RAFFLES INSTITUTION
2021 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	

CLASS		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions

14 September 2021
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided at the top of this page.
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.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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	/ 25
2	/ 10
3	/ 12
4	/ 28
Total	/ 75

This document consists of **23** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 Esters are sweet smelling compounds with widespread industrial applications.

(a) Simple esters are flammable liquids. The standard enthalpy change of combustion for some simple esters can be experimentally determined using the set-up shown in Fig. 1.1.

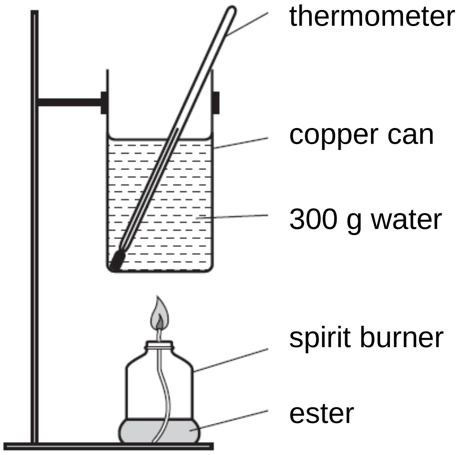


Fig. 1.1

Heat loss for such experiments are significant but can be taken into account by using the data collected from an initial experiment.

To determine the standard enthalpy change of combustion for ethyl ethanoate (M_r = 88.0), an initial experiment, Experiment 1, was carried out using methyl ethanoate (M_r = 74.0).

Experiment 1

Methyl ethanoate was combusted in a spirit burner which heated 300 g of water in a copper can as shown in Fig. 1.1. It was found that 0.980 g of methyl ethanoate was required to raise the temperature of the water in the copper can by 10.0 °C.

Table 1.1 provides some relevant data for the experiment.

Table 1.1

	mass / g	specific heat capacity / J g^{-1} K^{-1}
water	300	4.18
copper can	250	0.384

(i) Calculate the total heat energy gained by the water and the copper can in Experiment 1. You may assume that the water and copper can are in thermal equilibrium with each other.

[2]

(ii) The theoretical standard enthalpy change of combustion of methyl ethanoate is -1592 kJ mol^{-1}. Calculate the theoretical heat energy released by the mass of methyl ethanoate combusted in Experiment 1.

[1]

The same set-up was used to carry out Experiment 2 with ethyl ethanoate.

The following results were obtained.

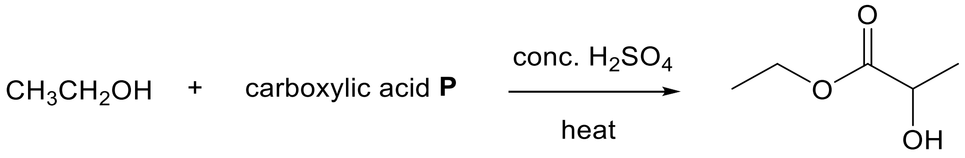
Experiment 2

- mass of ethyl ethanoate combusted = 0.948 g
- increase in temperature of 300 g of water = 11.5 °C

(iii) Calculate the standard enthalpy change of combustion for ethyl ethanoate in kJ mol^{-1}, taking into account the heat loss determined in Experiment 1. You may assume that the percentage heat loss in both Experiments 1 and 2 is the same.

[3]

(b) The structure of another simple ester commonly used as a water-soluble degreaser is shown below. It can be formed by heating ethanol and carboxylic acid **P** with concentrated sulfuric acid.



(i) The yield of the ester is found to be low due to the formation of side products. Two of the side products are **A** and **B**. **A** decolourises aqueous bromine and **B** is a neutral compound. Draw the structures of **A** and **B**.

A ($C_3H_4O_2$)

B ($C_6H_8O_4$) [2]

(ii) State and explain how the value of pK_a of **P** compares with that of propanoic acid.

