NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY

9729/03

Paper 3 Free Response

12 September 2024

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class 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.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question. Circle the question you attempted in the box below.

The use of an approved scientific calculator is expected, where appropriate.
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.

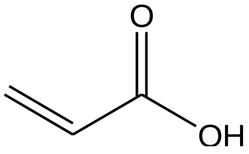
For Examiner's Use	
1	**/20**
2	**/20**
3	**/20**
4 or 5	**/20**
Total	**/80**

This document consists of **34** printed pages and **1** blank page.

Section A

Answer **all** questions in this section.

1 Acrylic acid is a major building block used in the manufacture of a wide range of industrial and consumer products. In 2022, the global market for acrylic acid was approximately 6.7 million tonnes valued at USD 14.1 billion.



acrylic acid

(a) One method of synthesising acrylic acid is by reacting propene and steam with palladium (Pd) catalyst in a fuel cell as shown in Fig. 1.1. Pd serves as both an electrode and a catalyst in the fuel cell.

Propene is pumped in at the Pd electrode, while air (as a source of oxygen) is pumped in at the other electrode (platinum, Pt). The cell is operated in the gas phase at 365 K and atmospheric pressure. Electricity is generated during the reaction, making the process economically viable.

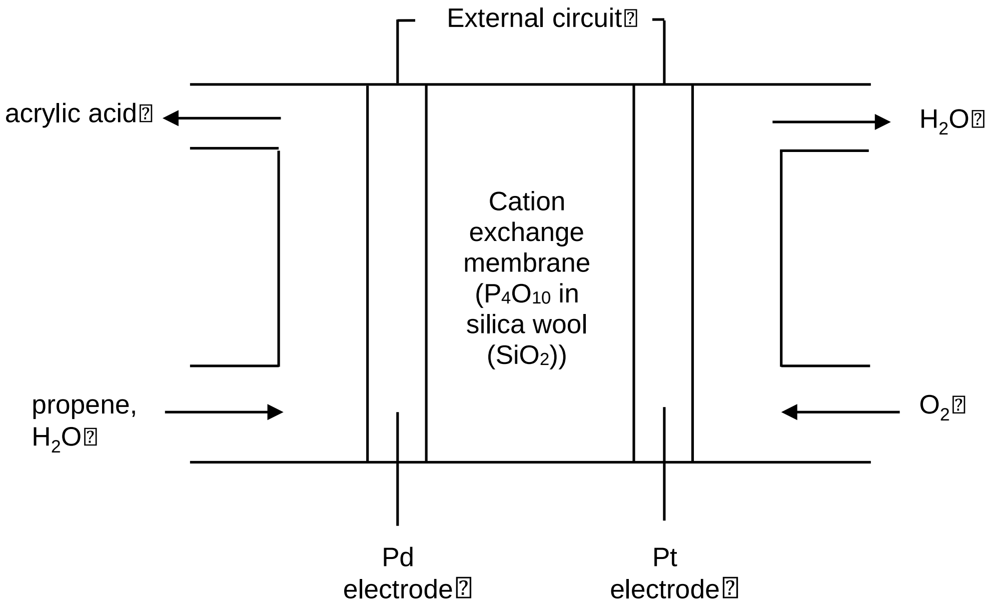


Fig. 1.1

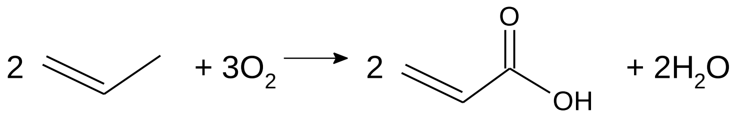
(i) Explain fully why Pd is suitable to serve **both** roles in the fuel cell. [2]

(ii) Write half-equations for the reactions occurring at the cathode and the anode in the fuel cell. State the polarities of each electrode. [3]

The cell potential of the fuel cell was measured to be +0.70 V under the operating conditions.

(iii) Use your answer in **(a)(ii)** and the *Data Booklet* to determine the electrode potential of the acrylic acid/propene half-cell. [1]

(iv) Calculate ΔG for the following overall equation of the fuel cell.



[2]

(v) Describe and explain how electrode potential of the oxygen/water half-cell will change when pH of the whole cell was increased slightly.

Given electrode potential of the acrylic acid/propene half-cell will be affected similarly, deduce the overall effect on the cell potential of the fuel cell. Explain your reasoning. [2]

(vi) Write an equation to show the acid-base reaction taking place in the cation exchange membrane when pH of the whole cell was increased via addition of $OH^-(aq)$ ions. [1]

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(b) Acrylic acid can be treated with different reducing agents to form different products as shown in Fig. 1.2.

