H

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.

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1	/20
2	/20
3	/20
4 or 5	/20
Total	/80

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

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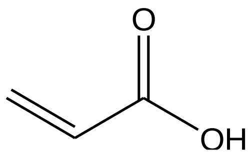
Section A

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.

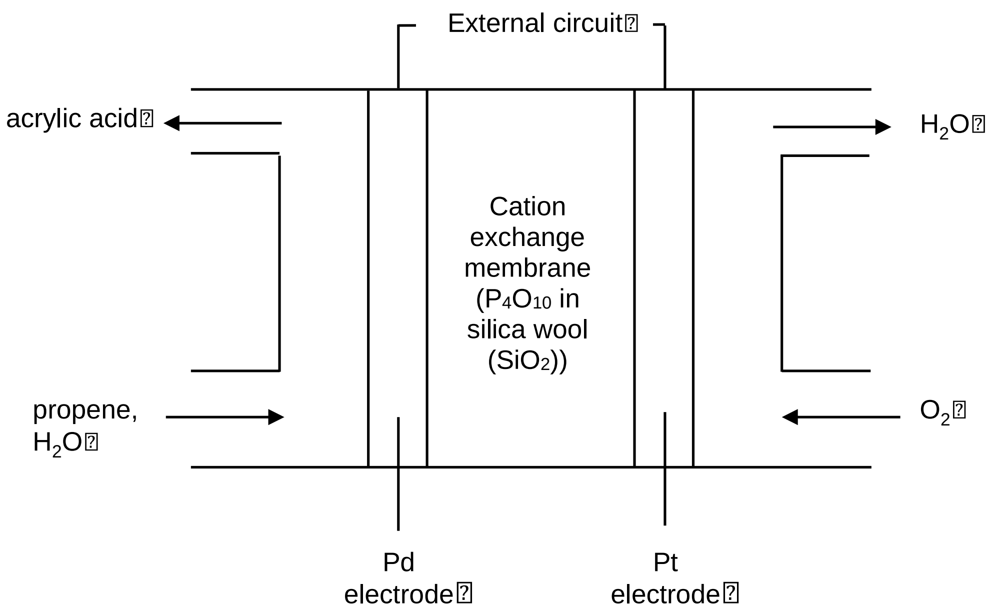


Fig. 1.1

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

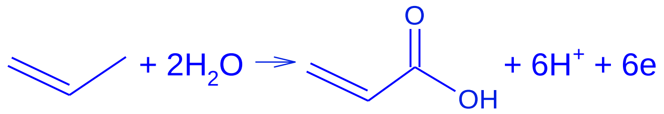
Pd is able to serve as an electrode as it is a good electrical conductor due to presence of delocalised valence electrons which can act as charge carriers. [1]

Pd is able to serve as a (heterogeneous) catalyst as it is a transition metal which contains partially filled (4)d subshell/orbitals which can accept electrons from the reactant molecule/ are able to form weak temporary bonds with reactant molecules during adsorption. [1]

(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]

[R] Cathode (+ve): $O_2 + 4H^+ + 4e \rightarrow 2\ H_2O$ [1]

[O] Anode (-ve):



OR $CH_2CHCH_3 + 2H_2O \rightarrow CH_2CHCOOH + 6H^+ + 6e$ [1]

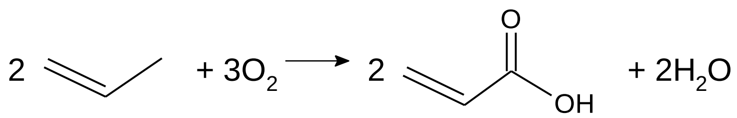
ecf 1m for equations if mixed up cathode and anode. BOD for C_3H_6.
[1] for correct polarity. No ecf.

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]

$E_{cell} = E_{[R]} – E_{[O]}$ = E(O_2/H_2O) – E(acrylic acid/propene)
+0.70 = +1.23 – E(acrylic acid/propene)
E(acrylic acid/propene) = +1.23 – 0.70 = + 0.53 V [1]

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



[2]

Electrons transferred when 3 moles O2 or 2 moles propene is reacted = 12 ecf (ii)
$\Delta G = – n F E_{cell}$ = – (12)(96500)(+0.70) = – 810600 [1] J mol^{-1}
[1] sign and units for both (iii) and (iv)

(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]

If pH is increased, <u>[H^+] decreases</u>,
<u>position of equilibrium of $O_2 + 4H^+ + 4e$ ∏ $2\ H_2O$ shifts left</u> to produce more H^+ i.e. oxidation is more favoured
<u>*E*(O_2/H_2O) becomes less positive.</u> [1]

Since <u>overall equation doesn't contain H^+ on either side</u>, it will not be affected by changes in [H^+] hence <u>E_{cell} remains unchanged</u>. [1] OR

Similarly, <u>E(acrylic acid/propene) becomes less positive</u> as POE of $CH_2CHCOOH + 6H^+ + 6e$ ∏ $CH_2CHCH_3 + 2H_2O$ shifts left when [H^+] decreases.

<u>E_{cell} = *E*(O_2/H_2O) – E(acrylic acid/propene)</u>. <u>The effect on *E*(O_2/H_2O) and E(acrylic acid/propene) cancels out</u> <u>as there are equal number of H^+ on either side of the overall equation</u>.

Accept also if student recognise equal H+ on either side of the overall equation AND $CH_3CHCOOH$ may react with OH^- at higher pH hence POE of overall equation shifts right and E_{cell} becomes more positive.

(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]

$P_4O_{10} + 12\ OH^- \rightarrow 4\ PO_4^{3-} + 6\ H_2O$ [1] Note SiO_2 reacts only with conc alkali.

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

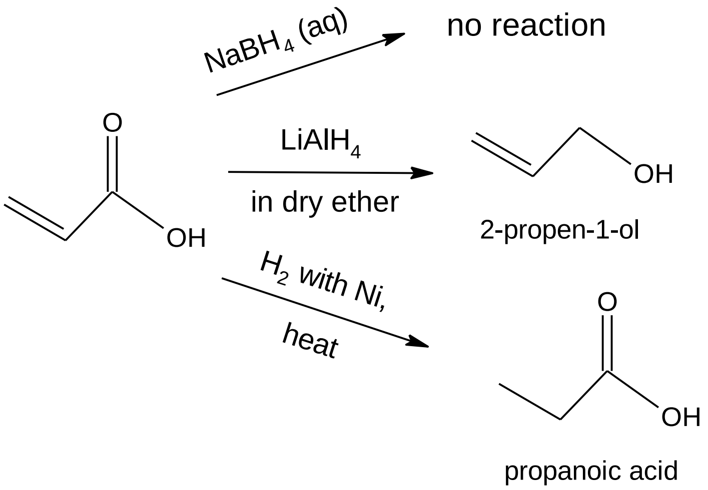


Fig. 1.2

(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]

$NaBH_4$ is a weaker reducing agent than $LiAlH_4$ as the B–H bond is shorter hence stronger than Al–H bond hence less easily broken to form H^- nucleophile OR B is more electronegative than Al hence B–H bond is less polar and H^- nucleophile is formed less readily hence no reduction occur with $NaBH_4$. [1]

$LiAlH_4$ supplies the H^- nucleophile which is able to attack the electron deficient carboxylic acid carbon to reduce it to a primary alcohol. [1] H^- nucleophile does not reduce alkene as C=C bonds are non-polar / they are repelled by electron rich C=C.

