UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
Cambridge International Level 3 Pre-U Certificate
Principal Subject

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

CHEMISTRY **9791/02**

Paper 2 Part A Written **May/June 2011**

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
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7	
Total	

This document consists of **19** printed pages and **1** blank page.

DC (SM/DJ) 34229/3

[Turn over

1 **(a)** **(i)** Sketches of the shapes of the atomic orbitals from the s, p and d subshells are shown below, in random order. Label **each** orbital using labels such as p_x, d_{xy}, etc.

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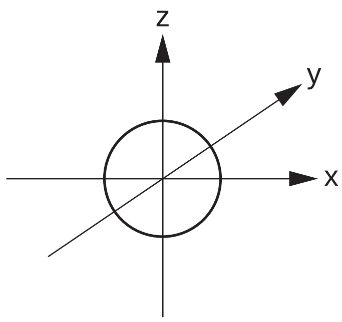

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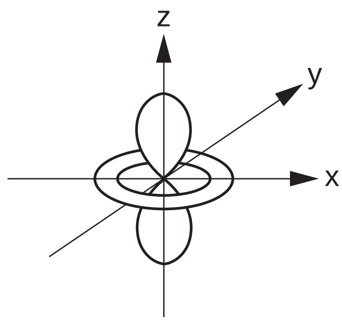

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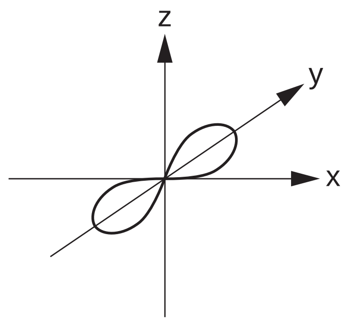

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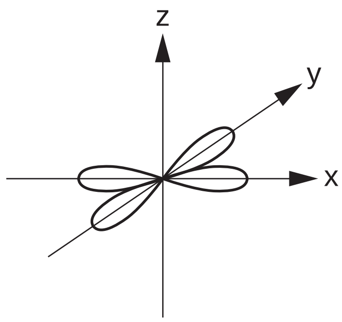

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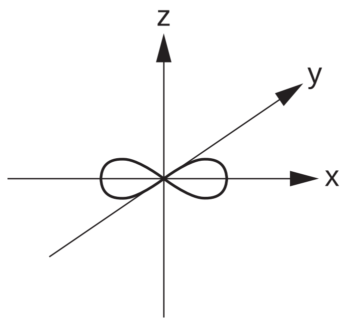

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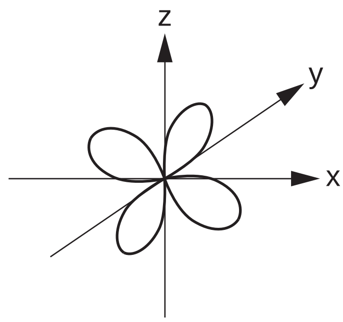

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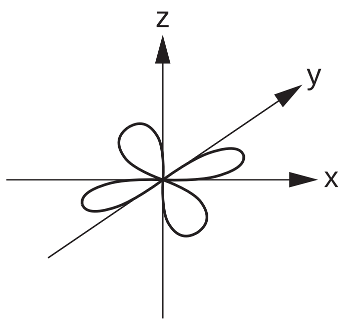

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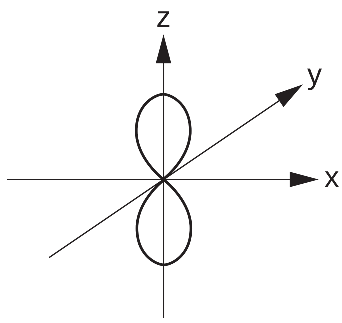

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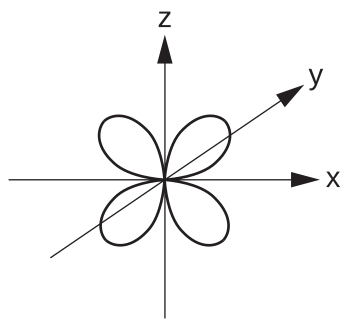


....

