Cambridge Pre-U

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 2010**

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	
1	
2	
3	
4	
5	
6	
7	
8	
Total	

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

1 Table 1.1 gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

Table 1.1

name	formula	molar mass / g mol^{-1}	density / g cm^{-3}	$\Delta_c H^{\ominus}$ (298 K) / kJ mol^{-1}	$\Delta_f H^{\ominus}$ (298 K) / kJ mol^{-1}
methanol	CH_3OH	32	0.793[a]	–726.0	–239.1
ethanol	C_2H_5OH		0.789[a]	–1367.3	–277.1
liquid hydrogen	H_2	2	0.0711[b]		
octane	C_8H_{18}		0.703[a]		–250.0

[a] At 298 K and 1 bar pressure.
[b] At 20 K and 1 bar pressure.

(a) Insert the missing molar mass values in the table. [1]

(b) Calculate the density of **gaseous** hydrogen at 298 K and 1 bar pressure.
Assume 1 mol of any gas occupies 24 dm^3 at 298 K and 1 bar pressure. Give your answer in g cm^{-3}.

..... g cm^{-3} [1]

(c) What is the value of the standard enthalpy of formation of hydrogen **gas**, H_2?

.....[1]

(d) Use the information in Table 1.2 to give the value of the standard enthalpy of combustion of hydrogen.

Table 1.2

name	$\Delta_f H^{\ominus}$ (298 K) / kJ mol^{-1}
water	–285.8
carbon dioxide	–393.5

.....[1]

(e) Write down the chemical equation that represents the standard enthalpy of combustion of octane. Include state symbols.

.....[2]

(f) Use the enthalpy of formation data in Table 1.1 and Table 1.2 to calculate the standard enthalpy of combustion of octane.

For Examiner's Use

.....[3]

(g) An important property of a fuel, especially when the fuel has to be lifted (such as in aviation), is the energy released on combustion *per gram* of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298 K for methanol and hydrogen gas.

(i) methanol

.....

(ii) hydrogen gas

.....[2]

(h) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion *per cm^3* of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for ethanol and octane.

(i) ethanol

.....

(ii) octane

.....[2]

(i) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with the other fuels.

.....

.....[1]

[Total: 14]

[Turn over

2 The Intel® super-fast 45 nm Core 2 processors are based on Penryn technology. This involves the use, for the first time in computer chips, of an oxide of hafnium.

For Examiner's Use

(a) This oxide of hafnium has the formula HfO_2. Calculate the percentage of hafnium by mass in this oxide.

.....% [1]

(b) Table 2.1 provides the electronegativity data for O and Hf.

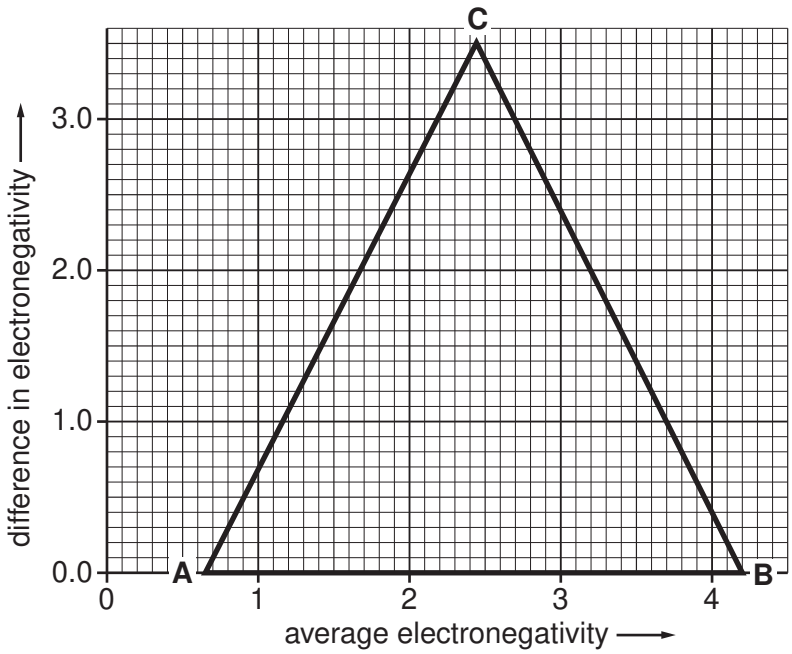
Table 2.1

element	electronegativity
O	3.61
Hf	1.16

Computer chips contain electrical conductors, semiconductors and insulators. On the van Arkel triangle mark the point corresponding to the oxide of hafnium and use this point to deduce its electrical properties. Ring the correct option.

