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

titration Number	1	2
final burette reading / cm^3	44.50	44.60
initial burette reading / cm^3	0.00	0.00
volume of **FA 1** used / cm^3	44.50	44.60
	✓	✓

[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.

$$\text{volume of FA 1 used} = \frac{44.50 + 44.60}{2} = 44.55 \text{ cm}^3$$

volume of **FA 1** = ... **44.55 cm^3** ..... [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**.

$$n_{C_2O_4^{2-}} \text{ in 10.0 cm}^3 \text{ of FA 2} = \frac{10.0}{1000} \times 0.200 = 2.000 \times 10^{-3} \text{ mol}$$

$$n_{MnO_4^-} \text{ reacted} = \frac{2}{5} n_{C_2O_4^{2-}} = \frac{2}{5} \times 2.000 \times 10^{-3}$$

$$= 8.00 \times 10^{-4} \text{ mol}$$

amount of MnO_4^- reacted = ... **8.00×10^{-4} mol** ..... [1]

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

$$\left[MnO_4^-\right] \text{ in FA 1} = \frac{n_{MnO_4^-}}{V_{MnO_4^-}} = \frac{8.00 \times 10^{-4} \text{ mol}}{\frac{44.55}{1000} \text{ dm}^3}$$

$$= 0.01796 \text{ mol dm}^{-3}$$

$$= 0.0180 \text{ mol dm}^{-3} \text{ (3 s.f.)}$$

concentration of MnO_4^- in **FA 1** = ... **0.0180 mol dm^{-3}** ..... [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.

The stable rate is due to **more Mn^{2+} ions being produced**. As the concentration of the Mn^{2+} catalyst increases it **cancels out** the effect of the drop in temperature.

[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.

$$\%\ \text{apparatus error for student's titration} = \frac{2 \times 0.05\ cm^3}{21.05\ cm^3} \times 100\% = 0.475\%$$

$$\%\ \text{apparatus error for my titration} = \frac{2 \times 0.05\ cm^3}{41.55\ cm^3} \times 100\% = 0.241\%$$

My titre value is more reliable since for the same absolute error of 0.05 cm^3 × 2, the **percentage error is smaller** for the titre reading in **(a)(ii)**.

[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

t	t_d / min	final burette reading / cm^3	initial burette reading / cm^3	volume of **FA 4** $V_{FA\,4}$ / cm^3
1 min 14 s	1.2	18.00	0.00	18.00
2 min 15 s	2.3	35.90	18.00	17.90
5 min 12 s	5.2	15.50	0.00	15.50
8 min 29 s	8.5	19.00	15.50	3.50
11 min 26 s	11.4	22.10	19.00	3.10
14 min 50 s	14.8	25.10	22.10	3.00

[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.