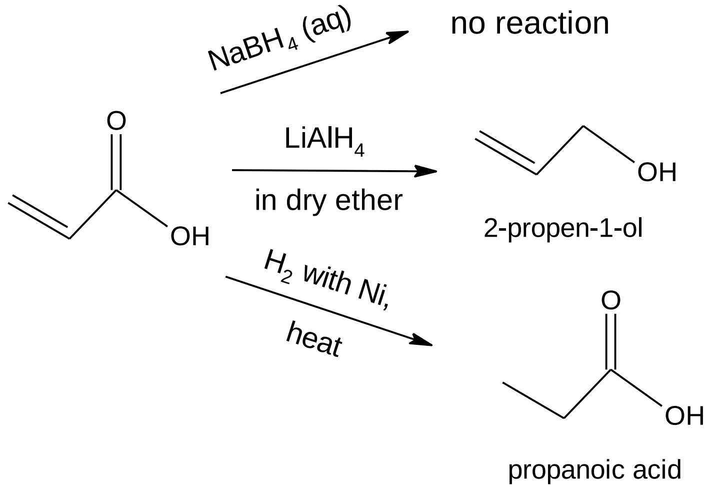

Fig. 1.2

(i) Suggest reasons to explain Fig. 1.2. You may find it helpful to discuss strength of reducing agents and how the reducing agents work in your answer. [3]

(ii) Acrylic acid has a pK_a of 4.25, while propanoic acid has a pK_a of 4.72. Explain why the pK_a of acrylic acid is lower than that of propanoic acid. [1]

(iii) Propanoic acid has the molecular formula $C_3H_6O_2$.

There are two isomeric esters with the same molecular formula as propanoic acid. Draw the structures of the esters and suggest a simple chemical test to distinguish them. [3]

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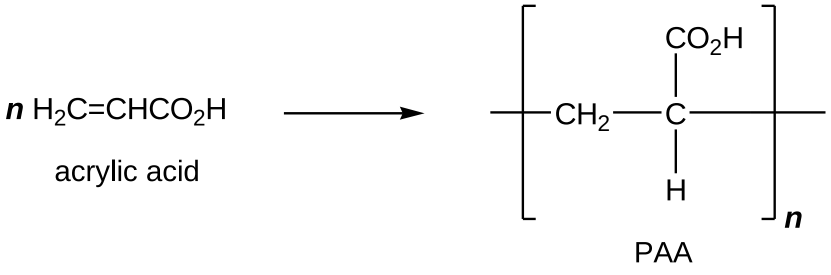
(c) Polymerisation is a process through which a large number of monomer molecules react together to form a long chain known as a polymer. Acrylic acid can be readily polymerised to form poly(acrylic acid), PAA, a useful material for making thickening agents and super absorbent polymers for use in diapers.



(i) There are two general types of polymerisation reactions: addition polymerisation and condensation polymerisation. Suggest, with explanation, the type of polymerisation that has taken place in the formation of PAA. [1]

(ii) PAA is a very effective thickening agent. In aqueous solutions of pH > 6, the polymer chain stretches out from a random coil formation. This causes the polymer to take up a lot more space, resisting the flow of the solvent molecules around it, hence, making the solution viscous.

By considering the interaction between the polymer chains, explain why the polymer chain stretches out and take up more space at pH > 6. [1]

[Total: 20]

2 Oxygen and sulfur belong to the same group. Although they share similar properties, they also behave differently due to different electronegativity.

(a) **(i)** Explain what is meant by the term *electronegativity*. [1]

(ii) Descending down a group, the electronegativity of atoms decreases. Explain the trend of electronegativity. [1]

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Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When dissolved in a gaseous organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

ring size	S_6	S_7	S_8
percentage by mass	0.32	0.76	98.92

The equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:

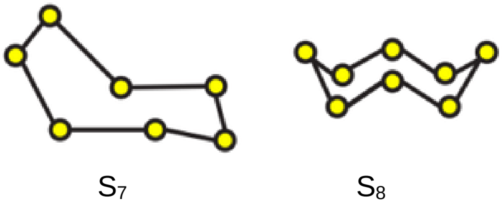
$$8S_7(g) \rightleftharpoons 7S_8(g)$$

(b) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1 dm^3 of an organic solvent. [2]

(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

(iii) At constant volume, the pressure of the system was increased, and the system was allowed to reach equilibrium. State and explain the effect on the composition of the reaction mixture, and the value of K_C. [2]

The shape of the S_7 and S_8 molecules are as follows.



(c) **(i)** Define the term *bond energy* with reference to the S–S bonds in S_8. [1]

(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, and considering the structures of the S_7 and S_8 molecules, calculate the enthalpy change for the reaction between S_7 and S_8.

