ANDERSON SERANGOON JUNIOR COLLEGE

2021 JC 2 PRELIMINARY EXAMINATION

NAME:_____ (   )   CLASS: 21 /_____

CHEMISTRY   **9729/03**

Paper 3 Free Response   **20 September 2021**

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces 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. 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

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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.

<table>
<tr><th colspan="5">For Examiner's Use</th></tr>
<tr><td rowspan="6">Paper 3</td><td>A1</td><td>/19</td><td>Paper 1 (15%)</td><td>/ 30</td></tr>
<tr><td>A2</td><td>/18</td><td>Paper 2 (30%)</td><td>/ 75</td></tr>
<tr><td>A3</td><td>/19</td><td>Paper 3 (35%)</td><td>/ 76</td></tr>
<tr><td>B4*</td><td>/20</td><td>Paper 4 (20%)</td><td>/ 55</td></tr>
<tr><td>B5*</td><td>/20</td><td>Percentage</td><td></td></tr>
<tr><td colspan="2">*Circle the question you have attempted</td><td>Grade</td><td></td></tr>
</table>

This document consists of **28** printed pages.

Section A

Answer **all** the questions from this section.

1 (a) SiH₄, PH₃ and H₂S are three compounds whose central atoms in their molecules are elements in Period 3 of the Periodic Table.

(i) State and explain the bond angles in the molecules of these three compounds. [4]

(ii) In this question, you may assume that phosphorus and hydrogen have the same electronegativity.
Draw the three molecules, SiH₄, PH₃ and H₂S and indicate for each one the polarity of each of the bonds it contains and the overall polarity of the molecule. [4]

(iii) State the properties of a gas necessary for it to approach ideal behavior. [2]

(iv) Of the three gases at 400 K, the behaviour of SiH₄ is closest to ideal gas behavior.

Suggest why H₂S deviate more from ideal behaviour than SiH₄. [1]

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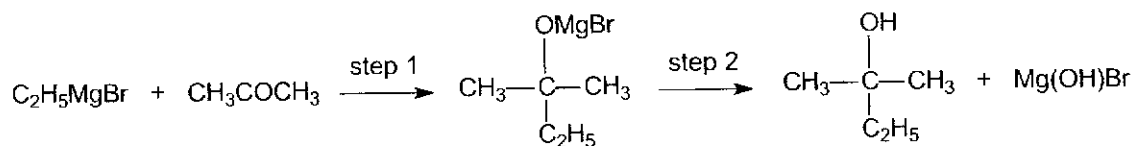...

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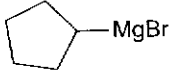
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9729/03/H2 **[Turn over**

(b) **(i)** Define the term *lattice energy*. [1]

(ii) Use the data in Table 1.1, together with relevant data from the *Data Booklet*, to calculate a value for the lattice energy of magnesium iodide, $MgI_2(s)$. Show your working.

Table 1.1

	value / kJ mol^{-1}
electron affinity of iodine, $I(g) + e^- \rightarrow I^-(g)$	-295.4
enthalpy change of sublimation of iodine molecules, $I_2(s) \rightarrow I_2(g)$	$+62.4$
standard enthalpy change of atomisation of Mg(s)	$+148$
standard enthalpy change of formation of $MgI_2(s)$	-364

[3]

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(c) Magnesium forms an important group of covalent compounds which are known as Grignard reagents. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic synthesis.

A typical example of the use of a Grignard reagent is the two–step reaction of C_2H_5MgBr with propanone, CH_3COCH_3 to form 2–methylbutan–2–ol.