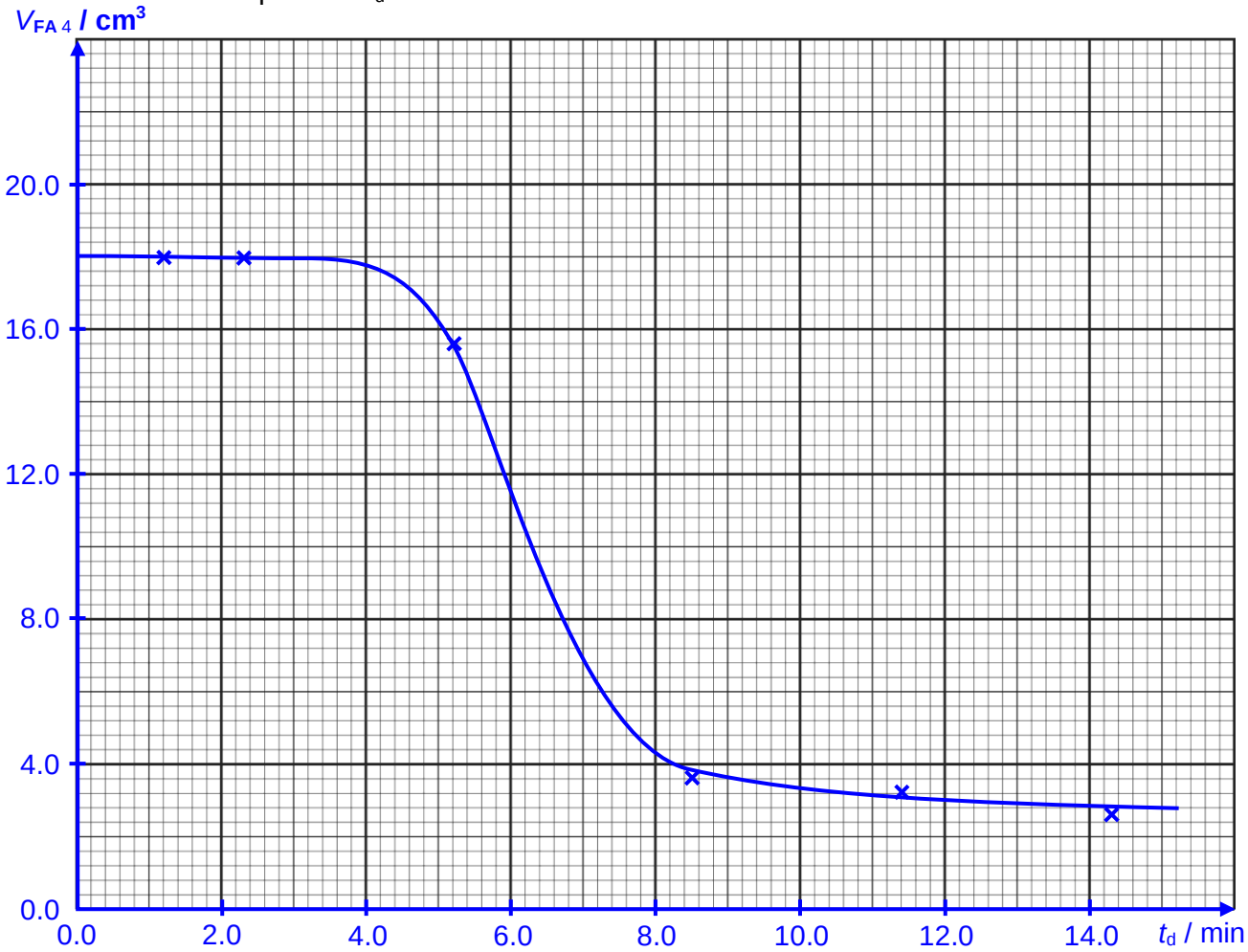

Fig. 2.1

volume of **FA 4** required at t_d = 0.0 min = ... **18.00 cm³** ..... cm³

[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**.

The **gradient** of the graph is **very gentle** (**almost straight**) **initially** as the reaction **starts slowly**, then the **magnitude of the gradient increases sharply** as the reaction **speeds up**, before finally **tapering off** as the reaction **slows down** towards the end. [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.

$$n_{S_2O_3^{2-}} \text{ reacted} = \frac{18.00}{1000} \times 0.0100 = 1.800 \times 10^{-4} \text{ mol}$$

$$2MnO_4^- \equiv 5I_2 \equiv 10S_2O_3^{2-}$$

$$n_{MnO_4^-} \text{ present in 10.0 cm}^3 \text{ of mixture} = \frac{2}{10} \times n_{S_2O_3^{2-}} = \frac{1}{5} \times 1.800 \times 10^{-4} \text{ mol}$$

$$= 3.600 \times 10^{-5} \text{ mol}$$

$$\text{initial } \left[MnO_4^-\right] \text{ in reaction mixture} = \frac{3.600 \times 10^{-5} \text{ mol}}{\frac{10.0}{1000} \text{ dm}^3} = 3.60 \times 10^{-3} \text{ mol dm}^{-3}$$

initial concentration of MnO_4^- in reaction mixture = **3.60 × 10^{-3} mol dm^{-3}** [1]

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

$$\left[MnO_4^-\right] \text{ in FA 1} = \frac{50.0 + 5.0 + 45.0 + 25.0}{25.0} \times 3.60 \times 10^{-3}$$

$$= \frac{125.0}{25.0} \times 3.60 \times 10^{-3}$$

$$= 0.0180 \text{ mol dm}^{-3}$$

concentration of MnO_4^- in **FA 1** = **0.0180 mol dm^{-3}** [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.

The concentration determined in **1(b)(ii)** by **titration is more accurate**.

All the **volume of solutions** used to prepare the reaction mixture in **2(a)(i)** are **measured using measuring cylinders** with a **lower degree of precision**, compared to the pipette and burette used in **1(b)(ii)**. [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**.

To **quench the reaction** between MnO_4^- and $C_2O_4^{2-}$, by reacting completely with the remaining MnO_4^-. [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.

