EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2020
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME							
CIVICS GROUP	1	9	–			INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

01 September 2020

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 12
2	/ 34
3	/ 9
Total	/ 55

This document consists of **17** printed pages and **3** blank pages.

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

For Examiner's Use

1 Standardisation of $KMnO_4$

FA 1 is approximately 0.02 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FA 2 is 0.200 mol dm^{-3} potassium ethanedioate, $K_2C_2O_4$
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4

$KMnO_4$ is not a primary standard as it cannot be obtained in a sufficiently pure state to allow its concentration to be determined by preparing a solution from a known mass of solid $KMnO_4$. However, it can be standardised by using potassium ethanedioate, $K_2C_2O_4$.

Acidified MnO_4^- ions oxidises $C_2O_4^{2-}$ ions as shown in equation **1**. The Mn^{2+} ions produced in equation **1** act as a catalyst for the reaction. This is an example of 'autocatalysis'.

equation **1** $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

In this question, you will perform a titration. The data from this titration will be used to determine the concentration of MnO_4^- ions in **FA 1**.

(a) Titration of FA 2 against FA 1

In this titration, **FA 1** is run from the burette into the conical flask containing **FA 2** and **FA 3**. Initially, the colour of the **FA 1** will take some time to disappear. After some **FA 1** has been added, sufficient $Mn^{2+}(aq)$ ions will be present to allow the reaction to occur faster.

The end-point is reached when a **permanent** pale pink colour is obtained.

(i) 1. Fill the burette labelled **FA 1** with **FA 1**.

2. Using a pipette, transfer 10.0 cm^3 of **FA 2** into the conical flask.

3. Using an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 3** to the same conical flask.

4. Heat this solution to about 65 ºC.

5. **Turn off your Bunsen burner.**

6. Run **FA 1** from the burette into this flask until a **permanent** pale pink colour is obtained.

7. Record your titration results in the space provided on page **3**. Make certain that your recorded results show the precision of your working.

8. Repeat points **1** to **6** as necessary until consistent results are obtained.

Results

For Examiner's Use

[6]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

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

(b) (i) The equation for reaction **1** between ethanedioate ions and manganate(VII) ions is given on page **2**.

Calculate the amount of manganate(VII) ions, MnO_4^-, reacted with the $C_2O_4^{2-}$ in 10.0 cm^3 of **FA 2**.

amount of MnO_4^- reacted = ... [1]

(ii) Determine the concentration, in mol dm^{-3}, of MnO_4^- in **FA 1**.

concentration of MnO_4^- in **FA 1** = ... [1]

For Examiner's Use

(c) For the titration in **(a)(i)** between ethanedioate ions $C_2O_4^{2-}$ and manganate(VII) ions MnO_4^-, the solution needs to be at least 65 ºC at the start. As cold **FA 1** is added, the temperature of the mixture decreases. However, this decrease in temperature does not cause the rate of reaction between $C_2O_4^{2-}$ ions and MnO_4^- to decrease.

Suggest an explanation for this.

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..... [1]

(d) A student performed the experiment in **(a)(i)** using a solution of $Na_2C_2O_4$ of lower concentration instead of **FA 2**. The student obtained a mean titre value of 21.05 cm^3.

Determine the percentage apparatus error in the student's titre value and your titre value in **(a)(ii)**.

State **and** explain which titre value is more reliable.

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..... [2]

[Total: 12]

For Examiner's Use

2 To investigate the reaction between manganate(VII) ions and ethanedioate ions.

In this experiment you will investigate the kinetics of the reaction between MnO_4^- and $C_2O_4^{2-}$ in equation **1**.

FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
FA 5 is 0.100 mol dm^{-3} potassium iodide, KI

You will need access to the **FA 1**, **FA 2** and **FA 3** solutions you used earlier.

You are also provided with a starch indicator.

You will add a measured volume of **FA 1** to a mixture consisting of measured volumes of **FA 2**, **FA 3** and deionised water and, at timed intervals, you will transfer aliquots (portions) of the reaction mixture.

