



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

CANDIDATE
NAME

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NUMBER

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CHEMISTRY

9791/02

Paper 2 Part A Written

May/June 2013

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.
 Electronic calculators may be used.
 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 | |
|--------------------|--|
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| Total | |

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



- 1 (a) Nitrogen and phosphorus are both found in Group 15.

Phosphorus forms more than one allotrope.

- (i) Draw a dot-cross diagram to show the bonding in nitrogen, N_2 . Show outer electrons only.

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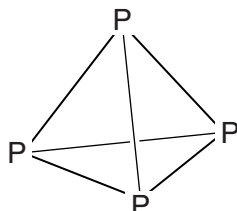
[1]

- (ii) What is meant by the term *allotrope*?

.....

..... [1]

- (iii) White phosphorus is a solid and exists as P_4 molecules with a tetrahedral structure as shown.



Using the data in Table 1.1 work out the enthalpy change for the following conversion. Include a sign in your answer.

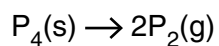


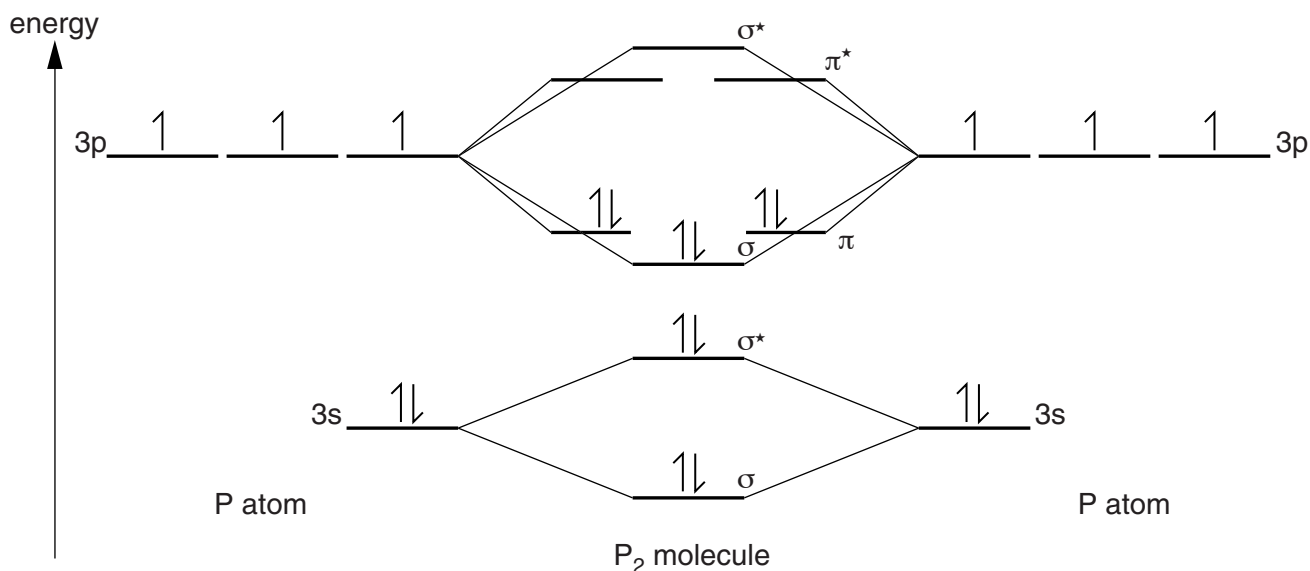
Table 1.1

| | energy change / kJ mol^{-1} |
|-----------------------------------|--------------------------------------|
| P–P bond energy | 198 |
| P≡P bond energy | 485 |
| enthalpy of vaporisation of P_4 | 12 |

$$\Delta_r H^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \text{ [3]}$$

sign

- (iv) Chemists have recently managed to prepare P_2 molecules in the solid state, trapped in an organic framework (reported in *Nature Chemistry*, 2010). The labelled molecular orbital diagram represents the bonding in P_2 , which has a bond order of 3.



Using similar techniques P_2^{2+} and P_2^+ were also trapped and characterised.

Using the molecular orbital diagram or otherwise, give the bond order in these species.