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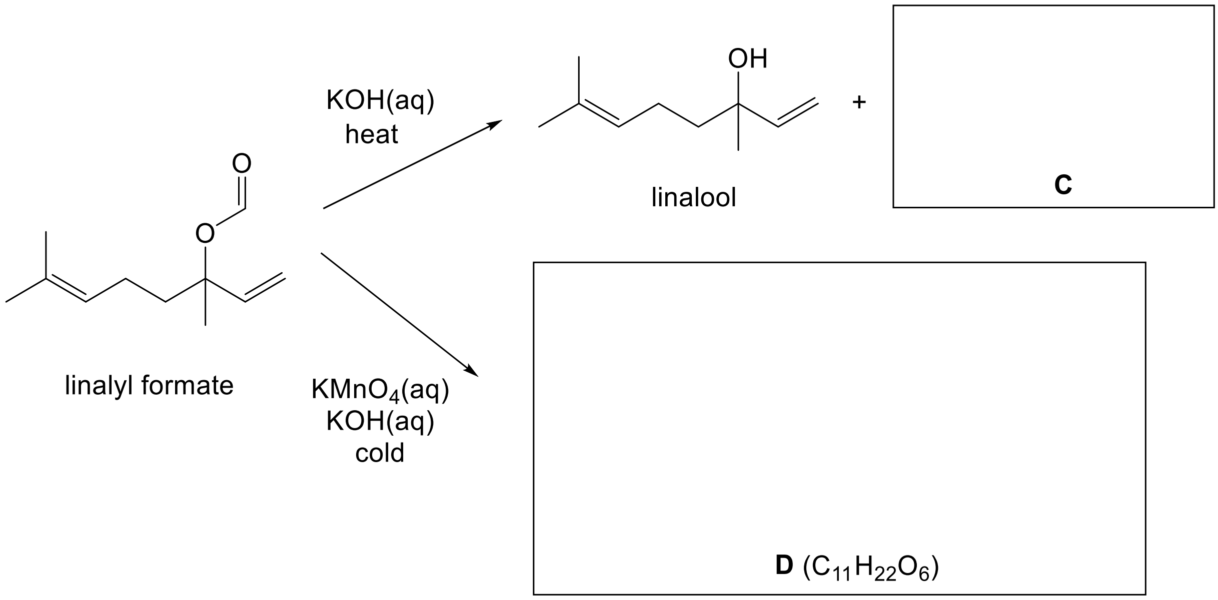
(iii) An aqueous solution containing 0.10 mol dm^{-3} of **P** has a pH of 2.43.

Calculate the value of pK_a for **P**.

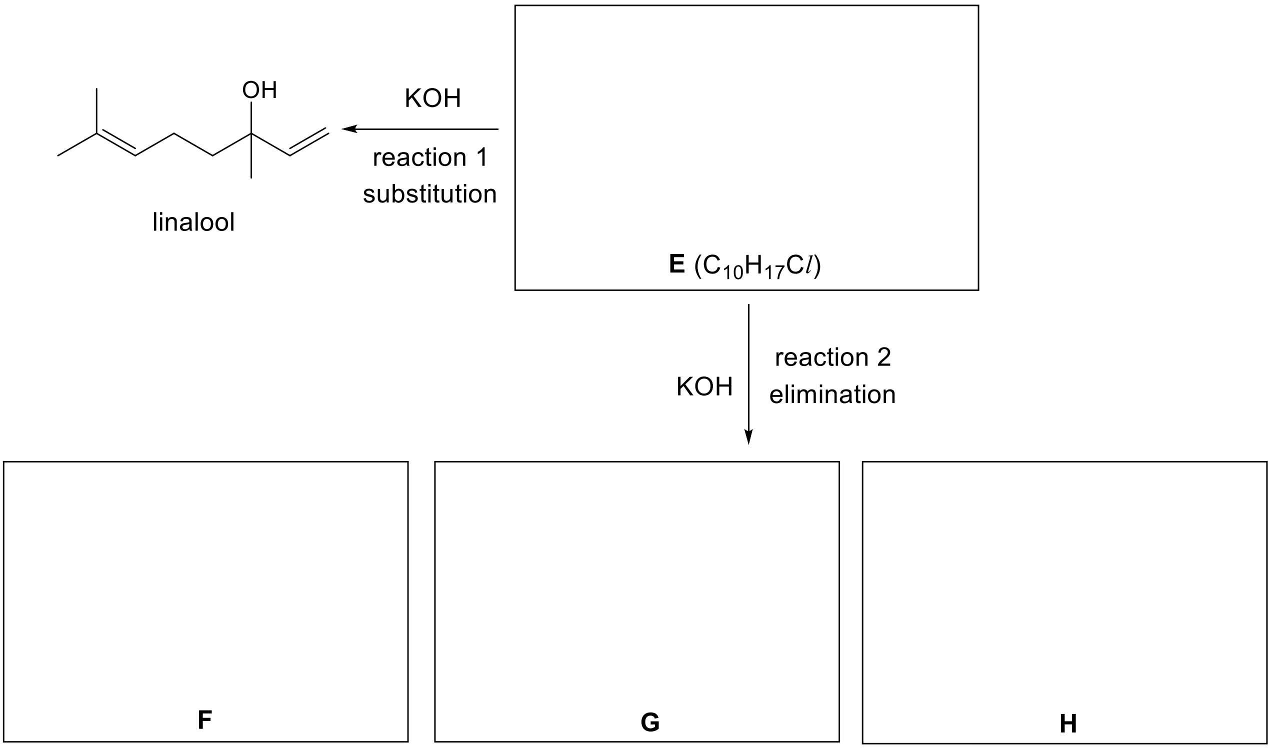
[2]