$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step 1}} CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{OMgBr}{|}}{C}} - CH_3 \xrightarrow{\text{step 2}} CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{OH}{|}}{C}} - CH_3 + Mg(OH)Br$$

(i) Suggest the type of reaction which occurs in step 2. [1]

(ii) Suggest the structural formula of the final organic product formed when [cyclopentyl]—MgBr is reacted with ethanal, CH_3CHO, in a similar two–step process. [1]

(iii) The Grignard reagent CH_3CH_2MgBr can be readily converted into a carboxylic acid by using carbon dioxide, as shown in the two–step reaction sequence in Fig. 1.1.

$$CH_3CH_2MgBr + CO_2 \xrightarrow{\text{step 1}} \text{compound A} \xrightarrow{\text{step 2}} \text{compound B} + Mg(OH)Br$$
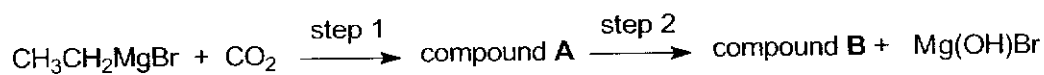
Fig. 1.1

Suggest the structural formula for compounds **A** and **B**. [2]

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(d) Two different complexes **F** and **G** can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Each complex contains a cobalt(III) ion bonded to six ligands, which can be either NH_3 or Cl^-. The cobalt(III) complexes in **F** and **G** are octahedral in shape and an octahedral arrangement is shown in Fig. 1.2.
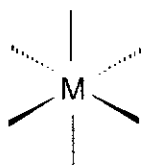
Fig. 1.2

2 mol and 1 mol of white precipitate are formed respectively when 1 mol each of the complexes **F** and **G** is treated separately with aqueous $AgNO_3$.

(i) Deduce the structural formulae of complexes **F** and **G**.   [2]

(ii) The cobalt(III) complex in **G** exhibits *cis–trans* isomerism, like alkenes.

Suggest the structure of the *trans* isomer, showing clearly how the ligands are bonded to the central metal ion.   [2]

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[Total: 23]

Question 2 starts on the next page.

2   (a)   Chlorine is a greenish yellow gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes as shown in Fig. 2.1.
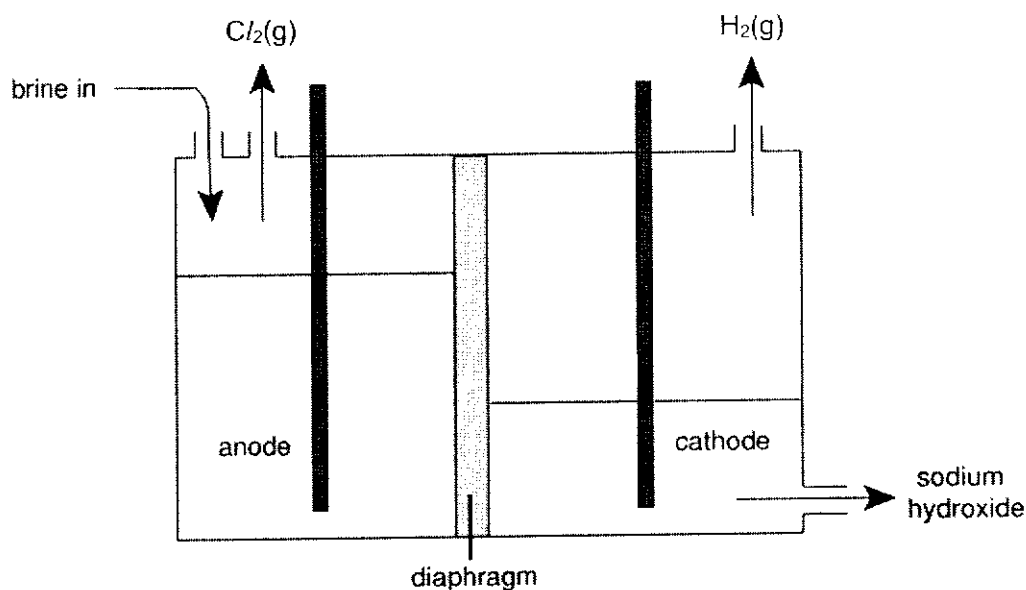
Fig. 2.1

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by–products.

(i)   Given the cathode reaction: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Write the ion-electron half-equation for the reactions taking place at the anode. Hence, construct the overall equation. You are to provide state symbols for all the equations.

