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

1 Identification of two cations

FA 1 is an aqueous solution containing two cations.

FA 2 is 20 cm^3 aqueous sodium hydroxide.

You will perform tests to identify the two cations in **FA 1**.

You are **not** expected to identify the anions.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

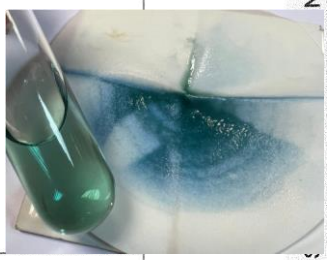
Test and identify any gases evolved.

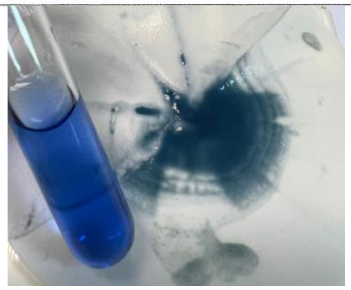
If there is no observable change, write **no observable change**.

(a) (i) Carry out the following tests. Carefully record your observations in Table 1.1.

Table 1.1

	tests	observations
1	Add 1 cm depth of **FA 1** into a clean boiling tube. Add 2 cm depth of **FA 2**, aqueous sodium hydroxide, slowly with shaking, to **FA 1**. Add all the remaining **FA 2** to the contents of the boiling tube and shake the boiling tube. Filter the mixture into a clean boiling tube. While waiting, proceed to test 2.	Blue green ppt formed upon addition of NaOH(aq) Blue green ppt remains insoluble in green solution Green filtrate Residue is blue ppt
2	Add 2 cm depth of **FA 1** into a clean test-tube. Add aqueous ammonia, slowly with shaking, until 4 cm depth of aqueous ammonia has been added. Filter the mixture into a clean test-tube.	Blue green ppt formed upon addition of $NH_3(aq)$. Grey green ppt remains insoluble in excess $NH_3(aq)$ Deep blue filtrate Residue is grey green ppt





[4]

(ii) Identify the two cations in **FA 1** and state the evidence for each cation by completing Table 1.2.

Table 1.2

cation	evidence
Cr^{3+}	In excess NaOH(aq), it gives a green filtrate. In excess NH_3(aq), grey green ppt is collected as residue.
Cu^{2+}	In excess NaOH(aq), blue ppt is collected as residue. In excess NH_3(aq), it gives a deep blue filtrate.

[2]

(b) (i) Carry out the following test on **FA 1**.

test	observations
To 2 cm depth of **FA 1** in a clean test-tube, add 2 cm depth of dilute sulfuric acid and one small spatula of powdered zinc. Filter the mixture into a clean test-tube.	Upon addition of Zn powder, vigorous effervescence of gas is observed. The gas "pops" with a lighted splint. A red suspension in observed. Green filtrate. Residue is a mixture of red brown solid and grey solid

[2]

(ii) Explain the reaction between powdered zinc and **FA 1** in **1(b)(i)**.

Redox reaction. Cu^{2+} is reduced to red brown Cu(s), Zn is oxidized to Zn^{2+}(aq)

Note: H_2(g) is produced via acid-metal reaction of Zn with H_2SO_4(aq), NOT with FA1 [1]

[Total: 9]

2 Determination of an enthalpy change of neutralisation by thermometric titration

FA 3 is 1.00 mol dm^{-3} sodium hydroxide, NaOH.
FA 4 is aqueous sulfuric acid, H_2SO_4.

You are to carry out a thermometric titration to determine the enthalpy change of neutralisation per mole of water formed when these solutions react. This involves adding volumes of aqueous sulfuric acid to a fixed volume of aqueous sodium hydroxide and measuring the temperature of the resulting solution.

(a) Prepare a table in the space provided on page 6 and record, to the appropriate level of precision:

- all volumes of **FA 4** added, *V*
- the maximum temperature, *T*, reached after each addition of acid, **FA 4**.