The concentration of MnO_4^- ions in each aliquot will be determined after adding the aliquot to an excess of potassium iodide solution and titrating the iodine produced (equation **2**) against sodium thiosulfate (equation **3**).

equation **2** $2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$

equation **3** $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

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

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

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

Leaving all of the titrations to be performed until after all the aliquots have been collected may cause you **time problems**.

In an appropriate format in the space provided on **page 6**, prepare a table in which to record for each aliquot

- the time of transfer, t, in minutes and seconds,
- the decimal time, t_d, in minutes, to 0.1 min, for example, if t = 4 min 33 s then t_d = 4 min + 33/60 = 4.6 min,
- the burette readings and the volume of **FA 4** added.

For Examiner's Use

1. Label the boiling-tubes, **1** to **6**.
2. Using a measuring cylinder, add about 10 cm^3 of **FA 5** to each boiling-tube.
3. Fill a burette with **FA 4**.
4. Using appropriate measuring cylinders, add 50.0 cm^3 of **FA 2**, 5.0 cm^3 of **FA 3** and 45.0 cm^3 of deionised water to the conical flask labelled **reaction mixture**
5. Using a measuring cylinder, add 25.0 cm^3 of **FA 1** to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its contents.
6. At approximately one minute, use a 10 cm^3 pipette to remove a 10.0 cm^3 aliquot of the reaction mixture.
7. **Immediately** transfer this aliquot into the boiling-tube labelled **1** and shake 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.
8. At approximately two minutes, repeat points **6** and **7**. Transfer this aliquot into the boiling-tube labelled **2**.
9. Repeat points **6** and **7** four more times at about three minute intervals, transferring the aliquots into the boiling-tubes labelled **3** to **6**.
10. Pour all of the contents of boiling-tube **1** into a clean 250 cm^3 conical flask. Wash out this boiling-tube and transfer the washings to the conical flask.
11. Titrate the iodine in this solution with **FA 4**. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator. The solution will turn dark blue-black. Continue the titration; the end-point is reached when the colour just disappears. Record your results.
12. Wash this conical flask thoroughly with water.
13. Repeat points **10** to **12** as required for each of the remaining boiling-tubes.

Results

[4]

For Examiner's Use

(ii) On the grid in Fig. 2.1, plot a graph of the volume of sodium thiosulfate, **FA 4**, on the *y*-axis, against time, t_d, on the *x*-axis. Draw the most appropriate line taking into account all of your plotted points.
Extrapolate (extend) this curve to t_d = 0.0 min, and determine the volume of **FA 4** required at t_d = 0.0 min.

