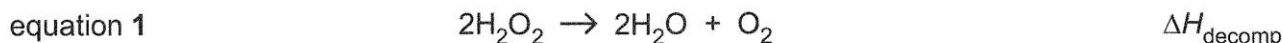


Answer **all** the questions in the spaces provided.

1 Determination of a value for an enthalpy change of decomposition, $\Delta H_{\text{decomp}}^1$

Hydrogen peroxide decomposes very slowly to form water and oxygen gas as shown in equation 1. The enthalpy change of decomposition, ΔH_{decomp} , for this reaction is exothermic.



Many transition element ions are able to catalyse the decomposition of hydrogen peroxide. Iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, is an effective catalyst for this reaction.

FA 1 is $0.850 \text{ mol dm}^{-3}$ aqueous hydrogen peroxide, H_2O_2 .

FA 2 is iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$.

The addition of **FA 2** to **FA 1** increases the rate of decomposition of H_2O_2 . This increase is sufficient to allow the maximum temperature change, ΔT_{max} , to be determined within a few minutes.

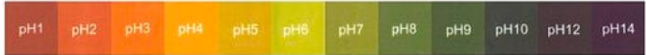
In this question, you will perform an experiment to determine a value for ΔT_{max} . You will then repeat this experiment and hence determine the average maximum temperature change, ΔT_{max}^1 .

You will use your value of ΔT_{max}^1 to calculate a value for the enthalpy change for the decomposition reaction shown in equation 1, $\Delta H_{\text{decomp}}^1$.

In **1(d)**, you will use data provided to determine another value for the maximum temperature change, ΔT_{max}^2 . You will then calculate a second value for the enthalpy change for the decomposition reaction shown in equation 1, $\Delta H_{\text{decomp}}^2$.

- (a) Perform the tests described in Table 1.1, and record your observations in the table. Test and identify any gases evolved.

Table 1.1

tests		observations
1.	Test the FA 2 solution using Universal Indicator paper.	Universal Indicator paper turns red / orange, indicating pH = 3 (match with chart provided)
2.	Put about a 2 cm depth of FA 1 into a test-tube. Add about a 2 cm depth of FA 2 to the same test-tube and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	 When yellow FA 2 is added to colourless FA 1, the solution turns brown. Vigorous effervescence of colourless, odourless gas. Gas relights a glowing splint. Gas is oxygen. After a few minutes, the reaction mixture turns yellow.
While you are waiting, continue with (b).		

[2]

(b) Determination of the average maximum temperature change, $\Delta T_{\max}^1$, for the catalysed decomposition of hydrogen peroxide, FA 1

You will follow the instructions to perform the experiment twice, run A and run B.

Record your results in Table 1.2.

- (i)
1. Using a measuring cylinder, transfer 50.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker.
 2. Stir and measure the temperature of this **FA 1**, $T_{\text{FA 1}}$.
 3. Using another measuring cylinder, measure 50.0 cm³ of **FA 2**.
 4. Stir and measure the temperature of this **FA 2**, $T_{\text{FA 2}}$.
 5. Add the **FA 2** from the measuring cylinder to the **FA 1** in the Styrofoam cup.
 6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. This could take several minutes. Record this temperature, $T_{\max}$.
 7. Replace the wet Styrofoam cup with a clean, dry Styrofoam cup. Repeat steps 1 to 6 to obtain a second value for $T_{\max}$.

Complete Table 1.2 by calculating values for the average of $T_{\text{FA 1}}$ and $T_{\text{FA 2}}$, T_{ave} , and $\Delta T_{\max}$ for each run.

Table 1.2

	run A	run B
$T_{\text{FA 1}}/^{\circ}\text{C}$	30.4	30.4
$T_{\text{FA 2}}/^{\circ}\text{C}$	30.5	30.4
$T_{\text{ave}}/^{\circ}\text{C}$	30.5	30.4
$T_{\max}/^{\circ}\text{C}$	38.9	38.8
$\Delta T_{\max}/^{\circ}\text{C}$	+8.4	+8.4

Determine the average maximum temperature change, $\Delta T_{\max}^1$.

$$\Delta T_{\max}^1 = \dots\dots\dots^{\circ}\text{C}$$

[2]





- (ii) Calculate the average heat change, q , for your experiment in **1(b)(i)** and hence determine a value for the enthalpy change, for the decomposition reaction shown in equation 1, $\Delta H_{\text{decomp}}^1$.