[2]

(ii)   Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell.   [3]

Using relevant data from the *Data Booklet*, explain why

(iii)   Dilute sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis.   [1]

(iv)   Unlike chlorine, fluorine gas cannot be manufactured in a similar way using concentrated sodium fluoride.   [1]

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(b) When the diaphragm in Fig, 2.1 is removed, the chlorine produced can react with the hydroxide ions to produce chloride, Cl^- and chlorate(V), ClO_3^-.

Using oxidation numbers, construct a balanced equation for this reaction. Show your working. [2]

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(c) The standard electrode potentials, $E^\ominus$, of different chlorine–containing species and hydrogen peroxide are shown in Table 2.1.

Table 2.1

	Half–equation	$E^\ominus$ / V
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
4	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77

Predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-. [3]

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Question 2 continues on the next page.

Glucose, $C_6H_{12}O_6$, is an ideal fuel for fuel cells because it is abundant in nature, renewable, non–toxic and easy to produce. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set–up is illustrated in Fig. 2.2.
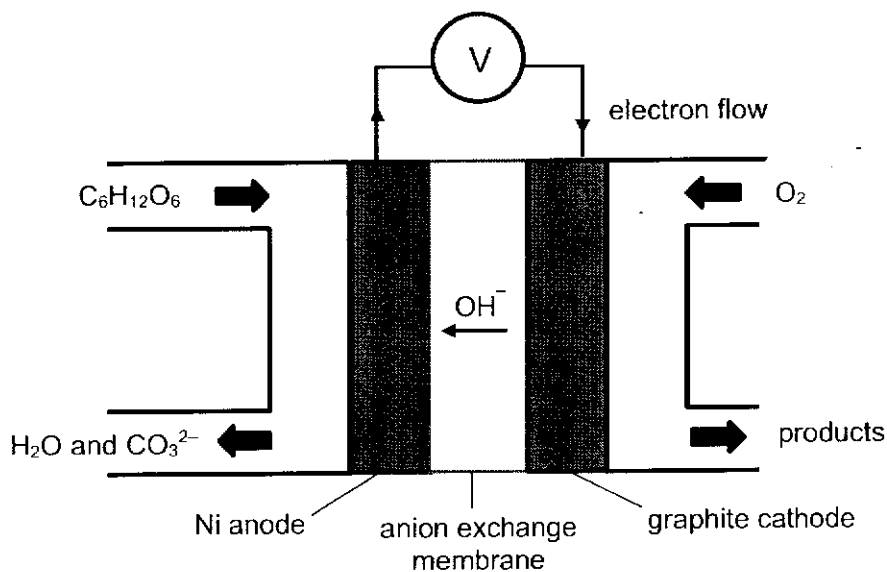
Fig. 2.2

At the anode, glucose is oxidised to carbonate ions, CO_3^{2-}, in an alkaline medium while oxygen gas is reduced at the cathode. The overall reaction occurring in the fuel cell is given below.

$$C_6H_{12}O_6 + 6O_2 + 12OH^- \rightarrow 6CO_3^{2-} + 12H_2O \qquad E^{\ominus}_{cell} = +0.85 \text{ V}$$
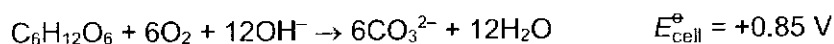
(d) **(i)** Calculate $\Delta G^{\ominus}$ for the overall reaction occurring in this fuel cell. [2]

(ii) Calculate the standard electrode potential for the half–equation for the reduction of CO_3^{2-} to $C_6H_{12}O_6$, using appropriate $E^{\ominus}$ value from the *Data Booklet*. [1]