[5]

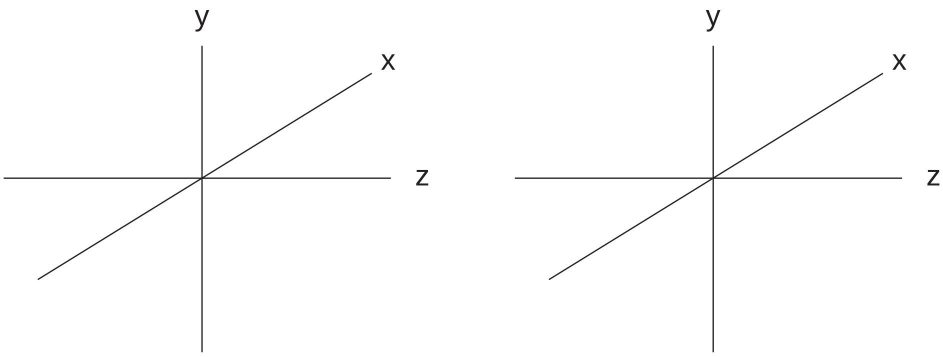
(ii) There are two elements in the first row of the d block whose gaseous atoms have all their 3d orbitals fully occupied. Name the two elements.

.... and .... [2]

(b) When the atomic orbitals from two atoms overlap a chemical bond may result. The p orbitals can overlap to form sigma (σ) or pi (π) bonds. When two atoms overlap the *z*-axis is used to define the internuclear axis.

For Examiner's Use

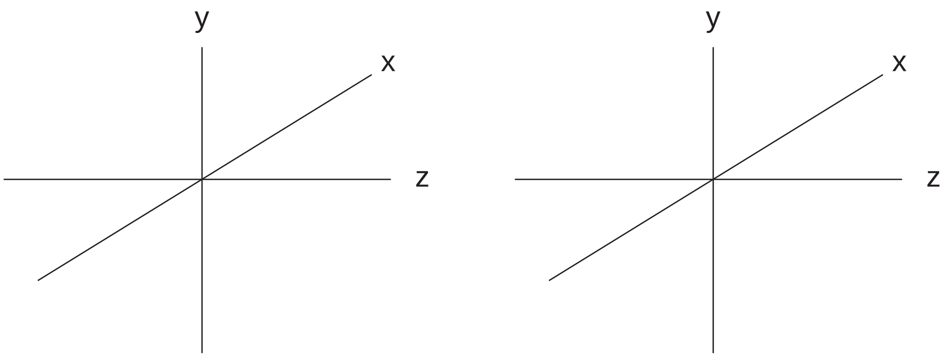
(i) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a sigma (σ) bond.



atom 1 atom 2

[1]

(ii) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a **single** pi (π) bond.



atom 1 atom 2

[1]

(c) Transition metal atoms such as chromium sometimes form bonds between themselves using their d orbitals. A compound containing a chromium-chromium quintuple bond (i.e. with a bond order of 5) was recently reported (*Nature Chemistry*, 2009).

(i) Complete the electron configuration of a chromium atom in the gas phase.

[Ar] .... [1]

(ii) The *z*-axis is used to define the internuclear axis of a chemical bond. Suggest which atomic d orbital can overlap with the same orbital on another atom to form a single sigma (σ) bond.

.... [1]

(iii) The d orbitals of one chromium atom can overlap with d orbitals of the same type on another chromium atom to form pi (π) bonds and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap the *z*-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in pi (π) bonds, and two different d orbitals that could be involved in delta (δ) bonds.

pi (π): .... and ....

delta (δ): .... and .... [2]

[Total: 13]

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2 **(a)** In theory, the reaction shown in equation 2.1 could be used to prepare SiF_4.

equation 2.1 $CF_4(g) + SiH_4(g) \rightarrow CH_4(g) + SiF_4(g)$

Bond enthalpy data is shown in Table 2.1.

Table 2.1

gas-phase bond	average bond enthalpy / $kJ\,mol^{-1}$
C–H	413
C–F	467
Si–H	318
Si–F	553

Calculate the enthalpy change of the reaction shown in equation 2.1. Include a sign and units in your answer. You are advised to show your working.