H_2 with Ni catalyst is able to reduce alkene as alkenes and hydrogen molecules can be adsorbed onto active sites of Ni catalyst for heterogeneous catalysis to take place. [1]

(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]

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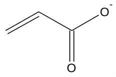
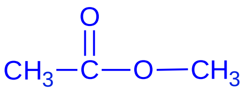
In  , the p orbital of oxygen overlaps with both the π electron cloud/orbital of the C=O and C=C bonds. This further disperses the negative charge, stabilising the conjugate base to a greater extent, making acrylic acid a stronger acid (with a lower pK_a). [1]

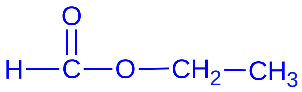
(iii) Propanoic acid has the molecular formula $C_3H_6O_2$.

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]

Test: I_2(aq), NaOH(aq), warm



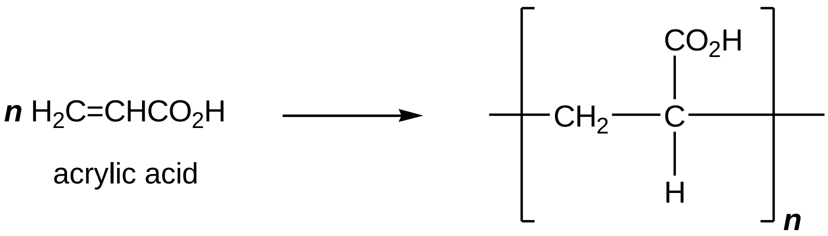
no yellow ppt formed.



yellow ppt formed.

[1] both esters
[1] D.Test (note $KMnO_4$ cannot be used as both methanol and methanoic acid will form CO_2 but we can BOD/ecf obs).
[1] observation

(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.



PAA

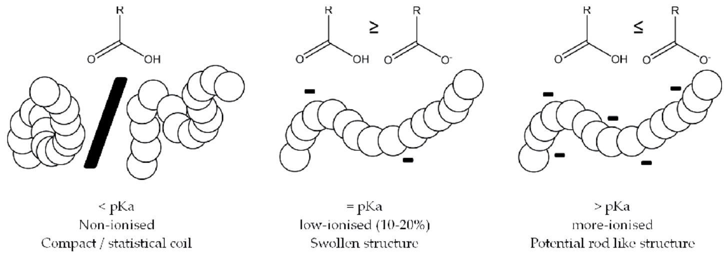
(i) There are two general types of polymerisation reactions: addition polymerisation and condensation polymerisation. Suggest, with explanation, the type of polymerisation that has taken place in the formation of PAA. [1]

<u>Addition polymersiation</u> as the <u>monomer/acrylic acid</u> contains an <u>unsaturated C=C/alkene</u> which becomes saturated in the polymer. [1] accept also it is not condensation polymerisation as there is no small molecule formed as a side product alongside the polymer.

(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]

At pH > 6 (above pK_a of acrylic acid), most of the COOH groups on PAA are deprotonated to form COO^-. The negative charges on the chain are in close proximity and they repel each other, causing the chain to spread out. [1] accept also hydrogen bonds are broken.



Comments: It was good that most students could identify and describe clearly the deprotonation of COOH. However, not many read the question carefully and picked up the important clue of "polymer chain" stretches out… take up a lot more space". Hence, a logical explanation should examine either repulsion of like charges (or alternatively breaking of hydrogen bonds upon deprotonation).

[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]

Electronegativity of an atom is a measure of its ability to attract the bonding/shared pair of electrons (or electron density) in a covalent bond towards itself. [1]

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

- Down a group, atomic radius increases/there are more electron shells between the nucleus and the outer shell electrons,
- So there is less attraction by the nucleus for the bonding/shared electrons [1]

Do not award "nuclear charge decreases"/reference to ions/ionic radius

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]

$$n(S_7) = \frac{\frac{0.76}{100} \times 1.00}{7 \times 32.1}$$
$$= \frac{0.0076}{224.7}$$
$$= 3.38 \times 10^{-5} \text{ mol}$$ **[1]**

$$n(S_8) = \frac{\frac{98.92}{100} \times 1.00}{8 \times 32.1}$$
$$= \frac{0.9892}{256.8}$$
$$= 3.85 \times 10^{-3} \text{ mol}$$ **[1]**

(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]

$$K_c = \frac{[S_8]^7}{[S_7]^8}$$ **[1]**

$$= \frac{\left[\frac{3.85 \times 10^{-3}}{1}\right]^7}{\left[\frac{3.38 \times 10^{-5}}{1}\right]^8}$$

$= 7.36 \times 10^{18}$ mol^{-1} dm^3 (ecf from (b)(i)) **[1]**

(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]

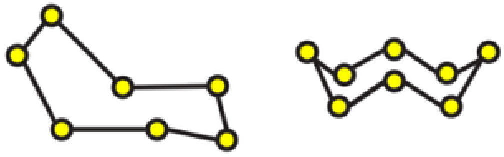
[1]

$8S_7(g) \rightleftharpoons 7S_8(g)$ (eqn not necessary for mk to be allocated)

By Le Chatelier's Principle, the equilibrium will shift right where there are less gas particles, so as to decrease the pressure of the system. Hence the mixture will consists of more S_8 **[1]**

K_C remains the same as temperature remains constant. **[1]**

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



S_7 S_8

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

The energy required to break 1 mole of covalent bonds between 2 sulfur atoms in a gaseous S_8 molecule. **[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]

Enthalpy change of reaction = (8 x 7 x 260.0) – (7 x 8 x 263.3)
= 14560 – 14744.8
= –185 kJ mol^{-1} **[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]

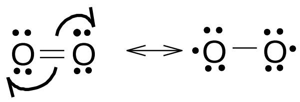
$\Delta G = -RT \ln K_c$
$= -8.31 \times 369 \times \ln(7.36 \times 10^{18})$
$= -1.33 \times 10^5$ J mol^{-1} [1] correct value + units for mk to be awarded

$\Delta G = \Delta H - T\Delta S$
$\Delta S = (\Delta H - \Delta G)/T$
$= \dfrac{-185 \times 10^3 - (-1.33 \times 10^5)}{369}$
$= -141$ J mol^{-1} K^{-1} [1] correct value + units for mk to be awarded

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.

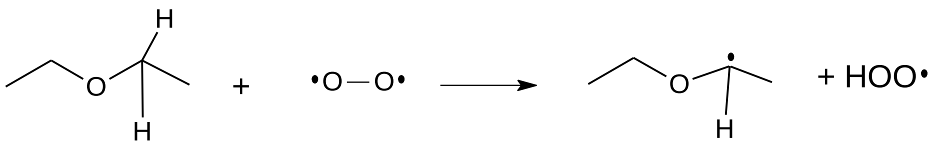
However, on prolonged storage, ethers tend to form explosive hydroperoxides. This is due to a process called autoxidation. Autoxidation of ethers proceeds by a free-radical chain reaction consisting of a series of steps – initiation, propagation, and termination in repetitive cycles.

A resonance form of the oxygen molecule can exist as a diradical. In this form, each oxygen has 7 electrons.



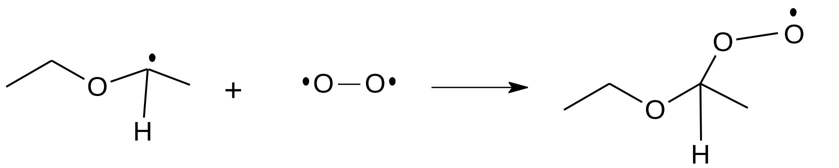
The initiation and propagation steps of the autoxidation of an ether, diethyl ether, $CH_3CH_2–O–CH_2CH_3$ is shown below. The hydroperoxide is mainly formed in the second propagation step.