(e) In the fuel cell, glucose molecules are adsorbed on the nickel anode surface prior to oxidation to carbonate ions. Fig. 2.3 shows how the E_{cell} varies with the concentration of glucose.
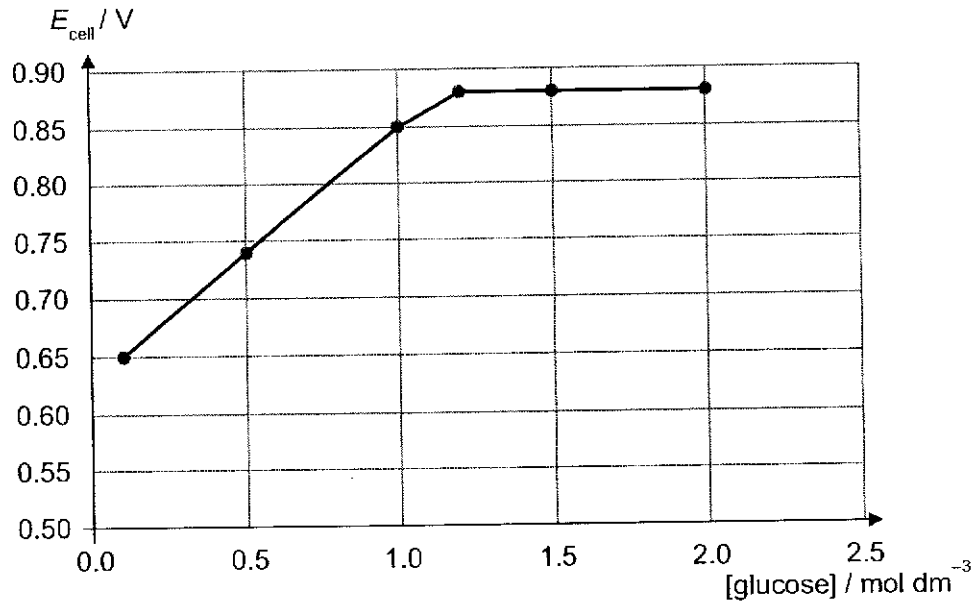
Fig. 2.3

Explain the shape of the graph. [2]

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(f) Beside the advantages mentioned in the question, suggest another possible advantage of using the glucose fuel cell compared to a hydrogen fuel cell. [1]

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[Total: 18]

3   Succinic acid, $HO_2CCH_2CH_2CO_2H$ is a diprotic acid, which serves as the precursor of certain biodegradable polymers of interest in tissue engineering applications. It is also commonly used as an acidity regulator in the food and beverage industry.

The two pK_a values associated with it are 4.2 (pK_{a1}) and 5.4 (pK_{a2}).

(a)   (i)   Butanoic acid, $CH_3CH_2CH_2CO_2H$ has a pK_a of 4.8.

With the aid of a diagram, explain why the pK_{a1} of succinic acid is lower than pK_a of butanoic acid.   [2]

(ii)   Calculate the pH of a 0.10 mol dm^{-3} solution of succinic acid (ignore the effect of pK_{a2} on pH).   [1]

(iii)   Determine the pH of the resulting solution when 30 cm^3 of 0.10 mol dm^{-3} KOH(aq) is added to 10 cm^3 of 0.10 mol dm^{-3} succinic acid.   [2]

(iv)   Hence using the information provided and your answers to (a)(ii) and (a)(iii), sketch the pH–volume curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} KOH(aq) is added to 10 cm^3 of 0.10 mol dm^{-3} succinic acid.
[No additional calculation is required.]   [3]

(b) Succinic acid can be synthesised from bromoethanal via a series of reaction.

Bromoethanal was reacted with HCN in the presence of KCN to form **W**, C_3H_4BrNO. **W** was then reacted with reagent **U** under appropriate condition to form **X**, $C_4H_4N_2O$.

Upon heating **X** with dilute hydrochloric acid, **Y**, $C_4H_6O_5$ was generated.

Y was then heated with concentrated sulfuric acid to form **Z** which is a dicarboxylic acid with molecular formula $C_4H_4O_4$. Subsequent introduction of $H_2(g)$ in the present of platinum catalyst will convert **Z** to succinic acid.

It is also known that when hot acidified $KMnO_4$ was added to **Z**, only an acidic gas was produced.