(c) Linalyl formate is a naturally occurring ester responsible for the characteristic apple smell. It can undergo various reactions under alkaline conditions using potassium hydroxide.



(i) Draw the structures of compounds **C** and **D** in the boxes above. [2]

Potassium hydroxide can also be used to bring about substitution and elimination reactions.



mixture of three isomeric alkenes ($C_{10}H_{16}$)

(ii) Draw the structures of **E, F, G and H** in the boxes above. [4]

(iii) Potassium hydroxide is said to function as a *nucleophile* in reaction 1 and a *Brønsted base* in reaction 2.

Using your understanding of the two terms in *italics*, describe one similarity and one difference between the two terms.

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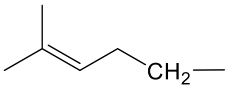
(iv) State the conditions required for reactions 1 and 2.

reaction 1: ………………………………………..

reaction 2: ……………………………………….. [2]

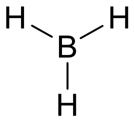
(v) Using an enantiomerically pure sample of **E**, describe the mechanism for reaction 1, showing clearly the stereochemistry of the reactant and products.

You may represent the group  as R– in your drawing.

[3]

[Total: 25]

2 Boron trihydride, BH_3, is an important reagent in the hydroboration-oxidation reaction, which converts an alkene to an alcohol. The structure of BH_3 is given below.



(a) **(i)** State the hybridisation of the boron atom in BH_3.

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(ii) By considering your answer in **(a)(i)** and the number of valence electrons around boron, explain why BH_3 is an electrophile.

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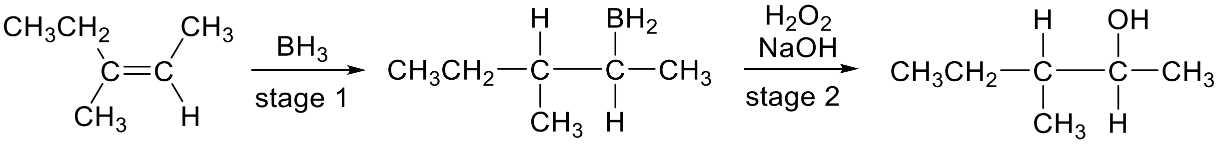
The hydroboration-oxidation reaction is a two-stage hydration reaction.

Stage 1: BH_3 adds across the alkene.
Stage 2: The $–BH_2$ group is replaced by an $–OH$ group.

The stages in the hydroboration-oxidation of 3-methylpent-2-ene are shown below.



(b) **(i)** For 3-methylpent-2-ene, it was proposed that **stage 1** proceeds via a two-step electrophilic addition mechanism. The first step of the mechanism produces a carbocation and a hydride ion, H^-.

By considering the electronegativity values in Table 2.1 and the information provided, draw the proposed two-step electrophilic addition mechanism for **stage 1**. Show all relevant charges and the movement of electron pairs by using curly arrows.

Table 2.1

element	electronegativity value
H	2.2
B	2.0

[2]

(ii) Markovnikov's rule states that for the addition of H–X to an asymmetric alkene, the H atom is added to the doubly bonded carbon with more hydrogen atoms.

