Cambridge Pre-U	**Cambridge Assessment International Education** Cambridge Pre-U Certificate

CANDIDATE NAME

CENTRE NUMBER

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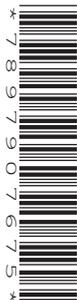
CHEMISTRY (PRINCIPAL)   **9791/02**

Paper 2 Part A Written   **May/June 2019**

                                         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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, 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, if you do not use appropriate units or if you do not give your answer to appropriate significant figures.
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	
Total	

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

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

Cambridge Assessment
International Education

[Turn over

1   The reaction of alkali metals with water is a common chemical demonstration. Alkali metals react with water as shown in the equation, where M represents the alkali metal.

$$M(s) \ + \ H_2O(l) \ \rightarrow \ MOH(aq) \ + \ \tfrac{1}{2}H_2(g)$$
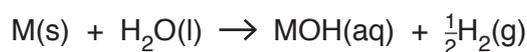
For each of the alkali metals the table shows:

- the standard enthalpy change at 298 K of atomisation, $\Delta_{at}H^{\ominus}$
- the standard enthalpy change at 298 K of hydration, $\Delta_{hyd}H^{\ominus}$
- the first ionisation energy, $\Delta_{IE1}H^{\ominus}$
- the standard enthalpy change at 298 K of reaction with water as given in the equation, $\Delta_rH^{\ominus}$.

alkali metal	$\Delta_{at}H^{\ominus}$ (M) /kJ mol^{-1}	$\Delta_{hyd}H^{\ominus}$ (M$^+$) /kJ mol^{-1}	$\Delta_{IE1}H^{\ominus}$ (M) /kJ mol^{-1}	$\Delta_rH^{\ominus}$ (M) /kJ mol^{-1}
Li	+160	−519	+519	−222
Na	+109	−406	+495	−184
K	+90	−322	+418	−196
Rb	+86	−301	+402	−195
Cs	+79	−276	+376	−203

(a) Define the enthalpy change of hydration, $\Delta_{hyd}H$.

   ....

   ....

   .... [3]

(b) (i) Write the equation for the first ionisation energy of M. Include state symbols.

   .... [1]

   (ii) Explain the trend in the first ionisation energy down the group.

   ....

   ....

   ....

   .... [3]

(c) (i) Calculate the enthalpy change for $Na(s) \rightarrow Na^+(aq) + e^-$.

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

(ii) Use the information in the table and your answer to **(c)(i)** to help you draw an enthalpy cycle for the reaction $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$. Show state symbols.

Calculate the enthalpy change per mole of hydrogen gas produced.

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

(d) There is particular interest in lithium as an energy source due to its low density.

Calculate the enthalpy change of reaction of lithium with water per gram of lithium.

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

(e) Lithium and sodium are both being considered for batteries for use on Mars and Venus as both planets have atmospheres consisting of over 95% carbon dioxide.

When used in these batteries, each metal undergoes a redox reaction with carbon dioxide as shown, where M represents the alkali metal.

$$4M + 3CO_2 \rightarrow 2M_2CO_3 + C$$
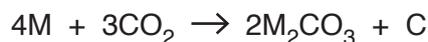
Use relevant oxidation numbers to explain which atoms have been oxidised and which atoms have been reduced.

atom oxidised .... change in oxidation number from .... to ....

atom reduced .... change in oxidation number from .... to ....

[2]

(f) Alkali metal carbonates undergo thermal decomposition in a similar way to Group 2 carbonates, though much higher temperatures are generally required.

(i) Write an equation for the thermal decomposition of an alkali metal carbonate, M_2CO_3.

.... [1]

(ii) Suggest why an alkali metal carbonate is more resistant to thermal decomposition than the Group 2 carbonate in the same period.

....

....

....

.... [3]

(iii) Only one alkali metal carbonate decomposes in a Bunsen burner flame. Suggest which one it is and the reason why.

....

.... [1]

[Total: 20]

2 Engines that drive modern torpedoes may use the Stored Chemical Energy Propulsion System, SCEPS, which utilises heat from the reaction of lithium with a flow of sulfur hexafluoride, SF_6, gas. This heat converts water to steam, driving the turbine that propels the torpedo.

(a) (i) Other than its reaction with lithium, SF_6 is normally considered to be chemically unreactive. Suggest, in terms of bond energy and dipoles, why the molecule is normally unreactive.

....

....

.... [2]

(ii) Selenium hexafluoride, SeF_6, has the same molecular shape as SF_6. The boiling point of SeF_6 is $–47\,°C$; the boiling point of SF_6 is $–64\,°C$.