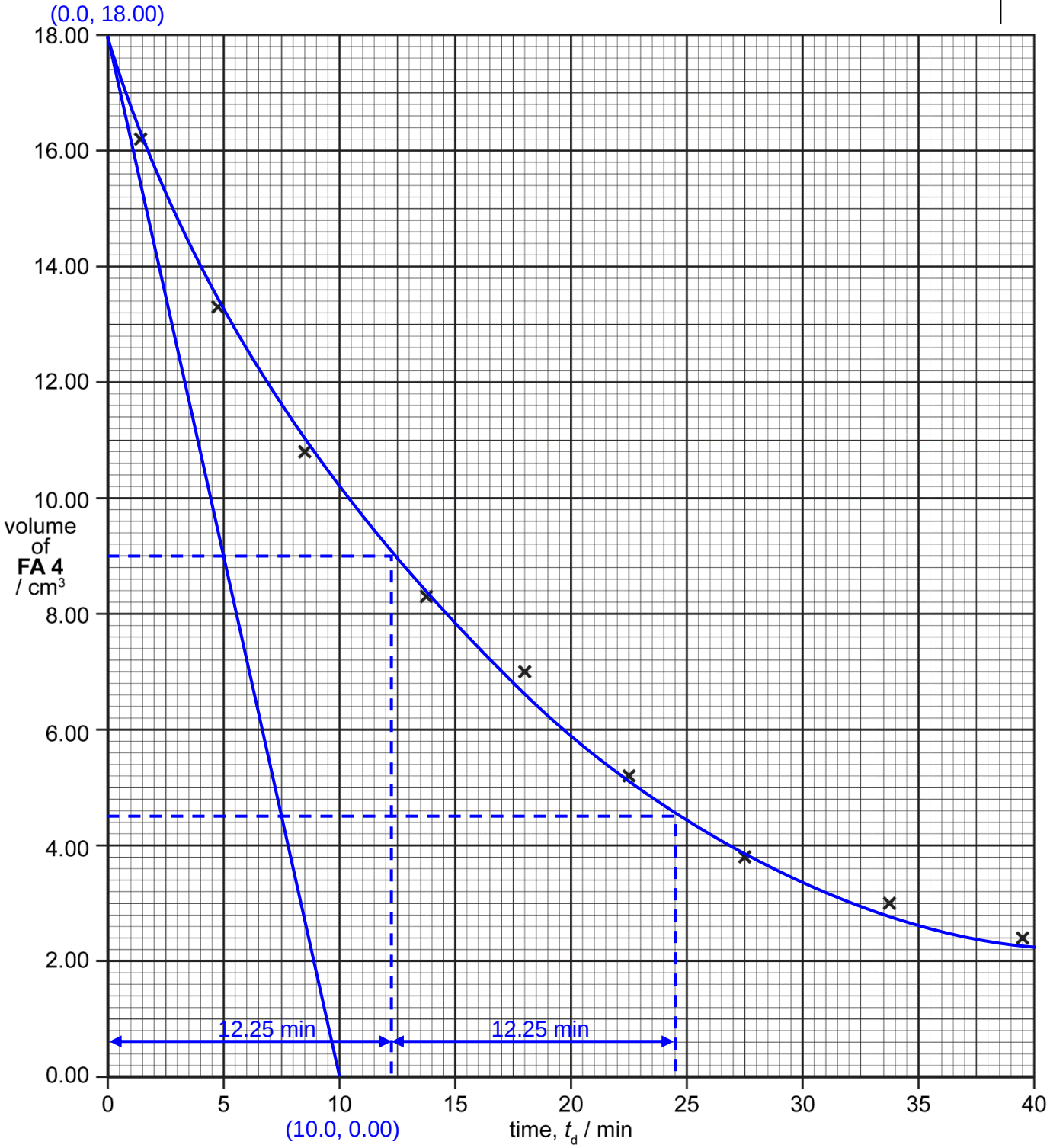

Fig. 2.2

[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.

$$\text{gradient} = \frac{18.00 - 0.00}{0.0 - 10.0}$$
$$= \frac{18.00}{-10.00}$$
$$= -1.80$$

gradient = **–1.80** $cm^3\ min^{-1}$ [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}.

