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

1 Determination of percentage by mass of ethanedioic acid in a mixture of sodium ethanedioate and ethanedioic acid

In this experiment, you are to determine the percentage by mass of ethanedioic acid in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment will be carried out in two parts.

In **Part One**, you will carry out a titration to find out the amount of ethanedioic acid, $H_2C_2O_4$, present in the mixture.

In **Part Two**, you will make use of the titration results to find out the total amount of ethanedioate ions, $C_2O_4^{2-}$, present in the mixture.

You will then use the values found in these two parts to calculate the percentage by mass of ethanedioic acid in **FA 1**.

FA 1 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FA 2 is 2.00 mol dm^{-3} sodium hydroxide, NaOH.
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 4 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

You are also provided with thymolphthalein solution.

Part One:

(a) Dilution of FA 2 solution

As the NaOH solution provided is too concentrated, you will have to dilute it before conducting the experiment.

1. Fill the burette labelled **FA 2** with **FA 2**.
2. Measure between 17.00 cm^3 to 17.50 cm^3 of **FA 2** into a 250 cm^3 volumetric (graduated) flask.
3. Record your burette readings in Table 1.1 below.
4. Fill the flask to the mark with deionised water, using a dropper when nearing the mark.
5. Stopper and mix the contents thoroughly by shaking to obtain a homogeneous solution. Label this solution **FA 5**.

Table 1.1

final burette reading / cm^3	
initial burette reading / cm^3	
volume of **FA 2** added / cm^3	

[1]

(b) Titration of FA 1 with FA 5

1. Fill the burette labelled **FA 5** with **FA 5**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Add 3 to 4 drops of thymolphthalein solution.
4. Run **FA 5** from the burette into the flask. The end-point is reached when the solution changes from colourless to a permanent pale blue colour. Record your titration results in Table 1.2 below.
5. Repeat steps 2 to 4 until consistent results are obtained and record your results in the table below.

Table 1.2

final burette reading / cm^3				
initial burette reading / cm^3				
volume of **FA 5** added / cm^3				

[4]

From your titrations, obtain a suitable volume of **FA 5**, to be used in your calculations. Show clearly how you obtained this volume.

suitable volume of **FA 5** = …….. [1]

Part Two:

(c) Titration of FA 1 with FA 4

(There is no need to carry out this experiment)

1. Fill the burette labelled **FA 4** with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask
3. Using a measuring cylinder, add 25 cm^3 of **FA 3** to the conical flask.
4. Place the conical flask on a tripod and gauze and heat to about 65 ^oC.
5. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
6. Run 1 cm^3 of **FA 4** from the burette into the flask and swirl until the colour of the potassium manganate(VII) has disappeared then continue the titration as normal until a permanent pale pink colour is obtained. This is the end-point. Record your titration results in the table below.
7. Repeat steps 2 to 6 until consistent results are obtained and record your results in Table 1.3 below.

Table 1.3

final burette reading / cm^3	36.20	36.30	36.40
initial burette reading / cm^3	0.90	1.30	1.10
volume of **FA 4** added / cm^3			
chosen values			

[1]

From the titrations above, obtain a suitable volume of **FA 4**, to be used in your calculations and place ticks below the chosen volumes of **FA 4**.
Show clearly how you obtained this volume.

suitable volume of **FA 4** = …….. [2]

Calculations

Show your working and appropriate significant figures in all of your calculations.

(d) (i) Using your values in **(a)**, calculate the concentration of NaOH in **FA 5** that you prepared.

concentration of NaOH in **FA 5** = ……..[1]

(ii) Using your answer from **(b)** and **d(i)**, calculate the amount of NaOH required to react with 25.0 cm^3 of **FA 1** in **Part One**.

amount of NaOH required = …….. [1]

(iii) The equation for the reaction between sodium hydroxide and ethanedioic acid is shown below

$$2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

Using your answer in **d(ii),** calculate the amount of ethanedioic acid present in 25.0 cm^3 of **FA 1**.

amount of $H_2C_2O_4$ in 25.0 cm^3 of **FA 1** = …….. [1]

(e) **(i)** Using your answer from **(c)**, calculate the amount of potassium manganate(VII) required to react with 25.0 cm^3 of **FA 1** in **Part Two**.

amount of $KMnO_4$ required = …….. [1]

(ii) The balanced equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is given below.