(i) State reagent **U** and the conditions required to convert **W** to **X**. [1]

(ii) Deduce the structures of **W**, **X**, **Y** and **Z**, explaining the reactions described. [7]

(iii) **Z** is known to exhibit stereoisomerism. Draw and label the **skeletal** formula of the stereoisomers of **Z**. [2]

(iv) Write a chemical equation to show the reaction between **Z** and hot acidified $KMnO_4$. [1]

[Total: 19]

18

Section B

Answer **one** question from this section.

4 (a) Cyanogen iodide, ICN exists as white crystals that react slowly with water to form hydrogen cyanide and one other acidic iodine–containing by–product. The oxidation number of iodine in the by–product is +1.

(i) State the molecular formula of the by–product. [1]

(ii) Draw the displayed structure of the by–product. · [1]

(iii) Cyanogen iodide, ICN, undergoes addition reactions with alkenes. With but–1–ene, isomer **D** is produced rather than isomer **E**.
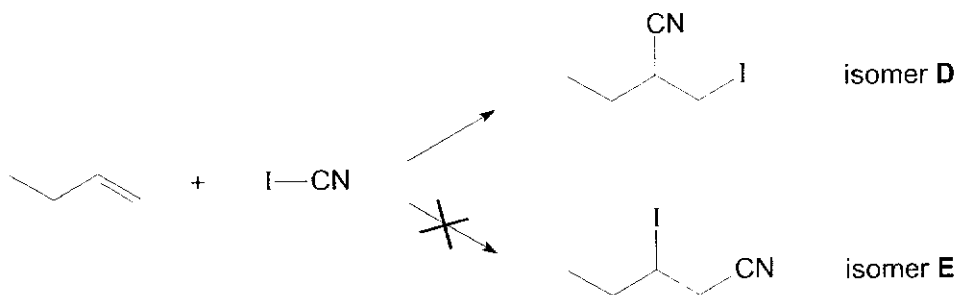
Fig. 4.1

Suggest a mechanism for this reaction. [2]

(iv) With reference to the mechanism and carbocation intermediate formed, explain the preferential production of isomer **D**. [1]

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(b) State how the reactivity of the halogens as oxidising agents varies down the group and relate these variation to relevant $E^⦵$ value.

Hence, deduce the products formed when F_2 and Br_2 is added separately to $NaCl(aq)$. [2]

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(c) Sodium, aluminium and sulfur are elements in Period 3 of the Periodic Table.

Use the oxides of these three elements to describe reactions that illustrate the variation in their acid–base behaviour. Write equations for all the reactions you describe. [5]

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(d) Table 4.1 lists the boiling points of some Period 3 oxides.

Table 4.1

compound	formula	boiling point / °C
sodium oxide	Na_2O	1950
silicon oxide	SiO_2	2230
sulfur dioxide	SO_2	−10
sulfur trioxide	SO_3	45

(i) Using structure and bonding, suggest reasons for the differences in boiling points of Na_2O, SiO_2 and SO_2. [3]

(ii) Account for the difference in boiling points between SO_2 and SO_3. [1]

(iii) SO_2 and SO_3 are sealed in separate containers and heated from room temperature to a temperature of 100 °C.

With reference to Table 4.1, explain which compound will show a greater change in entropy. [1]

(iv) When reacted with SO_3, PCl_3 produces a compound **J** with $M_r = 153.5$ and a by–product **K**. **J** is also produced when PCl_5 is reacted with a small amount of H_2O.