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

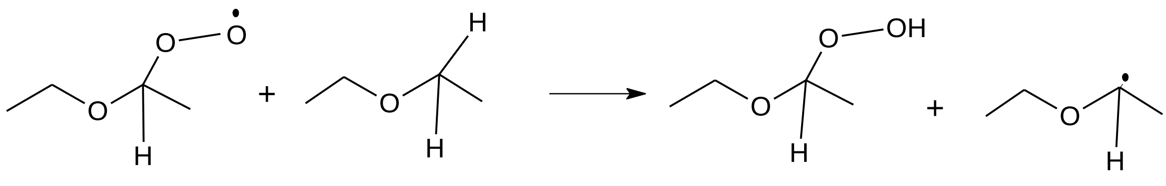


carbon centered radical

Propagation:



oxygen centered radical

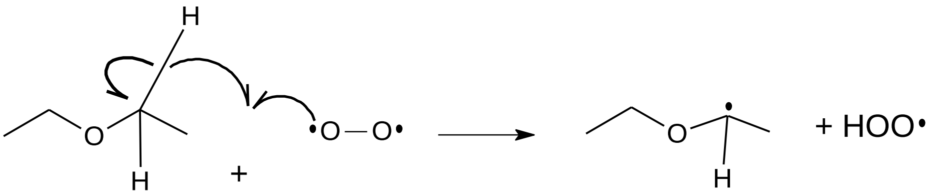


hydroperoxide

Fig. 2.1

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

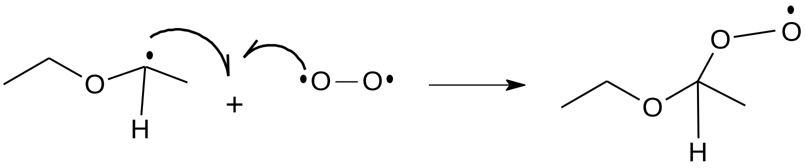
Initiation:



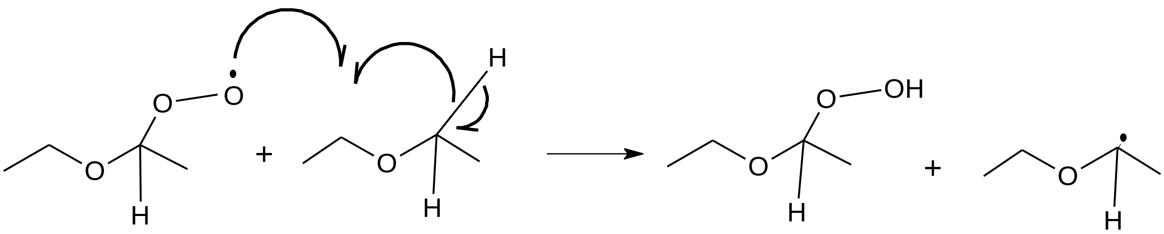
diethyl ether

carbon centered radical

Propagation:



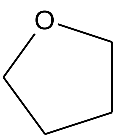
oxygen centered radical

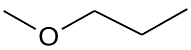


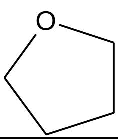
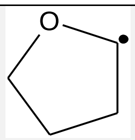
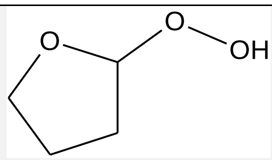
hydroperoxide

2 mks for all 3 equations with correct half arrows
1 mk for any 1 equation with correct half arrows

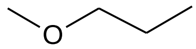
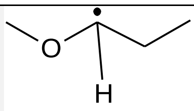
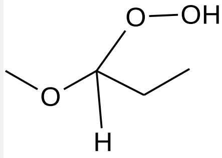
(ii) Give the most stable carbon centered radicals and hydroperoxides formed when the following ethers undergoes autoxidation. [3]

- 

- 

Ether	Carbon centered radical formed in initiation step	Hydroperoxide
		

[1] for both correct

	 [1]	 [1]	More stable 2^{O} radical should be formed

(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]

The peroxides act as an oxidising agent, the oxidation number of iron increases from +2 in $FeSO_4$ to +3 in $[Fe(H_2O)_5SCN]^{2+}$.

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

Shaking the sample with an acidified aqueous solution of potassium iodide/KI(aq). Add CCl_4 (or any other organic solvent) [1]

If peroxides are present, the Fe^{2+} will be oxidised to Fe^{3+}, and Fe^{3+} will reduce iodide ions to iodine. The CCl_4 solution will hence turn purple. [1]

[Total: 20]

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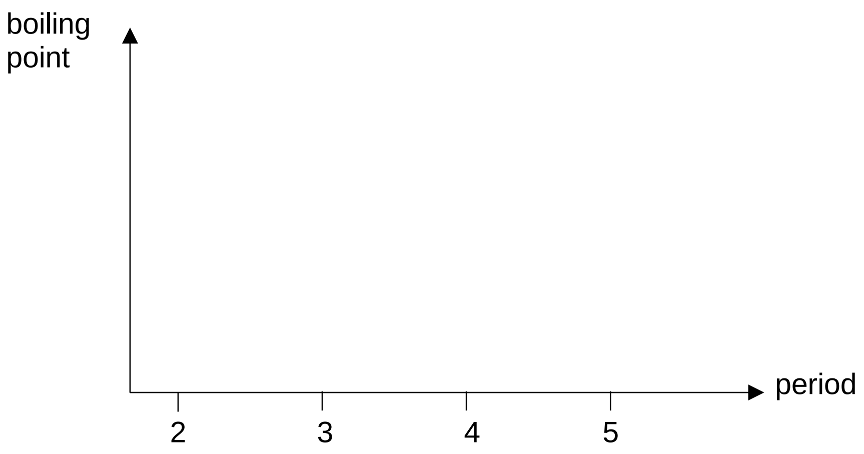
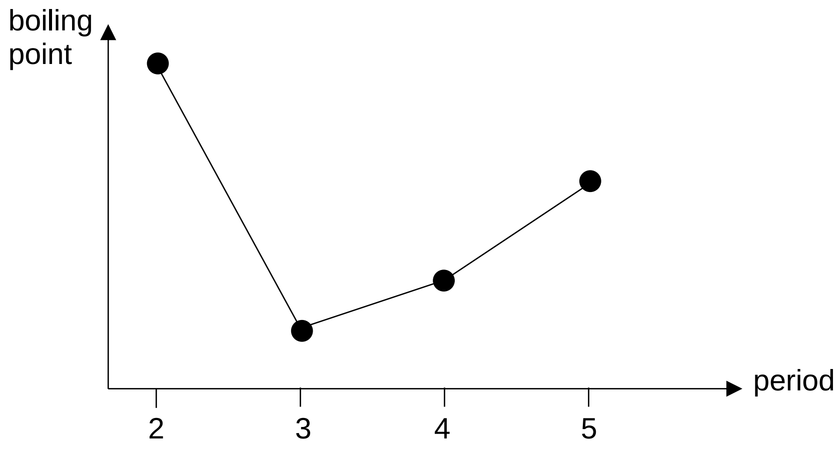
3(a) Sketch a graph on the axis provided to show the variation in the boiling points of group 15 hydrides from nitrogen to antimony. Explain this variation in terms of the structure and bonding of the group 15 hydrides. [4]



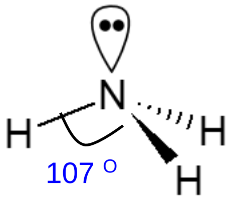


- Graph with appropriate labelling of the axis
- shape of the graph should be similar to what is described and explained below.
- Group 15 hydrides have simple molecular lattice structure.
- Down the group from PH_3 to SbH_3, the increase in number of electrons per molecule makes the molecule more polarisable and so
- instantaneous dipole-induced dipole, id-id forces between molecules become stronger. More energy is required to overcome the increasingly stronger id-id forces and
- boiling point increases.
- More energy is needed to break the
- stronger hydrogen bonds between NH_3 molecules than the weaker instantaneous dipoles-induced dipoles, id-id forces between PH_3 molecules, between AsH_3 molecules and between SbH_3 molecules.
- Hence the boiling point of NH_3 is much higher compared to the hydrides in its group.

