ACJC Prelim 2020 Paper 4 Answers

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} 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	17.00
initial burette reading / cm^3	0.00
volume of **FA 2** added / cm^3	17.00

[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	25.00	41.00		
initial burette reading / cm^3	1.00	17.00		
volume of **FA 5** added / cm^3	24.00	24.00		

[4]

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

Average titre = ½ (24.00 + 24.00)
= 24.00 cm^3

Suitable volume of **FA 5** = ……24.00 cm^3…….. [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 25cm^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 4 until consistent results are obtained and record your results in the **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	35.30	35.00	35.30	
chosen values	√		√	

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.

Average titre = ½ (35.30 + 35.30)
= 35.30 cm^3

Suitable volume of **FA 4** = ……35.30 cm^3…….. [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.

Volume of FA2 = 17.00 cm^3

Amount of NaOH in 250 cm^3 = 17.00 x 10^{-3} x 2.00
= 0.0340 mol

[NaOH] in FA5 = $\frac{0.0340}{250} \times 1000$
= 0.136 mol dm^{-3}

concentration of NaOH in **FA 5** = ……0.136 mol dm^{-3}……..[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**.

Vol in (b) x concentration from d(i) = amount of NaOH [1]

Amount of NaOH = 0.136 x 24.00 x 10^{-3}
= 0.00326 mol

amount of NaOH required = ……0.00326 mol …….. [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 NaOH in d(ii)/2 = amount of $H_2C_2O_4$ [1]

Amount of $H_2C_2O_4$ in 25.0 cm^3 = ½ x 0.003264
= 0.00163 mol

amount of $H_2C_2O_4$ in 25.0 cm^3 of **FA 1** = ……0.00163 mol….. [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**.

Volume in (c) x 0.0200 mol dm^{-3} = amount of $KMnO_4$ required [1]

Amount of $KMnO_4$ = $35.30 \times 10^{-3} \times 0.0200$
= 7.06×10^{-4} mol

amount of $KMnO_4$ required = ……7.06×10^{-4} mol.. [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 $KMnO_4$ from e(i) x 5/2 = amount of $C_2O_4^{2-}$ [1]

Amount of $C_2O_4^{2-}$ in 25.0 cm^3 = $\frac{5}{2} \times 7.06 \times 10^{-4}$ mol
= 0.001765 mol

amount of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1** = …….0.001765 mol …….. [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 in e(ii) – amount in d(iii) = amount of $C_2O_4^{2-}$ from $Na_2C_2O_4$

Amt of $C_2O_4^{2-}$ from $Na_2C_2O_4$ = 0.001765 – 0.00163
= 1.35×10^{-4} mol

amount of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 1** = ……1.35×10^{-4} mol …….. [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]

amount of ethanedioic acid from d(iii) x 90.0 = mass

Mass of ethanedioic acid = 0.00163 x 90.0
= 0.147 g

mass of ethanedioic acid in 25.0 cm^3 of **FA 1** = ……0.147 g…….. [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]

amount of sodium ethanedioate from e(iii) x 134.0 = mass

Mass of sodium ethanedioate = $1.35 \times 10^{-4} \times 134.0$
= 0.0181 g

mass of sodium ethanedioate in 25.0 cm^3 of **FA 1** = ……0.0181 g…….. [1]

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

mass in **f(i)**/(mass in **f(i)** + mass in **f(ii)**) x 100%

$$\% = \frac{0.1467}{0.0181 + 0.1467} \times 100$$
= 89.0 %

Percentage by mass of ethanedioic acid in **FA 1** = ……89.0 %…….. [1]

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

Maximum error = ±……0.05……..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.
……... [2]

Calculate % error using burette
0.10/25.0 x 100% = ±0.400%

Compare 0.24% < 0.40%, hence <u>student is incorrect</u>

(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.
……... [1]

Will not improve because the acid is used in excess [1]

[Total : 22]

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

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

	$H_2C_2O_4(aq) + aq \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq)$	$\Delta H_{dissociation}$
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, $\Delta H_{dissociation}$.

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, add **FA 6** into 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

t / min	*T* / °C	*t* / min	*T* / °C
0.0	28.0	5.5	37.6
0.5	28.0	6.0	37.2
1.0	28.0	6.5	36.9
1.5	28.0	7.0	36.6
2.0	28.0	7.5	36.3
2.5	28.0	8.0	36.0
3.0	--		
3.5	38.8		
4.0	38.6		
4.5	38.2		
5.0	38.0		

[2]