Bond order in $\text{P}_2^{2+} = \dots\dots\dots$ Bond order in $\text{P}_2^+ = \dots\dots\dots$ [2]

(b) Carbon and silicon are both members of Group 14.

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(i) What is meant by the term *first ionisation energy*?

.....

.....

..... [3]

(ii) Explain why the first ionisation energy of silicon is lower than that of carbon.

.....

.....

..... [3]

(iii) State the type of covalent bond typically seen in

- single bonds,
- additional bonds in a multiple bond. [1]

(iv) Carbon readily forms multiple bonds with itself, while silicon does not form these bonds so easily.

The first compound containing a Si=Si double bond was synthesised in 1972. One such compound contains the following percentages by mass.

C 41.3% H 10.3% Si 48.4%

Find the empirical formula of this compound and draw a possible structure, given that it contains only one Si=Si double bond.

structure empirical formula [3]

[Total: 17]

2 (a) Group 2 carbonates decompose when heated.

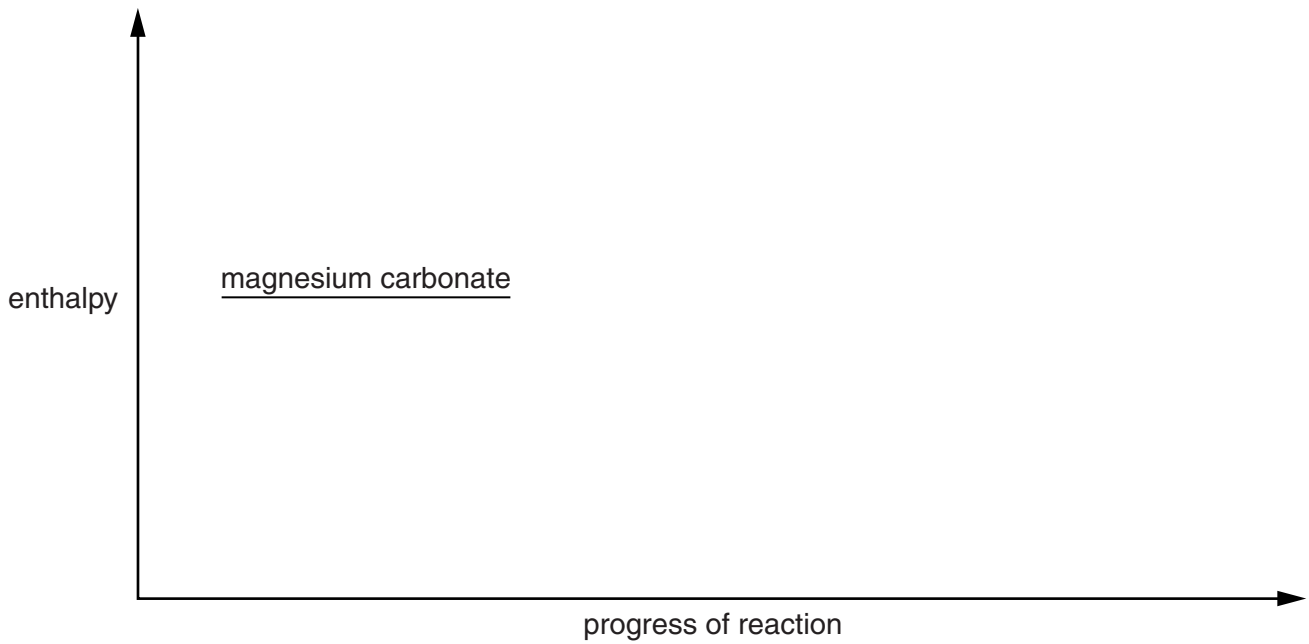
(i) Write the equation for the thermal decomposition of magnesium carbonate.

..... [1]

(ii) Complete the reaction profile diagram for the thermal decomposition of magnesium carbonate.

On the diagram, label

- the enthalpy change of reaction, $\Delta_r H$,
- the activation energy, E_a .



[3]

(b) There is a trend in the decomposition temperature of Group 2 carbonates as the group is descended.

State and explain this trend.

trend

explanation

.....

.....

.....

.....