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

Using your answer in **e(i),** calculate the amount of ethanedioate ions present in 25.0 cm^3 of **FA 1**.

amount of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1** = …….. [1]

(iii) Hence, calculate the amount of ethandioate ions which came from the sodium ethanedioate dissolved in 25.0 cm^3 of **FA 1**.

amount of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 1** = …….. [1]

(f) **(i)** Using your answer to **(d)(iii)**, calculate the mass of ethanedioic acid in 25.0 cm^3 of **FA 1**.

[A_r: H, 1.0; C, 12.0; O, 16.0]

mass of ethanedioic acid in 25.0 cm^3 of **FA 1** = …….. [1]

(ii) Using your answer to **(e)(iii)**, calculate the mass of sodium ethanedioate in 25.0 cm^3 of **FA 1**.

[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of sodium ethanedioate in 25.0 cm^3 of **FA 1** = …….. [1]

(iii) Calculate the percentage by mass of ethanedioic acid in **FA 1**.

percentage by mass of ethanedioic acid in **FA 1** = …….. [1]

(g) (i) State the maximum error in a single burette reading.

maximum error = ±……..cm^3 [1]

(ii) The percentage error of a 25.0 cm^3 pipette is ±0.24%.

A student suggested that using a burette to measure out 25.0 cm^3 of **FA 1** for the titration would give a more accurate result than using a pipette.

Is the student correct? Explain your answer.

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……[2]

(iii) A student decided to use a 25.0 cm^3 pipette instead of a 50 cm^3 measuring cylinder to measure the volume of **FA 3** in **Part Two**.

State and explain whether this change will improve the accuracy of the calculation of the percentage by mass of ethanedioic acid in the mixture.

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……[1]

[Total: 22]

2 Determination of the enthalpy change of dissociation, $\Delta H_{\text{dissociation}}$, of ethanedioic acid

Ethanedioic acid is a weak acid that dissociates partially in water as shown.

	$H_2C_2O_4(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq)$	$\Delta H_{\text{dissociation}}$
reaction 1	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	ΔH_1
reaction 2	$2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$	ΔH_2

In this experiment, you will measure the temperature of the contents of a polystyrene cup at timed intervals, both before and after hydrochloric acid is added. You will analyse your results graphically in order to determine an accurate value for the temperature change of the mixture, caused by hydrochloric acid reacting with sodium hydroxide.

You will use this value to calculate the heat evolved for the experiment, determine a value for the enthalpy change of reaction 1, ΔH_1 and use it together with the enthalpy change of reaction 2, ΔH_2, to calculate the enthalpy change of dissociation of ethanedioic acid, $\Delta H_{\text{dissociation}}$.

In an appropriate format in the space provided on page 11, prepare a table in which to record results for your experiment:

- all values of temperature, T, to an appropriate level of precision,
- all values of time, t, recorded to the nearest 0.5 min.

It is important that you measure each temperature at the specified time.

You are provided with the following

FA 2 is 2.00 mol dm^{-3} NaOH
FA 6 is 2.00 mol dm^{-3} HCl

Procedure

1. Using a 25 cm^3 measuring cylinder, measure out 20 cm^3 of **FA 6**.
2. Using a 50 cm^3 measuring cylinder, transfer 30 cm^3 of **FA 2** into the polystyrene cup supported in a beaker.
3. Stir **FA 2** in the cup gently with thermometer. Read and record its temperature, T at time, t = 0.0 min.
4. Continue to stir **FA 2**. Read and record T every half a minute.
5. At exactly three minutes, transfer **FA 6** to the polystyrene cup. Stir the mixture but do not read T.
6. Continue to stir the mixture gently. Read and record T at t = 3.5 min and every half minute until t = 8.0 min

(a) Results

[2]

(b) Plot a graph of temperature, T, on the y-axis, against time, t, on the x-axis on the grid in Fig. 2.1.

Use a scale of 1 large square to 1 min for the time axis and 1 large square to 2 ^{o}C for the temperature axis. The temperature axis need not start from zero.

Draw a best-fit straight line taking into account all of the points before t = 3.0 min.

Draw another best-fit straight line taking into account all of the points after the temperature of the mixture has started to fall steadily.

Extrapolate (extend) both lines to t = 3.0 min.