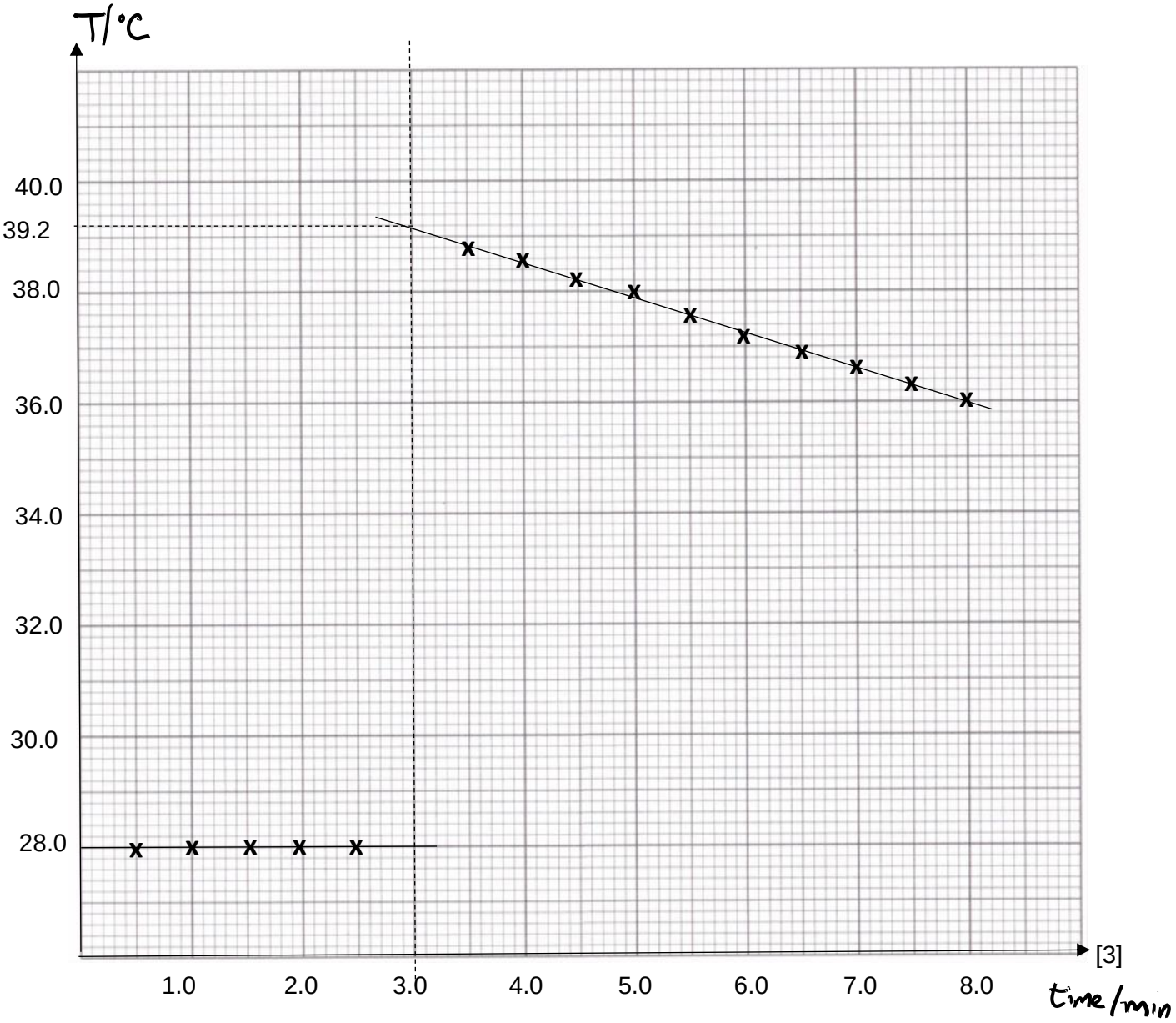
(b) Plot a graph of temperature, *T*, on the y-axis, against time, *t*, on the x-axis on the grid in Fig. 2.1.

Use a scale of 1 large square to 1 min for the time axis and 1 large square to 2 °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.



[3]

Fig. 2.1

(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} = ……28.0 ^{o}C……

T_{max} = ……39.2 ^{o}C ……

ΔT = ……11.2 ^{o}C ……

[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}.

q (heat released) = mcΔT
= (50)(4.18 J g^{-1} K^{-1})(39.2–28.0)
= 2341 J
= 2.34 kJ

[1]

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

Amount of HCl = 20.0/1000 x 2.0 = 0.0400 mol

Amount of NaOH = 30.0/1000 x 2.0 = 0.0600 mol

HCl is the limiting reagent as the amount of HCl required to completely react with NaOH is more than what is present.