[4]

- (c) The cement-making process involves the thermal decomposition of calcium carbonate. This process is the second largest emitter of greenhouse gases globally after power generation.

There is presently much interest in serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_x$, as a “green” cement which chemically absorbs carbon dioxide.

- (i) Deduce the value of x in $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_x$.

$x = \dots\dots\dots$ [1]

- (ii) Serpentine cement reacts with carbon dioxide to form water, silicon(IV) oxide and one other product.

Suggest the identity of the other product.

$\dots\dots\dots$ [1]

- (iii) Magnesium oxide can be considered to be an intermediate in the process in (c)(ii).

What type of chemical reaction takes place between magnesium oxide and carbon dioxide?

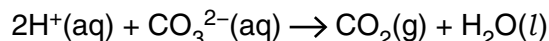
$\dots\dots\dots$ [1]

- (d) Dolomite is a carbonate-containing mineral with formula $\text{CaZ}(\text{CO}_3)_2$ where Z is a metal ion.

- (i) Use the formula of dolomite to determine the charge on the metal ion Z .

$\dots\dots\dots$ [1]

- (ii) Dolomite is insoluble in water but dissolves in acid. The ionic equation for the reaction between hydrogen ions and carbonate ions is shown.



A 5.00 g sample of dolomite is dissolved in 30.0 cm³ of 5.00 mol dm⁻³ hydrochloric acid, an excess.

The resulting solution is made up to 100 cm³ in a volumetric flask, using distilled water. 10.0 cm³ of this solution is titrated against a 0.100 mol dm⁻³ solution of sodium hydroxide. An average titre of 41.60 cm³ is obtained.

Calculate the amount, in mol, of excess hydrochloric acid in the 100 cm³ volumetric flask. Use an appropriate number of significant figures in your answer.

amount = $\dots\dots\dots$ mol [3]

- (iii) Calculate the amount, in mol, of hydrochloric acid that reacts with the 5.00 g sample of dolomite.

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Use*

amount = mol [2]

- (iv) Calculate the mass of carbonate ions in the 5.00 g sample of dolomite.

mass = g [2]

- (v) Determine the molar mass of the metal ion Z.

molar mass = g mol^{-1} [3]

[Total: 22]

3 (a) Fluorine forms simple molecular compounds with nearly all the non-metals.

(i) What is the name of the theory or model used to determine the shape of molecules?

..... [1]

(ii) Name the shape and give the bond angle in boron trifluoride.

name of shape

bond angle [2]

(b) Many non-metals form hypervalent compounds with fluorine.

(i) Explain what is meant by the term *hypervalent*.

.....
..... [1]

(ii) IF_7 is a hypervalent compound.

Name the shape and give the bond angles in the molecule.

name of shape

bond angles and [3]

(iii) Unlike IF_7 , BrF_7 is not known to exist. Suggest why IF_7 exists but BrF_7 does not.

.....
..... [1]

(c) The trioxide of xenon, XeO_3 , is simple molecular and hypervalent. It has three $\text{Xe}=\text{O}$ double bonds and a lone pair on the xenon atom.

(i) Deduce and name the shape of an XeO_3 molecule.

..... [1]

(ii) In 2011 xenon dioxide, XeO_2 , was synthesised for the first time (reported in the *Journal of the American Chemical Society*). Xenon dioxide exists as a polymer in which the oxygen atoms are bonded to xenon in a square planar arrangement.

Work out the number of

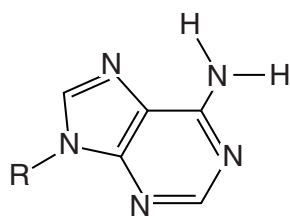
- bonding electron pairs around each Xe atom,
- lone pairs around each Xe atom. [2]

(d) Hydrogen-bonding is the interaction that holds the two strands of DNA together through its purine and pyrimidine bases.

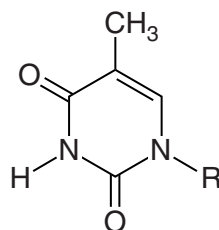
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(i) The structures of adenine and thymine are shown below (R indicates the DNA backbone).