Fig. 2.1 shows the outcome of the reaction in stage 1.

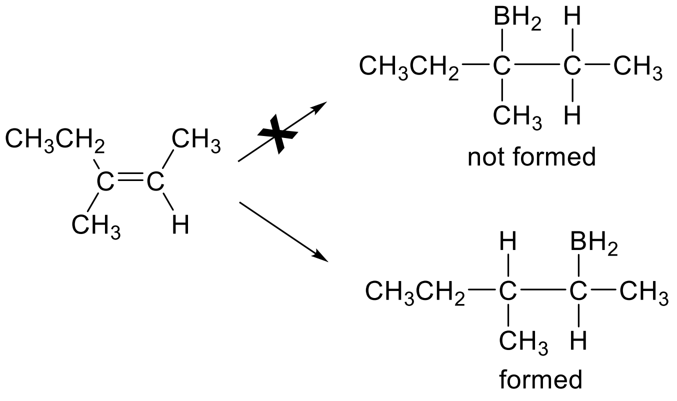


Fig. 2.1

With reference to the intermediate formed in your mechanism in **(b)(i)**, explain why the product formed does not follow Markovnikov's rule.

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(c) Further investigation into the stereochemistry of the product of **stage 1** suggested that the initially proposed two-step mechanism was inadequate.

The currently accepted mechanism involves the addition of BH_3 to either side of the plane of the alkene, where the following occur simultaneously.

- Breaking of the B–H bond and the π bond of the C=C.
- Formation of the C–B and C–H bonds.

(i) Fig. 2.2 represents the approach of BH_3 from the top side of the plane of the alkene to form compound **V**.

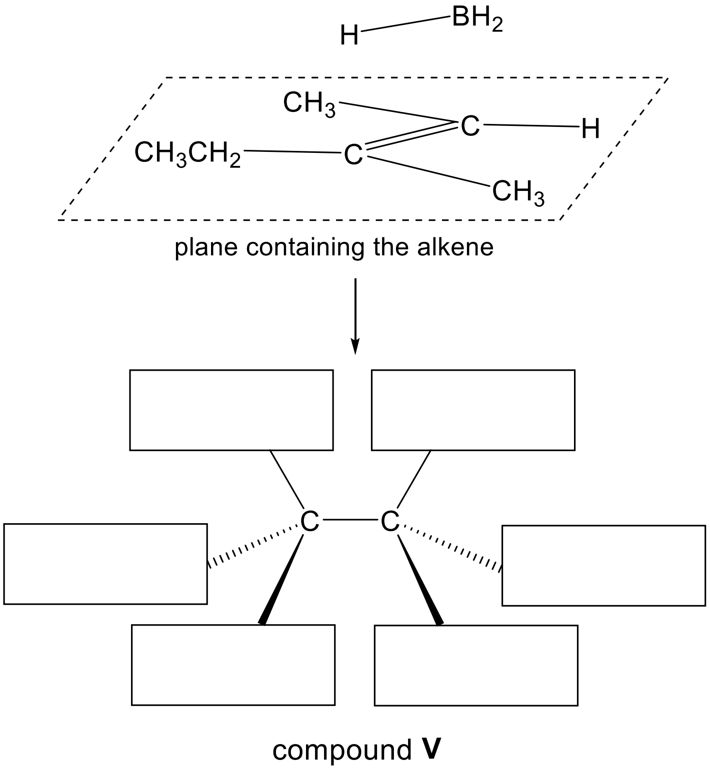

Fig. 2.2

Complete the structure of compound **V** in Fig. 2.2 to show the three-dimensional structure of the product formed. [1]

(ii) Another product, compound **W**, is formed from this mechanism.

State the relationship between compounds **V** and **W**.

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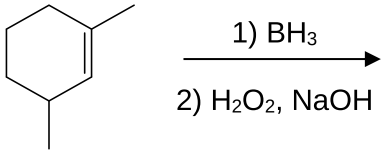
(d) **(i)** Suggest the structure of compound **Y** formed from the hydroboration-oxidation of compound **X**, ignoring stereochemistry.



X

Y

[1]

(ii) Compounds **X** and **Y** are separately heated with acidified potassium manganate(VII).