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

[1]

(iii) Using your answers in **(b)(ii)** and **(c)(ii)**, and given that:

$$\Delta G = -RT \ln K_c$$

calculate the entropy change of the reaction at 369 K. [2]

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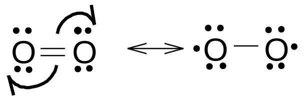
In organic chemistry, ethers are a class of compounds that contain an ether group; i.e. an oxygen atom connected to two alkyl or aryl groups. They have the general formula R–O–R’, where R and R’ represent alkyl or aryl groups. The C–O bonds in ethers are strong and are generally unreactive.

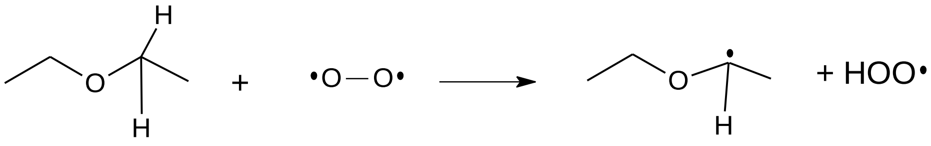
However, on prolonged storage, ethers tend to form explosive hydroperoxides. This is due to a process called autoxidation. Autoxidation of ethers proceeds by a free-radical chain reaction consisting of a series of steps – initiation, propagation, and termination in repetitive cycles.

A resonance form of the oxygen molecule can exist as a diradical. In this form, each oxygen has 1 unpaired electron.



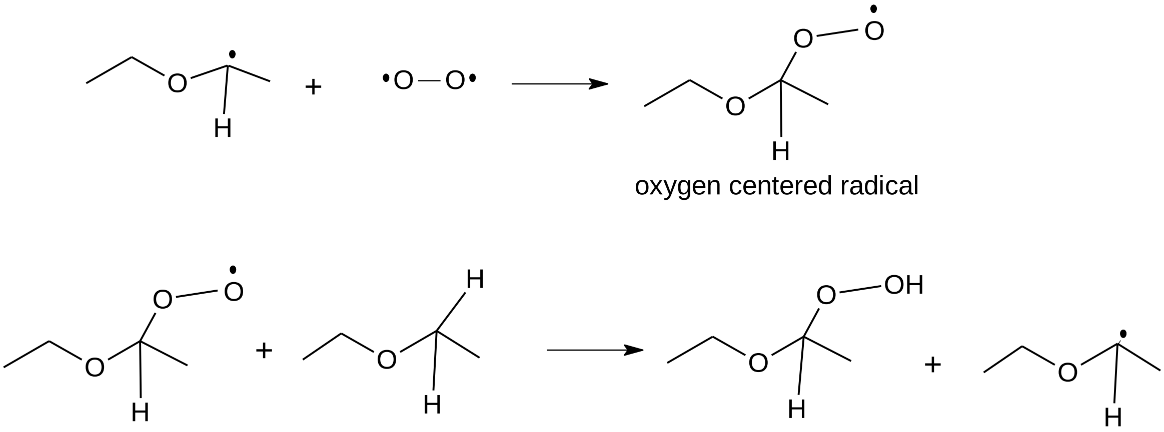
The initiation and propagation steps of the autoxidation of an ether, diethyl ether, $CH_3CH_2–O–CH_2CH_3$ is shown below. The hydroperoxide is mainly formed in the second propagation step.

Initiation: The alpha H (i.e. hydrogen atom on carbon adjacent to the oxygen) is abstracted by the radical.



carbon centered radical

Propagation:

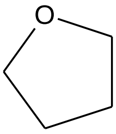
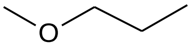


hydroperoxide

Fig. 2.1

(d) **(i)** On Fig 2.1, draw curly arrows in the steps above to complete the mechanism. [2]

(ii) Give the most stable carbon centered radicals and hydroperoxides formed when the following ethers undergoes autoxidation. [3]

- 
- 

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(e) The presence of peroxides in old samples of ethers may be detected by shaking them with a freshly prepared solution of acidified $FeSO_4$ followed by addition of KSCN. The formation of a blood red complex, $[Fe(H_2O)_5SCN]^{2+}$ indicates that peroxides are present.