Explain why SeF_6 has a higher boiling point than SF_6.

....

....

.... [2]

(b) (i) Alkali metal fluorides are considered to be ionic. Which alkali metal fluoride is generally considered to be the most ionic?

.... [1]

(ii) Draw a dot-cross diagram of LiF, showing **all** of the electrons.

Use dots for Li and crosses for F.

[2]

(c) The equation for the SCEPS reaction and some relevant standard enthalpy changes of formation are given.

$$8Li(s) + SF_6(g) \rightarrow Li_2S(s) + 6LiF(s) \quad \Delta_rH^\ominus = -2934\,kJ\,mol^{-1}$$

	SF_6	Li_2S
$\Delta_fH^\ominus$ (298 K)/kJ mol^{-1}	−1209	−447

(i) Calculate the standard enthalpy change of formation of LiF.

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

(ii) Exothermic reactions involving gases in a closed system sometimes run the risk of high pressures blowing apart the reaction vessel.

Why is that not a problem with this exothermic reaction?

....

.... [1]

(iii) Sketch a simple reaction profile energy diagram for the reaction. Label the activation energy and the enthalpy change of reaction with directional arrows.

The diagram does not need to be drawn to scale. Assume the reaction consists of just a single step.

[3]

(iv) In practice the lithium metal is in the liquid state while the reaction is proceeding in the torpedo. The standard enthalpy change of fusion of lithium is $3.00\,kJ\,mol^{-1}$.

Calculate the enthalpy change for the reaction when lithium is in the liquid state.

[The standard enthalpy change of fusion is the change in enthalpy required for the conversion of one mole of a solid to a liquid.]

.... $kJ\,mol^{-1}$ [2]

(d) In a torpedo, gaseous SF_6 reacts with lithium at a rate equivalent to $1.8\,dm^3\,s^{-1}$ at r.t.p.

Calculate the power in watts (W) of the heat output of this reaction.

Use $-2934\,kJ\,mol^{-1}$ for the enthalpy change of the reaction.

$[1\,W = 1\,J\,s^{-1}]$

....W [3]

[Total: 19]

3 Some laboratory glassware is made from Pyrex®, a borosilicate glass introduced in 1908 that can tolerate rapid changes in temperature. It is a mixture of four oxides: SiO_2, B_2O_3, Na_2O and Al_2O_3.

(a) (i) Calculate the percentage of silicon by mass in SiO_2.

Give your answer to 1 decimal place.

....% [1]

(ii) Elemental analysis of Pyrex® revealed the following compositions by mass.

element	% composition by mass in Pyrex®
Al	1.22
B	4.03
Na	2.97
Si	

Determine the percentage composition by mass of Al_2O_3 in Pyrex®. The relative formula mass of Al_2O_3 is 102.0.

....% [2]

(iii) Use your answers to **(i)** and **(ii)** and the information in the following table to determine the percentage composition by mass of oxygen in Pyrex®.

oxide	% by mass of the oxide in Pyrex®
Al_2O_3	
B_2O_3	13.0
Na_2O	4.00
SiO_2	

If you were unable to calculate answers to **(i)** and **(ii)**, use:

- 44.0% Si in SiO_2 by mass
- 3.00% Al_2O_3 in Pyrex® by mass.

These are **not** the correct answers.

....% [2]

(b) Use the electronegativity values in the table to determine which of these oxides in Pyrex® has the most covalent character.

atom	Na	Al	Si	B	O
electronegativity	0.9	1.6	1.9	2.1	3.6

The most covalent oxide is .... oxide. [1]

(c) The SiO_2 in laboratory glassware is attacked by molten sodium hydroxide.

(i) Write a balanced equation for this reaction.

.... [1]

(ii) What chemical property of silicon dioxide does this reaction show?

.... [1]

[Total: 8]

4 Many halogenoalkanes undergo nucleophilic substitution with hydroxide ions.

(a) Draw a dot-cross diagram for the hydroxide ion. Show outer electrons only.

[2]

(b) (i) Why is the carbon atom in the C–Cl bond susceptible to nucleophilic attack?

....

.... [1]

(ii) Write an equation to show the nucleophilic substitution reaction between chloroethane and sodium hydroxide. Use structural formulae.

.... [1]

(c) The ethoxide ion, $C_2H_5O^-$, behaves as a nucleophile in a similar way to OH^- ions. It reacts with many halogenoalkanes.

