

Cambridge Pre-U

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CHEMISTRY
9791/02

Paper 2 Part A Written

October/November 2020
2 hours 15 minutes

You must answer on the question paper.

You will need: Data booklet


INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

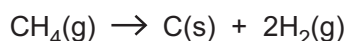
- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [].

For Examiner's Use	
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Total	

This syllabus is regulated for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

 This document has **20** pages. Blank pages are indicated.

- 1 The cracking of methane is carried out at high temperatures in the presence of a catalyst. The equation for this reaction is shown.



- (a) Data for this question are given.

standard enthalpy change of formation of methane	$-74.8 \text{ kJ mol}^{-1}$
standard enthalpy change of atomisation of carbon	$+716.7 \text{ kJ mol}^{-1}$
H–H bond energy	$+435.9 \text{ kJ mol}^{-1}$
standard enthalpy change of combustion of carbon	$-393.5 \text{ kJ mol}^{-1}$
standard enthalpy change of combustion of hydrogen	$-285.8 \text{ kJ mol}^{-1}$

- (i) Define the term *standard enthalpy change of formation*.

.....

.....

.....

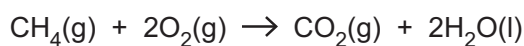
..... [3]

- (ii) Use the data to determine the C–H bond energy.

Give your answer to **one** decimal place.
Show your working.

$$E(\text{C–H}) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [3]$$

- (iii) Use the data to determine the standard enthalpy change of combustion of methane.
Show your working.



$$\Delta_c H^\ominus(\text{CH}_4) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [3]$$

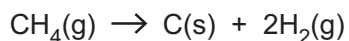
- (b) Chemists have developed a Ni-Fe-Co catalyst that lowers the temperature required for the cracking of methane.

Catalysts provide an alternative reaction route.

Why does the alternative reaction route allow the cracking of methane to operate at lower temperatures?

..... [1]

- (c) The cracking of methane is a source of hydrogen.



- (i) Calculate the atom economy of this reaction. Assume that hydrogen is the only utilised product.

atom economy = % [1]

- (ii) The hydrogen produced can be reacted with carbon monoxide to form methanol. Both hydrogen and methanol can be used as fuels.

Suggest the physical property of methanol that leads to many practical advantages of methanol over hydrogen as a fuel.

..... [1]

[Total: 12]

- 2 (a) Draw a dot-and-cross diagram for a molecule of hydrogen sulfide, H_2S .

Show outer electrons only.

[1]

- (b) (i) Predict the trend in the boiling points of the Group 16 hydrides from H_2S to H_2Se to H_2Te .

Explain your prediction in terms of the intermolecular forces involved.

.....

 [3]

- (ii) How does the boiling point of water compare with the boiling points of the other Group 16 hydrides?

..... [1]

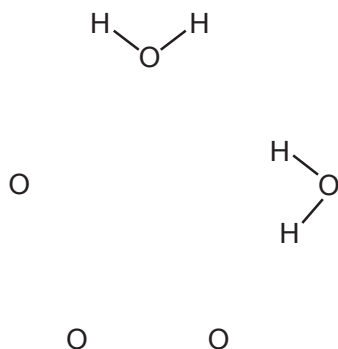
- (c) Chemists have found that the smallest droplet of water that is a 3-dimensional hydrogen-bonded network contains 6 water molecules (reported in *Science*, 2016).

Calculate the mass, in g, of this droplet.
 Show your working.

mass = g [2]

(d) A cluster of five water molecules forms a cyclic hydrogen-bonded network.

Complete the diagram below by drawing possible positions of O–H covalent bonds and hydrogen-bonds. Show the hydrogen-bonds with dashed lines.



[3]

[Total: 10]

3 Red phosphorus and white phosphorus are allotropes. Red phosphorus, P, is flammable and is used in emergency flares. White phosphorus has a molecular structure.

(a) Write the equation for the combustion of red phosphorus in excess oxygen.

..... [1]

(b) Define the term *allotrope*.

.....

 [2]

(c) White phosphorus has been used to create smoke screens.

(i) State the molecular formula of white phosphorus.