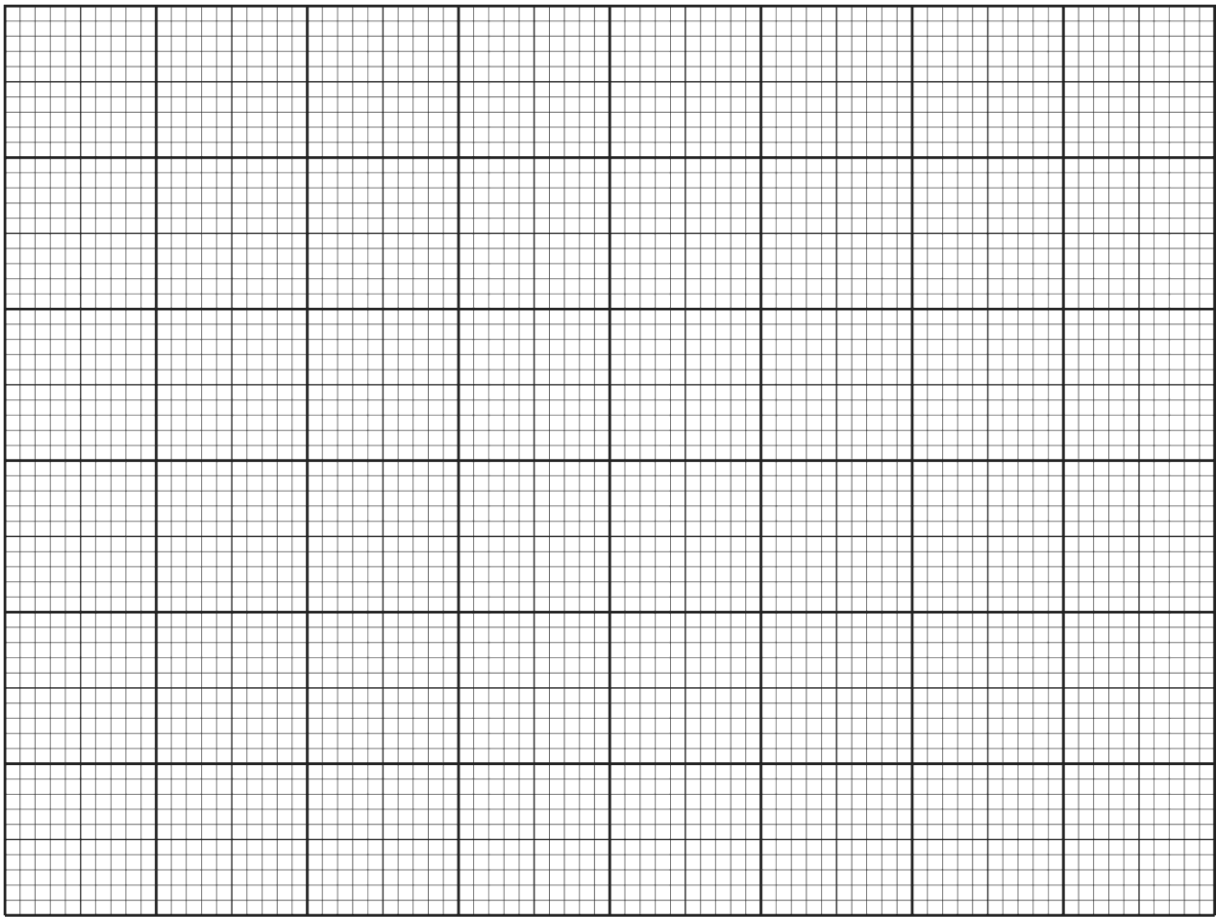

Fig. 2.1

volume of **FA 4** required at t_d = 0.0 min = ... cm^3

[4]

(iii) Consider the **shape** of the graph in Fig. 2.1.

Describe the shape and explain how it relates to the rate of the reaction in equation **1**.

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..... [1]

For Examiner's Use

(b) The concentration of MnO_4^- in **FA 1** can also be determined from the volume of **FA 4** used at t_d = 0.0 min.

(i) Determine the initial concentration, in mol dm^{-3}, of MnO_4^- in the reaction mixture.

initial concentration of MnO_4^- in reaction mixture = ... [1]

(ii) Determine the concentration, in mol dm^{-3}, of MnO_4^- in **FA 1**.

concentration of MnO_4^- in **FA 1** = ... [1]

(iii) You have earlier determined the concentration of MnO_4^- in **FA 1** in **1(b)(ii)** by direct titration between MnO_4^- and $C_2O_4^{2-}$.

By considering the apparatus used in the two experiments, suggest which of these two concentrations is more accurate. Explain your answer.

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..... [1]

(c) Besides enabling the concentration of MnO_4^- to be determined via the iodine produced, suggest another role of the excess potassium iodide, **FA 5**, used in point **7**.

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..... [1]

For Examiner's Use

(d) A student performed a similar experiment in much cooler conditions. In point **4**, she used the same volumes of **FA 2** and **FA 3** that you used but she also added 5.0 cm^3 of 1.00 mol dm^{-3} manganese(II) sulfate. She only added 40.0 cm^3 of deionised water, so the total volume used was the same as in your experiment.

On the grid in Fig. 2.2, the data from the student's experiment has been plotted.

(i) Draw the most appropriate line taking into account all of the plotted points. Extrapolate (extend) this curve to t_d = 0.0 min.

