Answer ALL questions.

Write your answers in the spaces provided.

1 The compound sulfuryl chloride is a colourless liquid with the formula SO_2Cl_2.

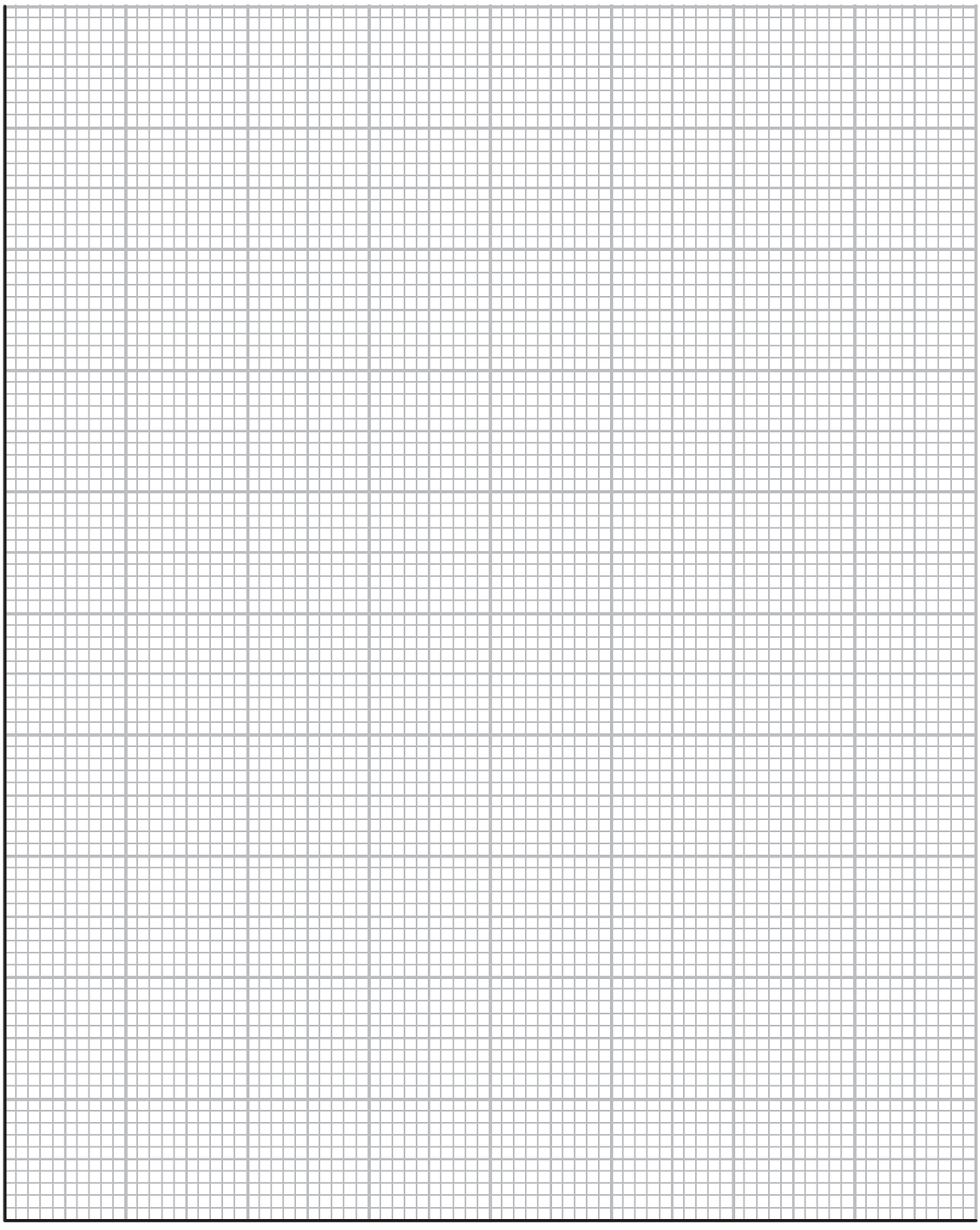
It decomposes at room temperature to form sulfur dioxide and chlorine.