..... [1]

(ii) Draw the 3-dimensional structure of a molecule of white phosphorus.

[1]

(d) A collaboration of European chemists suggested in 2016 that a phosphorus nitride, P_3N_5 , is a safer alternative to red phosphorus in emergency flares (published in *Angewandte Chemie International Edition*).

(i) P_3N_5 may be made by reacting phosphorus pentachloride with ammonium chloride. Construct the equation for this reaction.

..... [2]

(ii) State the trend, if any, in electronegativity on descending Group 15.

..... [1]

(iii) Give the oxidation numbers of phosphorus and nitrogen in P_3N_5 .

P N [1]

(iv) P_3N_5 undergoes complete hydrolysis when reacted with pressurised liquid water at 250°C . Construct the equation for this reaction.

..... [2]

- (v) When heated strongly, 1.00g of $\text{P}_3\text{N}_5(\text{s})$ decomposes to give an equimolar quantity of a different solid nitride of phosphorus. An unreactive gas is also produced which has a volume at room temperature and pressure of 147 cm^3 .

Use this information to work out:

- the amount, in mol, of P_3N_5 that reacts
- the amount, in mol, of gas produced
- a balanced equation for the reaction
- the empirical formula for the phosphorus nitride produced.

[4]

[Total: 15]

4 Halogens and halides undergo many redox reactions.

(a) State and explain the trend, if any, in oxidising power of halogens as the group is descended.

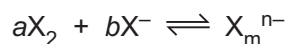
.....

 [4]

(b) Which halide ion has the greatest reducing power?

..... [1]

(c) Halogens, X_2 , and halides, X^- , can react together to form polyhalide ions, X_m^{n-} . These three species are in equilibrium.



(i) Express m and n in terms of a and b .

$m = \dots\dots\dots$ $n = \dots\dots\dots$ [1]

(ii) The most well-known polyhalide ion is the triiodide ion, I_3^- , which exists in equilibrium with iodine and iodide ions, as shown in the equation.

Explain why iodine has a much higher solubility in aqueous potassium iodide than it does in pure water.

.....

 [2]

(d) The concentration of aqueous iodine is commonly determined using sodium thiosulfate.

Write the equation for the reaction between iodine and sodium thiosulfate.

..... [1]

(e) It is possible to synthesise interhalogen ions such as ICl_4^- .

Deduce the shape of the ICl_4^- ion.

Explain why it has this shape.

shape

explanation

.....

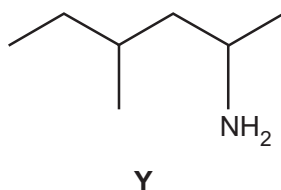
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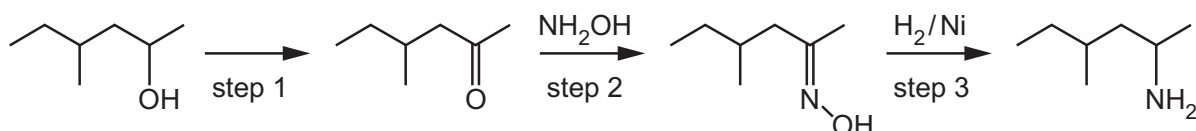
..... [3]

[Total: 12]

- 5 Compound Y is a banned performance-enhancing stimulant. Usain Bolt lost one of his three gold medals from the 2008 Olympics because one of the relay team later tested positive for this drug.



Compound Y may be prepared by the following three-step synthesis. Other products of each step are not shown.



- (a) (i) Give the molecular formula and the systematic name of the organic starting material in step 1.

molecular formula

systematic name [2]

- (ii) Suggest the reagent(s) necessary to carry out step 1.

..... [2]

- (iii) What type of reaction does the organic substance undergo in step 1?

..... [1]

- (b) (i) Deduce the identity of the other product in step 2.

..... [1]

- (ii) What type of reaction is step 2?

..... [1]

- (iii) During step 2 an intermediate is formed. Suggest the structure of this intermediate.

[1]

- (c) (i) Step 3 is a reduction. Use the functional group levels of the carbon attached to nitrogen to explain why it is a reduction.

.....
 [1]

- (ii) Suggest the identity of the other product in step 3.