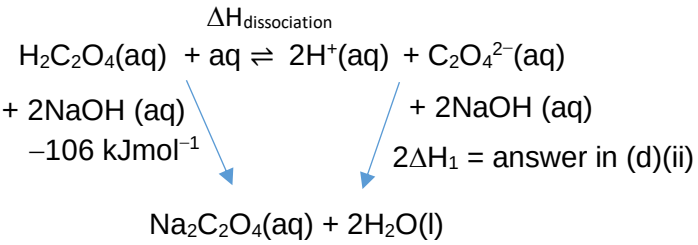
Amount of water formed = 0.0400 mol
Enthalpy change of reaction = –2.341/0.0400
= –58.5 kJ mol^{-1}

[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 $H_2C_2O_4(aq)$.



$$\Delta H_{dissociation} = -106 - 2\Delta H_1$$
$$= -106 - 2(-58.5)$$
$$= +11.0 \text{ kJmol}^{-1}$$

[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.	Universal indicator paper turns yellow/orange. pH = 4-5	
(ii)	To 0.5 cm depth of **FA 7**, add aqueous NaOH. Warm the mixture.	Off white ppt, turns brown on standing. Insoluble in excess NaOH (ppt will turn dark brown at the top) Gas evolved turned damp red litmus paper blue. Gas is NH_3	
(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.	White ppt formed. White ppt is insoluble.	White ppt formed. White ppt dissolved to form a colourless solution.

[4]

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

Cations in **FA 7** …**NH_4^+, Mn^{2+}**……..……..

Anion in **FA 7** …**SO_4^{2-}**……..[2]

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

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

H_3O^+ turns the Universal indicator paper orange/yellow.

[1]

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

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Since FA 7 also contains NH_4^+, the position of equilibrium above shifts left, thus $[OH^-]$ decreases. This causes ionic product of $[Mn^{2+}][OH^-]^2$ to fall below K_{sp}, hence no ppt was formed.

[1]

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

$BaC_2O_4(s) \rightleftharpoons Ba^{2+}(aq) + C_2O_4^{2-}(aq)$ ---(1)

$2H^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons H_2C_2O_4$

<u>Ionic product</u> $[Ba^{2+}][C_2O_4^{2-}]$ falls below K_{sp} <u>hence the ppt dissolves. OR</u>

<u>Position of equilibrium (1) shifts right, hence the white ppt dissolves.</u>

OR $BaC_2O_4 + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2C_2O_4$

BaC_2O_4 react with HNO_3 hence the ppt is soluble.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ ---(2)

As <u>sulfate is unable to react with H^+</u> since H_2SO_4 is a strong acid.

OR <u>As sulfate/$BaSO_4$ is unable to react with H^+</u> hence no change in $[SO_4^{2-}]$, ionic product remain above Ksp, ppt insoluble. [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 rate equation.

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 graphically analysing the results.

In one experiment, a student mixed $MnO_4^-(aq)$, 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 10s.

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

experiment	volume of $KMnO_4$, 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^3s^{-1}
1	10	0	10	10	1	10	1.00
2	8	2	10	10	1	10	0.800
3	6	4	10	10	1	10	0.600
4	4	6	10	10	1	10	0.400
5	2	8	10	10	1	10	0.200

Table 4.1

(a) State the volumes 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)
- 0.100 $moldm^{-3}$ sodium ethanedioate, $Na_2C_2O_4$
- 1.0 $moldm^{-3}$ dilute sulfuric acid
- 0.100 $moldm^{-3}$ Mn^{2+} ions
- 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.

[3]

Answer:

1. Add 10 cm^3 of **$KMnO_4$** into a 100 cm^3 conical flask using a 10 cm^3 measuring cylinder.
2. Add 10 cm^3 of **H_2SO_4** into the conical flask using the second 10 cm^3 measuring cylinder.
3. Add 1 cm^3 of Mn^{2+} into the conical flask using third 10 cm^3 measuring cylinder.
4. Swirl the mixture to mix well.
5. Add 10 cm^3 of solution **$Na_2C_2O_4$** using the fourth 10 cm^3 measuring cylinder, and start the stopwatch.

   NOTE: Step 1 and step 5 can switch.

6. Swirl the mixture gently and continuously until the purple colour disappears.
7. When the purple colour disappears, stop the stopwatch and record the time to the nearest second in table 1 above.

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

……..[1]

Rate is only <u>proportional to 1/t of a fixed volume of manganate(VII) ions is used</u>, since rate is measured by taking the time taken for the colour of manganate(VII) ions to disappear, rate is no longer proportional to 1/t.

OR

The <u>volume of manganate(VII) ions used in each experiment is different</u>, since rate is measured by taking the time taken for the colour of manganate(VII) ions to disappear, rate is no longer proportional to 1/t.

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

……..[1]

Water was added to top up to the <u>same total volume</u> for all experiments<u>.</u>

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

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' = $k[Mn^{2+}][C_2O_4^{2-}]^2$.

……..[2]

<u>Mn^{2+} is a catalyst</u> and <u>$C_2O_4^{2-}$ is in large excess</u> thus the $[Mn^{2+}]$ and $[C_2O_4^{2-}]$ <u>is constant/remains unchanged.</u>
OR
<u>Mn^{2+} and $C_2O_4^{2-}$ is in large excess</u> thus the $[Mn^{2+}]$ and $[C_2O_4^{2-}]$ <u>is constant/remains unchanged.</u>

(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).

[Total : 10]