Suggest the identity of **J** and **K** and construct equations for the production of **J** from PCl_3 and PCl_5. [3]

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[Total: 20]

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5 (a) The Strecker Synthesis is a preparation method for α–amino acids using aldehydes. In the process, α–aminonitriles, which are versatile intermediates to form α–amino acids via hydrolysis of the nitrile group.
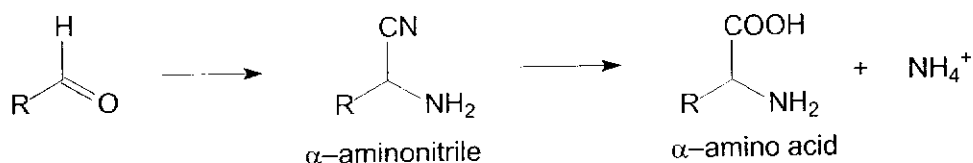
Alanine, 2–aminopropanoic acid, can be prepared from ethanal via Strecker Synthesis as shown in Fig. 5.1.
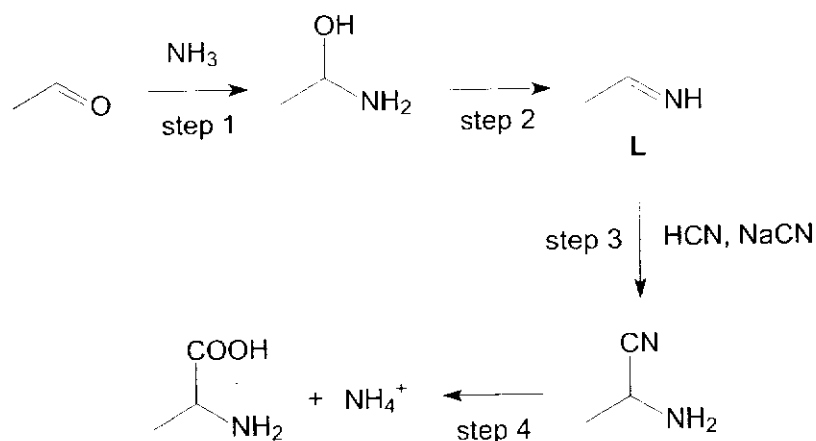
Fig. 5.1

(i) Alanine has a melting point of 213 °C while ethanal has a melting point of –124 °C. Suggest reasons for the difference in their melting points. [2]

(ii) Imines are the nitrogen analogues of aldehydes and ketones, containing a C=N bond instead of a C=O bond. Compound L in Fig 5.1 is one example of an imine.

Assuming the C=N bond of imines has the same reactivity as the C=O bond of carbonyl compounds, name and describe a mechanism for step 3 shown in Fig. 5.1. [3]

(iii) Explain why step 3 produces an equimolar mixture of enantiomers. [2]

(iv) Draw the enantiomers formed in step 3. [1]

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(b) Fig. 5.2 shows a five–step laboratory synthesis reaction scheme of protonated alanine from ethanol.
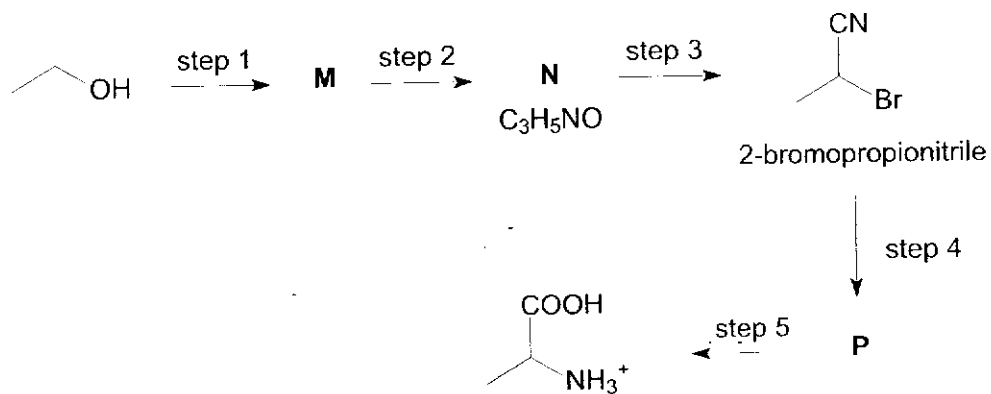
Fig. 5.2

Suggest the structures of the intermediates **M**, **N** and **P** and the reagents and conditions for steps 1 **and** 4. [5]

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(c) Ethanol can be synthesised from bromoethene with bromoethane as an intermediate.