Draw the organic products formed.

organic product of **X**

organic product of **Y**

[2]

[Total: 10]

3 This question is about the chemistry of vanadium and its ions.

(a) Vanadium(II) sulfate, VSO_4, and vanadium(III) sulfate, $V_2(SO_4)_3$, are common sources of vanadium ions with different oxidation states.

Explain, in terms of structure and bonding, whether VSO_4 or $V_2(SO_4)_3$ has a higher melting point.

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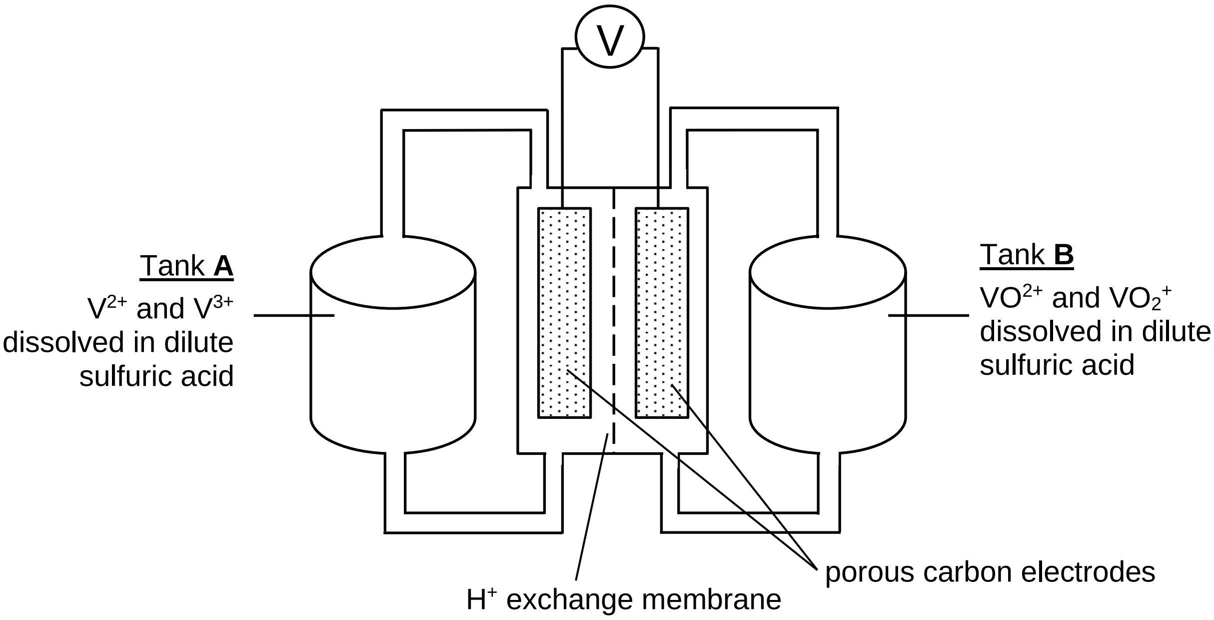
………[2]

(b) The vanadium-flow battery uses the redox couple V^{3+}/V^{2+} in one electrolyte tank and VO_2^{+}/VO^{2+} in another. Sulfuric acid is the electrolyte in both tanks.

The diagram shows a vanadium-flow battery set up under standard conditions.



(i) Calculate the $E^{\ominus}_{cell}$ for the reaction in the battery.

[1]

(ii) Explain the effect on E_{cell} if the battery was set up at a higher initial pH.

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(iii) With reference to the table below, suggest the colour change in each tank as the battery discharges.

vanadium ion	colour
V^{2+}	violet
V^{3+}	green
VO^{2+}	blue
VO_2^+	yellow

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(iv) Sulfuric acid is a source of H^+ ions which flow through the exchange membrane as the battery discharges.

Suggest the direction of the flow of H^+ through the membrane. Explain your answer.

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(v) Suggest an advantage of using *porous* carbon electrodes.

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(c) After the vanadium-flow battery runs flat, it can be recharged using an external power supply.

(i) Write the overall equation for the charging process.

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(ii) Calculate the $\Delta G^{\ominus}$ for the charging process, stating the units clearly.

[1]

[Total: 12]

Question 4 starts on the next page.

