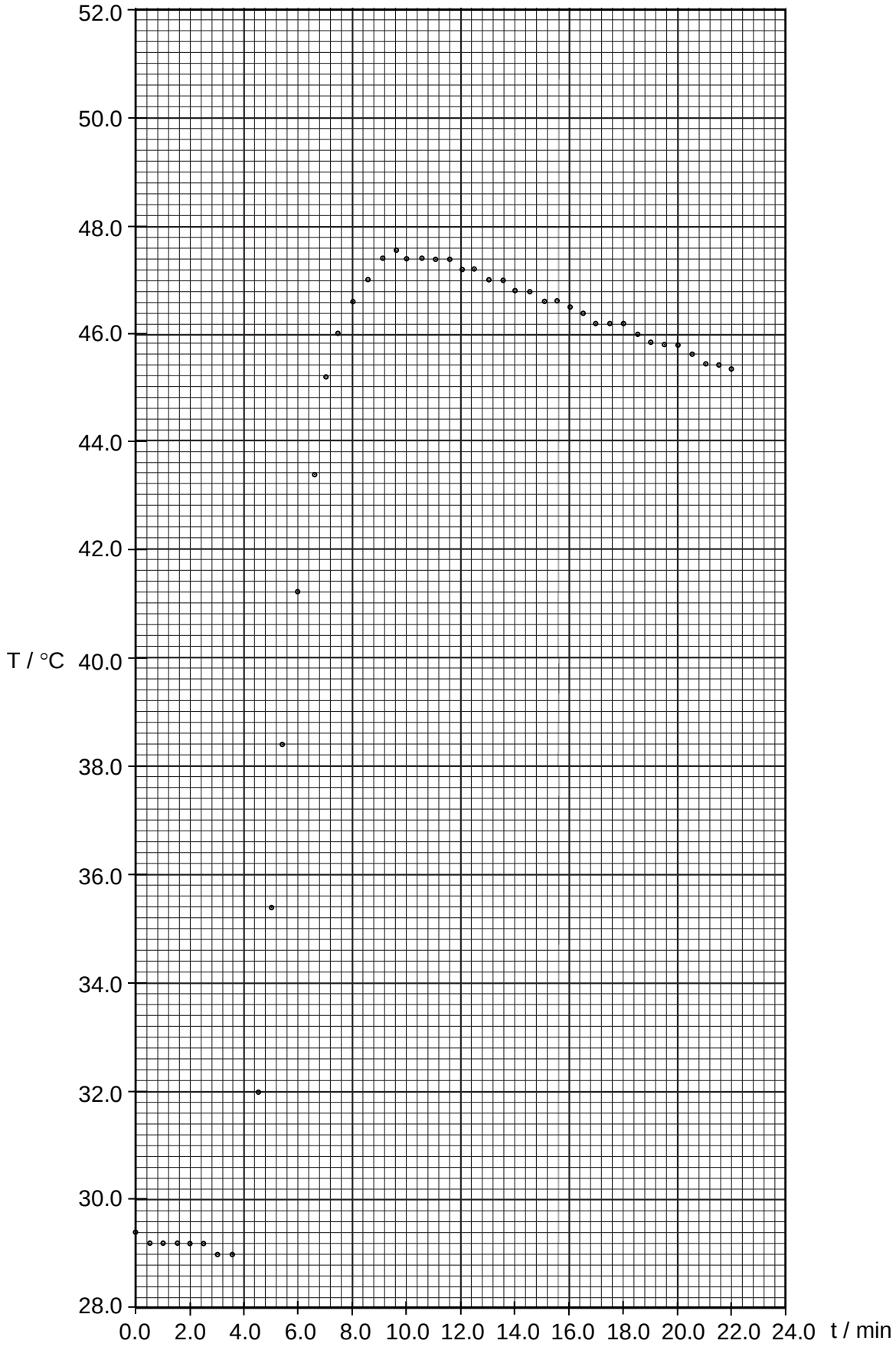

52.0
50.0
48.0
46.0
44.0
42.0
T / °C
40.0
38.0
36.0
34.0
32.0
30.0
28.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
t / min

Fig 2.2

(d) Planning

When solid hydrated barium chloride, $BaCl_2.\mathbf{x}H_2O$, dissolves in water, $Ba^{2+}(aq)$ and $Cl^-(aq)$ ions are formed.

The concentration of dissolved chloride ions in a solution can be determined by titration with aqueous silver nitrate of known concentration.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Potassium chromate(VI), $K_2CrO_4(aq)$, can be used as the indicator for the reaction. At the end–point of the titration, it forms a red precipitate in the presence of excess silver ions.

The solubilities, in mol dm^{-3}, of the various ionic solids at 20 °C are given in Table 2.2.

Table 2.2

	anion		
cation	Cl^-	CrO_4^{2-}	SO_4^{2-}
Ag^+	1.32×10^{-5}	6.63×10^{-5}	0.940
Ba^{2+}	1.72	1.10×10^{-5}	1.05×10^{-5}

E.g. the solubility of $AgCl$ at 20 °C = 1.32×10^{-5} mol dm^{-3}

Sulfuric acid must be added to the solution to prevent the $Ba^{2+}(aq)$ ions from interfering with the action of the potassium chromate(VI) indicator.