It is important that the volume of **FA 4** recorded is the total volume you have added up to the point when the temperature reading was made.

Note: If you overshoot on an addition, record the actual total volume of **FA 4** added up to that point.

Procedure

1. Place a polystyrene cup inside a second polystyrene cup and place both cups in a glass beaker. The retort clamp provided may be used to clamp the beaker to prevent it from tipping.

2. Use the pipette labelled **FA 3** to transfer 25.0 cm^3 of **FA 3** into the first polystyrene cup.

3. Fill the burette labelled **FA 4** with **FA 4**.

4. Stir the **FA 3** in the cup gently with the thermometer. Read and record its temperature.

5. Use the burette to add 2.00 cm^3 of **FA 4** to the cup and stir the mixture gently with the thermometer. Read and record both the maximum temperature and the actual total volume of **FA 4** added.

6. Repeat step 5 until a total of 24.00 cm^3 of **FA 4** has been added. For each addition of **FA 4**, read and record both the maximum temperature and the actual total volume of **FA 4** added up to that point.

Results

Total Vol of FA4 added/cm^3	Temp/°C
0.00	28.0
2.00	31.0
4.00	32.8
6.00	34.2
8.00	35.4
10.00	36.4
12.00	37.2
14.00	36.6
16.00	35.8
18.00	35.0
20.00	34.4
22.00	34.0
24.00	33.6

[3]

(b) Plot a graph of temperature, *T*, on the *y*-axis, against total volume of **FA 4**, *V*, on the *x*-axis on the grid in Fig. 2.1. Your scale on the *y*-axis should allow for extrapolation above the highest temperature recorded.

Draw two lines of best fit, taking into account the points when the temperature of the mixture was rising and the points when the temperature was falling. Each line should have a shape best suited to its plotted points.

Extrapolate (extend) both lines until they intersect.