(i) Which are the highest energy electrons of the oxygen atom in an ethoxide ion?

.... [1]

(ii) The nucleophilic substitution reaction between chloroethane and sodium ethoxide gives an ether, ethoxyethane.

$$CH_3CH_2Cl + CH_3CH_2ONa \rightarrow CH_3CH_2OCH_2CH_3 + NaCl$$
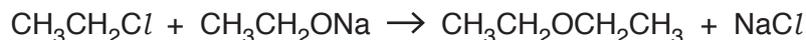
Calculate the atom economy of this reaction. Assume that only the ether product is utilised.

....% [1]

(iii) Suggest why fluoroethane does not undergo these substitution reactions.

....

.... [1]

(d) Using these nucleophilic substitution reactions it is possible to create cyclic ethers.
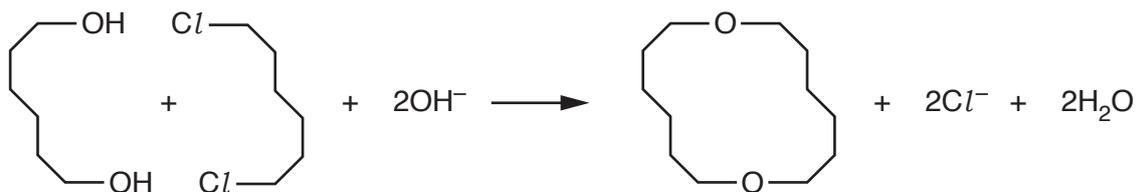
Suggest the purpose of the hydroxide in this reaction.

.. [1]

(e) Charles Pedersen was awarded the Nobel prize for using these reactions to synthesise a family of cyclic ethers called 'crown ethers'. Crown ethers attracted great interest because their cavities could bind other species.

One example of a crown ether is 12-crown-4, shown below. Its systematic name is 1,4,7,10-tetraoxacyclododecane.
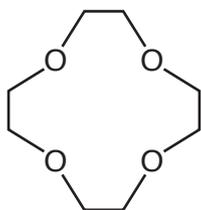
An example of the synthesis of a different crown ether is given.
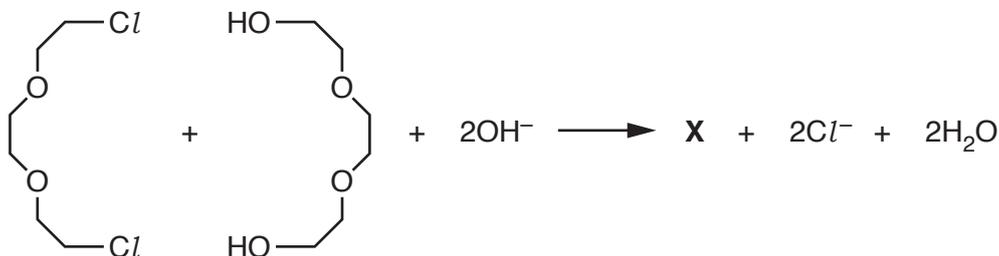
(i) Deduce the molecular formula of crown ether **X**.

molecular formula .... [1]

(ii) The crown ether, **X**, is known as 18-crown-6; its systematic name is 1,4,7,10,13,16-hexaoxacyclooctadecane. Suggest the structure of cyclic ether **X**.

[1]

(iii) 15-crown-5 can be made by the reaction shown.

$$C_6H_{12}O_2Cl_2 \;+\; C_4H_{10}O_3 \;+\; 2OH^- \longrightarrow 2Cl^- \;+\; 2H_2O \;+$$
$$\quad\;\;\textbf{Y} \qquad\qquad \textbf{Z}$$
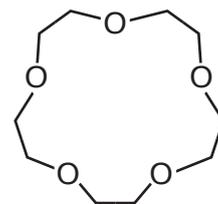
Draw the structures of starting materials **Y** and **Z**.

Y	Z

[2]

(iv) How many signals are there in the carbon-13 NMR spectrum of 15-crown-5?

.... [1]

(v) Complete the table by deducing the systematic name for 15-crown-5.

crown ether	systematic name
12-crown-4	1,4,7,10-tetraoxacyclododecane
15-crown-5	
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane

[1]

(vi) The relative yield of crown ether in these reactions is found to be dependent on which cation is present in the alkali used, as shown in the table.

alkali	yield of 15-crown-5	yield of 18-crown-6
NaOH	relatively high	relatively low
KOH	relatively low	relatively high

Suggest why each alkali is better suited to the synthesis of the different crown ethers.