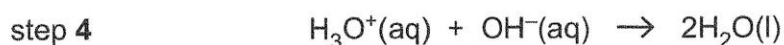
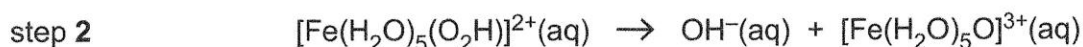
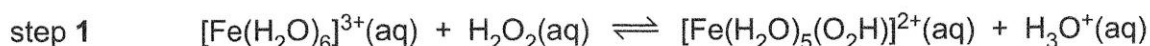
You should assume that the:

- decomposition of H_2O_2 in **FA 1** is complete when T_{max} is reached;
- specific heat capacity of the mixture is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$;
- density of the mixture is 1.00 g cm^{-3} .

$q = \dots\dots\dots$

$\Delta H_{\text{decomp}}^1 = \dots\dots\dots$ [3]

- (c) Steps 1 to 4 represent a possible mechanism for the catalysed decomposition of H_2O_2 . In this mechanism, the O_2H ligand on one of the complex ions represents the H-O-O^- ion and the O represents an oxygen atom.



- (i) Explain fully how you can tell that the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions are acting as a catalyst in this reaction, using evidence from your observations in Table 1.1 and from the mechanism.

.....

[3]





- (ii) The crystals of hydrated iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, used to prepare your sample of **FA 2** were pale violet in colour.

The colour of the **FA 2** solution obtained by dissolving these crystals is due to the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion reacting with a water molecule.

Complete the equation and explain how you deduced the products of this reaction, using your observations from test 1 in Table 1.1 to help you.



explanation

.....

.....

.....

[2]

- (iii) Explain the colour changes you observed for test 2 in Table 1.1, in terms of the complex ions involved in the mechanism.

.....

.....

.....

.....[1]





(d) **Determination of a value for an enthalpy change of decomposition, $\Delta H_{\text{decomp}}^2$, using a graphical method**

A student performed the experiment you performed in **1(b)(i)** but measured the temperature at timed intervals. The student added **FA 2**, containing the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ catalyst, to the **FA 1** at four minutes.

The results from this experiment are plotted on the grid in Fig. 1.1.

- (i) Draw two best-fit straight lines, the first taking into account the points before the **FA 2** was added and the second taking into account the points after the reaction had finished.

Extrapolate (extend) both lines to four minutes.

Determine a value for the maximum temperature change, ΔT_{max}^2 , at $t = 4.0$ min using the graph.

$$\Delta T_{\text{max}}^2 = \dots\dots\dots^\circ\text{C} \quad [2]$$

- (ii) Calculate a second value for the enthalpy change for the decomposition reaction shown in equation 1, $\Delta H_{\text{decomp}}^2$, using this value of ΔT_{max}^2 .

$$\Delta H_{\text{decomp}}^2 = \dots\dots\dots [1]$$

- (iii) State which of the temperature changes, ΔT_{max}^1 or ΔT_{max}^2 , is likely to be more accurate. Explain why your chosen value is likely to be the more accurate one.

.....

[1]