9 points – 4 marks; 6-8 points – 3 marks; 3-5 points – 2 marks; 2 points – 1 mark

(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]

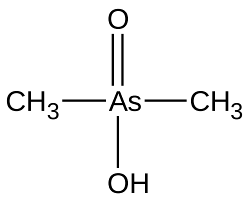
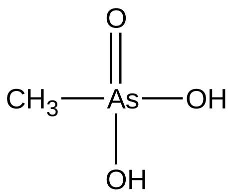


(ii) Explain why the bond angle decreases down the group for Group 15 hydrides from nitrogen to arsenic by considering the electronegativity of the central atom. [2]

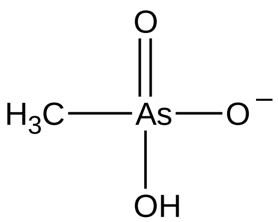
[1] The electronegativity of the central atom decreases from nitrogen to arsenic.
[1] As the less electronegative central atom tends to draw electron density of the bond-pair less towards itself, repulsion between bond pairs is increased by a decrease in the electronegativity of the central atom. This caused the bond pair of electrons to be further from the nucleus and exert less repulsion, causing the bond angle to be smaller.

(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		$(CH_3)_2AsO(OH)$	6.2	–
monomethylarsonic acid		$CH_3AsO(OH)_2$	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]



[1]

$CH_3AsO(OH)_2 + H_2O \overset{K_{a1}}{\rightleftharpoons} CH_3AsO(OH)O^- + H_3O^+$

$$K_{a1} = \frac{[CH_3AsO(OH)O^-][H_3O^+]}{[CH_3AsO(OH)_2]}$$

Ratio of $\dfrac{[CH_3AsO(OH)_2]}{[CH_3AsO(OH)O^-]} = \dfrac{[H_3O^+]}{K_{a1}}$

% of $CH_3AsO(OH)_2$ present at pH 7

$= \dfrac{[H_3O^+]}{[H_3O^+]+K_{a1}} \times 100 = \dfrac{10^{-7}}{10^{-7}+10^{-4.1}} \times 100 = 0.126\ \%$ [1]

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]

$[H^+] = \sqrt{10^{-4.1} \times 0.10} = 2.818 \times 10^{-3}$ mol dm^{-3}

pH = – lg 2.818×10^{-3} = 2.55

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

[1] At 5 cm^3, 1st maximum buffering capacity point where pH = pK_1 = 4.1

[1] At 10 cm^3, 1st equivalence point, solution contains $CH_3AsO(OH)O^-$ which is an (overall) acidic salt with pK_a = pK_2 ($CH_3AsO(OH)O^-$ is amphoteric with pK_b = 14 – 4.1 = 9.9 and pK_a = 8.7; since its pK_a < pK_b, hence it is more likely to act as an acid)

$CH_3AsO(OH)O^- + H_2O \rightleftharpoons CH_3AsO_3^{2-} + H_3O^+$ pK_2

$[CH_3AsO(OH)O^-] = \dfrac{\frac{10}{1000} \times 0.10}{\frac{20}{1000}}$ =0.05 mol dm^{-3}

pH = $-\lg\sqrt{0.05 \times 10^{-8.7}}$ = 5.00

[1] At 15 cm^3, 2nd maximum buffering capacity point, pH = pK_2 = 8.7

[1] At 20 cm^3, 2nd equivalence point, solution contains $CH_3AsO_3^{2-}$ which is a basic salt with pK_b = 14 – pK_2

$[CH_3AsO_3^{2-}] = \dfrac{\frac{10}{1000} \times 0.10}{\frac{30}{1000}}$ = 0.03333 mol dm^{-3}

pOH = $-\lg\sqrt{0.03333 \times 10^{-(14-8.7)}}$ = 3.388

pH = 14 – 3.388 = 10.61

[1] At 25 cm^3, solution contains 5 cm^3 excess NaOH

pH of the solution = pH of the excess 5 cm^3 of NaOH

$[OH^-]$ = conc. of the 5 cm^3 of excess NaOH in a total solution volume of 35 cm^3

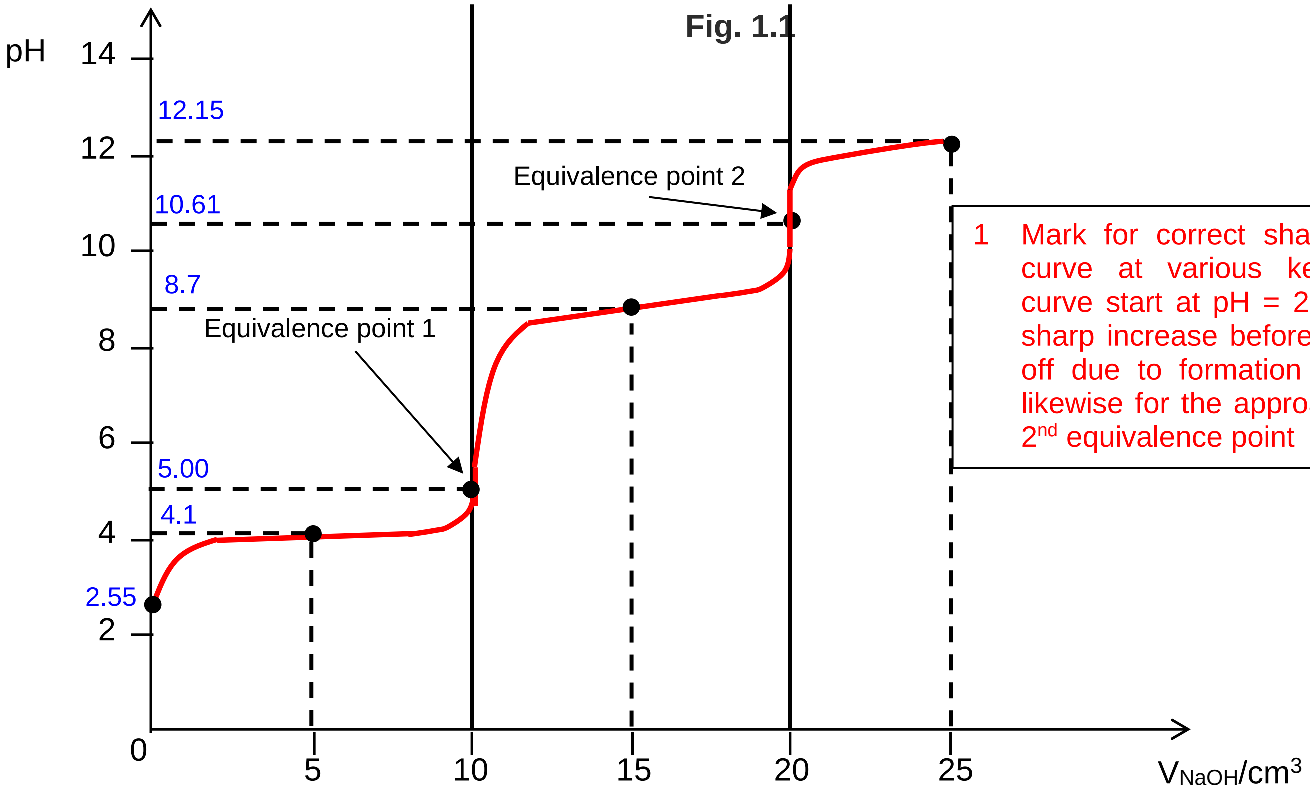
$= \dfrac{\frac{5}{1000} \times 0.10}{\frac{35}{1000}}$ 0.01428 mol dm^{-3}

pH = 14 – pOH = 14 – (–lg 0.01428) = 12.15

 [Turn Over

(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]