The oxide of hafnium is

conductor **semiconductor** **insulator**



[2]

(c) Use your van Arkel plot to decide whether the oxide of hafnium is best described as ionic, covalent or metallic. Ring the correct option below.

The oxide of hafnium is best described as

ionic **covalent** **metallic** [1]

(d) Elemental hafnium has neutron-absorbing properties that are useful in nuclear reactors. It can be extracted from the oxide, HfO_2, by the following reactions.

For Examiner's Use

reaction 1 reaction with hydrochloric acid
reaction 2 reduction of a product of **reaction 1** with magnesium

Write balanced equations for these reactions.

equation for **reaction 1**

.....

equation for **reaction 2**

.....[2]

[Total: 6]

3 The compound whose bonding most resembles pure ionic bonding is caesium fluoride.

(a) Write down the formula of caesium fluoride.

.....[1]

(b) Draw a dot-cross diagram to show the bonding in caesium fluoride. Show outer electrons only.

[2]

(c) Explain why caesium fluoride is the compound whose bonding most closely resembles pure ionic.

.....

.....[1]

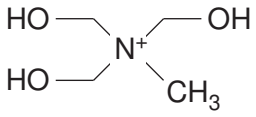
(d) Virtually all ionic compounds are solids at room temperature and pressure. However, researchers have designed ionic compounds whose ionic bonding is so weak that they are liquids under these conditions. Ionic liquids are often easy to handle as solvents as they are non-volatile; they have also recently found use in solar cells for this reason.

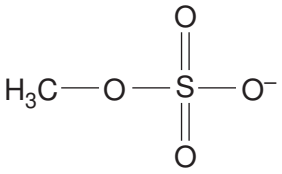
Explain what is meant by *non-volatile*.

.....[1]

(e) In the pure ionic bonding model, the ionic bond energy is proportional to the charge on each ion and inversely proportional to the distance between the charges, which are considered to be located at the centre of ions.

The structure of an ionic substance which is a liquid at room temperature and has been used in thermometers (reported in *Green Chemistry*, 2008) is shown below.





Suggest two features of these ions that account for the compound having such a low melting point.

1. .....

2. .....[1]

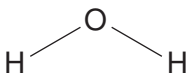
(f) Hydrogen-bonding is weaker than ionic or covalent bonding, but accounts for many important intermolecular attractions.

State two anomalous properties of water that are the result of hydrogen-bonding.

1. .....

2. .....[2]

(g) Draw a second molecule of water and a hydrogen-bond between the two molecules. Indicate the bond angle around the hydrogen atom involved in the hydrogen-bond. Include all relevant lone pairs and dipoles.



[3]

(h) Hydrogen-bonding is directional (i.e. a specific link between two atoms can be drawn) and has many applications in linking together molecules in an organised way. This linking has been put to use recently by researchers designing self-assembling surface networks for applications in nanotechnology (reported in *Nature*, 2008).

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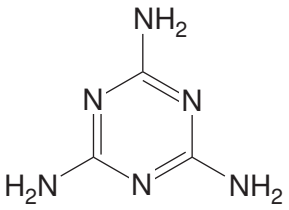
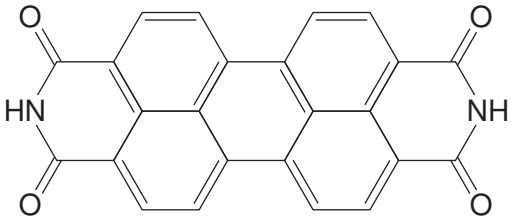


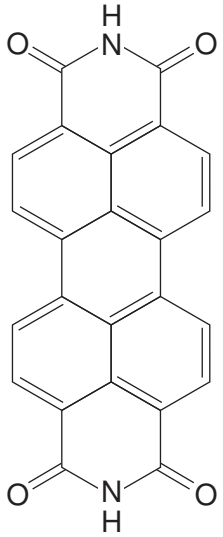
1,3,5-triazine-2,4,6-triamine (melamine)



perylene-3,4,9,10-tetracarboxylic diimide (PTCDI)

Fig. 3.1

The two molecules in Fig. 3.1 were chosen for the self-assembling network. A molecule of melamine and a molecule of PTCDI attach together strongly via three hydrogen bonds. Suggest where these **three** hydrogen-bonds form by drawing the melamine below in the correct orientation, with the hydrogen-bonds connecting the relevant atoms.