(i) How would $Ba^{2+}(aq)$ ions interfere with the action of this indicator?

……

…… [1]

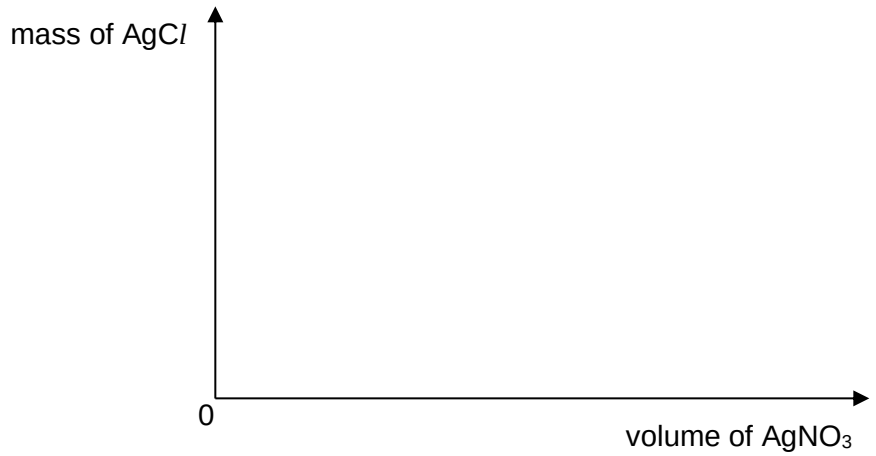
(ii) How does the addition of sulfuric acid prevent $Ba^{2+}(aq)$ ions from interfering with the action of this indicator?

……

…… [1]

(iii) In an initial rough titration, excess silver nitrate solution is added so that the end–point is exceeded.

Draw a sketch graph to show how the mass of silver chloride varies with the volume of silver nitrate added.



[1]

You are provided with the apparatus normally used in a school laboratory and the following materials:

3.00 g of hydrated barium chloride, $BaCl_2.\mathbf{x}H_2O$
0.050 mol dm^{-3} aqueous silver nitrate
1.0 mol dm^{-3} potassium chromate(VI) solution
1.0 mol dm^{-3} sulfuric acid

(iv) Describe how you would prepare a solution of barium chloride that is suitable for use in your titration. You should give details of any apparatus used.

……

……

……

……

…… [2]

(v) A known volume of the barium chloride solution you have prepared in **(d)(iv)** is transferred to a conical flask.

In what order should the other three solutions then be added to the flask?

first……

second……

third……

[1]

[Total: 18]

3 (a) Carry out the following tests on **FA 7** which contains **two** cations and **one** anion from the following list: NH_4^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, CO_3^{2-}, NO_3^-, NO_2^-, SO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, I^-.

Carefully record your observations in the space provided in Table 3.1.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved.

Table 3.1

	test	observations
1.	Add 1 cm depth of **FA 7** to a test–tube. Add aqueous ammonia slowly, with shaking, until no further change is seen. Filter the mixture and add dilute nitric acid drop–wise to the filtrate, until no further change is seen. *(You may continue with test 2, while waiting for the filtration process to complete.)*	
2.	Add 1 cm depth of **FA 7** to a test–tube. Add aqueous barium nitrate, followed by dilute nitric acid.	

[3]

Summary

Identify the ions present in **FA 7**. Use evidence from your observations in Table 3.1 to support your deductions on the identification of the cations in **FA 7**.

FA 7 contains the cations …… and ……

evidence ……..……..

.....

.....

.....

.....

FA 7 contains the anion …… [2]

FA 8 is an aqueous solution of $FeCl_3$.

(b) **(i)** Perform the tests described in Table 3.2, and record your observations in the table.

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

Table 3.2

	test	observations
1.	Add 1 cm depth of **FA 8** to a test–tube. Add **FA 4** slowly, with shaking, until no further change is seen. Leave it to stand.	
2.	Add 1 cm depth of **FA 8** to a test–tube. Add 1 cm depth of **FA 5**, with shaking, until no further change is seen.	
3.	Add 1 cm depth of **FA 8** to a test–tube. Add 1 cm depth of aqueous potassium iodide, with shaking, until no further change is seen.	

[2]

(ii) Explain your observation(s), in test 2 in Table 3.2, in terms of the chemistry involved.

……

……

…….. [2]

Table 3.3 gives some standard electrode potential values.

Table 3.3

electrode reaction	$E^{\ominus}$ / V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

(iii) Explain the observation(s), in test 3 in Table 3.2, in terms of the chemistry involved.

……

……

…….. [2]

(iv) Consider your observation(s) when aqueous potassium iodide was added to $FeCl_3$ solution in test 3 in Table 3.2. No such colour change was observed when aqueous potassium iodide was added to a solution containing $[Fe(CN)_6]^{3-}$ ions.

Use data from Table 3.3 to explain the observations and comment on the difference in observations in terms of the stability of the $[Fe(CN)_6]^{3-}$ ion and the iron–containing complex ion in $FeCl_3$.

……

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…….. [2]

(v) State what you would expect to observe when an equal volume of hexane is added to the mixture you have obtained in test 3 in Table 3.2.

……

……..… [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 anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and 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 on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

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

(d) Colour of halogens

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