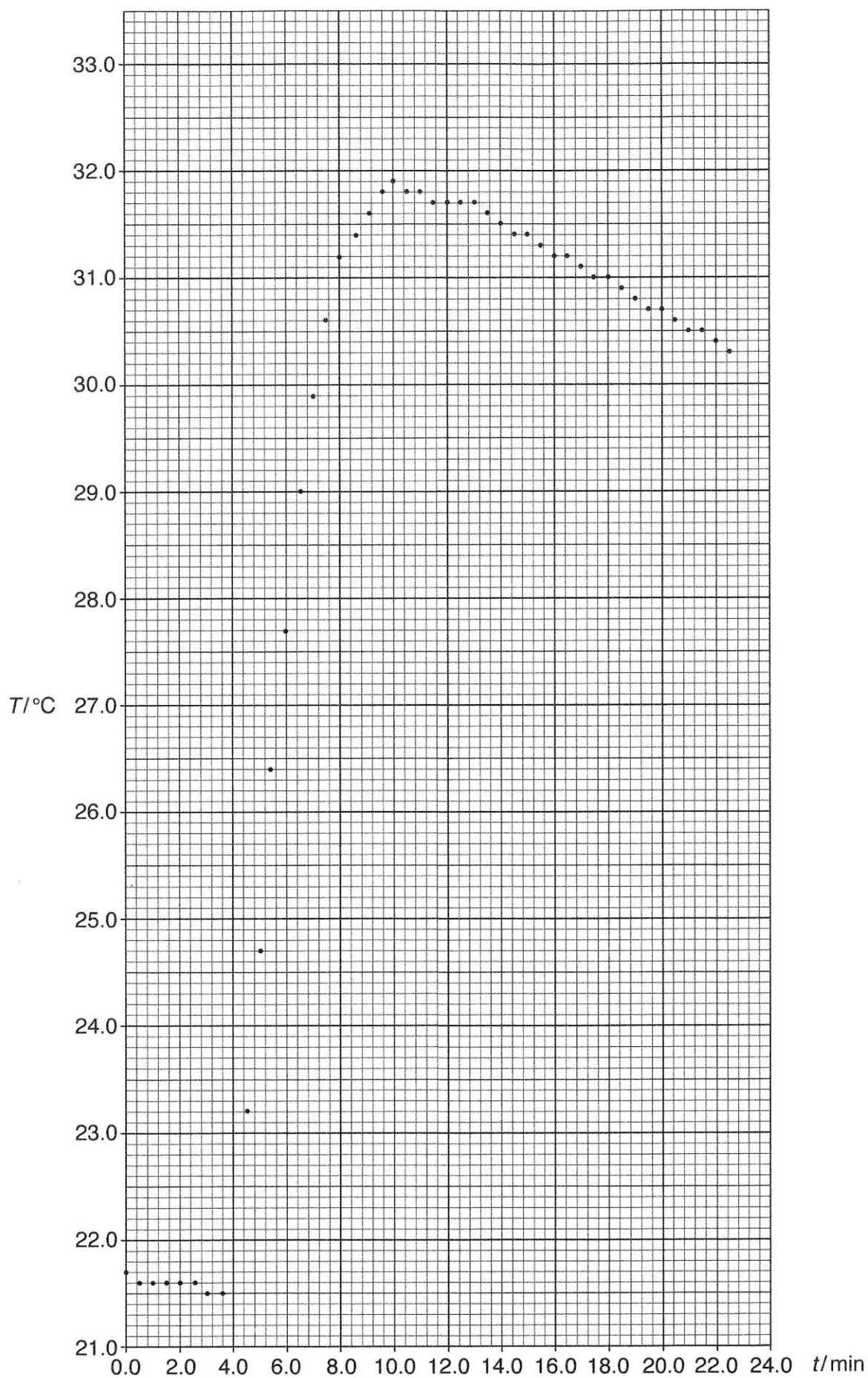


Fig. 1.1





2 Investigation of the kinetics of the catalysed decomposition of hydrogen peroxide

The concentration of **FA 1** is too high for the **FA 1** to be titrated directly against **FA 3**. A diluted solution of **FA 1** has been provided for you. This diluted solution is **FA 4**.

FA 3 is $0.0200 \text{ mol dm}^{-3}$ potassium manganate(VII), KMnO_4 .

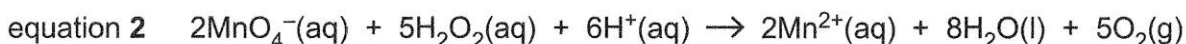
FA 4 is $0.170 \text{ mol dm}^{-3}$ aqueous hydrogen peroxide, H_2O_2 .

You are also provided with 0.2 mol dm^{-3} sulfuric acid, H_2SO_4 .

You will add a measured volume of **FA 2** to a measured volume of **FA 4** and, at timed intervals, you will transfer aliquots (portions) of the reaction mixture.