[2]

[Total: 13]

4 Chemists have recently found a way of making the strong, light-weight and thermally stable polymer, Kevlar®, to be antibacterial (reported in *Industrial & Engineering Chemistry Research*, 2008). This was achieved by coating it with another polymer, a fragment of which is shown in Fig. 4.1.

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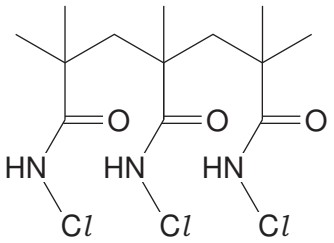

Fig. 4.1

(a) Draw the repeat unit of the polymer structure shown in Fig. 4.1.

[1]

(b) The polymer shown in Fig. 4.1 is made by the following reactions:

reaction 1	an addition polymerisation reaction of a monomer known as MAA
reaction 2	the substitution of a hydrogen atom in the polymer with a chlorine atom using bleach

Draw the structure of the monomer MAA.

[1]

(c) Not all the nitrogen atoms in the polymer end up bonded to a chlorine atom. The quantity of chlorine actually present in the polymer can be determined using **reactions 3**, **4** and **5**.

A known mass of polymer (written as XCONH–C*l*) is hydrolysed to convert the chlorine content of the polymer to chloric(I) acid, HOC*l*:

reaction 3 $XCONH–Cl + H_2O \longrightarrow XCONH_2 + HOCl$
(where X = remainder of polymer)

For Examiner's Use

The chlorine content is then 'converted' to iodine:

reaction 4 $HOCl + 2KI + H^+ \longrightarrow I_2 + KCl + H_2O + K^+$

The quantity of iodine is determined using a titration with sodium thiosulfate:

reaction 5 $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

(i) State the oxidation number of the chlorine in $HOCl$.

.....[1]

(ii) Given that **reaction 3** is a hydrolysis reaction, state the oxidation number of chlorine in the polymer.

.....[1]

(iii) Write ionic half equations for the oxidation and reduction processes in **reaction 4**.

oxidation .....

reduction .....[2]

In the analysis of a sample of polymer, 1.00 g of the polymer was hydrolysed (**reaction 3**).

The resulting mixture was reacted with excess acidified potassium iodide (**reaction 4**) and then made up to 100 cm^3 with distilled water.

10.0 cm^3 of this solution reacted with exactly 12.50 cm^3 of sodium thiosulfate solution of concentration 0.100 mol dm^{-3} (**reaction 5**).

(iv) Name a suitable indicator for this titration.

..... [1]

(v) Determine the amount (in moles) of sodium thiosulfate used in the titration.

..... mol [1]

(vi) Determine the amount (in moles) of iodine, I_2, in the titration.

..... mol [1]

(vii) Determine the mass of chlorine present in the sample of polymer.

.....[2]

[Total: 11]

For Examiner's Use

5 The scientific community was shocked at the recent claim of the discovery of an isotope of a new element with a mass number of 292 (published in *arXiv*, 2008): this is over 50 mass units higher than uranium, the heaviest known naturally-occurring element. There is a possibility that there is an 'island of stability' beyond the known Periodic Table at some very high atomic numbers.

(a) The authors of this claim suggested that the atomic number of the element is 122. How many neutrons are there in this isotope?

.....[1]

(b) If this element really exists then it will require a new block of the periodic table, corresponding to the occupancy of another type of subshell, beyond the *s*, *p*, *d* and *f*. This would be a *g* subshell, which is predicted to be found in the 5th shell of an atom, i.e. the 5g subshell.

Based upon the sequence of subshells in the Periodic Table, *s*, *p*, *d*, *f*, predict how many orbitals there are in a *g* subshell.

.....[1]

(c) Predict how many elements there would be in the first row of the *g*-block.

.....[1]

Below is a scheme of the 17 lowest energy subshells, which can be used to show the order in which the subshells are filled by electrons (the Aufbau principle).

1s 2s 3s 4s 5s 6s 7s

2p 3p 4p 5p 6p

3d 4d 5d

4f 5f

(d) List the order of filling subshells from 4p to 5d.