Fig. 1.1



1 Mark for correct shape of the curve at various key points: curve start at pH = 2.55 with a sharp increase before flattening off due to formation of buffer, likewise for the approach to the 2nd equivalence point

For Examiner's Use

(iv)

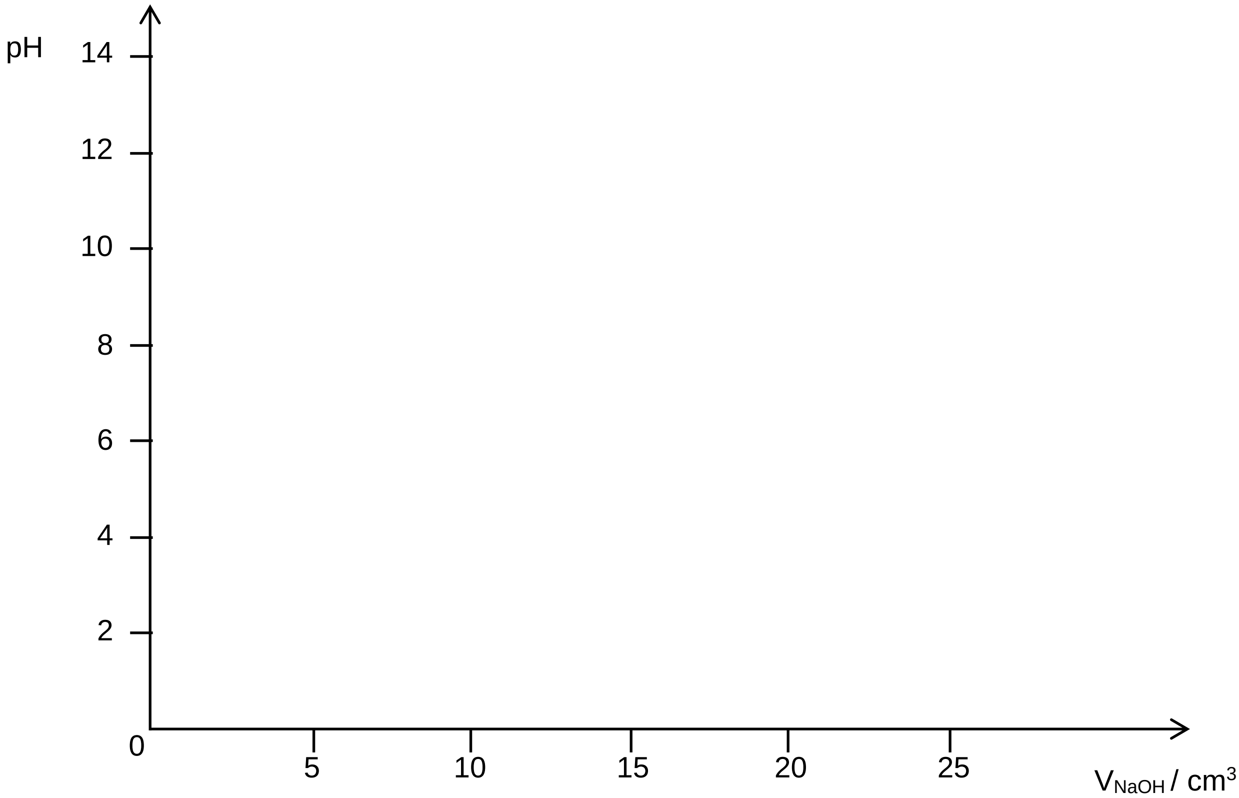
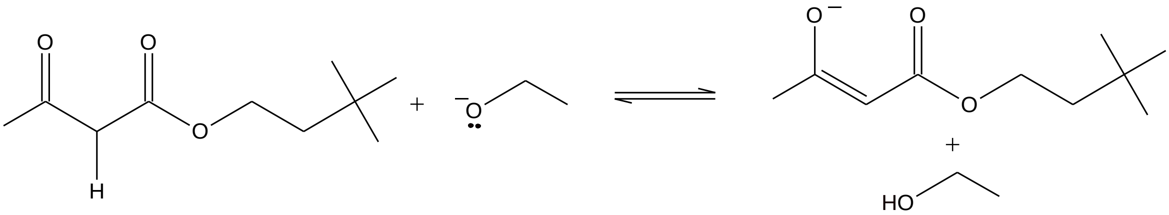


Fig. 3.1

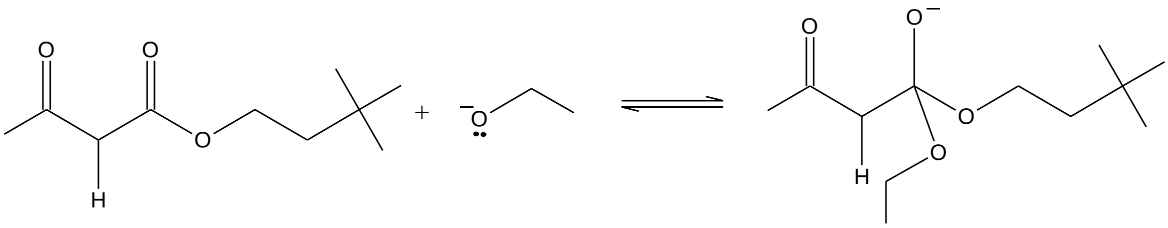
For Examiner's Use

(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**.



A

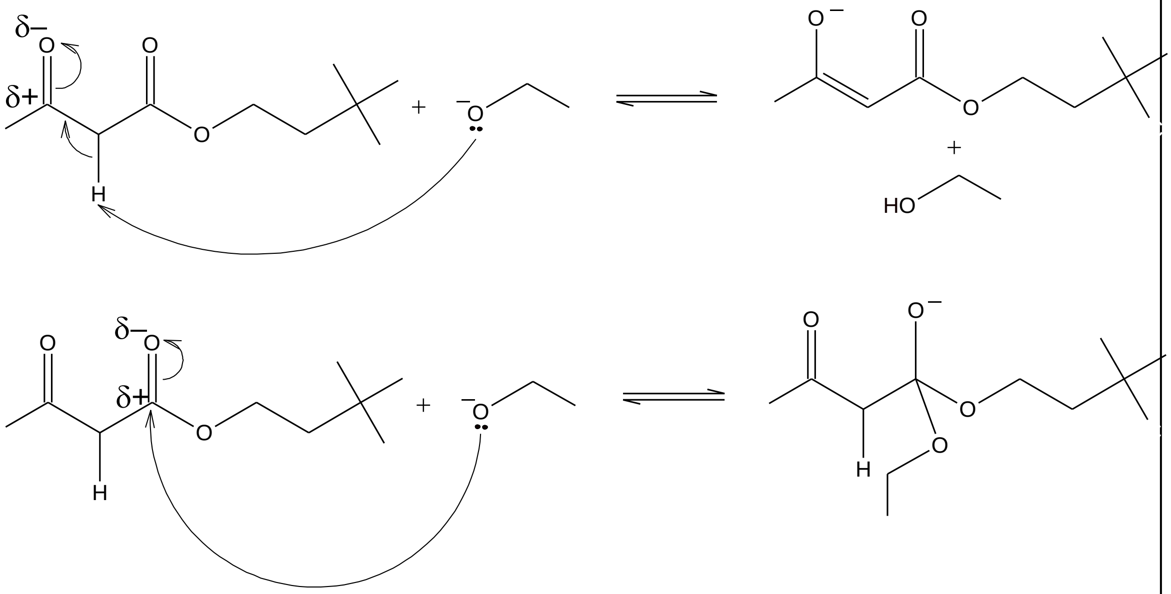
Fig. 3.2



A

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]



1 mark each

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

- In Fig. 1.2 , **A** acts as a Bronsted-Lowry acid.
- In Fig. 1.3, **A** acts as an electrophile.