(i) Identify the role of the peroxides when it reacts with acidified $FeSO_4$. Explain your answer. [1]

(ii) Suggest another simple chemical test to test for the presence of peroxides in ethers. State the observations for a positive test. [2]

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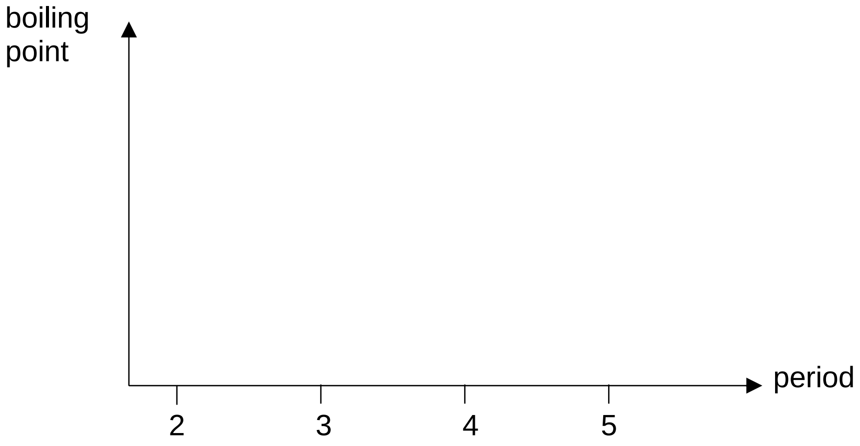
For Examiner's Use

3(a) Sketch a graph on the axis provided to show the variation in the boiling points of group 15 hydrides from nitrogen to antimony. Explain this variation in terms of the structure and bonding of the group 15 hydrides. [4]



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(b) The molecular shape of Group 15 hydrides from nitrogen to arsenic is the same. However, the bond angle decreases down the group.

(i) Draw a diagram to show the shape of a Group 15 hydride of nitrogen. Indicate the bond angle in your diagram. [2]

(ii) Explain why the bond angle decreases down the group for Group 15 hydrides from nitrogen to arsenic by considering the electronegativity of the central atom. [2]

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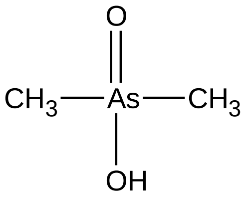
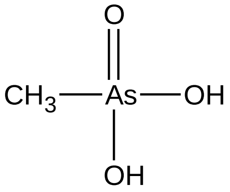
(c) The pK_a values of two common organic arsenic compounds, dimethylarsinic acid and monomethylarsonic acid are shown in Table 3.1.

Table 3.1

acid	structure	chemical formula	pK_1	pK_2
dimethylarsinic acid	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{\|}}{As}}-CH_3$	$(CH_3)_2AsO(OH)$	6.2	–
monomethylarsonic acid	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{\|}}{As}}-OH$	$CH_3AsO(OH)_2$	4.1	8.7

(i) Draw the structure of monomethylarsonic acid in its predominant form at pH 7. Hence, calculate the percentage of $CH_3AsO(OH)_2$ present in a solution at pH 7, to 3 decimal places. [2]

5.00 cm^3 portions of 0.10 mol dm^{-3} NaOH solution are progressively added to 10.0 cm^3 of 0.10 mol dm^{-3} monomethylarsonic acid solution until a total of 25.00 cm^3 of NaOH solution has been added.

(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of monomethylarsonic acid. Ignore the effect of pK_2 on the pH. [1]

(iii) Calculate the pH of the mixture for **each** 5.00 cm^3 addition of NaOH solution. [5]

(iv) Sketch the pH-volume added curve you would expect to obtain on Fig. 3.1 in **page 18** and label the various key points of the curve using the pH values you have calculated in **(c)(ii)** and **(c)(iii)**. [1]

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(iv)