(a) The rate of the decomposition of SO_2Cl_2 can be investigated by monitoring the concentration of SO_2Cl_2 as the reaction proceeds. The data in the table were collected from such a reaction.

Time / s	$[SO_2Cl_2]$ / mol dm^{-3}
0	0.500
1000	0.370
2000	0.290
3000	0.200
4000	0.150
5000	0.110
6000	0.090
7000	0.060
8000	0.040

(i) Plot a graph of these results.

(3)



(ii) Determine the order of reaction with respect to SO_2Cl_2 and hence write the rate equation for the reaction.
Show on your graph how you arrived at your answer.

(3)

(iii) Use your graph to find the rate of reaction when the concentration of SO_2Cl_2 is $0.200\ mol\ dm^{-3}$.
Hence calculate the rate constant, *k*, to an appropriate number of significant figures. Include units in your answer.

(4)

(b) Write a possible two-step mechanism for the reaction that is consistent with your rate equation and clearly identify the rate-determining step.

(2)

(Total for Question 1 = 12 marks)

2 A compound **Q** contains carbon, hydrogen and oxygen only.
It has a molar mass of 148 g mol^{-1}.

(a) Combustion analysis shows that when 0.952 g of **Q** is completely burned in excess oxygen, 2.83 g of carbon dioxide and 0.693 g of water are formed.

Use these data to determine the molecular formula of **Q**.

(5)

(b) Three qualitative tests are carried out on **Q**.
The results of each test are given in parts (i), (ii) and (iii).

State what can be deduced from each of these results.

(i) A very sooty flame is observed when a small sample of **Q** is burned in air.

(1)

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(ii) A yellow-orange precipitate is observed when a small amount of 2,4-dinitrophenylhydrazine is added to **Q**.

(1)

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(iii) No visible change is observed when a sample of **Q** is warmed with Tollens' reagent.

(1)

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(c) These data come from the proton NMR spectrum of **Q**.

Chemical shift of peak / ppm	Splitting pattern	Area under peak
7.5	complex multiplet	5
2.55	septuplet	1
1.25	doublet	6

(i) Deduce the structure of **Q**, using these data and your answers to (a) and (b).

Justify how all the data in the table supports your answer.

(7)

(Total for Question 2 = 15 marks)

3 Ethanedioic acid, $H_2C_2O_4.\mathbf{x}H_2O$, is a white, hydrated, crystalline solid.

A sample of 0.747 g of this solid is mixed with a small amount of dilute sulfuric acid and dissolved completely in distilled water. The volume is made up to exactly 250 cm^3 in a volumetric flask.

25.0 cm^3 of the resulting solution is titrated with a solution of manganate(VII) ions, $MnO_4^-(aq)$, of concentration 0.0105 mol dm^{-3}. The titration is repeated three more times.

During the titration, the ethanedioic acid is oxidised to form carbon dioxide and the managanate(VII) ions are reduced to Mn^{2+} ions.

(a) The steps followed in the titration are:

Step 1 A burette and pipette are rinsed.

Step 2 The burette is filled with the solution of manganate(VII) ions and the initial volume is recorded.

Step 3 25.0 cm^3 of the ethanedioic acid solution is measured using a pipette and transferred to a conical flask, which is warmed to 60 °C.

Step 4 The solution of manganate(VII) ions is added slowly, whilst swirling the flask.

Step 5 Distilled water is used to rinse any splashes on the inside of the flask.

Step 6 Near the end-point, the solution of manganate(VII) ions is added drop by drop.

Step 7 The volume of the solution of manganate(VII) ions is recorded at the end-point.

(i) State and justify what you would use in **Step 1** to rinse the burette.

(2)

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(ii) Describe how to measure the volume of the solution of manganate(VII) ions accurately in the burette in **Step 2**.

(2)

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(iii) Explain why the use of distilled water in **Step 5** will not affect the results of the titration.

(1)

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(b) Write half-equations for the reduction and oxidation reactions that occur during the titration.
Use these to construct an overall equation for the reaction. State symbols are not required.

(3)

(c) The results for the titration are shown in the table.