[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 O  N.

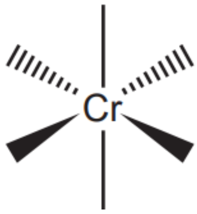
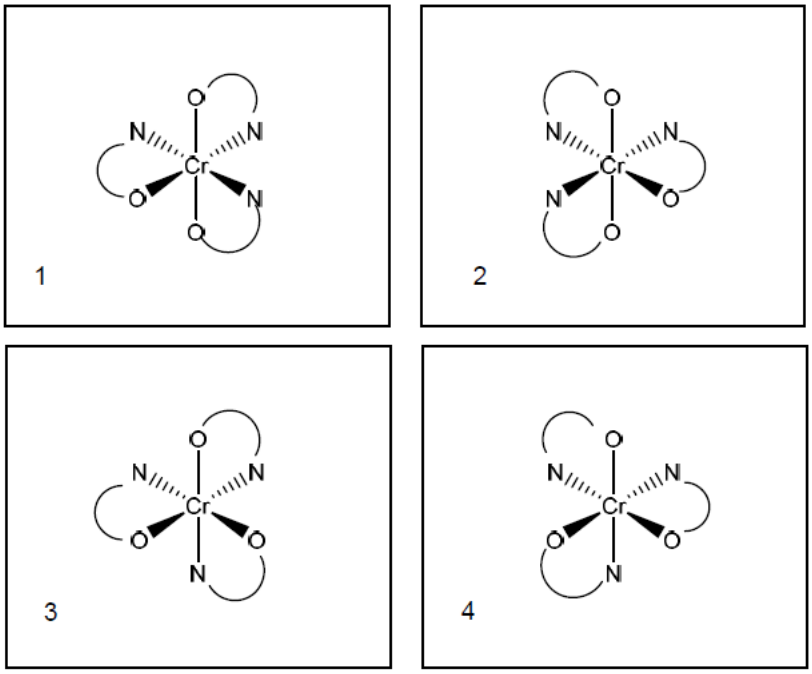


Fig. 4.1

[2]



[1] for two correct structures
[2] for two pairs of enantiomers drawn as mirror images

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....

 [Turn Over

(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.

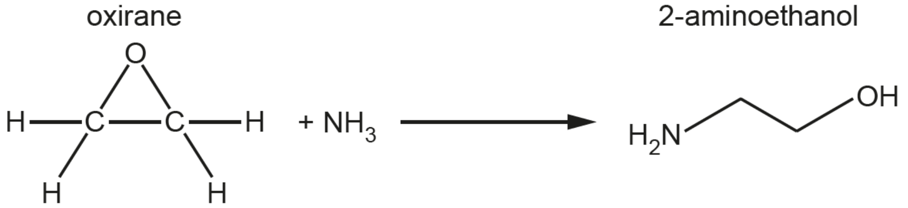


Fig. 4.2

(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.

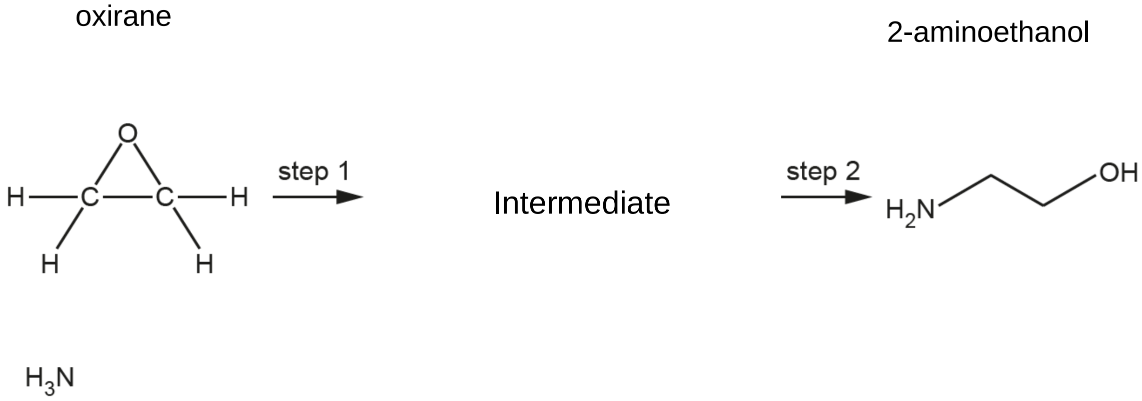
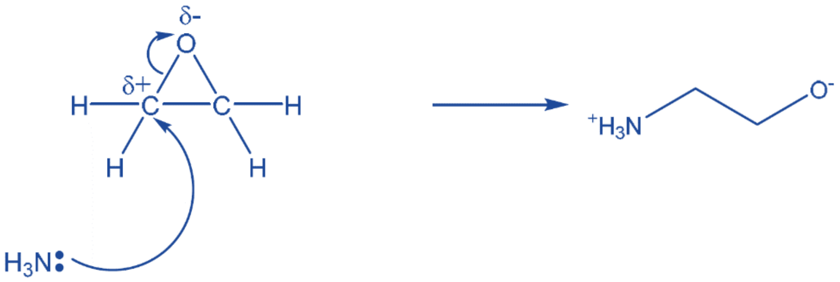


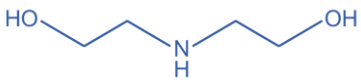
Fig. 4.3

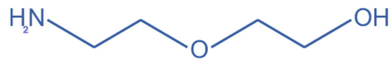
[2]



[1] for correct curly arrows, lone pairs of electrons, charges and partial charges
[1] for correct intermediate

(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]

E: 

[1] (alternatively:) 

Explanation (not required): There is a lone pair on the nitrogen atom / oxygen atom of 2 aminoethanol, this allows it to act as a nucleophile to attack the electron deficient carbon atom of oxirane, forming compound **E**.

Its formation can be minimised by increasing the concentration of NH_3 / excess NH_3/ limited oxirane. [1]

 [Turn Over

For Examiner's Use

(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]

The d_{x2-y2} and d_{z2} orbitals have lobes directed along the x, y, and z axes pointing toward the approaching ligands while d_{xy}, d_{yz} and d_{xz} orbitals have lobes that are directed between the axes along which the ligands approach.
Hence, electrons in the d_{x2-y2} and d_{z2} orbitals experience stronger repulsions from the lone pair of electrons in the ligands than those in the d_{xy}, d_{xz}, and d_{yz} orbitals. [1]

Therefore, d_{x2-y2} and d_{z2} will be the higher energy d-orbitals, while d_{xy}, d_{xz}, and d_{yz} will be the lower energy d-orbitals. [1]

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

Cu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$
Cu^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ [1]

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

- Cu^+ salt is white or colourless because its d orbitals are fully filled, and d-d transitions are not possible. Cu^{2+} salt is coloured because its d orbitals are partially filled.
- The presence of ligands causes the energy level of the five 3d orbitals to be split into two different levels.
- The energy difference, ΔE, corresponds to wavelengths in the visible spectrum.
- When light energy is absorbed by the substance, an electron is promoted from a d orbital of lower energy to one of higher energy. This is not possible for Cu^+.
- Unabsorbed wavelengths are transmitted and the colour of the complex is complementary to the colour absorbed.