It is necessary that you titrate each aliquot against **FA 3** **before** transferring the next aliquot.

Acidified KMnO_4 and H_2O_2 react as shown in equation 2.



(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 it until you have finished this experiment.

You should aim to transfer your first aliquot within the first three minutes of starting the reaction.

You should aim **not** to exceed a maximum reaction time of 25 minutes for this experiment.

In an appropriate format in the space provided, 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 $t = 4 \text{ min } 33 \text{ s}$ then $t_d = 4 \text{ min} + 33/60 \text{ min} = 4.6 \text{ min}$,
- the burette readings and the volume of **FA 3** added.

1. Fill a burette with **FA 3**.
2. Using a measuring cylinder, add 100.0 cm^3 of **FA 4** to the conical flask labelled **reaction mixture**.
3. Using a measuring cylinder, add 2.0 cm^3 of **FA 2** to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its contents.
4. Using a measuring cylinder, add 50.0 cm^3 of 0.2 mol dm^{-3} sulfuric acid to a second conical flask.
5. Transfer a 10.0 cm^3 aliquot (portion) of the reaction mixture to a 10 cm^3 measuring cylinder, using a dropping pipette.
6. **Immediately** transfer this aliquot into the second conical flask and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.
7. **Immediately** titrate the H_2O_2 in the second conical flask with **FA 3**. The end-point is reached when a permanent **pale** pink colour is obtained. Record your titration results.
8. Wash out the second conical flask with water.
9. Repeat steps 4 to 8 until a total of **five** aliquots have been titrated and their results recorded.



Results

Time of transfer, t (time at which reaction mixture is quenched)	1 min 40 s	4 min 50 s	7 min 54 s	11 min 17 s	15 min 6 s
Decimal time, t_d / min	1.7	4.8	7.9	11.3	15.1
Final burette reading / cm^3	40.00	47.50	14.55	24.80	30.80
Initial burette reading / cm^3	12.40	27.75	0.75	14.60	24.80
Volume of FA 3 added / cm^3	27.60	19.75	13.80	10.20	6.00

[4]

- (ii) Plot a graph of the volume of **FA 3** added, on the y -axis, against decimal time, t_d , on the x -axis on the grid in Fig. 2.1.

Draw the most appropriate best-fit curve taking into account all of your plotted points. Extrapolate (extend) this curve to $t_d = 0.0$ min.