$\Delta_r H^{\ominus}$ = ... [3]

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(b) The reaction shown in equation 2.1 is not observed to take place at room temperature and pressure. However, recent research (*Science*, 2008) has revealed a method of exchanging a fluorine atom bonded to carbon with a hydrogen atom bonded to silicon at room temperature and pressure. This was accomplished by introducing triethylsilyl cations, $(C_2H_5)_3Si^+$. The proposed mechanism contains the following steps.

step 1 $(C_2H_5)_3Si^+ + C_6F_5CF_3 \longrightarrow (C_2H_5)_3SiF + C_6F_5CF_2^+$

step 2 $(C_2H_5)_3SiH + C_6F_5CF_2^+ \longrightarrow (C_2H_5)_3Si^+ + C_6F_5CF_2H$

(i) Write down the overall equation shown by the reaction steps above.

.... [1]

(ii) State and explain the role of $(C_2H_5)_3Si^+$ in this process.

....

....

.... [2]

(c) Suggest why Si−F bonds have a higher average bond enthalpy than C−F bonds.

....

.... [1]

(d) Suggest why, despite the stronger Si−F bond, SiF_4 is more reactive than CF_4.

....

.... [1]

[Total: 8]

3 The following hard materials have all found use in body armour.

A*l*N Al_2O_3 B_4C SiC Si_3N_4 TiB_2 WC

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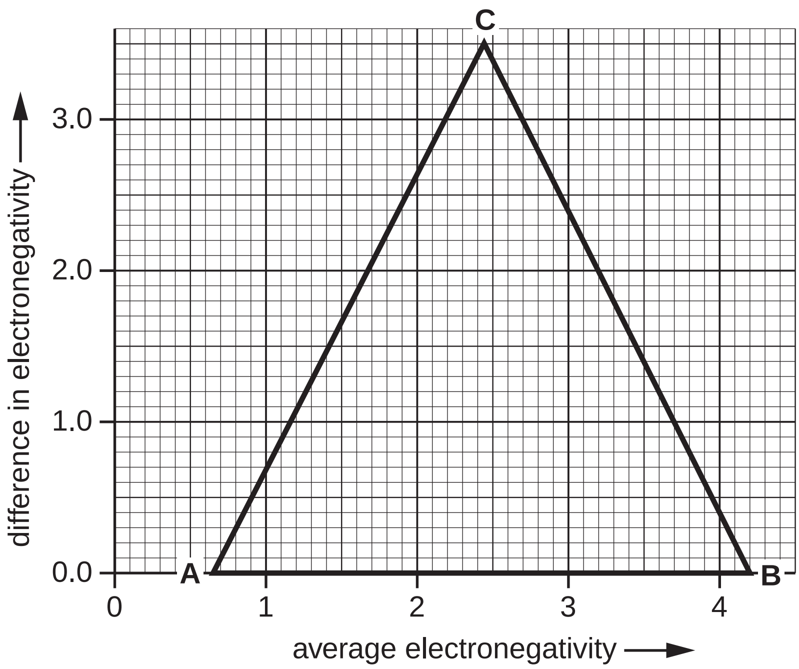
Table 3.1 gives the electronegativity values for the elements in these materials.

Table 3.1

element	electronegativity	element	electronegativity
titanium	1.4	boron	2.1
tungsten	1.5	carbon	2.5
aluminium	1.6	nitrogen	3.1
silicon	1.9	oxygen	3.6

(a) Plot on the van Arkel triangle the points corresponding to silicon carbide, SiC, and silicon nitride, Si_3N_4. Label your points, making it clear which is which. [2]



(b) Point **A** on the van Arkel triangle corresponds to metallic bonding. State the types of bonding that correspond to points **B** and **C**.

B .... **C** .... [1]

(c) Compare the bonding in silicon carbide, SiC, with silicon nitride, Si_3N_4, by circling the correct option.

SiC is **less metallic** **equally metallic** **more metallic** [1]

(d) Circle the correct response about the bonding in silicon carbide, SiC. The bonding in silicon carbide is best described as [1]

intermediate between metallic and covalent

metallic

intermediate between metallic and ionic

(e) Which of the hard materials, A*l*N, Al_2O_3 and TiB_2, is most intermediate between all three extremes of bonding?