.....[1]

(e) The subshells in the scheme above are those that are occupied by the elements up to uranium. Add to the above diagram the next four subshells that would be expected to be filled. [1]

(f) Following the Aufbau principle, how many electrons in the 5g subshell would element 122 be expected to have?

.....[1]

[Total: 6]

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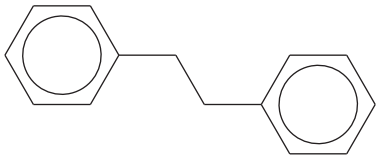
6 A survey in 2008 of the 24 million known organic compounds identified the most common structural motifs. The 3rd most popular shape (after the hexagon and pentagon) was based on the 1,2-diphenylethane molecule.

For Examiner's Use



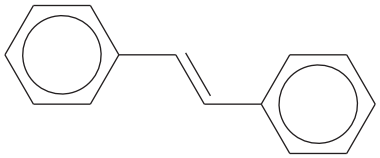
(a) How many signals would there be in the carbon-13 NMR spectrum of the 1,2-diphenylethane molecule?

.....[1]

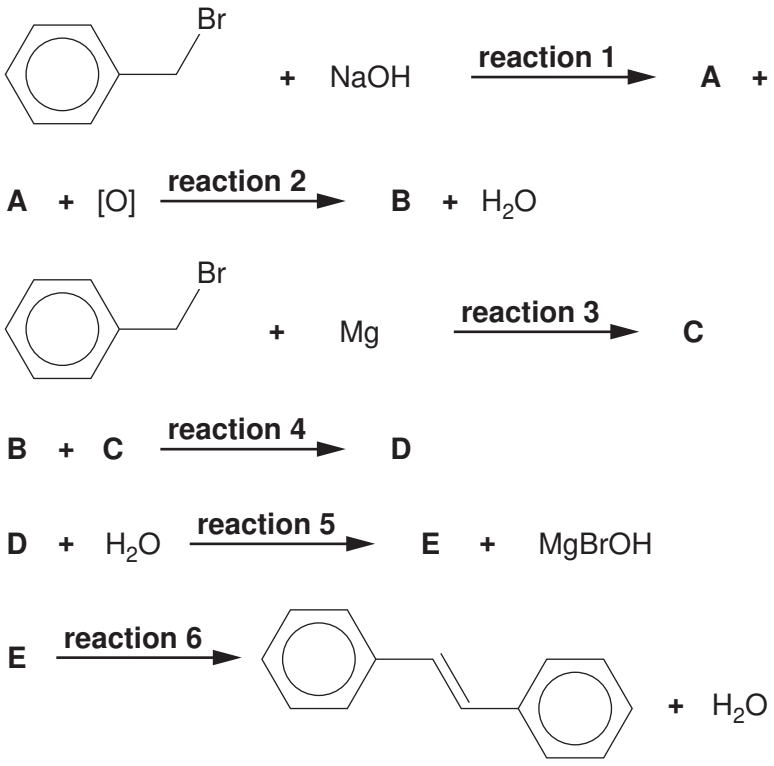
(b) If one of the hydrogen atoms on one of the phenyl groups of 1,2-diphenylethane is substituted with a chlorine atom, how many possible isomers would there be?

.....[1]

A closely related compound to 1,2-diphenylethane is 1,2-diphenylethene, commonly known as stilbene.



Stilbene can be synthesised from (bromomethyl)benzene according to the scheme below. The reactions are labelled **1** to **6** above the reaction arrows. The benzene ring does not take part in any of these reactions.



(c) **Reaction 2** is a partial oxidation. In the equation [O] represents the oxygen atom provided from some suitable reagents. Suggest such a reagent.

.....[1]

(d) What is the name of the **type** of compound produced in **reaction 3**?

.....[1]

(e) Classify the **type** of reaction in **1**, **5** and **6**.

reaction 1 .....[1]

reaction 5 .....[1]

reaction 6 .....[1]

(f) Draw the structures of unknowns **A** to **E**.

A

[1]

B

[1]

C

[1]

D

[1]

E

[1]

[Total: 12]

7 Nitrogen forms a variety of oxides and halides.

For Examiner's Use

(a) Nitrogen triiodide, NI_3, is an explosive that detonates with a snap even when only touched lightly. Given that the electronegativity value for nitrogen is 3.07 and for iodine is 2.36, indicate below the dipole in an N–I bond.

N–I

[1]

(b) (i) Nitrogen trifluoride, NF_3, can be prepared by reacting ammonia with fluorine. In this reaction the fluorine oxidises the nitrogen in ammonia while the oxidation number of hydrogen is unchanged.