The bromine atom in bromoethane is very reactive while the bromine atom in bromoethene is unreactive.

Suggest two reasons for the unreactivity of the bromine atom in bromoethene. [2]

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(d) Oxides of sodium and sulfur both react with water.

Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

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(e) Describe and explain how the thermal stability of hydrogen halides varies down Group 17.

[3]

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[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.

1 **(a)** SiH_4, PH_3 and H_2S are three compounds.

(i) State and explain the bond angles in the molecules of these three compounds.

[4]

To **minimise repulsion**, the **valence electron pairs** around a **central atom** are **arranged as far apart** as possible. **Lone pairs exert greater repulsion than bond pairs.** [1]

There are **4 bond pairs** and **(0 lone pair)** around Si. Hence, SiH_4, is tetrahedral with a bond angle of **109.5°**. [1]

There are **3 bond pairs** and **1 lone pair** around P. **Since lone pair–bond pair repulsion is greater than bond pair–bond pair repulsion**, PH_3 is trigonal pyramidal with a bond angle of **107°**. [1]

There are **2 bond pairs** and **2 lone pairs** around S. Since **lone pair–lone pair repulsion is greater than lone pair–bond pair repulsion** which is greater than bond pair–bond pair repulsion, H_2S is bent with a bond angle of **104.5°**. [1]

(ii) Phosphorus and hydrogen have same electronegativity.
Draw the three molecules SiH_4, PH_3 and H_2S and indicate for each one the polarity of each of the bonds it contains and the overall polarity of the molecule.

[4]

overall: non polar	overall: polar	overall: polar
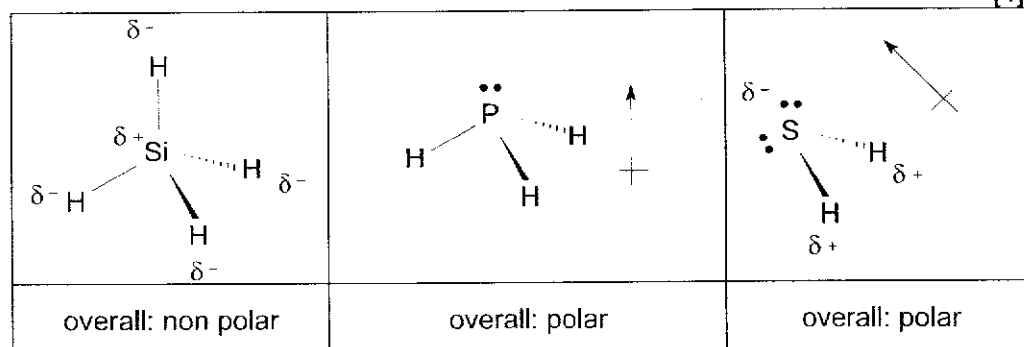
Note: must indicate the polarity of each bond as question mentioned it.

[1]: all 3 correct drawings
[1]: polarity of each of the bonds
[1]: overall polarity of each molecule
[1]: correct direction of polarity for PH_3 and H_2S

Thinking process
Electronegativity increases across a Period. As P and H have same electronegativity, Si will be less electronegative than H while S is more electronegative than H.

(iii) State the properties of a gas necessary for it to approach ideal behavior.

[2]

Intermolecular forces of attraction between gas molecules are **negligible**. [1]

The **volume of the gas particles/molecules** is **negligible** compared to the **volume of the container.** [1]

(iv) Of the three gases at 400 K, the behaviour of SiH_4 is closest to ideal gas behavior.