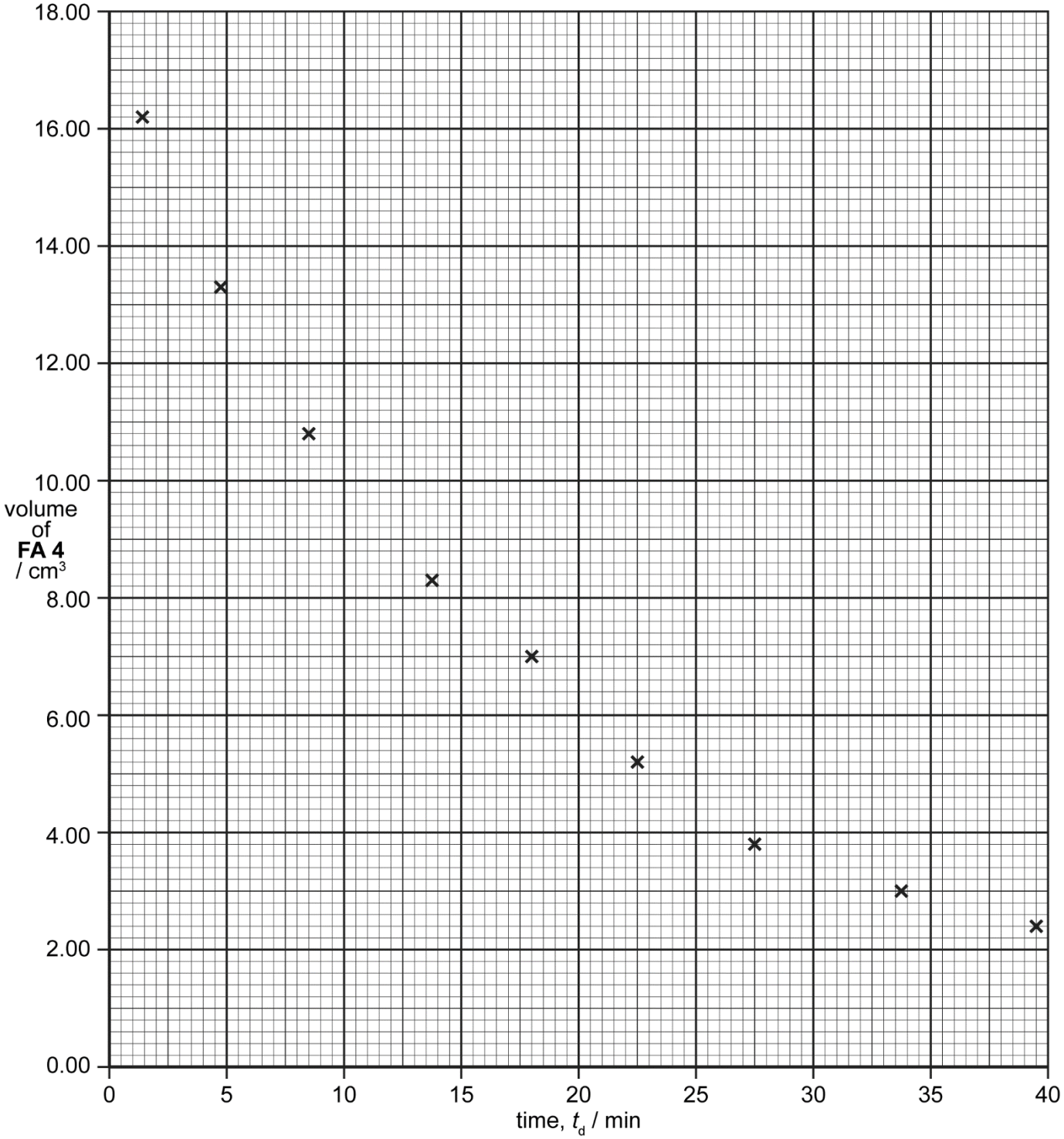

Fig. 2.2

[1]

The **initial rate** of change of the concentration of MnO_4^-, $[MnO_4^-]$, can be determined from the gradient of the tangent to the graph in Fig. 2.2 at time t_d = 0.0 min.

For Examiner's Use

(ii) Draw a tangent to your graph in Fig. 2.2 at time t_d = 0.0 min.

Determine the gradient of this line, showing clearly how you did this.

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

(iii) 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 $S_2O_3^{2-}$ ions required = ... mol min^{-1} [1]

(iv) Determine the amount of MnO_4^- reacting per minute and hence deduce the rate of change of $[MnO_4^-]$ at t_d = 0.0 min, in mol $dm^{-3}\ min^{-1}$.

rate of change of $[MnO_4^-]$ at t_d = 0.0 min = ... mol $dm^{-3}\ min^{-1}$ [5]

For Examiner's Use

(e) It has been claimed that the reaction in equation **1** is first order with respect to [MnO_4^-].