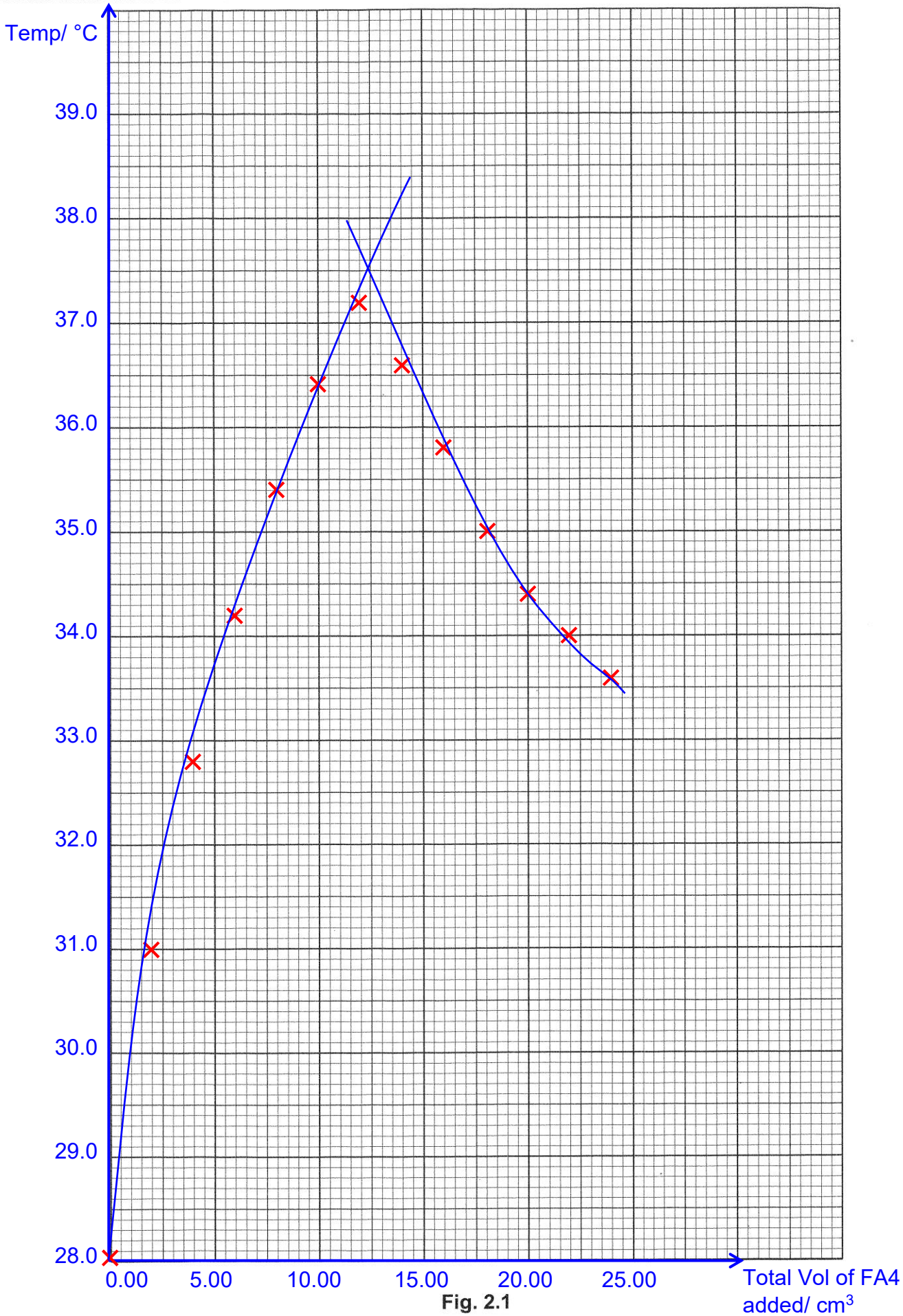


Fig. 2.1

[3]

(c) From your graph, read the initial temperature of **FA 3**, $T_{initial}$, and the maximum temperature of the mixture, T_{max}.

Use these values to calculate the temperature change in the reaction, ΔT.

Read the volume of **FA 4** added, V_{neut}, at the maximum temperature of the mixture.

Record all these values below.

$T_{initial}$ = 28.0 °C

T_{max} = 37.5 °C

ΔT = +9.5 °C

V_{neut} = 12.50 cm^3

[4]

(d) Calculate the heat change, q, at the point of neutralisation in your experiment, using the values you calculated 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 1.0 $g cm^{-3}$.

$q = m_{aq} c \Delta T$

$= (25.0 + 12.50) \times 4.18 \times (+9.5)$

$= 1489$ J

Note: m_{aq} is the total mass of aq solution at point of neutralisation.

ΔT in °C is the same as ΔT in K

q = ... [2]

(e) Calculate the enthalpy change of neutralisation, ΔH_{neut}, per mole of water formed.

The equation for the reaction is shown.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

Include the sign of ΔH_{neut} in your answer.

Amount of NaOH used = $\frac{25.0}{1000} \times 1.00 = 0.025$ mol = Amount of H_2O formed

$\Delta H_n = -\frac{mc\Delta T}{\text{mol of } H_2O \text{ formed}}$

$= -\frac{1489}{0.025}$

$= -59565$ J $mol^{-1} \approx -59.6$ kJ mol^{-1}

Note: ΔT is +ve, ΔH is -ve

ΔH_{neut} = ... [4]

(f) The enthalpy change of neutralisation for potassium hydroxide reacting with hydrochloric acid is the same as that for sodium hydroxide reacting with sulfuric acid. Explain why.

ΔH_n is defined as H^+ (aq) + OH^-(aq) $\longrightarrow$ H_2O(l). KOH and NaOH are strong bases that dissociates completely to give OH^-(aq). HCl and H_2SO_4 are strong acids that dissociates completely to give H^+(aq). The ionic equations for both acid-base reactions are the same. [2]

(g) **(i)** Suggest why the magnitude of ΔH_{neut} obtained by this method is lower than the magnitude of the true ΔH_{neut}.