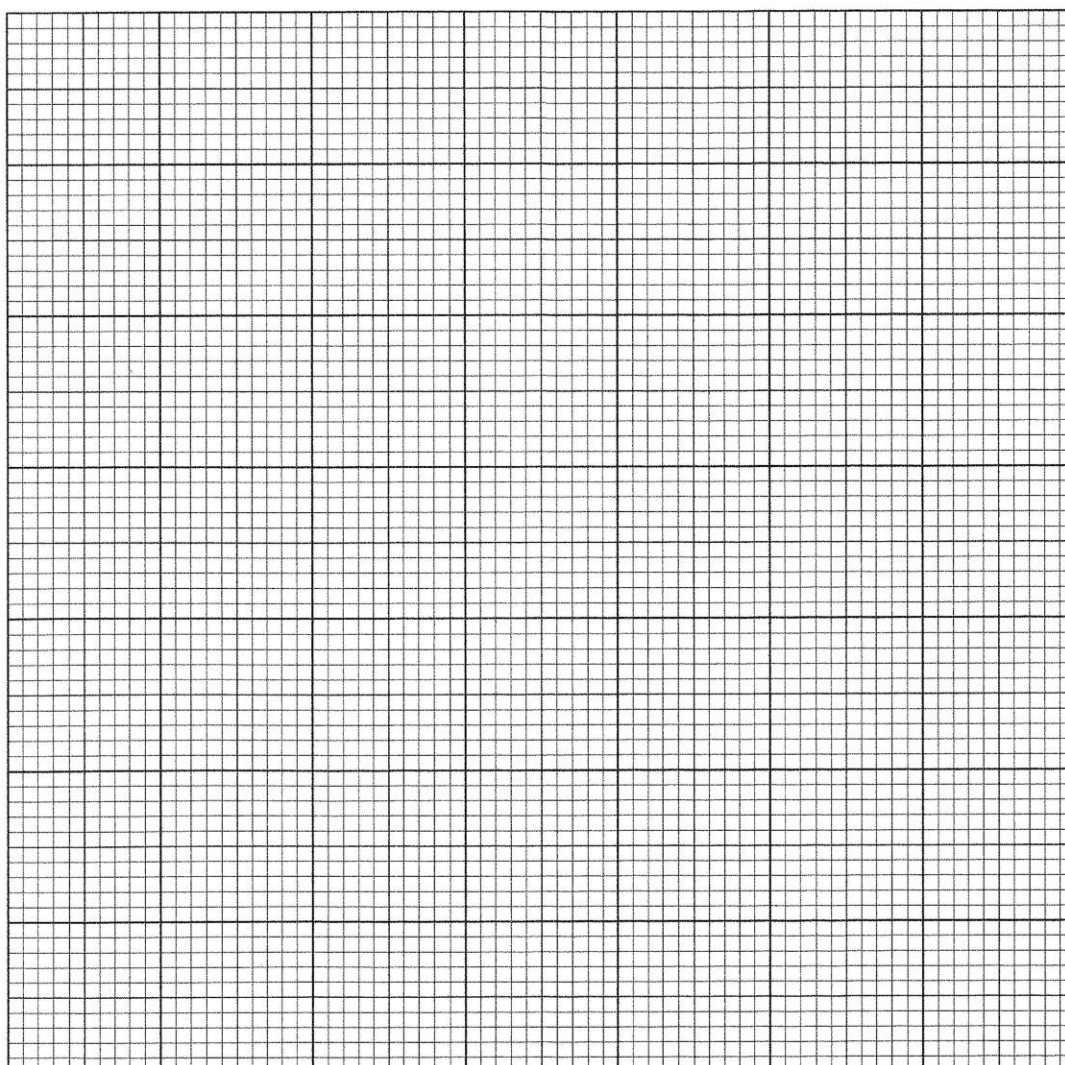


Fig. 2.1





- (i) Draw a tangent to your graph in Fig. 2.1 at time $t_0 = 0.0$ min.

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

- rate of change of the amount of MnO_4^- ions required = mol min^{-1} [1]

- rate of change of $[\text{H}_2\text{O}_2]$ at $t_d = 0.0 \text{ min} = \dots\dots\dots \text{mol dm}^{-3} \text{ min}^{-1}$ [2]

- State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 2.1 to support your answer.

[2]



(c) Planning

The decomposition of hydrogen peroxide, shown in equation 1, is also catalysed by the enzyme catalase, present in liver.

The rate equation for this decomposition is shown.

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{catalase}]$$

If the concentration of the catalase is kept constant, the rate equation becomes

$$\text{rate} = k'[\text{H}_2\text{O}_2]$$

where $k' = k[\text{catalase}]$.

The activation energy, E_a , and the pre-exponential factor, A , which is a constant, can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

T is the reaction temperature in kelvin.

k' is the rate constant at a chosen temperature.

The procedure you followed in **2(a)(i)** can be modified to investigate the effect of temperature, T , on the rate of decomposition of H_2O_2 . The activation energy, E_a , and the pre-exponential factor, A , can be graphically determined.

Plotting $\ln k'$ against $\frac{1}{T}$ gives a straight line of best fit. The gradient of this line is $\frac{-E_a}{R}$, where R is the molar gas constant.

- (i) Plan an investigation, based on the experiment described in **2(a)(i)**, to determine the effect of temperature, T , on the rate of decomposition of H_2O_2 with catalase.

You may assume that you are provided with

- 500 cm³ of 0.170 mol dm⁻³ hydrogen peroxide, H_2O_2 ,
- a piece of liver,
- a scalpel (knife),
- 0.0200 mol dm⁻³ potassium manganate(VII), KMnO_4 ,
- 0.2 mol dm⁻³ sulfuric acid, H_2SO_4 ,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the reactants and conditions that you would use,
- the apparatus that you would use in addition to that specified in **2(a)(i)**,
- the procedure that you would follow and the measurements that you would take,
- how you would determine the initial rate for each experiment.