$$\text{rate of change of amt of } S_2O_3^{2-} = \text{gradient} \times \left[S_2O_3^{2-}\right]$$
$$= -1.80\ cm^3\ min^{-1} \times 0.0100\ mol\ dm^{-3} \times 10^{-3}\ dm^3\ cm^{-3}$$
$$= -1.80 \times 10^{-5}\ mol\ min^{-1}$$

rate of change of the amount of $S_2O_3^{2-}$ ions required = **-1.80×10^{-5}** 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}.

$$2MnO_4^- \equiv 5I_2 \equiv 10S_2O_3^{2-}$$

$$\text{rate of change of amt of } MnO_4^- = \frac{2}{10} \times \text{rate of change of amt of } S_2O_3^{2-}$$
$$= \frac{1}{5} \times -1.80 \times 10^{-5}\ mol\ min^{-1}$$
$$= -3.60 \times 10^{-6}\ mol\ min^{-1}$$

$$\text{rate of change of } \left[MnO_4^-\right] = \frac{-3.60 \times 10^{-6}\ mol\ min^{-1}}{\frac{10.0}{1000}\ dm^3}$$
$$= -3.60 \times 10^{-4}\ mol\ dm^{-3}\ min^{-1}$$

rate of change of $[MnO_4^-]$ at t_d = 0.0 min = **-3.60×10^{-4}** 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.

I **agree** with the claim.

The **volume of FA 4** used is **directly proportional to the [MnO_4^-]**. Hence it is a

[reactant]-time graph.

From the graph, the **half-life, $t_{1/2}$ is constant** at **12.25 min**.

..... [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.

Extrapolation of **Fig. 2.1** would give a more reliable value due to the **almost**

straight line / very gentle gradient at the start of the graph. *or*

Extrapolation of **Fig. 2.2** would give a more reliable value as there are **more data**

points in **Fig. 2.2** (especially at the start of the graph).

..... [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.

A catalyst increases the rate constant of a reaction by providing an **alternative reaction pathway** with **lower activation energy**.

[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}.

Repeat with a different volume, *e.g.* 10 cm^3 of **FA 6**, while total volume is constant.

Determine initial rate and compare when $[Mn^{2+}]$ changes, how the initial rate changes.)

Repeat with two different volume of **FA 2**, while total volume is kept constant.

Determine initial rate and compare when $[C_2O_4^{2-}]$ changes, how the initial rate changes.

Temperature must be kept constant using a thermostatically controlled water bath

Then find k_{cat}.

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.	 white ppt white ppt dissolves to give a colourless solution white ppt dissolves to give a colourless solution
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.	 white ppt turns brown on standing brown ppt turns dark brown on warming Dark brown ppt dissolves to give a red solution

[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 Add $AgNO_3$ to **FA 2**, followed by bench dilute H_2SO_4
If the K_{sp} of Ag_2SO_4 is lower, the ppt appear to remain
If the K_{sp} of Ag_2SO_4 is higher, the ppt will dissolve

or add $AgNO_3$ one drop at a time to equal volumes of **FA 2** and SO_4^{2-} (of same concentration)
The first to form a ppt will have the lower K_{sp} [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 White ppt obtained, which dissolves in dilute sulfuric acid to give a clear colourless solution.

salt with lower K_{sp} **$Ag_2C_2O_4$** [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.

Oxidation of $C_2O_4^{2-}$ [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.

Mn^{2+} is oxidised to a higher oxidation state, which is capable of oxidising $C_2O_4^{2-}$ to CO_2 (while it is reduced back to Mn(II)) [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

Marking Procedures

Hierarchy to be used in calculating mean titres in question 1(a)(i):

- value of 2 identical titres
- average of titres within 0.05 cm^3
- average of titres within 0.1 cm^3, etc.

Use the selected titres to determine the mean titre for the end-point.

Note: For calculations, the principle of no double penalty (error carried forward) applies. For connecting parts, marking from point of first penalty onwards will be based on correct method only.