In this experiment, heat lost to the environment is not accounted for. Hence the ΔT recorded is smaller than expected and ΔH calculated would also be smaller in magnitude. [1]

(ii) Suggest **two** improvements to the method that would give a more accurate value for ΔH_{neut}.

Use a lid for the cup / use a draught shield to reduce heat lost to the environment.

Collect more data points near V_{neut} (e.g. at interval of 1 cm^3) so that we could better estimate the T_{max} and V_{neut} using graphical method. [2]

(h) Your value of V_{neut} could be used to calculate the concentration of the sulfuric acid. Explain why a conventional titration using an indicator gives a more accurate volume of neutralisation for this calculation.

This method collects data when volume of H_2SO_4 used is increased at 2 cm^3 interval, we use graphical method to estimate the volume of neutralisation. [1]

However, in a conventional titration, we can control and add volume of H_2SO_4 slowly when approaching the end point, and hence obtain a more accurate volume of neutralisation.

[Total: 22]

3 Determination of the formula of an organic acid

FA 3 is 1.00 mol dm^{-3} sodium hydroxide, NaOH.
FA 5 is an aqueous solution of 6.00 g dm^{-3} of an organic acid with the formula $HOOC(CH_2)_nCOOH$.

You are to dilute a sample of **FA 3** and titrate **FA 5** with this diluted sample to find:

- the concentration of the acid in **FA 5** in mol dm^{-3}
- the M_r of the acid and hence the value of n.

Solution **I** is thymolphthalein.

(a) (i) Procedure

1. Using the pipette labelled **FA 3**, transfer 25.0 cm^3 of **FA 3** into a 250 cm^3 volumetric flask.
2. Make the solution up to the mark with deionised water and shake well to mix.
3. Label this solution **FA 6**.
4. Fill a clean burette with **FA 6**.
5. Using a clean pipette, transfer 25.0 cm^3 of **FA 5** into a 250 cm^3 conical flask.
6. Add a few drops of solution **I** to the conical flask. Replace the cap on the container of **I** after use.
7. Run **FA 6** from the burette into the conical flask. The end-point is reached when the solution changes from colourless to a permanent **pale** blue colour.
8. Record your titration results in Table 3.1.
9. Repeat steps 5 to 8 until consistent results are obtained.

Results

Table 3.1

final burette reading / cm^3	25.50	25.40			
initial burette reading / cm^3	0.00	0.00			
volume of **FA 6** added / cm^3	25.50	25.40			

[5]

(ii) From your titration results, obtain a suitable volume of **FA 6** to be used in your calculation. Show clearly how you obtained this volume.

Average volume of FA6 used = $\frac{25.50+25.40}{2}$ = 25.45 cm^3

volume of **FA 6** = ... cm^3 [1]

(b) (i) The equation for the reaction in the titration is shown.

$$2NaOH + HOOC(CH_2)_nCOOH \rightarrow NaOOC(CH_2)_nCOONa + 2H_2O$$

Calculate the concentration of $HOOC(CH_2)_nCOOH$ in **FA 5** in mol dm^{-3}.

Concentration of NaOH in FA6 = $\frac{25.0}{250} \times 1.00 = 0.100$ mol dm^{-3}

Amount of NaOH used = $\frac{25.45}{1000} \times 0.100 = 0.002545$ mol

Amount of acid in 25.0 cm^3 = ½ × 0.002545 = 0.0012725 mol

Concentration of acid = $\frac{0.0012725}{(25/1000)} = 0.0509$ mol dm^{-3}

concentration of **FA 5** = ... mol dm^{-3} [2]

(ii) Determine the M_r of $HOOC(CH_2)_nCOOH$ and hence the value of n.
[A_r: H, 1.0; C, 12.0; O, 16.0]

M_r of acid = $\frac{6.00}{0.0509} = 117.9$ (1 d.p.)

M_r of $HOOC(CH_2)_nCOOH$ = ...