..... [1]

- (d) A student suggested that compound **Y** could be prepared directly from the starting material in step 1 by reacting it with ammonia, NH_3 .

- (i) State the property of ammonia that makes this a reasonable suggestion.

..... [1]

- (ii) A second student suggested that the first student's proposal might work better if the reaction with ammonia was carried out in the presence of acid.

Explain why the addition of acid does not enable ammonia to substitute the $-\text{OH}$ group in this proposed reaction.

.....
 [1]

- (e) Compound **Y** has low solubility in water but much higher solubility in dilute hydrochloric acid.

- (i) State which intermolecular interaction takes place between **Y** and water that leads to some solubility.

..... [1]

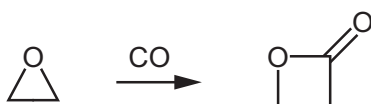
- (ii) Like ammonia, amines are bases. Compound **Y** reacts with dilute hydrochloric acid to form a substance with high solubility in water.

Draw the structure of this substance.


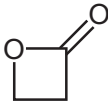
[1]

[Total: 14]

- 6 In 2016 a US chemical company developed a catalytic process for reactions involving cyclic organic compounds. One such reaction is shown.

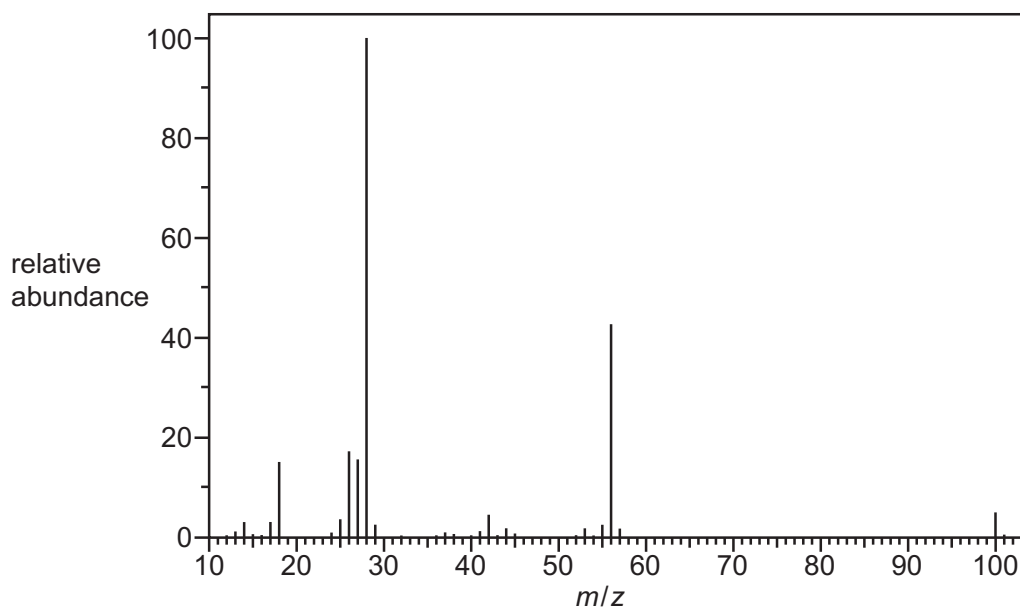


- (a) Complete the table to show the number of carbon environments and the number of hydrogen environments in each molecule.

molecule	number of carbon environments	number of hydrogen environments
		
		

[3]

- (b) The same company also developed molecule **A**. The mass spectrum of **A** is shown.



A was found to have the following composition by mass: 48% carbon, 4% hydrogen, 48% oxygen.

- (i) Determine the empirical formula of **A**.

..... [1]

(ii) Determine the molecular formula of **A**.