State whether you agree or disagree with this claim. Use evidence from the graph in Fig. 2.2 to support your answer.

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..... [2]

(f) Similar to **2(b)**, to determine the concentration of MnO_4^- in **FA 1**, the volume of **FA 4** required at t_d = 0.0 min can also be determined by extrapolating the graph in Fig. 2.2.

State and explain whether extrapolation of the plot in Fig 2.1 or Fig 2.2 would gave a more reliable value for the volume of **FA 4** required at t_d = 0.0 min.

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..... [1]

For Examiner's Use

(g) Planning

A catalyst works primarily by increasing the rate constant of a reaction. In the case of a homogeneous catalyst, it usually takes part in the reaction, but is regenerated at the end. In doing so, a catalyst may also increase the rate of reaction directly by manifesting in the rate equation itself.

(i) Explain how a catalyst increases the rate constant of a reaction.

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..... [1]

(ii) Plan an investigation, based on the experiment described in **2(a)(i)** and **2(d)** to determine order of reaction with respect to $[Mn^{2+}]$ and $[C_2O_4^{2-}]$, and hence determine the rate constant, k_{cat}, for the Mn^{2+}-catalysed reaction.

You may assume you are provided with the same chemicals and apparatus in **2(a)(i)** and **2(d)**.

In your plan, you should include details of

- the reactants and conditions that you would use,
- the apparatus you would use in addition to that specified in **2(a)(i)**,
- the procedure that you follow and the measurements that you would take,
- an outline of how you would use your results to determine order of reaction with respect to $[Mn^{2+}]$ and $[C_2O_4^{2-}]$, and determine the value of k_{cat}.

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For Examiner's Use

[8]

[Total: 34]

For Examiner's Use

3 Investigation of reactions involving the ethanedioate ion $C_2O_4^{2-}$.

FA 6 is 0.250 mol dm^{-3} manganese(II) sulfate, $MnSO_4$

You will need access to the **FA 2** and **FA 3** you used earlier.

(a) Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.1

	tests	observations
1.	Add 1 cm depth of **FA 2** to a test-tube. Add 10 drops of aqueous silver nitrate. Divide the mixture. To one part, add dilute nitric acid. To the other part, add aqueous ammonia.	
2.	Add ten drops of **FA 6** to a boiling-tube. Add five drops of aqueous sodium hydroxide dropwise. Gently warm the boiling-tube until no further change is observed and allow the mixture to cool. Mix half a test-tube full of **FA 2** and 1 cm depth of **FA 3** in a test-tube. Add the mixture in the test-tube into the cooled boiling-tube and shake.	

[4]

For Examiner's Use

(b) Silver(I) ions form sparingly soluble salts with many anions, such as halides, carbonate and sulfate. The precipitate formed in test 1 in Table 3.1 is silver(I) ethanedioate, $Ag_2C_2O_4$.

(i) The solubility product, K_{sp}, of silver(I) ethanedioate and silver(I) sulfate differs by approximately one million (10^6) times.

Describe a test, using only **FA 2** and the bench reagents provided, which will allow you to identify which of the two salts has the lower K_{sp}.

State how you will decide which salt has the lower K_{sp}.

test .....

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..... [2]

(ii) Perform the test you describe in **3(b)(i)** using the **FA 2** solution provided.

Record your observations and hence deduce which salt has the lower K_{sp}.

observations .....

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salt with lower K_{sp} .....
[1]

(c) A small amount of carbon dioxide is produced in test 2 in Table 3.1, when the acidified sodium ethanedioate in the test-tube is mixed with the contents in the boiling tube. It is unlikely that you will have noticed this.

(i) State the type of reaction that produces the CO_2 gas.

..... [1]

(ii) Based on your answer to **3(c)(i)** and using the Qualitative Analysis Notes on pages 19–20, suggest what happened to the manganese(II) sulfate upon addition of NaOH(aq) and warming.

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..... [1]

[Total: 9]

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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

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) 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