Show both the hydrogen bonds linking these bases.



adenine

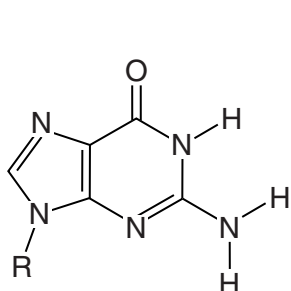


thymine

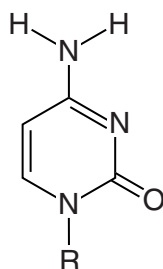
[2]

(ii) A Janus wedge is a molecule that can insert itself between a purine and a pyrimidine base in DNA using hydrogen-bonding interactions to each base. (It is named after the Roman god Janus who had two faces.)

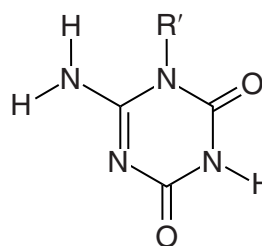
The structures of guanine, cytosine and a Janus wedge are shown. (R' indicates the remainder of the Janus wedge structure.)



guanine



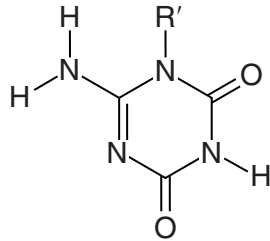
cytosine



Janus wedge

The guanine forms **three** hydrogen bonds with the Janus wedge, while the cytosine forms **two**.

Re-draw the guanine and cytosine on the next page, showing all the hydrogen bonds between the three molecules. The Janus wedge is drawn for you.



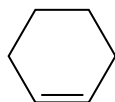
Janus
wedge

[3]

[Total: 16]

4 Cyclohexene behaves as a typical alkene.

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(a) (i) Give the name of the type of polymerisation that cyclohexene undergoes.

..... [1]

(ii) Draw, using a skeletal formula, a section of the polymer consisting of three repeat units.

[2]

(iii) A sample of cyclohexene is polymerised to a relative molecular mass of 2500, on average.

Calculate the number of complete cyclohexene units that polymerise in each polymer molecule on average. Show your working.

number of cyclohexene units = [1]

(b) Cyclohexene will react with bromine at room temperature.

(i) Write the equation for the reaction.

..... [1]

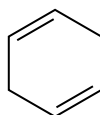
(ii) Show the structure of the product. Ignore any stereochemistry.

[1]

(iii) Give the name of the product.

..... [1]

- (c) Cyclohexa-1,4-diene also displays reactivity typical of alkenes. Its structure is shown.



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Draw the structures of all possible products of the reaction when one molecule of cyclohexa-1,4-diene completely reacts with two molecules of **hydrogen bromide**.

Ignore any stereochemistry.

[2]

- (d) When a **bromine** molecule adds across a C=C double bond the two bromine atoms bond to opposite faces of the molecule.

Draw all different possible products when one molecule of cyclohexa-1,4-diene reacts with two molecules of bromine.