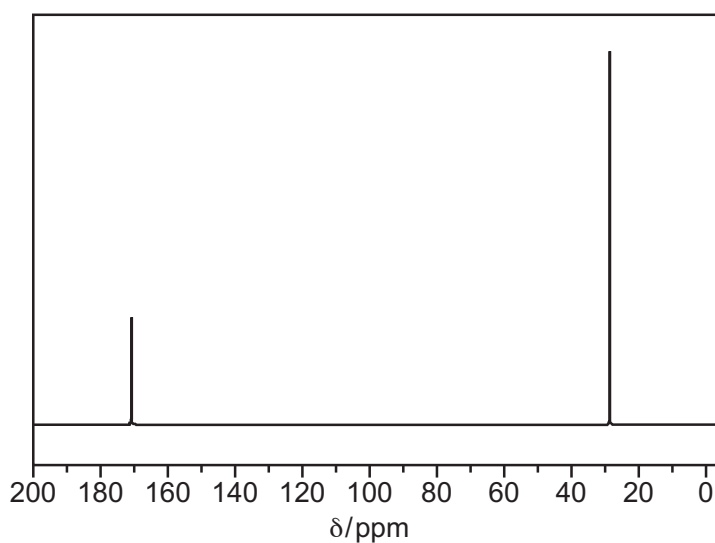
..... [1]

(iii) Suggest the formula of the fragments causing each of the signals at the following m/z values.

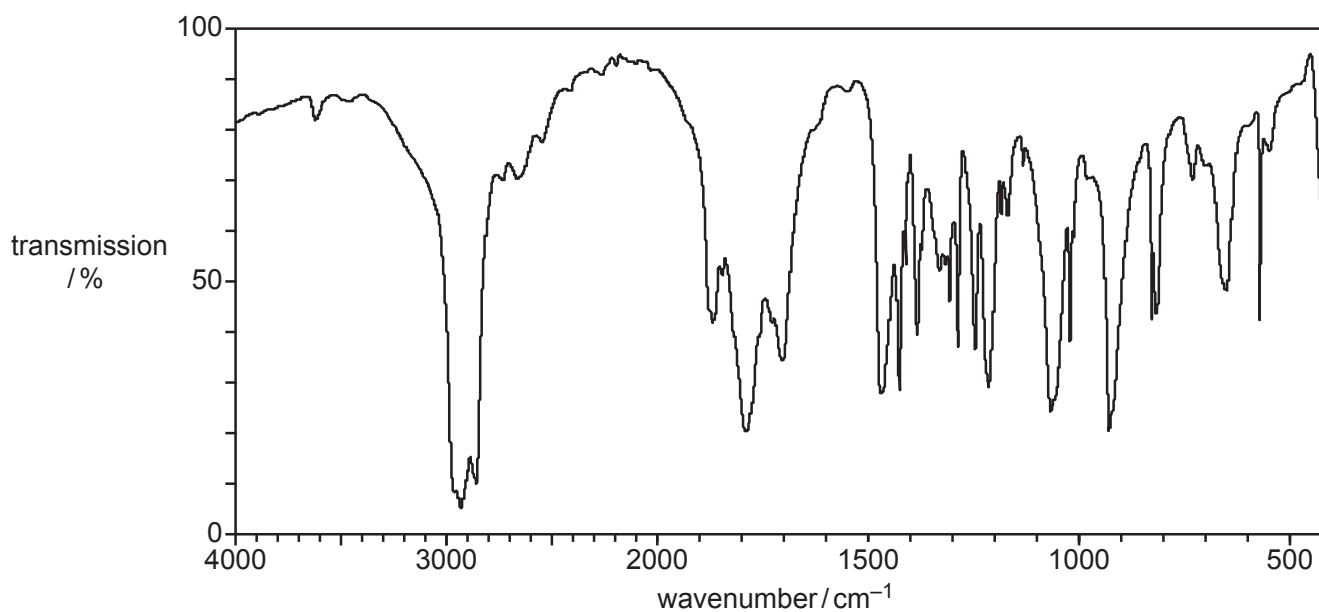
$m/z = 28$ $m/z = 56$ [2]

(c) The carbon-13 NMR and infra-red spectra of **A** are given.

^{13}C NMR



IR



- (i) Use the carbon-13 NMR spectrum to identify the carbon environments in **A**.

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

- (ii) There is only one hydrogen environment in **A**.

Suggest the structure of **A**.