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
1(a)(i)	PDO Layout **P1**	Tabulates initial and final burette readings and volume added in the titration table. Tables has correct headers and units. *Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers.* *Where units have not been included in the header, there should be the appropriate unit for <u>each entry</u> in the table.* *Do NOT award this mark if any final and initial burette readings are inverted or 50 is used as the initial burette reading* for titration table.	1	**1**
	PDO Record **P2**	All the final/initial burette readings, for all accurate titres in the titration table, are recorded to the nearest 0.05 cm^3. *Treat all titres as "accurate" unless labelled 'rough' or first titre is recorded to ta lower precision than subsequent titres.*	1	**2**
	MMO Quality **M1**	Has at least two <u>uncorrected</u> titres for end-points within 0.10 cm^3.	1	**3**
*A student's 'rough'/'trial' titre value can be considered by the examiner when selecting titre values for the mean titre calculation **if** the student has 'validated' this value either by ticking it or by using it in an expression in **(a)(ii)**. (By doing either of these, the student has declared it to be no longer a 'rough'/'trial' value).*				
	MMO Quality Accuracy **M2** **M3** **M4**	Calculate the student's mean titre as described on page **21**. Award **MR4** to **MR6** based on the difference, Δ *titre*, between Student's and Teacher's mean titre. Give 3 marks if this difference if ≤ **0.20** Give 2 marks if this difference is > **0.20 but ≤ 0.40** Give 1 mark if this difference is **> 0.40** but ≤ **0.60** Give 0 marks for a difference **> 0.60**	3	**4** **5** **6**

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
1(a)(ii)	MMO Decision **M5**	Student obtains appropriate "average", to 2 d.p., from any experiments with uncorrected end-point titre values within 0.20 cm^3. *Do not award this mark if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.* *Do **not** award this mark if there are arithmetic errors in the table.*	1	**7**
1(b)(i)	ACE Interpret **A1**	$nC_2O_4^{2-} = 10 \times 10^{-3} \times 0.200 = 2 \times 10^{-3}$ $nMnO_4^-$ reacted = $2 \times 10^{-3} \times 2/5 = 8 \times 10^{-4}$	1	**8**
1(b)(ii)	ACE Interpret **A2**	(Let mean titre = V_m) $[MnO_4^-]$ in **FA 1** = $8 \times 10^{-4} \div (V_m \times 10^{-3}) = 0.8 \div V_m$	1	**9**
1(c)	ACE Interpret **A3**	The stable rate is due to more Mn^{2+} ions being produced. As the concentration of the Mn^{2+} catalyst increases it cancels out the effect of the drop in temperature.	1	**10**
1(d)	ACE Interpret **A4** **A5**	% apparatus error in the student's titre = $\frac{2\times0.05}{21.05}\times100\% = \frac{0.10}{21.05}\times100\% = \underline{0.475\%}$ % apparatus error in titre in **(a)(ii)** = $\frac{2\times0.05}{V_m}\times100\% = \frac{0.10}{V_m}\times100\%$ The titre value in **(a)(ii)** is more reliable due to the smaller % apparatus error.	1 1	**11** **12**
2(a)(i)	PDO Layout **P3**	Tabulates time, initial and final burette readings, volume added and decimal time, t_d. Table must have correct headers and units. *Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers.* *Where units have not been included in the header, there should be the appropriate unit for <u>each entry</u> in the table.* *Table need not be populated.* *One table (for both burette readings and times) or two tables (one for burette readings and one for times and volume of **FA 4**) may be present but must meet all the requirements above.*	1	**13**

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
	MMO Record **M6**	Records **all** • burette readings and volumes added to 0.05 cm^3 • *transfer times in minutes and seconds – to 1 s* • *correctly calculated values of* t_d • t_d values to 0.1 min	1	**14**
	MMO Collecting **M7**	6 sets of results	1	**15**
	M8	Five out of six aliquots are transferred within ±30 seconds of the suggested times.	1	**16**
2(a)(ii)	PDO Layout **P4**	Correct axes, labels and units; scale uses over half the graph paper in both axes. Do not award this mark if an awkward scale is used that makes plotting/reading difficult.	1	**17**
	P5	Plotting – within ±½ small square. Check all points; put ticks if correct.	1	**18**
	MMO Quality **M9**	Graph line shows a smooth transit from concave (gradient increasing) to convex (gradient decreasing). *DO NOT allow if clearly anomalous points have been included*.	1	**19**
	MMO Manipu **M10**	Line correctly extrapolated to meet *y*-axis **and** volume of **FA 4** required at t_d = 0.0 min correctly read from intercept to within ±½ small square.	1	**20**
2(a)(iii)	ACE Interpret **A6**	Describes the shape of the graph showing that the reaction starts slowly, speeds up and then slows down towards the end.	1	**21**
2(b)(i)	ACE Interpret **A7**	(Let volume of **FA 4** required at t_d = 0.0 min = $V_{\mathbf{FA\,4}}$) $nS_2O_3^{2-}$ reacted = $(V_{\mathbf{FA\,4}} \times 10^{-3}) \times 0.01 = V_{\mathbf{FA\,4}} \times 10^{-5}$ $nMnO_4^-$ present in 10 cm^3 of mixture = $nS_2O_3^{2-} \times 2/10 = 2 \times V_{\mathbf{FA\,4}} \times 10^{-6}$ initial $[MnO_4^-]$ in mixture = $2 \times V_{\mathbf{FA\,4}} \times 10^{-6} \div (10 \times 10^{-3}) = 2 \times V_{\mathbf{FA\,4}} \times 10^{-4}$	1	**22**
2(b)(ii)	ACE Interpret **A8**	$[MnO_4^-]$ in **FA 1** = $(50+5+45+25)/25 \times (2 \times V_{\mathbf{FA\,4}} \times 10^{-4}) = V_{\mathbf{FA\,4}} \times 10^{-3}$	1	**23**