Titration	Volume of titre / cm^3
1	23.35
2	22.65
3	23.00
4	22.75

Select the appropriate titres and calculate their mean.

(1)

(d) Calculate the number of moles of water, **x**, in 1 mol of solid ethanedioic acid.

(5)

(e) A student carrying out the titration missed the end-point of the reaction and hence added too much of the solution of manganate(VII) ions.

Deduce what effect this would have on the student's value of the number of moles of water, **x**.

(2)

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(Total for Question 3 = 16 marks)

4 The halogenoalkane, 2-chloro-2-methylpropane, is prepared from 2-methylpropan-2-ol.

Step 1 Concentrated hydrochloric acid (in excess) and 2-methylpropan-2-ol (0.20 mol) are placed into a large conical flask. The flask is stoppered and then gently swirled for about 20 minutes.

Step 2 The mixture is transferred to a separating funnel and the lower aqueous layer is discarded.

Step 3 Sodium hydrogencarbonate solution is added to the separating funnel. The funnel is swirled carefully. The tap is opened frequently to release any build up of pressure. The lower aqueous layer is discarded.

Step 4 **Step 3** is repeated until there is no evidence of a build up of pressure.

Step 5 The product is transferred to a conical flask and anhydrous sodium sulfate is added, whilst swirling the flask.

Step 6 The product is filtered to remove the anhydrous sodium sulfate and then distilled, collecting the fraction that boils between 50 and 52 °C.

(a) Explain what causes the 'build up of pressure' in **Step 3**.
Write an equation for the reaction that takes place. State symbols are not required.

(2)

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(b) State the role of the anhydrous sodium sulfate in **Step 5** and describe how to tell when a sufficient amount has been added.

(2)

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(c) Explain the effect of **Steps 3** and **4** on the percentage yield for the preparation.

(2)

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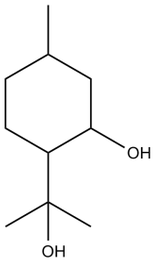
(d) Complete the mechanism for the reaction between concentrated HCl and 2-methylpropan-2-ol by showing the formation of the intermediate, its formula and its reaction to produce the product. Show appropriate lone pairs. **(4)**

(Total for Question 4 = 10 marks)

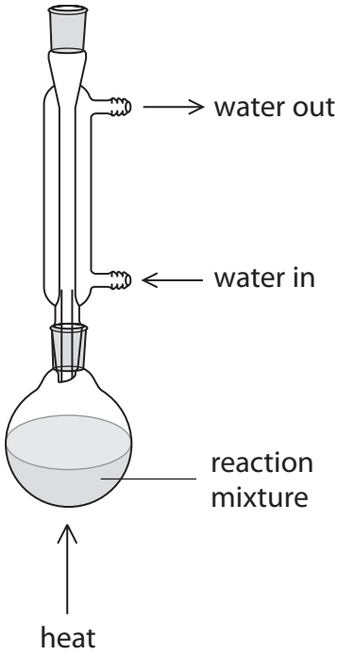
5 Alcohols contain the hydroxyl functional group. They can be oxidised using appropriate reagents and conditions.

Alcohol **Y** contains two hydroxyl groups.

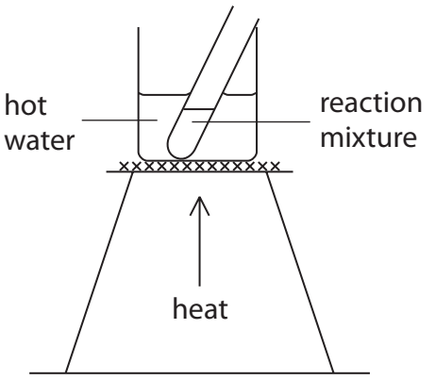


Alcohol **Y** can be oxidised by heating it with sodium dichromate(VI) solution and sulfuric acid.

*(a) A student suggested two possible techniques for heating the reaction mixture.



Technique A



Technique B

Evaluate all aspects of the two techniques and justify which one is more appropriate to just show that alcohol **Y** is able to be oxidised.

(6)

(b) Explain, using information from the Data Booklet, whether hydrochloric acid is a suitable alternative to sulfuric acid in the reaction mixture.