.... [1]

(f) Scientists have recently characterised metallic behaviour in VO_2 above 68 °C (*Nature Nanotechnology*, 2009). The same behaviour was not found in V_2O_5. By considering this case and the electrical properties of diamond and graphite suggest three **general** deficiencies in the predictive power of the van Arkel triangle.

1 ....

2 ....

3 .... [3]

[Total: 9]

For Examiner's Use

4 **(a)** Phosphorus forms a pentachloride, PCl_5. This exists as a simple molecule in the gas phase.

(i) Draw the structure of PCl_5 in the gas phase, including hashed and wedged bonds where necessary.

On your diagram label the bond angles. Name the shape of the molecule.

name of shape .... [4]

(ii) PCl_5 reacts with water to form phosphoric acid, H_3PO_4. What **type** of reaction is taking place between PCl_5 and water?

.... [1]

(iii) Write down the oxidation number of phosphorus in phosphoric acid.

.... [1]

(iv) Suggest **one** advantage that phosphoric acid has over sulfuric acid as a reagent for dehydrating alcohols to form alkenes.

....

.... [1]

(v) Write out a displayed formula for sulfuric acid, showing all of the chemical bonds.

[1]

(b) (i) Phosphorus oxychloride, $POCl_3$, is an intermediate compound formed during the reaction between PCl_5 and water. Write the equation for the reaction of PCl_5 with water to form phosphorus oxychloride.

.... [1]

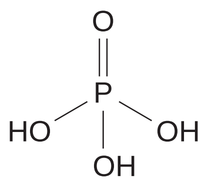
(ii) Reactions of covalent chlorides with water can be rationalised as step-wise replacement of –Cl with –OH. Complete the three-step reaction sequence for the formation of phosphorus oxychloride from phosphorus pentachloride.

step 1 $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$

step 2 ....

step 3 .... [2]

(c) The structure of phosphoric acid, H_3PO_4, is shown below.



(i) Phosphoric acid may dimerise to produce diphosphoric acid, $H_4P_2O_7$, and water. The reaction involves the condensation of an –OH group from each H_3PO_4 molecule to create an oxygen bridge between the two phosphoric acid units. Draw the structure of diphosphoric acid.

[1]

(ii) This condensation reaction may continue to give triphosphoric acid, $H_5P_3O_{10}$, and tetraphosphoric acid. Give the molecular formula of tetraphosphoric acid.

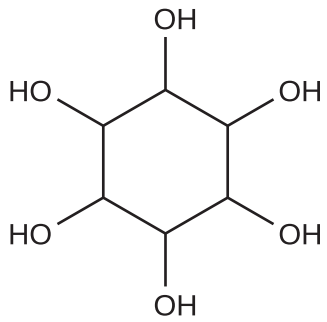
.... [1]

(iii) Give a general formula for polyphosphoric acids containing *n* phosphorus atoms.

.... [1]

(d) Recent research from a group led by Nobel-prize winning chemist Jean-Marie Lehn (*Proceedings of the National Academy of Science, USA,* 2009) has shown that a compound containing three cyclic diphosphates can improve the body's capacity for exercise. The compound is a derivative of inosotol, which is shown below.

For Examiner's Use



inosotol

(i) Give the empirical formula of inosotol.

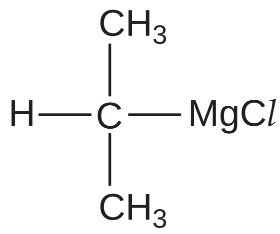
.... [1]

(ii) In the new compound each pair of adjacent oxygen atoms from the inosotol molecule is part of a cyclic diphosphate ester. The overall charge of the inosotol-cyclic-phosphate species is 6−. Suggest a structure for the compound.

[2]

[Total: 17]

5 **(a)** Grignard reagents are commonly used in synthesis to create carbon-carbon bonds. The structure is shown of the Grignard reagent formed from the reaction of 2-chloropropane and magnesium. Show the dipole on the relevant bond to carbon.



[1]

(b) Which three of the following terms describe a Grignard reagent? Circle the three correct answers.

reducing agent	**acid**	**oxidising agent**
base	**electrophile**	**nucleophile**

[3]

(c) The Grignard reagent from part **(a)** reacts with ethanal.

(i) Draw the structure of the organic product of this reaction.

[1]

(ii) Identify any chiral carbon atoms in the product with an asterisk (*). [1]

(iii) Name this organic product.