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
2(b)(iii)	ACE Interpret **A9**	Concentration determined by titration in **1(b)(ii)** is more accurate, as volume of solutions used to prepare reaction mixture in **2(a)(i)** are measured using measuring cylinders of lower precision.	1	**24**
2(c)	ACE Interpret **A10**	To quench the reaction.	1	**25**
2(d)(i)	PDO Manipu **P6**	Graph line is a smooth curve of best fit. *DO NOT allow if the fourth, the fifth and the sixth points have <u>all</u> been included.* **and** line correctly extrapolated to meet *y*-axis at 18.00 cm^3.	1	**26**
2(d)(ii)	PDO Manipu **P7**	Gradient line touches the curve at the t_d = 0.0 **and** it is a tangent at this point. *DO NOT allow this mark if the line is not tangential, does not touch the curve or covers/crosses part of the curve.*	1	**27**
	PDO Manipu **P8**	Clear indication of **correct** co-ordinates <u>from graph</u> **or** correct vales of *volume* and of *time* used (measured to ±½ small square) **and** gradient correctly calculated. *Allow this mark if a 'tangent' is a straight line that has failed to satisfy the criteria for mark* **26** *Ignore missing working, incorrect/missing units or sig figs errors at this point.*	1	**28**
2(d)(iii)	ACE Interpret **A11**	(Let the gradient be G) rate of change of the amt of $S_2O_3^{2-}$ ions required = G × 10^{-3} × 0.0100 = G × 10^{-5}	1	**29**
2(d)(iv)	ACE Interpret **A12** **A13**	rate of change of the amt of MnO_4^- at t_d = 0.0 min = G × 10^{-5} × 2/10 = 2G × 10^{-6} rate of change of [MnO_4^-] at t_d = 0.0 min = 2G × 10^{-6} ÷ (10 × 10^{-3}) = 2G × 10^{-4}	1 1	**30** **31**
	PDO Display **P9**	Shows working in **all** calculations in **1(b)**, **1(d)**, **2(b)(i)**, **2(b)(ii)**, **2(d)(ii)**, **2(d)(iii)** and **2(d)(iv)**. All calculations must be relevant although they may not be complete or correct. *Any calculation not attempted loses this mark.*	1	**32**