(2)

(c) Draw the **skeletal** formula of the organic product formed by the oxidation of alcohol **Y**.

(1)

(Total for Question 5 = 9 marks)

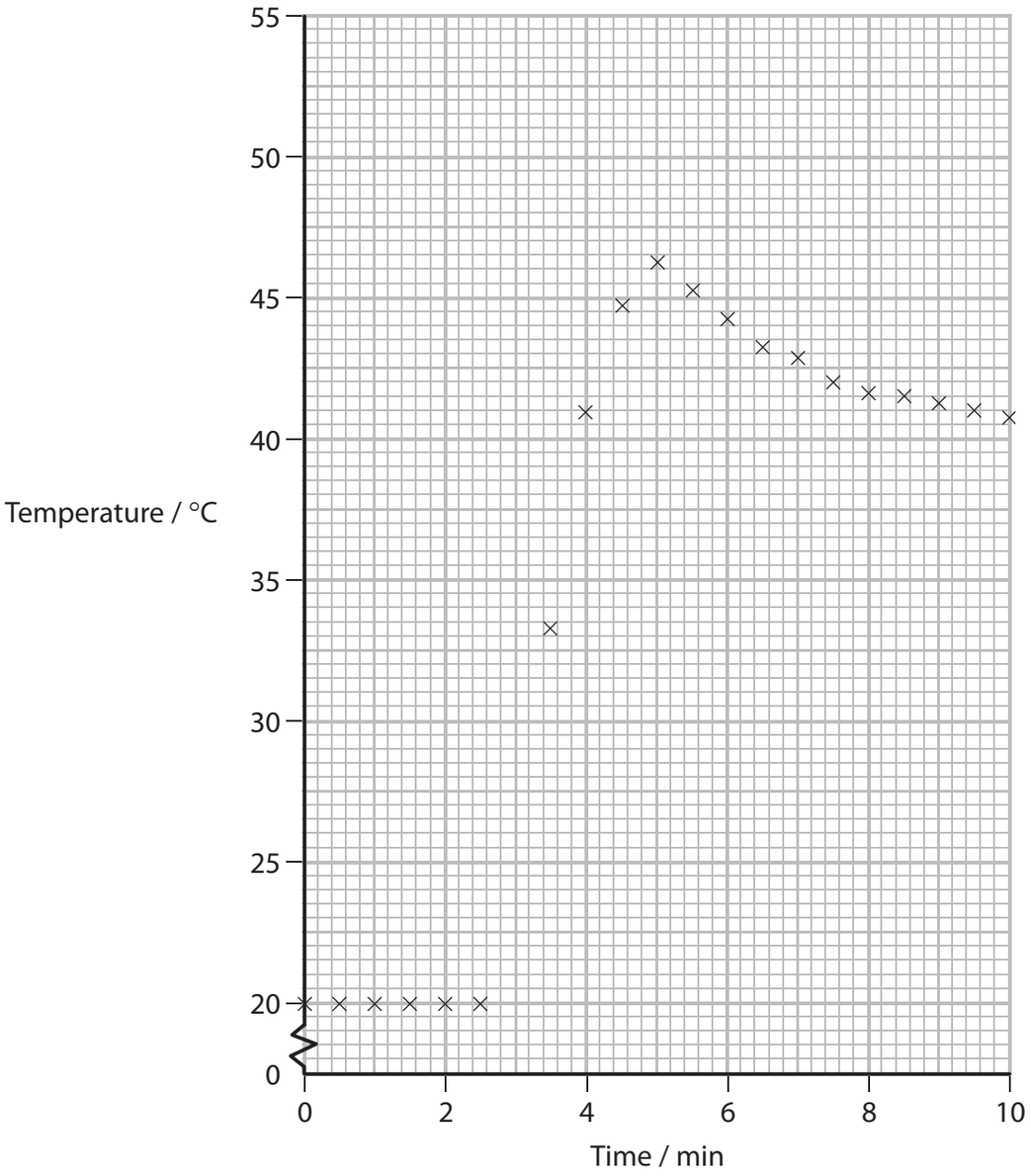
6 An experiment is carried out to determine the enthalpy change of the reaction between copper(II) sulfate solution and zinc.