4 Modern submarines are able to remain underwater for months without the need to surface for air due to advanced air purification technologies, which provide the crew with a continuous supply of oxygen gas and remove carbon dioxide from the air.

(a) The primary source of oxygen gas comes from an electrical oxygen generator. It works by the electrolysis of seawater, which contains NaC*l*.

Electrolysis of seawater produces both oxygen and chlorine gases at the anode.

Anode:
$2Cl^- \rightarrow Cl_2 + 2e^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Cathode:
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

The anode and cathode are separated by a membrane which prevents the reaction between Cl_2 and OH^-.

In an experiment, a sample of seawater was electrolysed over a period of 120 h. During the experiment, no additional seawater was introduced.

Fig. 4.1 shows how the concentration of dissolved chloride ions changes in that time.

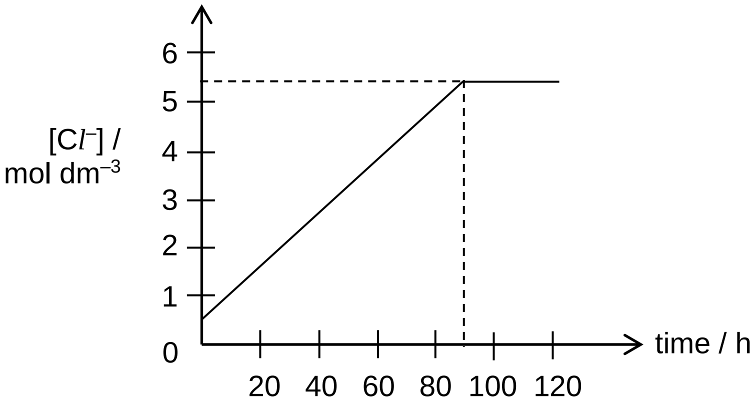

Fig. 4.1

(i) Describe the trend observed in Fig. 4.1 when the sample of seawater was electrolysed from 0 to 90 h.

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(ii) By considering the reactions at the cathode and anode, explain the trend described in **(a)(i)**.

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(iii) Apart from the evolution of gases, state what will be observed in the electrolytic setup from 90 to 120 h.

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(iv) Suggest how the composition of the products at the anode will change as the experiment proceeds from 0 to 120 h.

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An advancement to this method involves adding NaOH to the sample of seawater prior to electrolysis.

At high concentration of NaOH (~6.0 mol dm^{-3}), two observations were made.

Observation 1: The concentration of dissolved chloride ions was significantly reduced.

Observation 2: Only oxygen gas was produced at the anode. No chlorine gas was produced.

(v) Explain **observation 1** using concepts of solubility equilibria.

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(vi) *Use of the Data Booklet is relevant to this question.*

Describe two ways in which the high concentration of NaOH favoured the production of oxygen gas while preventing the production of chlorine gas, as seen in **observation 2**.

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(b) An electrical fault could render the electrical oxygen generator inoperable. Hence, crew members would ignite an “oxygen candle” to chemically produce oxygen gas.

An oxygen candle is a thermally insulated cylinder, which contains a homogeneous mixture of Fe metal and solid $NaC\mathit{l}O_3$. The head of the cylinder contains an igniter, which consists of a nail coated with 0.050 g of solid phosphorus.

When inserted into the cylinder, friction against the solid phosphorus starts an exothermic reaction with oxygen gas.

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

The heat released initiates a more controlled exothermic reaction between Fe and oxygen gas, which generates sufficient heat to decompose $NaC\mathit{l}O_3$, producing oxygen gas.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

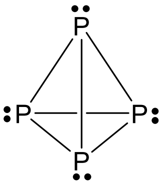
$$NaC\mathit{l}O_3(s) \rightarrow NaC\mathit{l}(s) + {}^{3}/_{2}O_2(g)$$

The contents of each oxygen candle weigh 15.0 kg and contain 88.0% $NaC\mathit{l}O_3$ and 4.0% Fe. Other inert binding materials take up the rest of the mass.

(i) Calculate the net volume of oxygen released, measured at room temperature and pressure, when 1 oxygen candle is ignited. You may ignore the reaction of phosphorus in your calculations.

[3]

(ii) Phosphorus exists as molecules made up of four atoms in a tetrahedron.