M_r of $HOOC(CH_2)_nCOOH = 117.9$

$90 + 14n = 117.9$

$14n = 27.9$

$n \approx 2$

n = ... [2]

[Total: 10]

4 Planning: Measuring the activation energy for a reaction

Bromate(V) ions react with bromide ions in the presence of an acid to form bromine.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The rate of the reaction may be followed by a 'bromine clock' method, by adding two other substances:

- a small amount of phenol, which reacts immediately with the bromine produced, removing it from solution as a precipitate

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$$

- methyl red indicator, which is decolourised by bromine.

As soon as all the phenol has been used up by the bromine released, excess bromine decolourises the methyl red indicator so there is a sudden change in colour from red to colourless.

The activation energy, E_a, for the reaction may be calculated by measuring the time for the solution to turn colourless at different temperatures.

You may assume you are provided with:

- $75\,cm^3$ of $0.10\,mol\,dm^{-3}$ potassium bromide, KBr
- $75\,cm^3$ of $0.02\,mol\,dm^{-3}$ potassium bromate, $KBrO_3$
- $75\,cm^3$ of $0.2\,mol\,dm^{-3}$ sulfuric acid, H_2SO_4
- solid phenol, C_6H_5OH (**corrosive** and **toxic by skin absorption**)
- methyl red indicator
- the equipment normally found in a school or college laboratory.

(a) Describe how you would make $75\,cm^3$ of a solution of phenol of approximate concentration $0.01\,mol\,dm^{-3}$ for your experiment. State any safety precautions you would take.
[A_r: H, 1.0; C, 12.0; O, 16.0]

Amount of phenol required = $\frac{75}{1000} \times 0.01 = 0.00075$ mol

Mass of phenol required = $0.00075 \times (12.0 \times 6 + 1.0 \times 6 + 16.0) = 0.0705$ g

1) As solid phenol is corrosive and toxic by skin absorption, wear a pair of glove and lab coat before the start of the procedure. Careful to avoid any skin contact with phenol.

2) Using a 100 cm^3 beaker and electronic balance, weigh out 0.07g of solid phenol.

3) Measure 75 cm^3 of deionised water using a 100 cm^3 measuring cylinder, add deionised water slowly into the beaker, stir with a glass rod to speed up the dissolution process.

Note: Question requires us to prepare a **75 cm^3** solution of **approximate** 0.01 mol dm^{-3}.

We do not need to use a volumetric flask for preparation as its typical size is 100 or 250 cm^3

[4]

(b) In order to calculate E_a, the following equation is used

$$\ln\left(\frac{1}{t}\right) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + c$$

where R is the molar gas constant
and c is a constant for the reaction.

Plan an experiment to collect sufficient data to plot a graph of $\ln(1/t)$ against $1/T$ where

- t is the time for the reaction mixture to turn colourless
- T is the reaction temperature in kelvin.

In your plan you should use the solution of phenol you planned to make and the solutions provided. The concentrations of the reactants and phenol solution are chosen so that mixing equal volumes of them gives a mixture with a suitable mole ratio for this method.

Your plan should include brief details of:

- the apparatus you would use
- the procedure you would follow
- the measurements you would take
- how the data measured would be used to determine values needed for the plotting of the graph.

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Methodology:

Repeat 5 experiments with varying temperatures and other variables kept constant (such as volume of each reactant used).

Note: Question stated that each reactant should be used in equal volumes.

Mixing KBr and $KBrO_3$ will cause reaction to start.

The reactants should be put into a thermostatically controlled water bath to achieve a desired temperature before starting the reaction.

Recall: Every 10 °C increase in temperature will cause rate of reaction to double, hence the temperature chosen should not be of a very wide range.