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

The procedure is:

- measure out 25.0 cm^3 of 0.720 mol dm^{-3} copper(II) sulfate solution, using a pipette, into a polystyrene cup
- weigh out an excess of zinc granules
- place a thermometer into the cup. Stir and record the temperature to the nearest 0.1 °C every 30 seconds, for 2½ minutes
- at 3 minutes, add the zinc granules to the cup
- gently stir the mixture and record the temperature every 30 seconds until a total time of 10 minutes is reached.

The data collected is shown on the graph.



(a) Extrapolate the graph and hence determine the maximum temperature change for the reaction.

(2)

Maximum temperature change = ... °C

(b) (i) Explain why an extrapolation is required to determine an accurate measure of the maximum temperature change.

(2)

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(ii) Explain how the experiment could be amended to allow a value for the maximum temperature change to be determined without the need for an extrapolation.

(2)

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(c) Calculate the enthalpy change for the reaction, $\Delta_r H$. Give your answer to an appropriate number of significant figures.

(4)

(d) The accepted value of $\Delta_r H$ for this reaction is –217 kJ mol^{-1}.

(i) Calculate the percentage error in this experiment.

(1)

(ii) Give reasons why the experimental value calculated in (c) is different from the accepted value.

(2)

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(iii) In the same experiment, another student used a polystyrene cup that contained some distilled water left over from rinsing the cup.

Explain what effect, if any, this would have on the value for the enthalpy change calculated by this student, compared to the answer in (c).

(2)

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(Total for Question 6 = 15 marks)

7 The element vanadium exists in a variety of oxidation numbers in its compounds.

(a) Calculate the oxidation number of vanadium in the compound NH_4VO_3.

(1)

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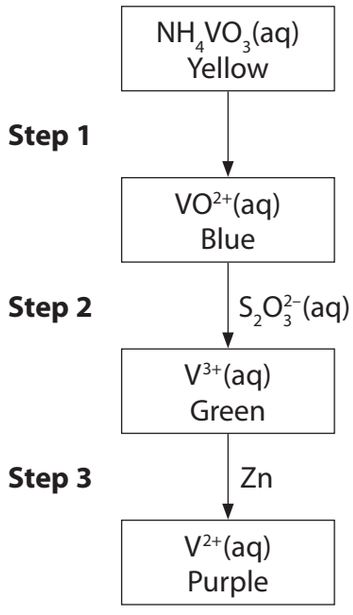
(b) NH_4VO_3 forms VO_2^+ in solution and can be reduced stepwise to form the ion, $V^{2+}(aq)$.



(i) Use the Data Booklet to give a suitable reducing agent for **Step 1** in order to only produce the blue solution.

(1)

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(ii) Give a possible reason why the reducing agent you choose may not be suitable.

(1)

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(iii) Explain what you would see during **Step 1**.

(2)

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(iv) Justify the choice of reducing agent for **Step 2**.
Write an equation for the reaction. State symbols are not required.

(2)

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(c) The solid compound V_2O_5 is used as a heterogenous catalyst in industry to speed up the reaction between oxygen and sulfur dioxide gas.

The reaction has two stages:

Stage 1 $SO_2(g) + V_2O_5(s) \rightarrow SO_3(g) + 2VO_2(s)$

Stage 2 $2VO_2(s) + ½O_2(g) \rightarrow V_2O_5(s)$

(i) Write the equation for the overall reaction. State symbols are not required.

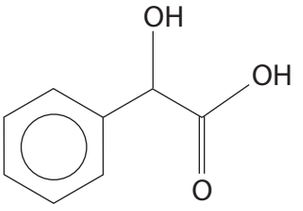
(1)

*(ii) Explain the catalytic behaviour of V_2O_5 in this reaction.

(6)

(Total for Question 7 = 14 marks)

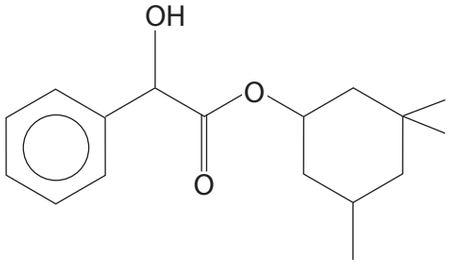
8 The compound mandelic acid is used in cosmetic skin peels.