[3]: 5 points, [2]: 3 to 4 points, [1]: 1 to 2 points

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

The electronic configuration of Cu^{2+} and Mn^{3+} is different, thus the extent of repulsion between the ligands and the electrons around the metal centre is different, resulting in an energy gap, ΔE, of a different magnitude. This implies that the light absorbed by the manganese complex is different from the light absorbed by the copper complex, thus the complement colour observed for each complex will be different.

For Examiner's Use

(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.

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

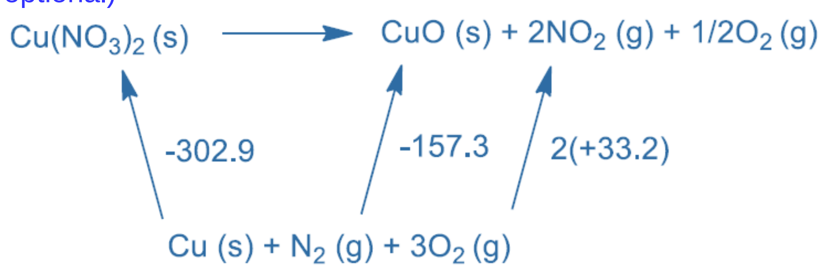
Table 4.1 lists the $\Delta H_f^{\ominus}$ values for some compounds.

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]

(Cycle optional)



$\Delta H^{\ominus} = \Delta H^{\ominus}_f$ (products) − $\Delta H^{\ominus}_f$ (reactants)
= (−157.3) + 2(+33.2) − (−302.9) = +212 kJ mol^{-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]

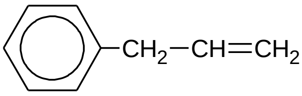
$\Delta S^\ominus = S^\ominus$ (products) − $S^\ominus$ (reactants)
= 92.4 + ½ (205.2) − 2(42.6) = +109.8 J mol^{-1} K^{-1} = +110 J mol^{-1} K^{-1} [1]
Given that $\Delta H^\ominus$ is positive and $\Delta S^\ominus$ is positive, using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, when high temperature is used, the magnitude of $T\Delta S^\ominus$ is greater than the magnitude of $\Delta H^\ominus$, $\Delta G^\ominus$ becomes negative and the reaction is spontaneous. Thus, high temperature favours the formation of Cu_2O. [1]

(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.

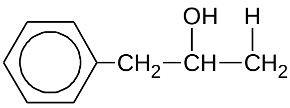
A hydrocarbon **R**, C_9H_{10}, does not exhibit stereoisomerism. When **R** is reacted with steam and phosphoric acid at 300 °C and 60 atm, compound **S**, $C_9H_{12}O$, is obtained which gives a yellow solid when reacted with alkaline aqueous iodine.

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**, $C_9H_{10}O$.

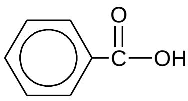
Draw the structures of **R**, **S**, **T** and **U**. [4]



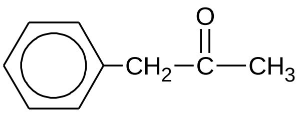
R



S



T



U

[4]

[Total: 20]

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]

Lewis bases are electron pair donors. [1]
Example: $CH_3CH_2NH_2 + H^+ \rightarrow CH_3CH_2NH_3^+$ [1]

Do not accept NH_3

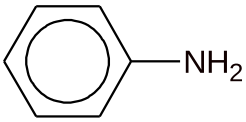
(ii) Describe and explain the relative basicities of methylamine, dimethylamine, and trimethylamine in the gas phase. [2]

Increasing basicity: methylamine, dimethylamine, trimethylamine [1]

There are 3 electron-donating methyl groups in trimethylamine (tertiary amine), 2 electron-donating methyl groups in dimethylamine (secondary amine) and 1 electron-donating methyl group in methylamine (primary amine). As the number of electron-donating groups present increases, the electron-density on N atom increases. This resulted in increasing availability of the lone pair of electron for donation to an empty orbital. [1]

(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]

$$K_b = \frac{[NH_3^+OH][OH^-]}{[NH_2OH]}$$ [1]

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

Increasing basicity: phenylamine, hydroxylamine, ammonia, ethylamine

- **$CH_3CH_2NH_2$ is a stronger base than NH_3.**
In $CH_3CH_2NH_2$, the electron-donating CH_3CH_2– group increases the electron density on the N atom. Hence, lone pair of electrons on N atom is more available than the lone pair of electrons on N atom in NH_3 for dative bonding with H^+.[1]

- **Phenylamine is a weaker base than NH_3.**
In phenylamine, the p-orbital of the N atom overlaps with the π orbital of the benzene ring, resulting in the delocalisation of the lone pair of electrons on N atom into the benzene ring thus decreasing its availability for dative bonding with H^+.[1]

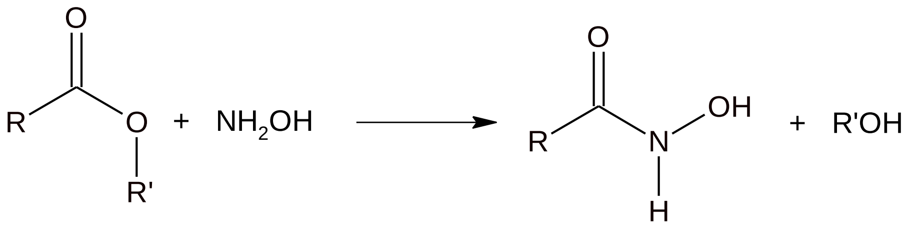
- **Hydroxylamine is a weaker base than ammonia.**

The presence of electron-withdrawing –OH group will further decrease the electron density on N atom. So the lone pair of electrons on N atom is less available for dative bonding with H^+. Hence hydroxylamine is less basic than ammonia. [1]

- **Phenylamine is a weaker base than hydroxylamine.**

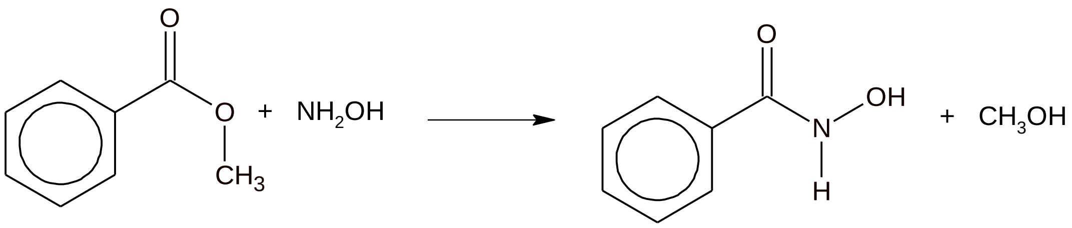
The delocalisation of electrons in phenylamine is more significant compared to the electron-withdrawing – OH group in hydroxylamine. Hence the lone pair of electrons on N atom in phenylamine is less available for dative bonding with H^+. [1]

(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]



[1]

R = benzene ring, R' = CH_3
Nucleophilic substitution [1]

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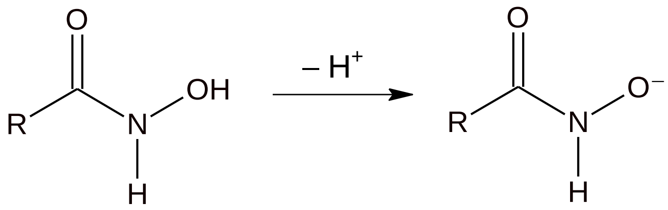
(d) Hydroxamic acid deprotonates to form hydroxamate anion.