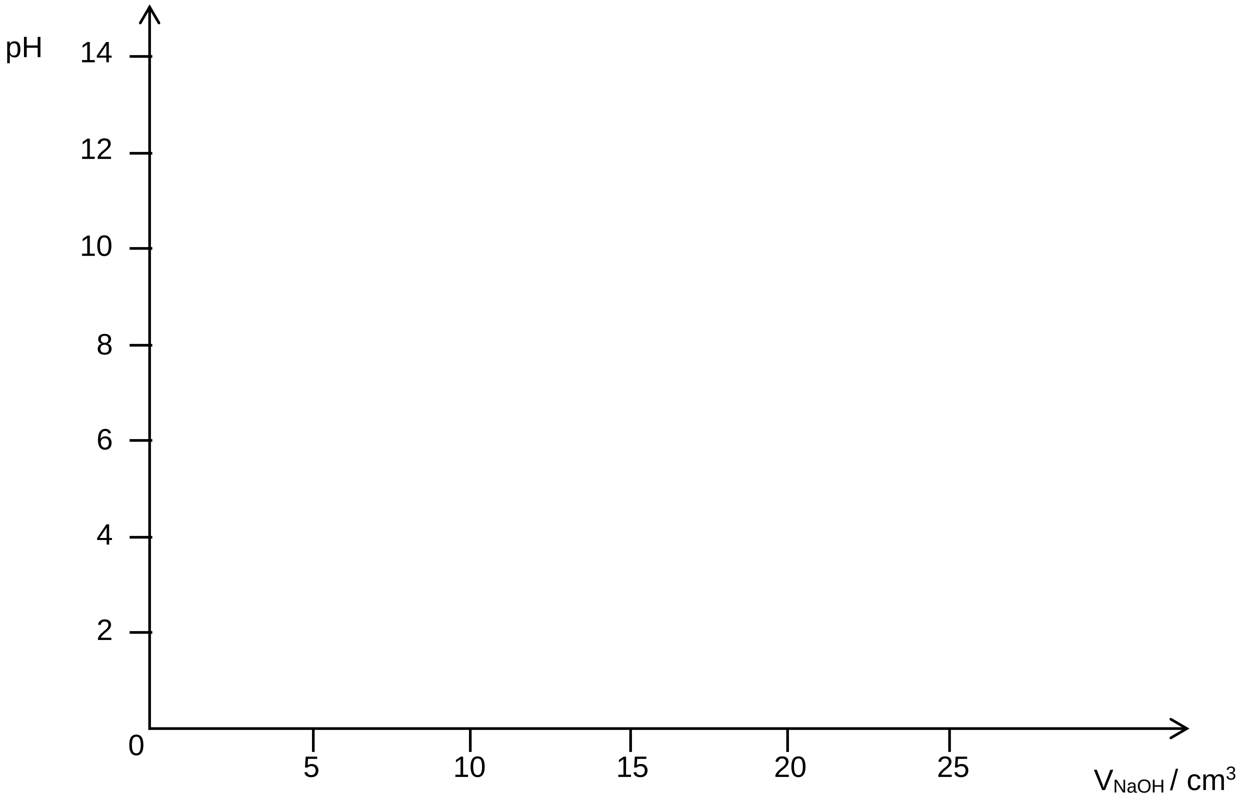

Fig. 3.1

(d) **A** can act as an electrophile or as a Bronsted-Lowry acid. Fig. 3.2 and Fig. 3.3 show the reactions of **A**.

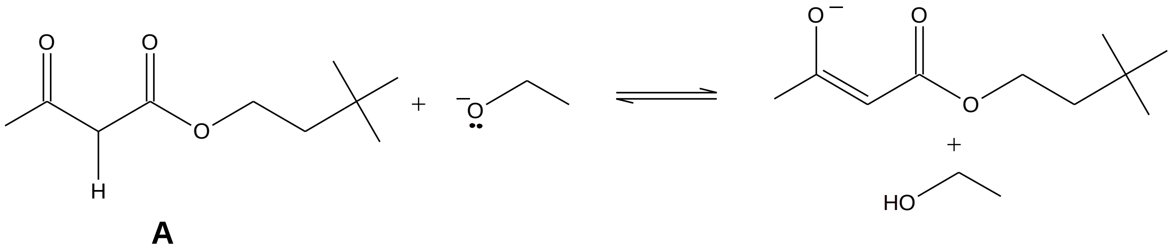

Fig. 3.2

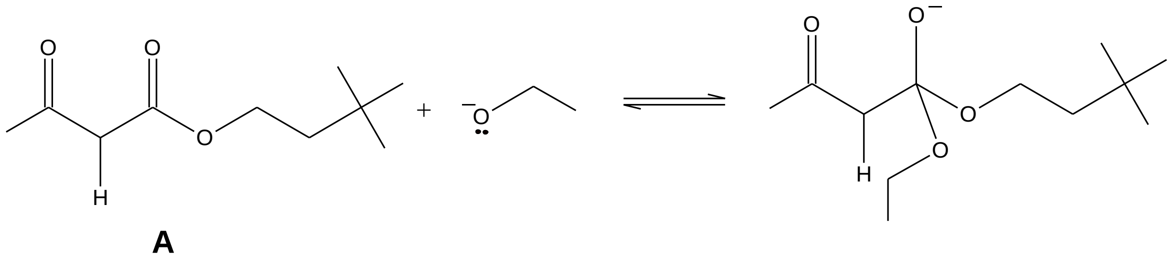

Fig. 3.3

(i) On Fig. 3.2 and Fig. 3.3, draw curly arrows to show the mechanism for the respective reactions. Show all relevant dipoles in your answer. [2]

(ii) Hence state the role of **A** for each reaction. [1]

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[Total: 20]

Section B

Answer **one** question from this section.