[2]

[Total: 11]

- 7 Thionyl chloride, SOCl_2 , is a liquid at room temperature which readily reacts with water and alcohols. Like PCl_5 , SOCl_2 can be used to substitute an $-\text{OH}$ group of an alcohol with a $-\text{Cl}$ group. Hexan-1-ol reacts with SOCl_2 to form 1-chlorohexane as shown.



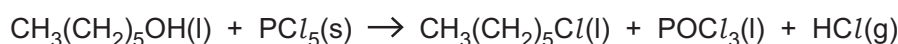
A student carries out the following procedure to prepare pure 1-chlorohexane, starting from hexan-1-ol.

- step 1 Distil approximately 50 cm^3 of SOCl_2 and collect the distillate.
- step 2 Place 22 cm^3 , an excess, of the distillate into a flask and very slowly add 10.20 g of hexan-1-ol dropwise.
- step 3 Place the condenser into the top of the flask and insert an open-ended tube loosely packed with anhydrous calcium chloride granules into the top of the condenser. Heat the mixture under reflux for approximately 60 minutes.
- step 4 Set up the apparatus for distillation and heat. Collect the product which distils between 131°C and 135°C .
- step 5 Place the product into a suitable piece of apparatus and, in turn, wash the product with:
- distilled water
 - aqueous sodium carbonate
 - distilled water (for a second time).
- step 6 Transfer the product to a conical flask. Add anhydrous magnesium sulfate, seal the flask and leave for several hours.

Some properties and some hazards of relevant materials are given.

substance	M_r	density / g cm^{-3}	boiling point / $^\circ\text{C}$	hazards
hexan-1-ol, $\text{CH}_3(\text{CH}_2)_5\text{OH}$	102.0	0.820	158	flammable, skin irritant
thionyl chloride, SOCl_2	119.1	1.66	79	corrosive, dangerous in contact with water
1-chlorohexane, $\text{CH}_3(\text{CH}_2)_5\text{Cl}$	120.5	0.879	135	flammable, skin irritant

- (a) SOCl_2 and PCl_5 can both be used to chlorinate alcohols. They are similarly reactive, costly and difficult to handle safely. The equation for the reaction between hexan-1-ol and PCl_5 is shown.



- (i) Suggest an advantage of using SOCl_2 instead of PCl_5 .

.....
 [1]

- (ii) Suggest why thionyl chloride in particular requires distillation before use. Include an equation in your answer.

.....

 equation [2]

- (iii) In addition to wearing a lab coat and eye protection, give **two** safety precautions that should be taken by the student during the procedure.

.....
 [2]

- (iv) The SOCl_2 used in step 2 is in excess. Calculate by how many moles SOCl_2 is in excess. Show your working.

..... mol [3]

- (b) Suggest why hexan-1-ol is added very slowly and dropwise to SOCl_2 in step 2.

.....
 [1]

- (c) The student did not use a solvent in the procedure. Another student decided to do this preparation using a solvent.

- (i) Suggest an advantage of using a solvent in this reaction.

.....
 [1]

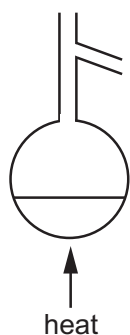
- (ii) Suggest a suitable solvent that could be used for this reaction.

..... [1]

(d) Suggest why an open-ended tube loosely packed with anhydrous calcium chloride granules is used in step 3.

.....
 [1]

(e) Complete the diagram of the apparatus needed for step 4.



[4]

(f) Step 5 involves three washing stages.

(i) Which apparatus should be used to carry out step 5?

..... [1]

(ii) Suggest which chemicals are removed in each of these washing stages.

first washing with distilled water

washing with aqueous sodium carbonate

second washing with distilled water

[3]

(g) Anhydrous magnesium sulfate is added in step 6.

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

..... [1]

(ii) How is the appearance of the anhydrous magnesium sulfate likely to change after being mixed with the product?

..... [1]

- (h) Identify **two** further steps in the correct order which are needed to obtain pure 1-chlorohexane from the conical flask after step 6.

step 7

step 8

[2]

- (i) The student obtained 6.60 g of pure 1-chlorohexane. Calculate the percentage yield of the reaction.
Show your working.

percentage yield % [2]

[Total: 26]

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