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
	PDO Display **P10**	Shows appropriate significant figures (3 or 4 sf) in **all** final answers in **1(b)**, **1(d)**, **2(b)(i)**, **2(b)(ii)**, **2(d)(ii)**, **2(d)(iii)** and **2(d)(iv)**. *Any calculation not attempted loses this mark.*	1	**33**
	PDO Display **P11**	Shows appropriate units in **all** answers in **1(a)(ii)**, (cm^3); **1(b)(i)**, (mol); **1(b)(ii)**, (mol dm^{-3}); **1(d)**, (%); **2(b)(i)**, (mol dm^{-3}) and **2(b)(ii)**, (mol dm^{-3}) *Any calculation not attempted loses this mark.*	1	**34**
2(e)	ACE Interpret **A14**	States/establishes a direct proportionality between the volume of thiosulfate added and [MnO_4^-].	1	**35**
	A15	Selects and compares at least two pairs of half-life values to prove rate order of 1.	1	**36**
2(f)	ACE Interpret **A16**	Extrapolation of Fig. 2.1 is more reliable due to almost straight line/very gentle gradient at the start. **or** Extrapolation of Fig. 2.2 is more reliable as there are more data points.	1	**37**
2(g)(i)	Plan **Pl 1**	A catalyst provides an alternative pathway with lower activation energy.	1	**38**
2(g)(ii)	Plan			
	Pl 2	Use same procedure, but **control temperature** using thermostatically controlled water bath.	1	**39**
	Pl 3	Repeat with **another volume** of 1.00 mol dm^{-3} $MnSO_4$.	1	**40**
	Pl 4	Repeat with **another volume** of **FA 2** (0.200 mol dm^{-3} $K_2C_2O_4$), while keeping volume of Mn^{2+} same as one of the two previous set.	1	**41**
	Pl 5	Volume of 1.00 mol dm^{-3} $MnSO_4$ chosen must be larger than **5 cm^3**, **and** volume of **FA 2** chosen must be larger than **25 cm^3** (each corresponding to an initial concentration of 0.04 mol dm^{-3} which is 10 times that of MnO_4^-)	1	**42**
	Pl 6	Select appropriate volume of deionised water so that **total volume** is 125 cm^3.	1	**43**
	Pl 7	Calculate and compare **initial rate** to find order w.r.t. [Mn^{2+}] and [$C_2O_4^{2-}$].	1	**44**
	Pl 8	Determine the **initial** [MnO_4^-], [$C_2O_4^{2-}$] and [Mn^{2+}] in the **mixture** for one set of experiment, and	1	**45**
	Pl 9	Use **rate equation**, rate = $k_{cat}[MnO_4^-]^{\mathbf{1}}[C_2O_4^{2-}]^x[Mn^{2+}]^y$, to determine k_{cat}.	1	**46**

Qn	Skilled assessed	Marking scheme	Mark	Mark ref
3(a)	MMO/PDO Collecting			
	M11	White ppt dissolves to give a colourless solution with dil. HNO_3.	1	**47**
	M12	White ppt dissolves to give a colourless solution with aq. NH_3.	1	**48**
	M13	White ppt turns brown on standing **and** brown ppt turns dark brown on warming.	1	**49**
	M14	Dark brown ppt dissolves to give a red solution.	1	**50**
3(b)(i)	Plan			
	Pl 10	Add aq. $AgNO_3$ to **FA 2**, followed by bench dil. H_2SO_4, **or**		
		Add aq. $AgNO_3$ one drop at a time to equal volumes of **FA 2** and SO_4^{2-} (of same concentration)	1	**51**
	Pl 11	If ppt remains, K_{sp} of Ag_2SO_4 is lower; If ppt dissolves, K_{sp} of Ag_2SO_4 is higher, **or**		
		The first to form a ppt will have the lower K_{sp}.	1	**52**
3(b)(ii)	Plan	White ppt obtained, which dissolves in dil. H_2SO_4 to give a colourless solution, **or**	1	**53**
	Pl 12	**FA 2** gives a white ppt before dil. H_2SO_4		
3(c)(i)	ACE Interpret **A17**	Oxidation of $C_2O_4^{2-}$.	1	**54**
3(c)(ii)	ACE Interpret **A18**	Mn(II) is oxidised to higher oxidation state.	1	**55**

MMO = 14
PDO = 11
ACE = 18
Plan = 12

APPARATUS FOR EACH CANDIDATE

1. Six(6) Pyrex hard glass, clean and dry test-tubes (125 × 15 mm)
2. Six(6) Pyrex hard glass, clean and dry boiling-tubes (140 × 26 mm)
3. One(1) test-tube rack
4. One(1) test-tube holder
5. Two(2) burettes of capacity 50 cm^3, one of which with blue graduation is labelled **"FA 1"**
6. One(1) burette stand and clamp
7. Two(2) filter funnels
8. One(1) pipette of capacity 10 cm^3
9. One(1) pipette filler
10. Two(2) measuring cylinder of capacity 10 cm^3
11. One(1) measuring cylinder of capacity 25 cm^3
12. Two(2) measuring cylinder of capacity 50 cm^3
13. Three(3) conical flasks of capacity 250 cm^3, one of which is labelled **"reaction mixture"**
14. Two(2) beakers of capacity 250 cm^3, one of which is labelled **"for boiling tubes"**
15. One(1) stopwatch, reading to at least 0.1 s
16. One(1) thermometer with range –10 ºC to +110 ºC, graduated to 1 ºC
17. One(1) Bunsen burner
18. One(1) lighter
19. One(1) heat-proof mat (e.g. wire gauze)
20. One(1) tripod stand
21. Five(5) dropping pipettes
22. One(1) glass rod
23. One(1) white tile
24. One(1) delivery tube fitted with rubber stopper [for test-tube (125 × 15 mm)]
25. Two(2) wooden splints
26. Two(2) pieces of blue and red litmus papers each
27. Two(2) pieces of plain filter paper strips
28. Two(2) pieces of filter paper (diameter ≈ 11 cm)
29. Paper towels
30. One(1) pair of safety goggles
31. One(1) marker pen suitable for writing on glass
32. One(1) wash bottle of deionised water, labelled **"deionised water"**
33. One(1) test-tube brush
34. One(1) large brush (for cleaning conical flask)