4(a) The ions of transition elements form complexes with ligands.

$^{-}OCH_2CH_2NH_2$ is a bidentate ligand.

The complex $[Cr(OCH_2CH_2NH_2)_3]$ exhibits stereoisomerism. Using the 3-dimensional diagram in Fig. 4.1, draw four stereoisomers of $[Cr(OCH_2CH_2NH_2)_3]$.

Represent the ligand $^{-}OCH_2CH_2NH_2$ by using $\overparen{\text{O}\qquad\text{N}}$.

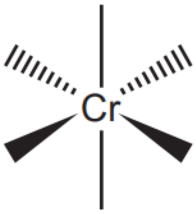

Fig. 4.1

[2]

(b) The complex $[Cr(OCH_2CH_2NH_2)_3]$ is formed by reacting $Cr^{3+}(aq)$ with the conjugate base of 2-aminoethanol. A synthesis of 2-aminoethanol is shown in Fig. 4.2.

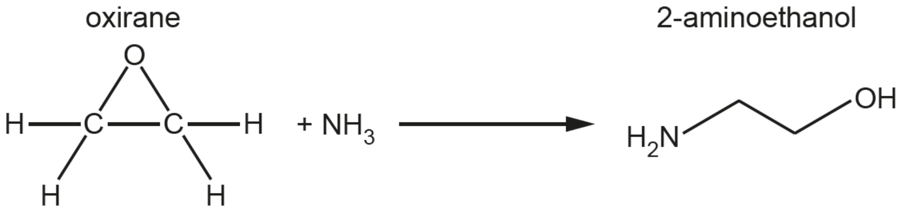

Fig. 4.2

(i) Suggest the mechanism for step 1 of the reaction of oxirane with ammonia in Fig. 4.3. Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.

Draw the structure of the organic intermediate.

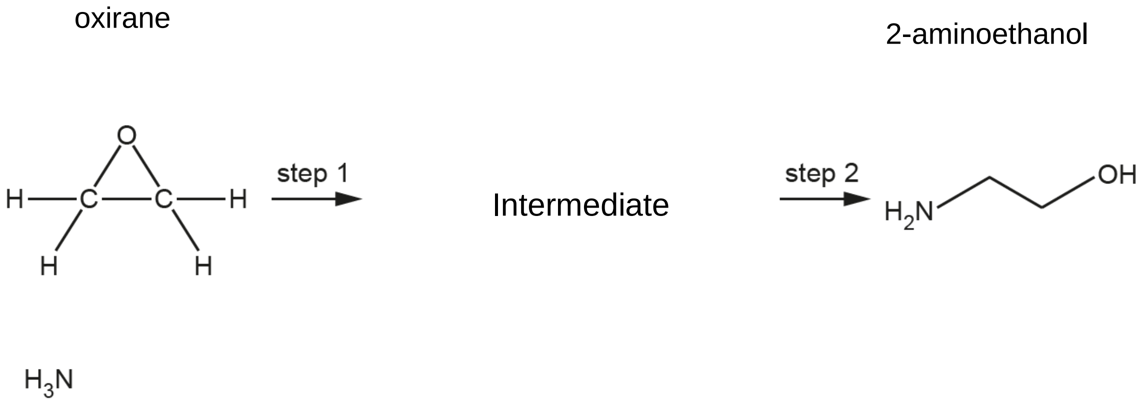

Fig. 4.3

[2]

(ii) A small amount of by-product **E**, $C_4H_{11}O_2N$, is produced during the reaction shown in Fig. 4.2. Compound **E** is basic. Draw the structure of compound **E** and suggest how its formation can be minimised. [2]

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(c) Copper forms two common series of compounds, one containing copper(II) ions and the other containing copper(I) ions.
Copper(II) salts are usually coloured, whereas copper(I) salts are usually white or colourless.
The complex ion $[Cu(H_2O)_6]^{2+}$ is blue, whereas the complex ion $[Mn(H_2O)_6]^{3+}$ is red. Both of these complexes are octahedral.
In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(i) State and explain why the d orbitals split into two energy levels in an octahedral complex, including which of the d orbitals are in each energy level. [2]

(ii) State the full electronic configurations of a copper(II) ion and a copper(I) ion. [1]

(iii) Explain why copper(II) salts are usually coloured, whereas copper(I) salts are usually white or colourless. [3]

(iv) Suggest why $[Cu(H_2O)_6]^{2+}$ and $[Mn(H_2O)_6]^{3+}$ have different colours. [1]

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(d) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry for imparting blue, green or red tints to glasses, glazes and enamels.

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate.

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

Table 4.1 lists the $\Delta H_f^{\ominus}$ values for some compounds.