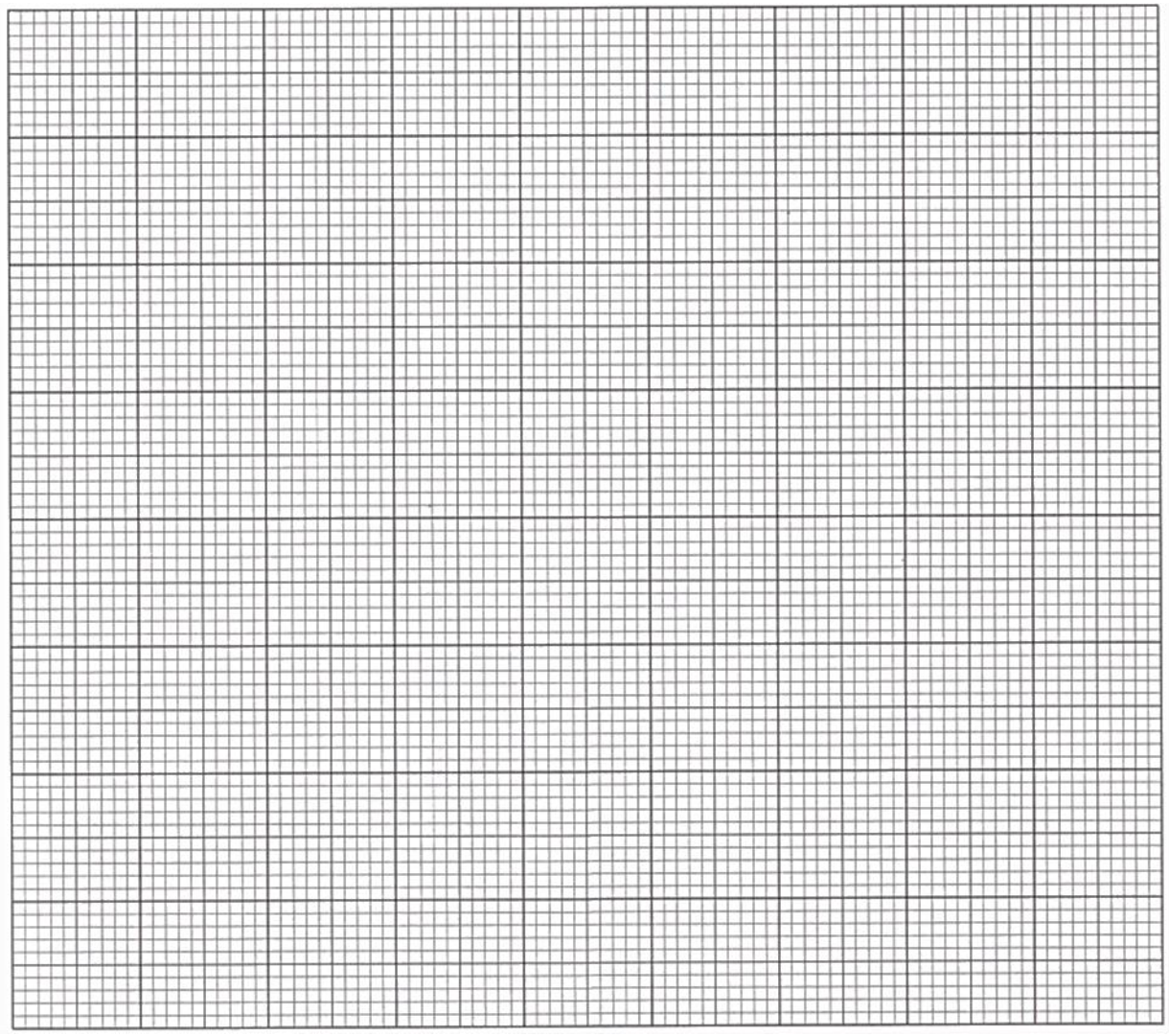

Fig. 2.1

[3]

(c) From your graph, read the minimum temperature, T_{min}, and the maximum temperature, T_{max}, at t = 3.0 min. Record these values in the spaces provided.

Deduce the temperature change, ΔT, at t = 3.0 min.

T_{min} = ...

T_{max} = ...

ΔT = ...

[2]

(d) **(i)** Calculate the heat evolved for your experiment using the value you deduced in **(c).**

You should assume that the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1} and that the density of the solution is 1.00 g cm^{-3}.

heat evolved = ……..[1]

(ii) Hence, calculate the enthalpy change of reaction 1, ΔH_1.

ΔH_1 = ……..[2]

(e) The enthalpy change of reaction 2, ΔH_2, is given below.

$$2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l) \quad \Delta H_2 = -106 \text{ kJ mol}^{-1}$$

Use your experimental result for ΔH_1 and the given value of ΔH_2 to construct an energy cycle to determine $\Delta H_{dissociation}$ of $H_2C_2O_4(aq)$.

$\Delta H_{dissociation}$ = ……..[3]

[Total: 13]

3 Qualitative Analysis

(a) You are to perform the tests given in Table 3.1 on **FA 7** and **FA 8**.