It can be easily ignited with friction due to its high reactivity.

With reference to its structure and VSEPR theory, explain why phosphorus is highly reactive.

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(iii) Phosphorus, sulfur and chlorine are consecutive elements in Period 3.

Using structure and bonding, explain why phosphorus and sulfur are solids, while chlorine is a gas at room temperature.

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(iv) Briefly explain how the first ionisation energies compare between

- phosphorus and sulfur,
- sulfur and chlorine.

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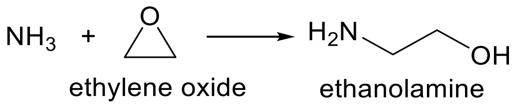
(c) In submarines, carbon dioxide is removed by treating the air with an aqueous solution of ethanolamine, $HOCH_2CH_2NH_2$.

Ethanolamine is produced industrially by the nucleophilic substitution reaction between ammonia and ethylene oxide.



Ethylene oxide can be prepared in a 3-step process shown in Fig. 4.2.

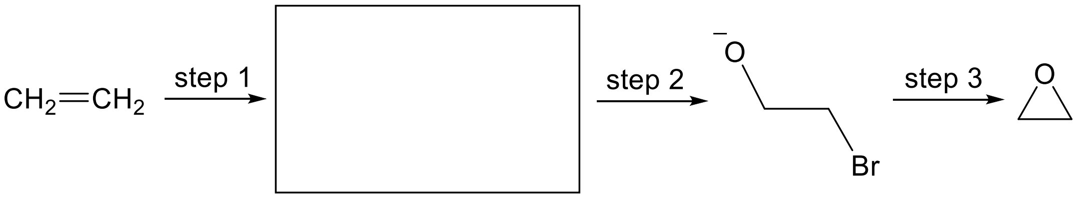


Fig. 4.2

(i) Draw the structure of the intermediate in Fig. 4.2. [1]

(ii) State the reagents and conditions required for steps 1 and 2.

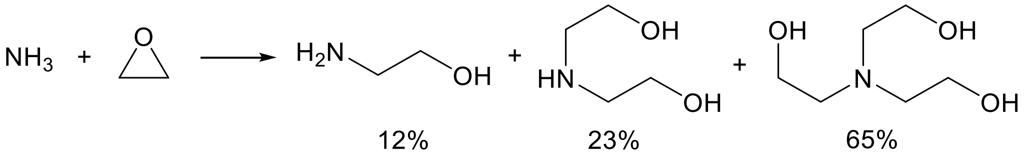
step 1: ……………………………………………..

step 2: …………………………………………….. [2]

(iii) On Fig. 4.2, draw the mechanism of the reaction in step 3.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [1]

When ammonia and ethylene oxide were reacted in a 1:1 ratio, a mixture of products was obtained.



(iv) Suggest and explain how the reaction conditions can be modified to increase the proportion of ethanolamine in the product mixture.

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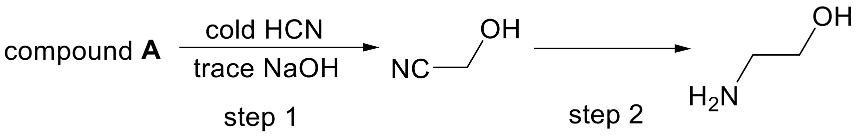
An alternative route to prepare ethanolamine, which produces fewer side products, is shown below.



(v) State the IUPAC name of compound **A**.

…………………………………………………………………………………………… [1]

(vi) State the reagents and conditions required for step 2.

step 2: …………………………………………… [1]

In a submarine, carbon dioxide in the air is continuously removed by cycling the air through a two-chamber system, shown in Fig. 4.3, containing aqueous ethanolamine.