(a) Draw a reaction scheme, including reagents, to show how mandelic acid can be synthesised in **two** steps from benzenecarbaldehyde (benzaldehyde), C_6H_5CHO.

(3)

(b) The compound cyclandelate is used to treat a condition called Raynauld's disease, which affects blood flow to the body's extremities, such as fingers and toes. The structure of cyclandelate is

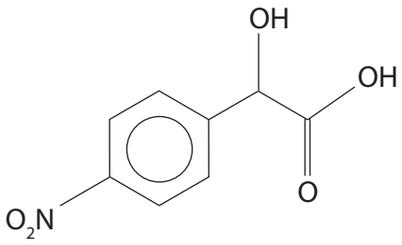


Draw the structure of a compound that could react with mandelic acid to form cyclandelate. Name the reaction type that occurs.

(2)

Type of reaction.....

(c) A derivative of mandelic acid, 4-nitromandelic acid, is used as a solid phase support in the synthesis of peptides.



Draw the mechanism for the formation of 4-nitromandelic acid from mandelic acid.

(4)

(Total for Question 8 = 9 marks)

9 An experiment to determine the equilibrium constant for the reaction between sodium fluoride solution and magnesium hydroxide is carried out.

100 cm^3 of sodium fluoride solution, of concentration 0.250 mol dm^{-3}, is added to a conical flask. Excess solid magnesium hydroxide is added and the mixture is left for 24 hours to reach equilibrium.

The mixture is filtered and 25.0 cm^3 of the solution is removed and titrated with hydrochloric acid.

11.70 cm^3 of 0.100 mol dm^{-3} HCl(aq) is required to neutralise the NaOH formed.

(a) Draw a dot-and-cross diagram of the ions in $Mg(OH)_2$.
Show outer electrons only.

(2)

(b) (i) Use the data to calculate the equilibrium constant, K_c for the reaction between NaF and $Mg(OH)_2$.
Give your answer to an appropriate number of significant figures and give the units, if any.

$$2NaF(aq) + Mg(OH)_2(s) \rightleftharpoons 2NaOH(aq) + MgF_2(s)$$

(5)

(b) (ii) The experiment was repeated on different days.
Justify whether this would improve the reliability of the data collected.

(1)

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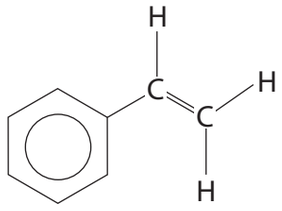
(Total for Question 9 = 8 marks)

10 The compound phenylethene (styrene) is used in the manufacture of polymers.



A simple test for the alkene functional group, such as that in styrene, is the addition of a small amount of bromine dissolved in cyclohexane.

(a) (i) State the colour change you would expect to see in this test.

(1)

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(ii) Explain what happens to the bromine molecule as it gets close to the alkene functional group.

(2)

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(iii) Give the type of reaction that occurs and draw the structure of the product formed in the test for the alkene functional group.

(2)

Type of reaction.....

Structure

(iv) Draw the repeat unit of the polymer formed from phenylethene.

(1)

(b) Both polystyrene and paper can be used to manufacture cups. Some people argue that using polystyrene for cups is more sustainable than using paper.

Evaluate the data in the table and hence justify which material you think is more sustainable.

(6)

	Paper cup	**Polystyrene cup**
Raw materials (per cup)		
Wood or bark	26 g	0 g
Petroleum fractions	2.2 g	3.4 g
Energy used (per tonne of material made)	980 kwh	280 kwh
Water released into environment (per tonne of material made)	120 m^3	2.5 m^3
Air emissions (per tonne of material made)		
Chlorine / chlorine dioxide	0.4 kg	0 kg
Sulfides / sulfur dioxide	11 kg	3.5 kg
Hydrocarbons	0 kg	40 kg

(Total for Question 10 = 12 marks)

TOTAL FOR PAPER = 120 MARKS