....

.... [1]

(f) The structures given in part **(e)** for 12-crown-4 and 15-crown-5 show that the members of this family of crown ethers share the same empirical formula.

(i) Deduce this empirical formula. .... [1]

(ii) It is possible to make crown ethers directly from a monomer. The molecular formula of the monomer is the same as the empirical formula of the crown ethers.

The monomer contains only single bonds. Suggest its structure.

[1]

(g) If 2-chlorobutane is heated with sodium hydroxide, three isomeric products with molecular formula C_4H_8 could be formed in an elimination reaction.

(i) Write an equation using molecular formulae to describe this reaction.

.... [1]

(ii) State two reaction conditions that would favour an elimination reaction over a substitution reaction.

1. ....

2. ....
[2]

(iii) Draw displayed structures of the three possible products of this reaction and name each one.

| 1	2	3
name	name	name

[3]

[Total: 23]

5 Compound **C** was extracted from a badger secretion used to mark its territory. Elemental and qualitative analysis revealed the following information.

test	result
elemental analysis	empirical formula is C_3H_6O
bromine water	no change
2,4-DNPH (Brady's reagent)	no change
acidified dichromate(VI)	solution turned green

The mass spectrum, infrared spectrum and ^{13}C NMR spectrum are given.

mass spectrum
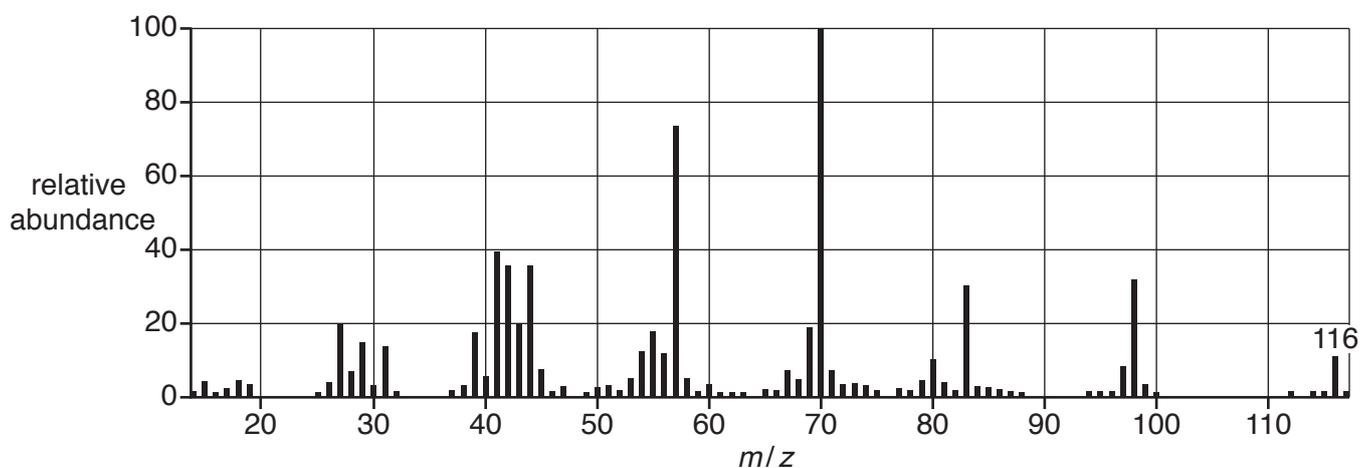
IR spectrum
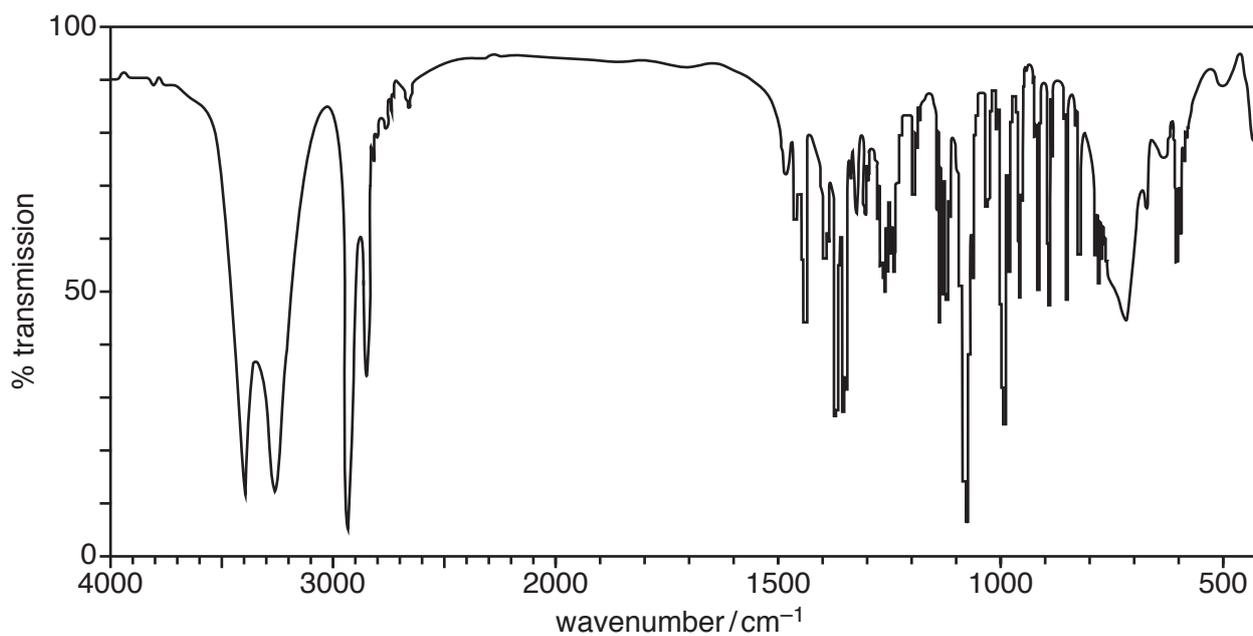
^{13}C NMR spectrum
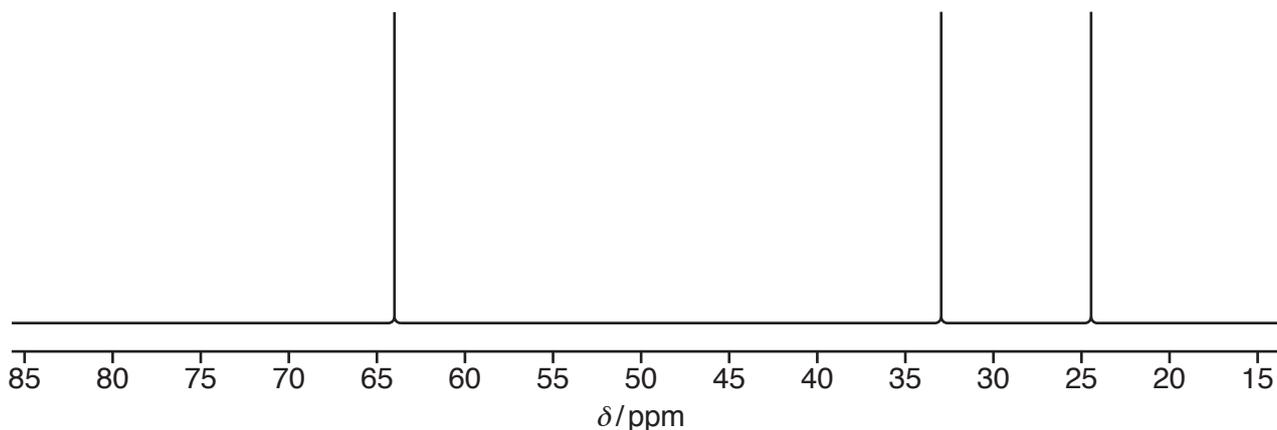
(a) Deduce the molecular formula of compound **C**.

molecular formula .... [1]

(b) (i) The two tests that showed no change prove the absence of two functional groups in compound **C**. Identify these two functional groups.

....

.... [2]

(ii) What additional information does the result of the test with acidified dichromate(VI) indicate about compound **C**?

....

.... [1]

(c) What does the ^{13}C NMR spectrum suggest about the individual carbon environments in compound **C**?

....

....