Give the equation for this reaction.

.....[1]

(ii) Nitrogen trifluoride is used to etch silicon in microelectronics. It is decomposed to its elements and the fluorine is used to attack the silicon.

Give the equation for the decomposition of nitrogen trifluoride.

.....[1]

(iii) Nitrogen trifluoride is a molecule that has attracted controversy recently for its possible potent contribution to the greenhouse effect. Draw the dot-cross diagram of this molecule; only include outer electrons. State the shape and the bond angle.

shape .....

bond angle ..... [3]

(iv) Whereas nitrogen trifluoride is reasonably easy to handle, nitrogen trichloride is an extremely dangerous explosive. Suggest why nitrogen trifluoride is more stable than the other nitrogen trihalides.

.....

.....[1]

(c) N_2O_5 is a less well-known oxide of nitrogen.

For Examiner's Use

(i) N_2O_5 is the anhydride of nitric acid, which means that it reacts with water to produce the acid. Write an equation for N_2O_5 reacting with water.

.....[1]

(ii) N_2O_5 can be made by reacting nitric acid with a dehydrating agent such as phosphorus(V) oxide. Bearing in mind that phosphorus(V) oxide is the anhydride of phosphoric acid, H_3PO_4, write an equation for the reaction between nitric acid and phosphorus(V) oxide.

.....[2]

(iii) In the solid state N_2O_5 is an ionic compound. Given that N_2O_5 is sometimes known as 'nitronium nitrate' write the ionic formula representation of N_2O_5.

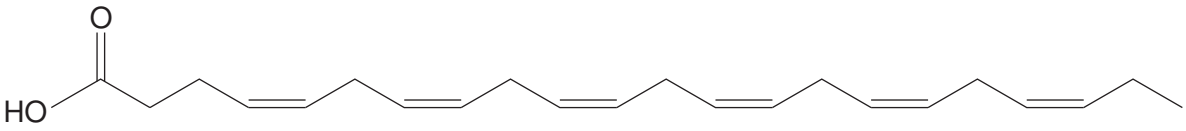
.....[1]

[Total: 11]

8 Evidence is accumulating that omega-3 oils help to protect us from schizophrenia and depression, and even improve learning and memory. Omega-3 oils are glyceryl esters of omega-3 fatty acids.

For Examiner's Use

One omega-3 fatty acid is cervonic acid.

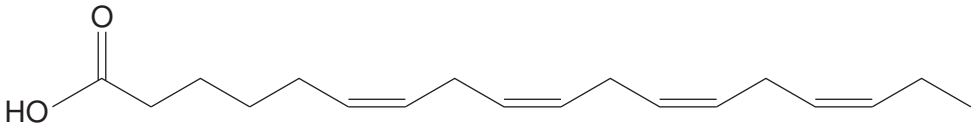


cervonic acid

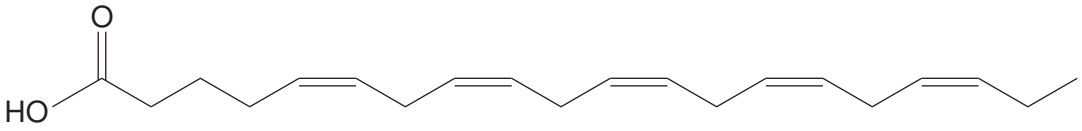
(a) Which configuration of the C=C double bonds is present in this molecule?

.....[1]

The systematic name of cervonic acid (ignoring geometric isomerism) is docosa-4,7,10,13,16,19-hexaenoic acid. "Docosa" indicates that there is a 22-carbon chain. The numbers indicate the carbon atom where the C=C double bonds start, counting from the carboxylic acid (–COOH) functional group. "Hexaen" indicates that there are six double bonds in the chain. Two other omega-3 fatty acids are stearidonic acid and timnodonic acid.



stearidonic acid



timnodonic acid

(b) "Octadeca" indicates that there is an 18-carbon chain. Write down the systematic name for stearidonic acid. Ignore the geometric isomerism.

.....[1]

(c) How many geometric isomers are there of timnodonic acid, including the molecule shown?