35. Seven(7) capped containers/vials:

GHS label	Label	Minimum Capacity	Vial Size
–	**FA 1**	200 cm^3	–
–	**FA 2**	150 cm^3	–
–	**FA 3**	200 cm^3	–
–	**FA 4**	150 cm^3	–
–	**FA 5**	100 cm^3	–
–	**FA 6**	–	B43/24 TC
–	**starch indicator**	–	B43/24 TC

COMMUNAL BENCH REAGENTS (ONE SET PER BENCH)

	GHS label	Reagent	Preparation
1.	–	dilute hydrochloric acid	2.0 mol dm^{-3}
2.		dilute nitric acid	2.0 mol dm^{-3}
3.		dilute sulfuric acid	1.0 mol dm^{-3}
4.		dilute sodium hydroxide	2.0 mol dm^{-3}
5.		aqueous ammonia	2.0 mol dm^{-3}
6.		limewater	freshly prepared & saturated
7.	–	aqueous barium nitrate	0.10 mol dm^{-3}
8.	–	aqueous silver nitrate	0.05 mol dm^{-3}
9.	–	aqueous potassium manganate(VII)	0.02 mol dm^{-3}
10.	–	aqueous potassium iodide	0.10 mol dm^{-3}
11.	–	aluminium foil	1 cm × 1 cm; 2 pieces

(i) Item 11 should be placed in a plastic vial (e.g. B121) or in a plastic bag labelled as **"aluminium foil"**.

(ii) Recommend for Centres to prepare about 100 cm^3 of each bench reagent (per set) and to top up at the end of each shift where necessary.

CHEMICALS FOR EACH CANDIDATE

	GHS pictogram (for SS to take note of when handling the stock chemicals)	**Label**	**Preparation**	**Per candidate**
1		**FA 1**	Dissolve **3.16 g** of $KMnO_4$ in about 250 cm^3 of deionised water, then add deionised water to 1 dm^3. Dispense this solution into capped container labelled **"FA 1"**.	200 cm^3
2		**FA 2**	Dissolve **36.85 g** of **potassium oxalate monohydrate, $K_2C_2O_4·H_2O$** in about 250 cm^3 of deionised water and make up to 1 dm^3 with deionised water. Dispense this solution into capped container labelled **"FA 2"**.	150 cm^3
3		**FA 3**	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of deionised water with continuous stirring. Make the solution up to 1 dm^3 with deionised water. **Care:** *concentrated sulfuric acid is very corrosive.* Dispense this solution into capped container labelled **"FA 3"**.	200 cm^3
4	–	**FA 4**	Dissolve **2.482 g** of **sodium thiosulfate-5-water**, **$Na_2S_2O_3·5H_2O$** in deionised water and make up to 1 dm^3 with deionised water. Dispense this solution into capped container labelled **"FA 4"**.	150 cm^3
5	–	**FA 5**	Dissolve **16.6 g** of potassium iodide in deionised water and make up to 1 dm^3 with deionised water. Dispense this solution into capped container labelled **"FA 5"**.	100 cm^3
6	–	**FA 6**	Dissolve **42.26 g** of **manganese(II) sulfate monohydrate, $MnSO_4·H_2O$** in deionised water and make up to 1 dm^3 with deionised water. Dispense this solution into capped container labelled **"FA 6"**.	5 cm^3

	GHS pictogram (for SS to take note of when handling the stock chemicals)	**Label**	**Preparation**	**Per candidate**
7	–	**starch indicator**	Add **20.0 g** of **soluble starch** to 500 cm^3 of **boiling** deionised water. Stir until a clear solution is obtained and make up to 1 dm^3 using hot deionised water. Dispense this solution into capped container labelled **"starch indicator"**.	10 cm^3