Table 4.1

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Cu_2O(s)$	–168.6
$CuO(s)$	–157.3
$Cu(NO_3)_2(s)$	–302.9
$NO_2(g)$	+33.2

Calculate the $\Delta H^{\ominus}$ for this reaction, using suitable $\Delta H_f^{\ominus}$ values from Table 4.1. [1]

(ii) Copper(II) oxide can be formed by heating copper metal in oxygen. Depending on the temperature used, copper(II) oxide may decompose to copper(I) oxide as shown.

$$2CuO(s) \rightleftharpoons Cu_2O(s) + \tfrac{1}{2}O_2(g) \qquad \Delta H^{\ominus} = +146 \text{ kJ mol}^{-1}$$

Table 4.2 lists the $S^{\ominus}$ values for some compounds.

Table 4.2

Compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Cu_2O(s)$	92.4
$CuO(s)$	42.6
$O_2(g)$	205.2

- Calculate the $\Delta S^{\ominus}$ for the reaction using suitable $S^{\ominus}$ values from Table 4.2. $S^{\ominus}$ can be used in the same manner as $\Delta H^{\ominus}$ in a Hess' law cycle.
- Hence, suggest whether the reaction is more spontaneous at a low or a high temperature. Explain your reasoning. [2]

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(e) Some transition element ions such as manganate(VII) and dichromate(VI) ions are highly oxidising and are often used as reagents for organic reactions as seen below.

A hydrocarbon **R**, C_9H_{10}, does not exhibit stereoisomerism. When **R** is reacted with steam and phosphoric acid at 300 °C and 60 atm, compound **S**, $C_9H_{12}O$, is obtained which gives a yellow solid when reacted with alkaline aqueous iodine.

When compound **S** is heated under reflux with acidified potassium manganate(VII) solution, it gives compound **T**, $C_7H_6O_2$. Additionally, **S** can be heated under reflux with acidified potassium dichromate(VI) solution to give compound **U**, $C_9H_{10}O$.

Draw the structures of **R**, **S**, **T** and **U**. [4]

[Total: 20]

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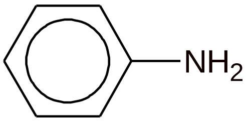
5(a) Amines are Lewis bases.

(i) Explain what is meant by this statement. Illustrate your answer with an equation for a suitable reaction of an amine of your choice. [2]

(ii) Describe and explain the relative basicities of methylamine, dimethylamine, and trimethylamine in the gas phase. [2]

(b) The K_b values of four bases, at 25 °C, are shown in Table 5.1.

Table 5.1

base	formula	K_b / mol dm^{-3}
ammonia	NH_3	1.8×10^{-5}
hydroxylamine	NH_2OH	8.7×10^{-9}
ethylamine	$CH_3CH_2NH_2$	4.5×10^{-4}
phenylamine		7.4×10^{-10}

(i) Write the K_b expression for hydroxylamine. [1]

(ii) Explain the relative magnitudes of the K_b values in Table 5.1. [4]

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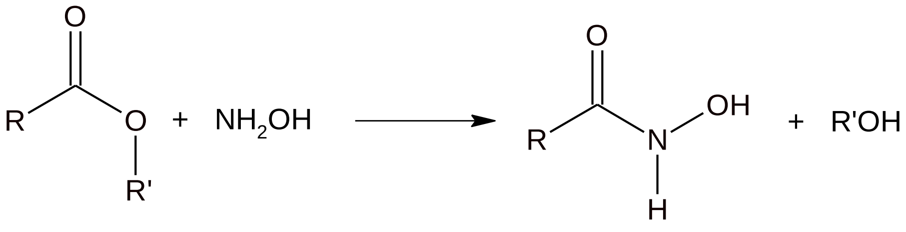
(c) Hydroxamic acid can be produced by reacting hydroxylamine, NH_2OH, with ester.



hydroxamic acid

Using the above information, write a balanced equation for the reaction between methyl benzoate and hydroxylamine. State the type of reaction involved. [2]

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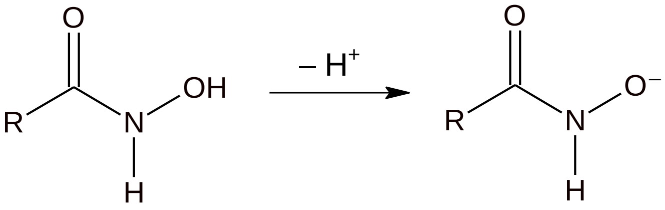
(d) Hydroxamic acid deprotonates to form hydroxamate anion.



hydroxamic acid hydroxamate

(i) Hydroxamate anion can act as a *bidentate ligand* to form stable chelates. Explain the term in *italics*. [1]

The addition of benzohydroxamate anion, $C_6H_5CONHO^-$ to a solution of Fe^{3+}(aq) produces a deep red solution which is a hexa-coordinated iron(III) complex.