.....[1]

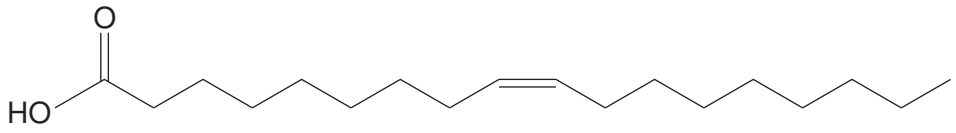
(d) What is the name of the intermolecular force that will operate between the hydrocarbon chains? Ring the correct option. [1]

permanent dipole-permanent dipole

hydrogen bonding

instantaneous dipole-induced dipole

(e) Another fatty acid that is believed to have beneficial health effects is oleic acid.



oleic acid

"Omega" is the **last** letter of the Greek alphabet. By comparing oleic acid, which is **not** an omega-3 acid, with the omega-3 fatty acids in part **(a)**, suggest what "omega-3" relates to in the structure of these oils and fatty acids.

.....

.....[1]

(f) It is possible to differentiate between different types of fatty acids and oils in the laboratory by measuring the degree of unsaturation in the hydrocarbon chains. Halogens react with alkenes in an addition reaction.

Draw the structure of the product when propene reacts with Br_2 and name it systematically.

structure
name

[2]

(g) Table 8.1 shows information about various fatty acids.

Table 8.1

fatty acid	molecular formula	molar mass / g mol^{-1}	number of C=C double bonds
cervonic acid	$C_{22}H_{32}O_2$	328	6
stearidonic acid	$C_{18}H_{28}O_2$	276	4
timnodonic acid	$C_{20}H_{30}O_2$	302	5
oleic acid		282	1

(i) The degree of unsaturation in a fatty acid is commonly expressed by the mass of iodine that reacts with 100.0 g of the acid. Use the information in Table 8.1 to calculate the mass of iodine that would react with 100.0 g of cervonic acid. Use an appropriate number of significant figures in your answer.

.....[2]

[Turn over

(ii) Write the molecular formula of oleic acid in Table 8.1. [1]

For Examiner's Use

(h) The interhalogen compound ICl also reacts with alkenes in an addition reaction. It is commonly used as *Wijs' reagent*, a 0.100 mol dm^{-3} solution of ICl in glacial ethanoic acid. ICl reacts faster with alkenes than the pure halogens and so can be used to determine volumetrically the unsaturation in fatty acids and oils.

(i) Suggest why ICl reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

.....

.....

.....[1]

For the volumetric determination, 30 minutes is required for the reaction between the fatty acid and Wijs' reagent to go to completion. A common solvent for Wijs' reagent and the fatty acids is 1,1,1-trichloroethane.

You are to design an experiment using Wijs' reagent to identify an unknown fatty acid that is one of cervonic acid, stearidonic acid or timnodonic acid. You have 0.100 g of the unknown acid dissolved in 20 cm^3 of 1,1,1-trichloroethane.

You should aim to produce data that is as accurate as possible using conventional laboratory methods.

You should use the information in Table 8.1.

(ii) The first part of the experiment involves adding an accurately known excess of Wijs' reagent to the fatty acid solution. The amount of Wijs' reagent should be at least 25% greater than the maximum amount that could be required to react with the fatty acid.

Work out a suitable volume of Wijs' reagent to add to the fatty acid solution and explain how you would add this quantity in the laboratory.

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For Examiner's Use

After this reaction is complete, 10 cm^3 of a 2.0 mol dm^{-3} aqueous solution of KI is added to the non-aqueous fatty acid solution to convert the excess $IC\ell$ to iodine, I_2.

$$IC\ell + KI \longrightarrow I_2 + KC\ell$$

This quantity of KI(aq) should be a large excess. Next, 100 cm^3 of deionised water is added to the mixture. The iodine is distributed between the aqueous and non-aqueous phases.

(iii) The second part of the experiment involves determining the amount of iodine generated by the excess $IC\ell$. This is done using a 0.100 mol dm^{-3} solution of sodium thiosulfate, $Na_2S_2O_3$.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

The whole mixture is reacted with sodium thiosulfate in one batch since the iodine is distributed between the phases. In this reaction considerable shaking is needed to ensure adequate mixing of the phases.

Write out a method for both parts of the experiment that a fellow student could follow. The original fatty acid solution comes in a small sample bottle that is nearly full. Include safety considerations.

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[Turn over

For Examiner's Use

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.....[8]

(iv) Explain how you would work out the identity of the fatty acid given the volume of thiosulfate obtained from the experiment.

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.....

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.....[4]

[Total: 27]