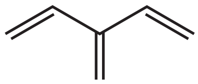
....[1]

(d) Solvents that are employed for Grignard chemistry need to be rigorously dried. By considering the dipole on the O−H bonds in water, suggest what organic product results from getting the Grignard compound in part **(a)** wet.

[1]

(e) Recent research (*Angewandte Chemie International Edition*, 2009) has produced the first practical synthesis of dendralenes. Dendralenes are acyclic conjugated polyalkenes. An example is shown.

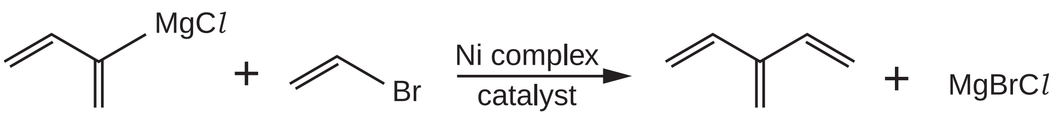
For Examiner's Use



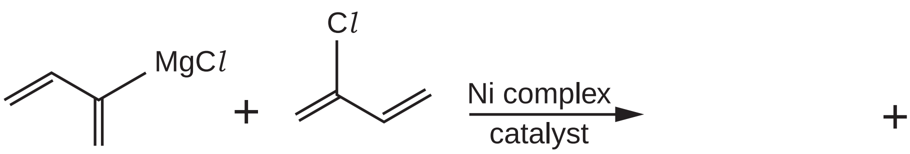
(i) What is the molecular formula of this compound?

.... [1]

(ii) The breakthrough was the discovery of the nickel complex that catalysed the process. An example of their dendralene synthesis is shown.



Complete the equation below by inserting the skeletal formula of the organic product and the formula of the inorganic product.



[2]

(iii) The Grignard reagent from part **(e)(ii)** can also react with 1,1-dichloroethene in the presence of the nickel complex catalyst. Draw the skeletal formula of the dendralene product.

[2]

[Total: 13]

6 **(a)** Chemists from the University of Cambridge have used Au_{55} nanoparticles to catalyse a reaction of oxygen with phenylethene (styrene), $C_6H_5{-}CH{=}CH_2$, (*Nature*, 2008). Three products, **A**, **B** and **C**, were observed. Use the following observations to complete the structure of **A**, **B** and **C**.

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- The phenyl ($C_6H_5{-}$) group remains unchanged in **A**, **B** and **C**.
- **A** has the molecular formula C_7H_6O;

  B and **C** both have the molecular formula C_8H_8O.
- When warmed with Tollens' reagent (ammoniacal silver nitrate) compound **A** produces a silver mirror but compounds **B** and **C** do not.
- The infra-red spectra of compounds **A** and **B** each have an intense peak at around 1700 cm^{-1} but that of compound **C** does not.
- None of the compounds' infra-red spectra show any broad signals above 3000 cm^{-1}.
- Compound **C** is the most reactive and unstable of the three. It contains a ring of three atoms.

structure of **A**

$C_6H_5{-}$

structure of **B**

$C_6H_5{-}$

Structure of **C**

$C_6H_5{-}$

[3]

(b) **(i)** Draw a dot-cross diagram for the hydroxonium ion, H_3O^+, showing only outer-shell electrons.

[2]

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(ii) Alkyl oxonium ions are analogues of H_3O^+ where the oxygen atom is bonded to alkyl groups rather than to hydrogen atoms. The tripropyl oxonium ion is a typical alkyl oxonium ion.

- Write down the molecular formula of the tripropyl oxonium ion.

  ....

- Deduce the m/z of the molecular ion peak in its mass spectrum.

  ....

- Deduce the number of signals in its ^{13}C NMR spectrum.

  .... [3]

(iii) Oxatriquinane is an alkyl oxonium ion whose synthesis was reported recently (*Journal of the American Chemical Society*, 2008). It was found to be surprisingly stable in water, and has:

- a molecular formula of $C_9H_{15}O^+$
- only two signals in its ^{13}C NMR spectrum
- no carbon-carbon multiple bonds
- multiple rings in its structure.

Suggest a structure for oxatriquinane.