.... [2]

**(d)** Suggest the structure of compound **C**.

[2]

[Total: 8]

6 Triiodomethane, CHI_3, is a yellow crystalline solid with a melting point of 119 °C. It is insoluble in water. Its trivial name is iodoform. It is made when any molecule containing the

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-$$ group is in the presence of aqueous iodine and aqueous sodium hydroxide. The remainder of the organic molecule is given the symbol R in the equation, where R can be H or an alkyl group.

$$CH_3COR + 3I_2 + 4NaOH \rightarrow CHI_3 + RCOONa + 3NaI + 3H_2O$$

A student researched instructions for making iodoform and followed a procedure in which aqueous iodine is not added as a reagent. The first four steps are shown.

step 1 Add 1.10 cm³ of ethanal into a 250 cm³ conical flask containing 10.0 g of potassium iodide, 25 cm³ of water and 10 cm³ of 2.0 mol dm⁻³ aqueous sodium hydroxide.

step 2 Slowly add, with swirling, an excess of 150 g dm⁻³ aqueous sodium chlorate(I), NaClO(aq). Allow to stand for 5 minutes.

step 3 Filter under reduced pressure using a Buchner funnel. Rinse the residue with distilled water. Leave under suction for a further 5 minutes.

step 4 Collect the residue and dissolve it in a minimum quantity of hot ethanol. Then allow the mixture to cool to room temperature.

The table gives the relative formula masses and hazards of the chemicals involved.

compound	relative formula mass	hazards
ethanal	44.0	flammable, serious health hazard
iodoform	393.7	moderate health hazard
potassium iodide	166.0	low hazard
sodium hydroxide	40.0	corrosive
sodium chlorate(I)	74.5	corrosive
ethanol	46.0	flammable

(a) In this procedure to make iodoform, no iodine is added as a reagent. Suggest why, in **step 2**, adding the sodium chlorate(I) to the mixture from **step 1** generates iodine.

....

.... [1]

(b) Suggest the purpose of:

(i) leaving the mixture to stand for 5 minutes in **step 2**

....

.... [1]

(ii) rinsing the residue with distilled water in **step 3**

....

.... [1]

(iii) leaving under suction for a further 5 minutes in **step 3**.

....

.... [1]

(c) What is the name of the technique described in **step 4**?

.... [1]

(d) (i) What is the final practical step necessary to obtain a sample of pure iodoform?

.... [1]

(ii) Apart from spectral techniques, what could the student do to check the purity of the product?

.... [1]

(iii) In which step is the sodium methanoate by-product removed?

.... [1]

(e) The student wears eye protection and a lab coat. Based on the information in the table, what additional precaution should be taken:

(i) when handling sodium hydroxide and sodium chlorate(I)

.... [1]

(ii) when heating ethanol?

.... [1]

(f) (i) The limiting reagent in this procedure is ethanal. It has a density of $0.788\,g\,cm^{-3}$.

Calculate the maximum mass of iodoform that could be obtained.

Give your answer to 3 significant figures.

....g [3]

(ii) In **step 2**, 0.0700 mol of sodium chlorate(I) is added to make the excess of aqueous iodine.

Calculate the volume of the 150 g dm^{-3} sodium chlorate(I) solution required.

Give your answer to the nearest cm^3.

....cm^3 [2]

(g) The student suspected that there were impurities and ran an infrared spectrum of the product. The spectrum showed a broad peak at 3300–3400 cm^{-1} and a peak at 1700 cm^{-1}.

Suggest what impurities caused these peaks.

peak at 3300–3400 cm^{-1} ....

peak at 1700 cm^{-1} ....

[2]

(h) A different procedure to make iodoform involves aqueous iodine as a reagent.

When an aqueous solution of iodine is required, the iodine is usually dissolved in aqueous potassium iodide, KI(aq), instead of dissolving in water alone. The I_2 reacts with I^- to form the triiodide ion, I_3^-. Aqueous triiodide behaves chemically like aqueous iodine.

Suggest the advantage of dissolving iodine in KI(aq) to form I_3^-(aq).

....

.... [1]

(i) Both iodoform-making procedures can also be used to convert the H_3C—CH— group to iodoform. In these reactions the –OH group is first oxidised to a carbonyl group.

$$\overset{\displaystyle OH}{\overset{\displaystyle |}{H_3C-CH-}}$$

The formation of iodoform can be used as a test for the presence of the $CH_3CH(OH)$– group in alcohols. When carrying out these tests, the student's procedure using KI/NaClO is considered superior to the I_2 procedure in **(h)**.

(i) Suggest why the KI/NaClO procedure is considered superior to the I_2 procedure.

....

.... [1]

(ii) Why would ethanol be an unsuitable choice of solvent in these tests?

....

.... [1]

(j) Iodine can react with cold aqueous sodium hydroxide in a disproportionation reaction in the same way as chlorine.

(i) Write an equation for this reaction of iodine with sodium hydroxide.

.... [1]

(ii) State what a disproportionation reaction is.

....

.... [1]

[Total: 22]

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