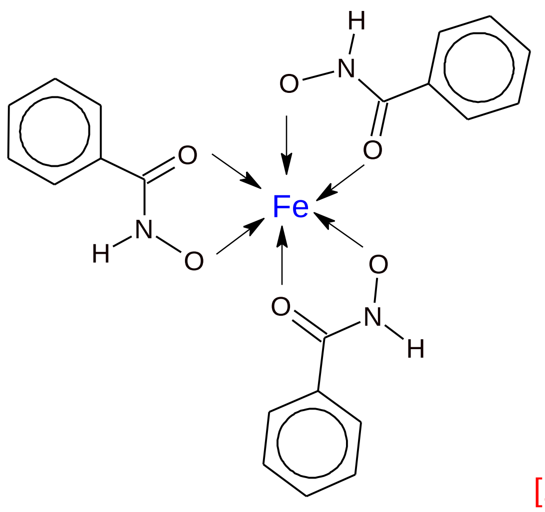
hydroxamic acid hydroxamate

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

Bidentate ligand consists <u>2 lone pairs of electrons</u> to form <u>2 dative bonds</u> with central metal atom/ion to form complex. [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]

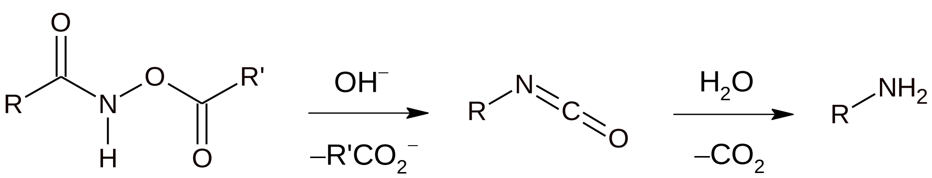


[1]

<u>Ligand exchange</u> where H_2O ligands are replaced by benzohydroxamate anion. [1]

$[Fe(H_2O)_6]^{3+} + 3C_6H_5CONHO^-$ ∏ $[Fe(C_6H_5CONHO)_3] + 6H_2O$ [1]

(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.



hydroxamate ester isocyanate amine

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

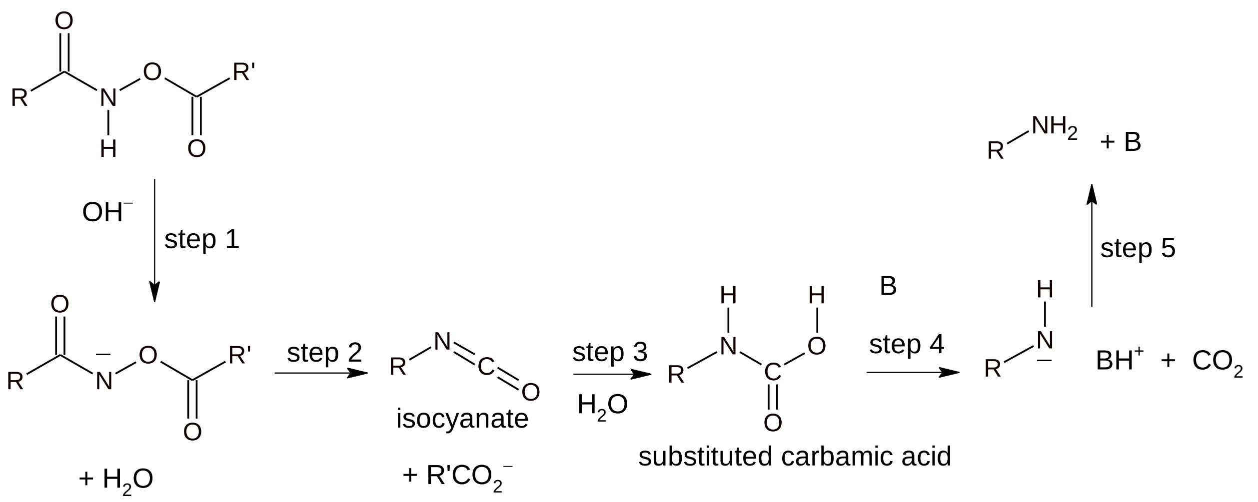


Fig. 5.1

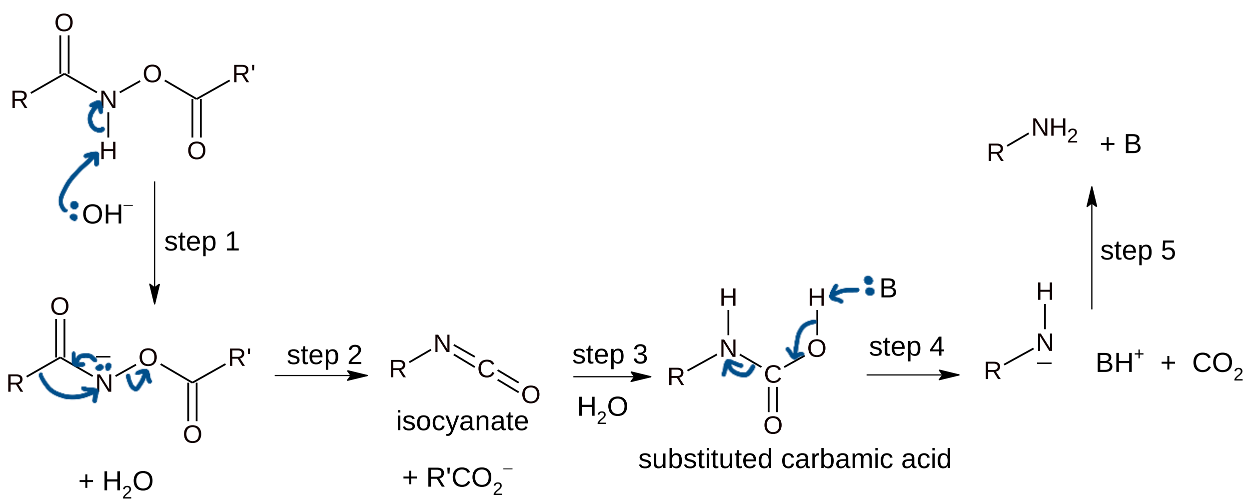
Step 1: Hydroxamate ester is converted to its conjugate base by removing a proton using a base, OH^-.

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 an amine, RNH_2, and CO_2.

(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]



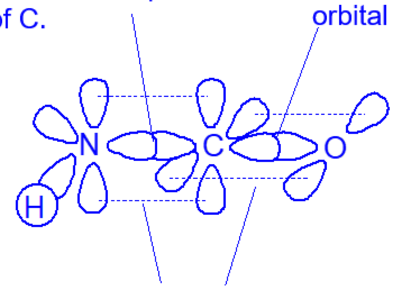
Each step [1] x 3

(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]

σ bond in N = C formed via head-on overlap of sp^2 orbital from N and sp orbital of C.

σ bond in C = O formed via head-on overlap of sp orbital from C and sp^2 orbital of O.

N – H σ bond formed via head-on overlap of sp^2 orbital from N and 1s orbital of H.



Correct identification of orbitals for H, N, C and O. [1]

Type of orbital overlap and bonds formed [1]

π bond in N = C and C = O formed via side-on overlap of p orbitals from N and C, C and O respectively.

[Total: 20]

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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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[End of Paper]