(ii) Draw a structure of the hexa-coordinated iron(III) complex. Suggest the type of reaction and write an equation for the reaction occurring. [3]

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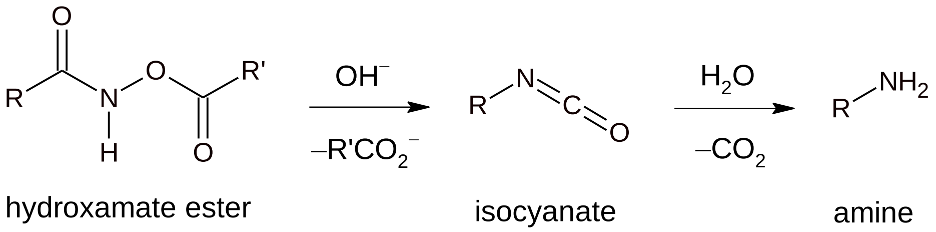
(e) The Lossen rearrangement is the conversion of a hydroxamate ester to an isocyanate. The isocyanate can further react with water to produce an amine.



The mechanism for the Lossen rearrangement is shown in Fig. 5.1.

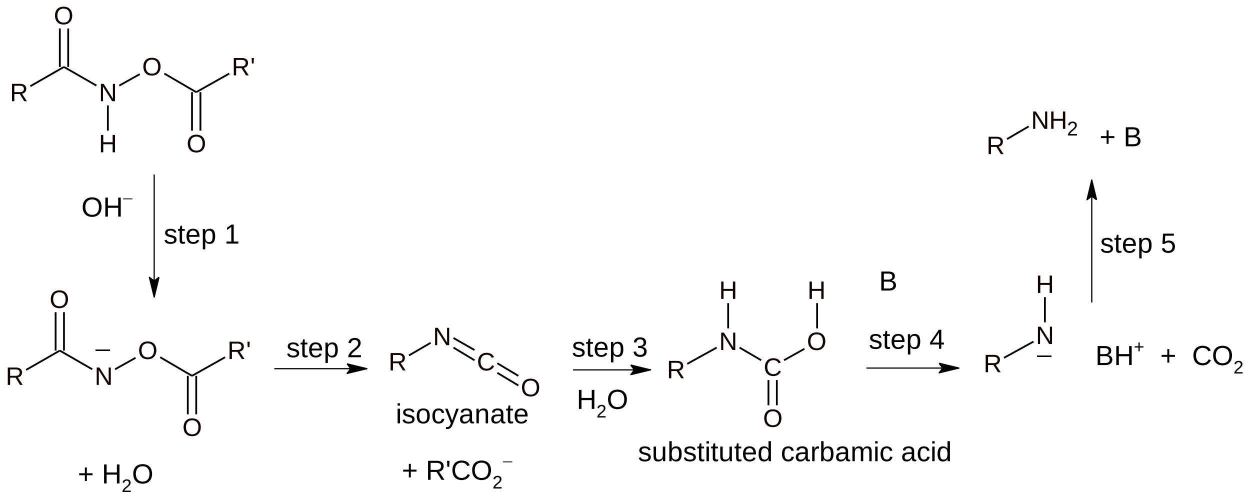


Fig. 5.1

Step 1: Hydroxamate ester is converted to its conjugate base by removing a proton using a base, OH^-.

Step 2: Spontaneous rearrangement of the conjugate base releases a carboxylate anion, $R'CO_2^-$, to produce the isocyanate.

Step 3: The isocyanate is hydrolysed by water to form an intermediate which undergoes proton transfer to produce a substituted carbamic acid, RNHCOOH.

Step 4: The removal of a proton from the substituted carbamic acid, RNHCOOH, using a base, B, will result in the formation of conjugate acid, BH^+, CO_2, and RNH^-,

Step 5: The conjugate acid, BH^+ will react with RNH^- to produce an amine, RNH_2 and regenerate the base, B.

(i) Using the above information, complete the mechanism for steps 1, 2 and 4 in the above reaction on Fig 5.1. Show all curly arrows and lone pairs. [3]

(ii) Isocyanic acid, HN=C=O contains both σ bonds and π bonds.
By reference to the hybridisation of the carbon atom and orbital overlap, describe the covalent bonding in isocyanic acid. Assume that both nitrogen and oxygen atoms in HN=C=O are sp^2 hydridised. You may use a labelled diagram to illustrate your answer. [2]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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