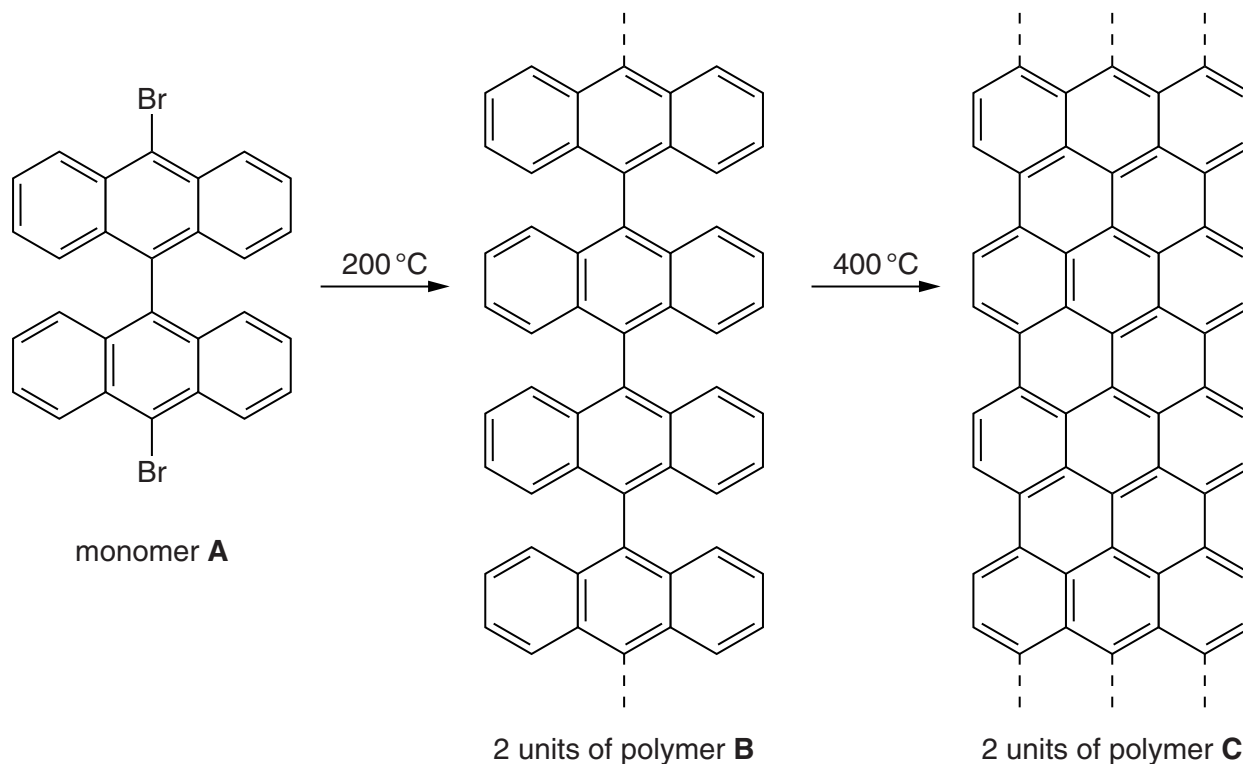
Show the six-membered carbon ring as a hexagon in the plane of the paper and use hashed and wedged bonds to bromine to show the stereochemistry.

[3]

(e) A graphene sheet is a layer of graphite.

A recent development has been the synthesis of graphene ribbons (reported in *Nature*, 2010). A reaction scheme is shown.

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(i) When monomer **A** is polymerised to make **B** there is also another product, **X**.

Give the molecular formula of **X**.

X is [1]

(ii) In the transformation of polymer **B** into polymer **C**, another product, **Y**, is produced.

Give the molecular formula of **Y**.

Y is [1]

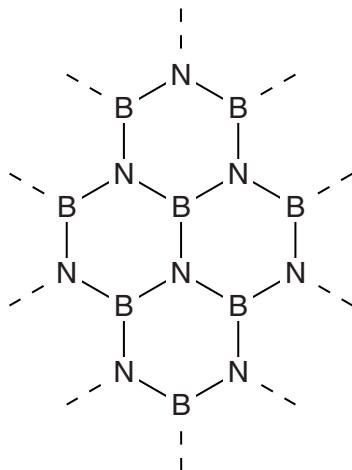
(iii) Deduce the number of moles of **X** and **Y** produced per mole of monomer **A**.

number of moles of **X** number of moles of **Y** [2]

- (iv) Boron nitride, BN, forms sheets similar to graphene except they contain dative covalent bonds as well as covalent bonds.

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Add all the possible dative covalent bonds between the atoms shown in the structure below.



[2]

- (v) Boron nitride can also form a giant covalent structure in which each atom has four single bonds.

Suggest the name of another substance which has this type of structure.

..... [1]

[Total: 19]

- 5 Grignard reagents are formed readily by iodoalkanes. This question concerns the conversion of a ketone, pentan-2-one, to a tertiary alcohol using a Grignard reagent.

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Table 5.1 summarises the volatilities and hazards of the reagents and the organic product.

Table 5.1

| substance | volatility | hazard |
|--------------------|--------------|--|
| iodoethane | moderate | flammable; toxic; respiratory irritant |
| ethoxyethane | high | flammable; harmful |
| magnesium turnings | non-volatile | flammable |
| pentan-2-one | low | flammable; harmful |
| product alcohol | very low | flammable; irritant |

- (a) (i) What are the **two** most important safety measures to guard against the hazards of these materials? You can assume that the experimenters are wearing gloves, eye protection and lab coats.