[illegible]This image shows a single sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

[7]

You do **not** need to perform any of the calculations.

[2]



(iii) Sketch the graph you would expect to obtain from 2(c)(ii) on the axes in Fig. 2.2.

Explain your answer.

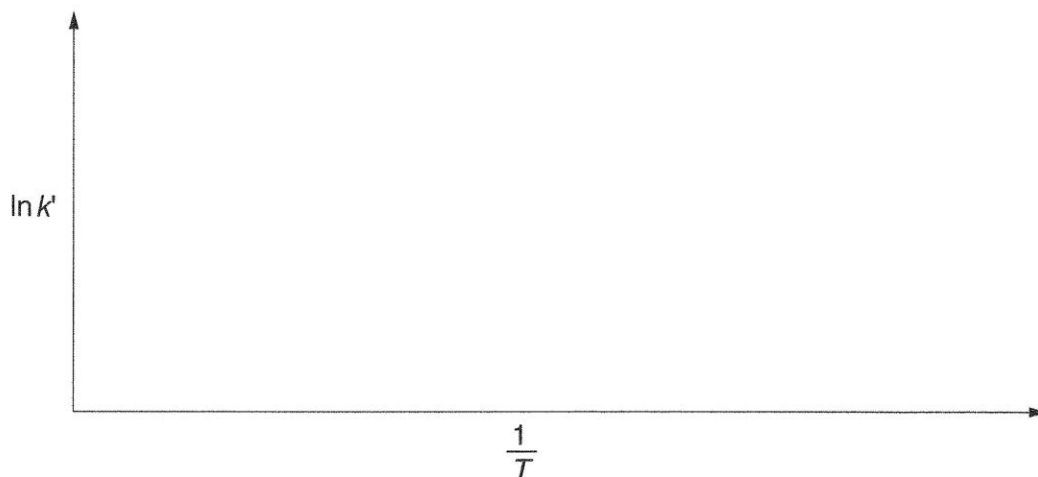


Fig. 2.2

explanation

 [2]

(iv) Describe how you would use your graph to determine values for E_a and A .

E_a

 [3]

[Total: 29]





3 Investigation of some redox reactions involving transition element ions

FA 5 is aqueous cobalt(II) chloride, CoCl_2 .

- (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 deionised water to a boiling tube until it is about one quarter full. Add aqueous sodium hydroxide to a second boiling tube until it is about one quarter full. Gently heat the second boiling tube until the liquid just starts to boil. Add one drop of FA 3 to each boiling tube and shake them thoroughly. Observe the mixtures until no further changes are seen.	Addition of purple FA 3 to deionised water gives a pink solution. Addition of purple FA 3 is added to hot NaOH(aq) gives pink solution which turns blue then green.
While you are waiting, continue with test 2.		
2.	Add ten drops of FA 5 to a test-tube. Add aqueous ammonia dropwise, with shaking, until no further change is seen. Then add about 1 cm depth of FA 1 and shake the mixture thoroughly.	Addition of $\text{NH}_3(\text{aq})$ to pink FA 5, a blue-green precipitate is formed, which dissolved partially in excess $\text{NH}_3(\text{aq})$ to give a brown solution. When FA 1 is added, vigorous effervescence of a colourless, odourless gas is observed, which relights a glowing splint. The gas is oxygen. The blue-green precipitate turns dark brown precipitate and the brown solution turns darker brown.

[4]





(b) Consider your observations in Table 3.1.

- (i) A small amount of oxygen is produced in one of the boiling tubes used in test 1 in Table 3.1. It is unlikely that you will have noticed this.

Suggest an explanation for the colour changes you observed in test 1 in Table 3.1, in terms of the physical and chemical changes occurring.

Identify the boiling tube in which the oxygen is produced.

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..... [2]

- (ii) The original colour of **FA 5** is due to the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions in the solution.

Identify, from your observations, the cobalt-containing species formed during test 2 in Table 3.1.

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..... [2]

- (iii) Compare the role of hydrogen peroxide in test 2 in Table 3.1 with its role in equation 2, on page 8. Explain your answer in terms of oxidation state changes.

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..... [1]

[Total: 9]