FA 7 contains two cations and one anion and **FA 8** is aqueous sodium ethanedioate, $Na_2C_2O_4$.

Record details of any colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should be identified by a test, described in the appropriate place in the table provided. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Table 3.1

Tests	observations	
	FA 7	**FA 8**
(i) Test the **FA 7** solution using Universal Indicator paper.		
(ii) To 0.5 cm depth of **FA 7**, add aqueous NaOH. Warm the mixture.		
(iii) To 1 cm depth of **FA 7** and **FA 8** in separate test-tubes, add aqueous barium nitrate dropwise, until no further change. Add dilute nitric acid.		

[4]

(b) (i) Based on your observations, state the identity of the cations and anion in **FA 7**.

Cations in **FA 7** ……

Anion in **FA7** ……[2]

(ii) Write an equation to explain the observation in test **(a)(i)** for **FA 7**.

…… [1]

(iii) When a student added a few drops of aqueous ammonia to **FA 7,** no precipitate was formed. Explain his observation.

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……[1]

(iv) Explain your observations for **FA 7** and **FA 8** in test **(a)(iii)** with the aid of equations.

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……[2]

[Total: 10]

4 Planning

The reaction between manganate(VII) ions, MnO_4^- and ethanedioate ions, $C_2O_4^{2-}$ in the presence of Mn^{2+} catalyst and excess dilute sulfuric acid has the following rate equation.

$$\text{rate} = k[MnO_4^-]^n[Mn^{2+}][C_2O_4^{2-}]^2$$

The overall equation is as follows.

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

The kinetics of the reaction can be studied by determining the time taken for the colour of MnO_4^- to disappear.

In this method, the rate of the reaction $\propto \frac{V_M}{t}$

where V_M = volume of MnO_4^-, t = time taken for colour of MnO_4^- to disappear

The order of reaction with respect to MnO_4^-, n, can be determined by performing a number of experiments with varying volumes of MnO_4^- and then analysing the results graphically.

In one experiment, a student mixed 10 cm^3 of $MnO_4^-(aq)$, 10 cm^3 of $C_2O_4^{2-}(aq)$, 10 cm^3 of $H_2SO_4(aq)$ and 1 cm^3 of $Mn^{2+}(aq)$ in a conical flask.

The time taken for the colour of MnO_4^- to disappear was 10 s.

The table for you to record the data is given below.

experiment	volume of MnO_4^-, V_M/cm^3	volume of water /cm^3	volume of $C_2O_4^{2-}$ /cm^3	volume of H_2SO_4 /cm^3	volume of Mn^{2+} /cm^3	t/s	$\frac{V_M}{t}$ /$cm^3\,s^{-1}$
1	10	0	10	10	1	10	
2	8		10	10	1		
3	6		10	10	1		
4	4		10	10	1		
5	2		10	10	1		

Table 4.1

(a) State the volume of water used for each experiment in Table 4.1 above.

[1]

(b) Plan a procedure that you would follow to determine the time taken for the colour of MnO_4^- to disappear in **experiment 1**.

You may assume that you are provided with the following solutions

- 0.001 moldm^{-3} potassium manganate(VII), $KMnO_4$,
- 0.100 moldm^{-3} sodium ethanedioate, $Na_2C_2O_4$,
- 1.0 moldm^{-3} dilute sulfuric acid, H_2SO_4,
- 0.100 moldm^{-3} manganese(II) ions, $Mn^{2+}(aq)$,
- deionised water,
- the equipment normally found in a school or college laboratory.

In your plan, you should include brief details of:

- the apparatus you would use,
- the procedure you would follow,
- the measurements you would make.

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(c) **(i)** Explain why the rate of the reaction is **not** proportional to $\frac{1}{t}$.

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……[1]

(ii) Explain why the volume of MnO_4^-, V_M is proportional to $[MnO_4^-]$.

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……[1]

(iii) The rate equation of the reaction is given by

$$\text{rate} = k[MnO_4^-]^n[Mn^{2+}][C_2O_4^{2-}]^2.$$

Suggest why the rate equation can be simplified to rate = $k'[MnO_4^-]^n$ where $k' = k[Mn^{2+}][C_2O_4^{2-}]^2$.

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……[2]

(iv) Given that n = 1, and the rate of the reaction $\propto \frac{V_M}{t}$, complete Table 4.1 by calculating the values of

(I) $\frac{V_M}{t}$ for experiment 1 to 5.

(II) t, using the $\frac{V_M}{t}$ values you calculated in (I).

[2]

[Total: 10]

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 → (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