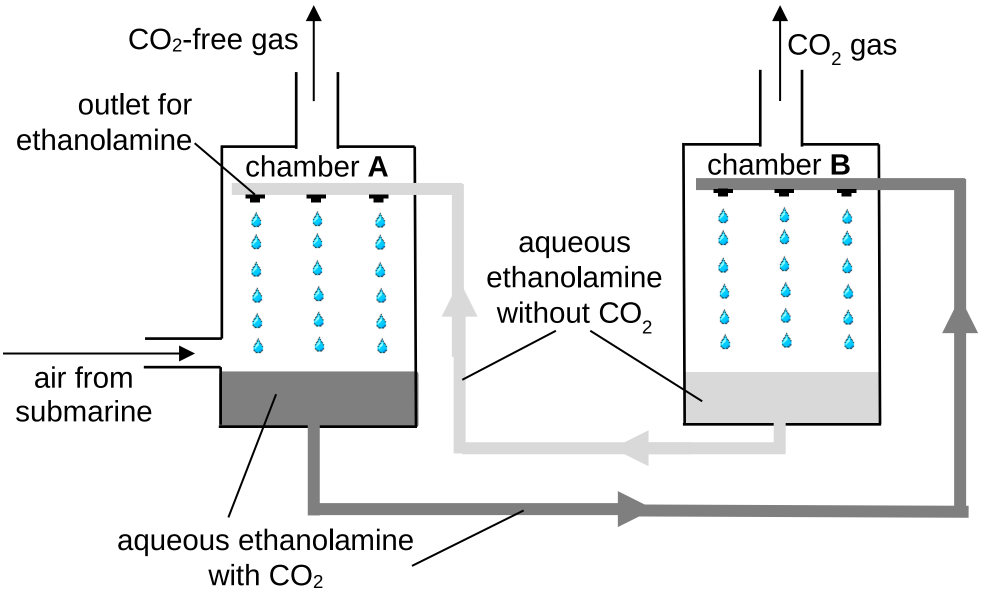


Fig. 4.3

In the chambers, ethanolamine undergoes a reversible reaction with carbon dioxide as shown in Fig. 4.4.

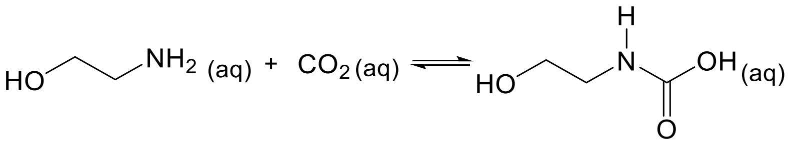


Fig. 4.4

The equilibrium constant, K_c, of this reaction varies with temperature and is illustrated in Fig. 4.5.

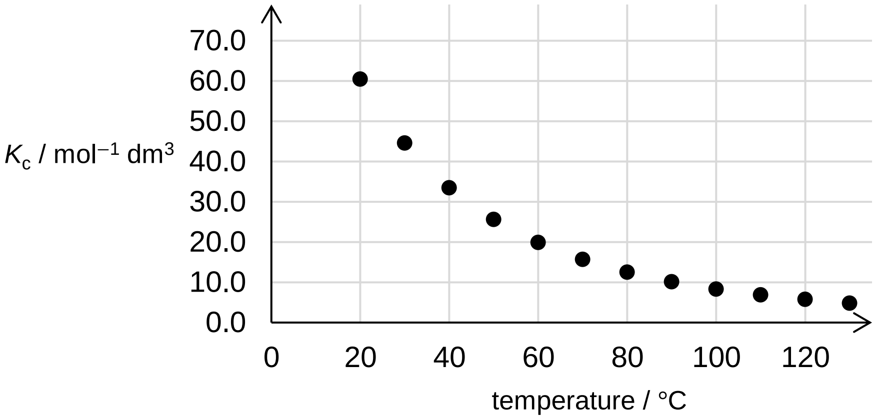


Fig. 4.5

(vii) The two chambers need to have a temperature difference of at least 40 °C to function optimally.

Using information from page 22, suggest suitable temperatures at which chambers **A** and **B** should be maintained.

temperature in chamber **A**: …………………………………………..

temperature in chamber **B**: …………………………………………..

Explain your choice of temperatures for each chamber.

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(d) Carbon dioxide can also be removed by passing air from the submarine through calcium hydroxide, which reacts with carbon dioxide to form calcium carbonate.

Calcium carbonate can be heated to form carbon dioxide and calcium oxide, which can be used to regenerate calcium hydroxide.

Barium hydroxide is not used because barium carbonate does not decompose easily on heating, requiring significantly higher temperatures.

Explain why barium carbonate requires a significantly higher temperature for decomposition compared to calcium carbonate.

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