.....

 [2]

- (ii) The day before the experiment anhydrous calcium chloride is added to the iodoethane, sodium wire is added to the ethoxyethane and the glassware is left in an oven.

Suggest the single purpose of these three precautions.

.....
 [1]

Step one

1.50 g of magnesium turnings is added to a pear-shaped flask with an equimolar quantity of iodoethane and 20 cm³ of ethoxyethane.

Table 5.2 gives some physical properties of the reagents and the organic product.

Table 5.2

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| substance | formula | molar mass /g mol ⁻¹ | density /g cm ⁻³ | solubility in water | boiling point /°C |
|--------------------|--|---------------------------------|-----------------------------|---------------------|-------------------|
| iodoethane | C ₂ H ₅ I | 156 | 1.93 | slightly soluble | 72 |
| ethoxyethane | C ₂ H ₅ OC ₂ H ₅ | 74 | 0.713 | slightly soluble | 35 |
| magnesium turnings | Mg | 24.3 | 1.74 | insoluble | 1110 |
| pentan-2-one | C ₅ H ₁₀ O | 86 | 0.814 | slightly soluble | 102 |
| product alcohol | | | 0.823 | slightly soluble | 143 |

(b) (i) Calculate the amount, in mol, of magnesium used.

amount = mol [1]

(ii) Calculate the volume of iodoethane required to react with the magnesium.

volume = cm³ [2]

(iii) Suggest the role of the ethoxyethane.

..... [1]

Step two

A crystal of iodine is added to the mixture from **step one** to activate the magnesium, and this mixture is refluxed.

(c) (i) Suggest why elevated temperatures and long periods of time are required for reactions such as this.

.....

 [2]

(ii) Give the structural formula of the Grignard reagent that is the product of **step two**.

..... [1]

Step three

The mixture from **step two** is allowed to cool and 6.0 cm³ of pentan-2-one is added dropwise. The mixture is then gently heated under reflux.

- (d) (i) Draw the structure of the product of the reaction between the Grignard reagent and pentan-2-one which is present at the end of **step three**.

[1]

- (ii) Show with a calculation that the Grignard reagent is in excess. Assume that the reaction between magnesium and iodoethane in **step two** had 100% yield. Use your answer to **(b)(i)**.

[2]

Step four

The mixture from **step three** is cooled using an ice bath, and then 25 cm³ of 4 mol dm⁻³ hydrochloric acid is slowly added.

- (e) (i) Draw the structure of the tertiary alcohol produced by the reaction with dilute hydrochloric acid.

[1]

- (ii) What organic by-product results from the addition of the hydrochloric acid?

..... [1]

- (iii) Suggest why the mixture is cooled before adding the hydrochloric acid.

.....
..... [1]

Step five

The mixture from **step four** is added to a separating funnel. The lower aqueous layer is separated and shaken successively with two 10 cm³ portions of ethoxyethane, retaining the ethoxyethane extracts and combining them with the original ethoxyethane layer.

- (f) (i) Using the data in Table 5.2, explain why the ethoxyethane forms a layer above the aqueous layer.

.....
 [2]

- (ii) Suggest the purpose of shaking the aqueous layer with ethoxyethane.

.....
 [1]

Step six

The combined ethoxyethane layer is washed successively with 20 cm³ of

1. water,
2. saturated sodium hydrogencarbonate solution,
3. 1 mol dm⁻³ aqueous sodium thiosulfate,
4. saturated sodium chloride solution.

- (g) The water and the three aqueous solutions used to wash the ethoxyethane layer are each intended to remove a particular impurity, either by dissolving or by chemical reaction followed by dissolving.

Suggest the impurity removed in each step.

1. water [4]
2. saturated sodium hydrogencarbonate
3. sodium thiosulfate
4. saturated sodium chloride

Step seven

The ethoxyethane layer is allowed to stand over anhydrous magnesium sulfate.

(h) What is the purpose of the anhydrous magnesium sulfate?

..... [1]

(i) Using the data in Table 5.2, describe how you would obtain a pure sample of the product alcohol.

.....

.....

..... [2]

[Total: 26]

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