[1]

(c) Chemists have recently synthesised the smallest "beakers" for carrying out chemical reactions (*Nature Chemistry*, 2009). The "beakers" are the junctions from a network of hollow polymer nanofibres. The volume of the beakers is about $4 \times 10^{-18}\,dm^3$.

(i) A "beaker" is full of a solution of glucose of concentration $5 \times 10^{-4}\,mol\,dm^{-3}$. Calculate the amount (in moles) of glucose in the "beaker".

.... mol [1]

(ii) Use your answer to part **(i)** to calculate the number of glucose molecules in the "beaker".

.... [1]

[Total: 11]

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7 **(a)** Simple esters are flammable liquids. Flammability is affected by volatility. Write the following homologous series in order of boiling point, assuming molecular masses are similar.

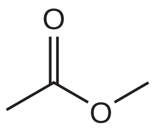
alcohols **alkanes** **esters**

highest boiling point ....

↑ ....

lowest boiling point .... [1]

(b) **(i)** The structure of methyl ethanoate, $C_3H_6O_2$, is shown below.



Write an equation for the complete combustion of methyl ethanoate.

.... [1]

(ii) Define *standard enthalpy change of formation*.

....

....

.... [3]

(iii) Use the standard enthalpy changes of combustion, $\Delta_c H^{\circ}$, in Table 7.1 to calculate the standard enthalpy change of formation of methyl ethanoate.

Table 7.1

	$\Delta_c H^{\circ}$ / kJ mol^{-1}
carbon	–393.5
hydrogen	–285.8
methyl ethanoate	–1592.1

.... kJ mol^{-1} [3]

(c) A student used the apparatus shown in Figure 7.1 to carry out experiments to determine the standard enthalpy change of combustion for ethyl ethanoate.

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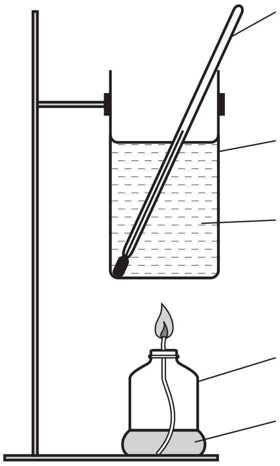

Fig. 7.1

- mass of copper pot is 250 g
- volume of water is 300 cm^3

An initial experiment was carried out using methyl ethanoate. This ester was combusted in a spirit burner underneath a copper can so that the flame from the burner heated 300 cm^3 of water in the can. It was found that 0.980 g of ester was required to raise the temperature of the water in the can by 10.0 °C.

(i) Describe how this initial experiment was carried out to collect the data that gave these results.

....

....

....

....

....

....

....

....

....

.... [6]

For Examiner's Use

(ii) Calculate the total thermal energy in kJ gained by the water and the copper can in this initial experiment. The specific heat capacities of water and copper are 4.18 and 0.384 $J\,g^{-1}\,K^{-1}$, respectively.

Take the density of water to be 1.00 $g\,cm^{-3}$. Assume that the water and copper are in thermal equilibrium with each other. Express your answer to the appropriate number of significant figures.

.... [3]

(iii) Using the $\Delta_c H^{\ominus}$ value in Table 7.1, calculate the total theoretical thermal energy in kJ released by the mass of methyl ethanoate combusted in this initial experiment.

.... kJ [2]

(iv) Heat losses are significant but can be taken into account by using the known value of $\Delta_c H^{\ominus}$ of −1592.1 $kJ\,mol^{-1}$ for methyl ethanoate. A similar experiment with ethyl ethanoate produced the following results.

mass of ethyl ethanoate combusted = 0.948 g

increase in temperature of 300 cm^3 water = 11.5 °C

Calculate the most accurate possible value for the standard enthalpy change of combustion for ethyl ethanoate.

.... $kJ\,mol^{-1}$ [4]

For Examiner's Use

(d) Outline **four** improvements that could increase the accuracy of the raw data recorded in these experiments.

....

....

....

....

....

....

....

....

....

.... [4]

(e) In terms of the ease of lighting and the appearance of the flame how does methyl ethanoate compare to decyl ethanoate ($CH_3COOC_{10}H_{21}$)?

ease of lighting ....

.... [1]

appearance of flame ....

.... [1]

[Total: 29]

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