Procedure:

1. Using a 10 cm^3 measuring cylinder, measure 10.0 cm^3 of KBr(aq) and transfer into a 250 cm^3 conical flask labelled reaction mixture.
2. To the same conical flask, use separate 10 cm^3 measuring cylinders to add 10.0 cm^3 of H_2SO_4 (aq) and 10.0 cm^3 of phenol solution to the reaction mixture.
3. Add 3 drops of methyl red indicator into the conical flask labelled reaction mixture.
4. Using another 10 cm^3 measuring cylinder, add 10.0 cm^3 of $KBrO_3$(aq) to a different conical flask B.
5. Set the thermostatically controlled water bath to at a temperature of 35 °C.
6. Place both conical flasks into the thermostatically controlled water bath and use a 1 °C division thermometer for each conical flask to check the solution has reached the desired temperature.
7. After both solutions has reached the desired temperature, transfer the content of conical flask B into the conical flask labelled reaction mixture. Start the stopwatch and swirl the mixture thoroughly to mix its contents. Put the conical flask back into the thermostatically controlled water bath.
8. Stop the stopwatch when the red colouration of the reaction mixture is decolourised. Record the time taken to the nearest seconds.
9. Repeat steps 1 to 8 using different temperatures of water bath, such as 40°C, 45°C, 50°C, 55°C.
10. Use the data collected to calculate the values of $\frac{1}{\text{time}}$, ln ($\frac{1}{\text{time}}$), T (K) and $\frac{1}{T}$ / K^{-1}

    Temperature of 35°C will be converted to T(K) = (35 + 273) K

Expt	Temp /°C	Time / s	$\frac{1}{\text{time}}$ / s^{-1}	ln ($\frac{1}{\text{time}}$)	T / K	$\frac{1}{T}$ / K^{-1}
1	35					
2	40					
3	45					
4	50					
5	55					

(c) (i) Sketch the graph that you would expect to obtain on the axes in Fig. 4.1.

The equation for the graph is

$$\ln\left(\frac{1}{t}\right) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + c$$

where R is the molar gas constant
and c is a constant for the reaction.

Let $\ln(\frac{1}{t})$ be Y and $\frac{1}{T}$ be X,

Equation becomes Y = $\frac{-E_a}{R}$ X + c

It follows the shape of a straight line graph where gradient is $\frac{-E_a}{R}$ and c is the Y-intercept

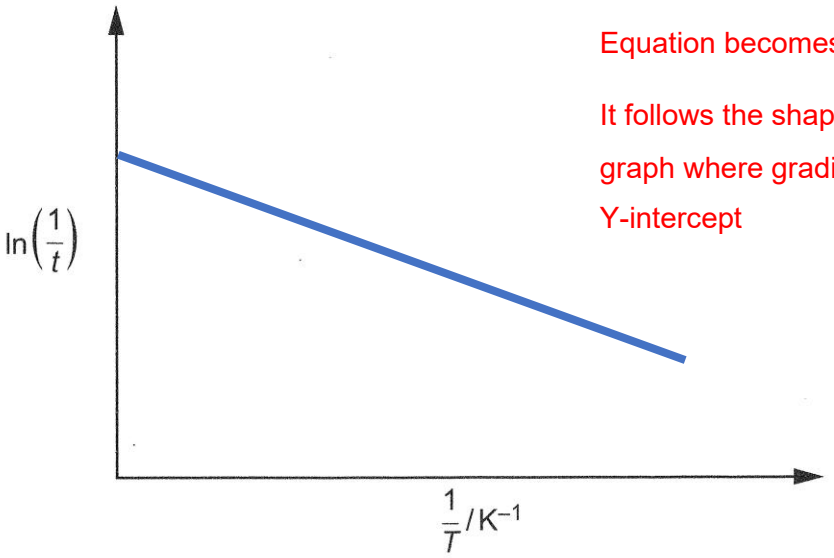

Fig. 4.1

[1]

(ii) Describe how you would use your graph to determine the value of E_a.

Use two points on the straight line to calculate the gradient of the line

gradient of the line is $\frac{-E_a}{R}$

E_a = gradient of graph × (−8.31) [1]

[Total: 14]