Suggest why H_2S deviate more from ideal behaviour than SiH_4. [1]

H_2S is polar and has <u>stronger permanent dipole-permanent dipole attractions</u> <u>between its molecules</u>. Hence, it has <u>more significant intermolecular forces</u> and deviate more from ideal behaviour. [1]

(b) **(i)** Define the term *lattice energy*. [1]

The amount of heat **evolved** when **one mole** of the solid ionic compound is formed from its constituent **free gaseous ions** under standard conditions of **298 K and 1 bar**. [1]

(ii) Use the data in Table 1.1, together with data from the *Data Booklet*, draw an energy cycle to calculate a value for the lattice energy of magnesium iodide, $MgI_2(s)$. Show your working.

Table 1.1

	value / kJ mol^{-1}
electron affinity of iodine, $I(g) + e^- \rightarrow I^-(g)$	−295.4
enthalpy change of sublimation of iodine molecules, $I_2(s) \rightarrow I_2(g)$	+62.4
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of $MgI_2(s)$	−364

[3]

[1]

Hess Law:
LE = $\Delta H_f^\ominus$ − [$\Delta H_{at}^\ominus$(Mg) + 1st IE(Mg) + 2nd IE(Mg) + $\Delta H_{sub}^\ominus$ + BE (I-I) + 2EA(I)] [1]
   = (-364) − [+148 + 736 + 1450 + 62.4 + 151 + 2 x (-295.4)]
   = **-2320kJ mol^{-1}** [1]

(c) Magnesium forms an important group of covalent compounds which are known as Grignard reagents. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic synthesis.

A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3 to form 2-methylbutan-2-ol.

$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step 1}} CH_3-\underset{\underset{C_2H_5}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3 \xrightarrow{\text{step 2}} CH_3-\underset{\underset{C_2H_5}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + Mg(OH)Br$$
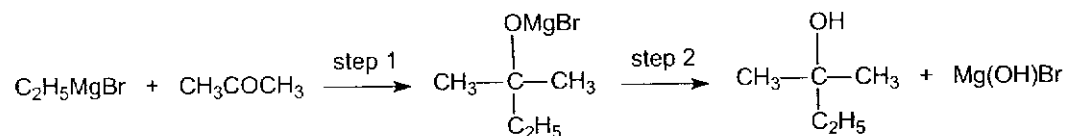
(i) Suggest the type of reaction which occurs in step 2. [1]

Hydrolysis [1]

(ii) Suggest the structural formula of the final organic product formed when
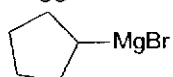
[cyclopentyl]—MgBr

is reacted with ethanal, CH_3CHO, in a similar two-step process. [1]

[cyclopentyl]—$\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}$—$CH_3$

[1]
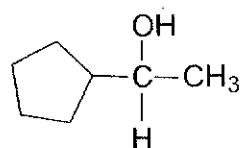
(iii) The Grignard reagent CH_3CH_2MgBr can be readily converted into a carboxylic acid by using carbon dioxide.

Given the two-step reaction sequence for this conversion

$$CH_3CH_2MgBr + CO_2 \xrightarrow{\text{step 1}} \text{compound } \mathbf{A} \xrightarrow{\text{step 2}} \text{compound } \mathbf{B} + Mg(OH)Br$$
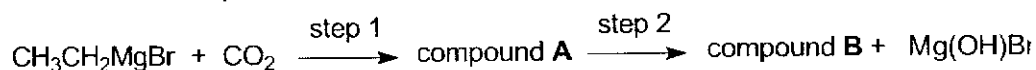
Draw the structural formula of compound **A** and **B**. [2]

$$CH_3CH_2\underset{\underset{O}{\diagdown\!\!/}}{\diagup}C-OMgBr \qquad\qquad CH_3CH_2\underset{\underset{O}{\diagdown\!\!/}}{\diagup}C-OH$$
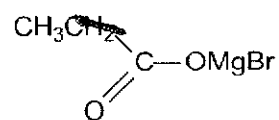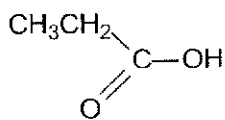
Compound A [1] Compound B [1]

C (c) F and G are ionic compounds which contain six-coordinate Co^{3+} complex ions, whose ligands
L are either NH_3 or Cl^-. The complexes of E and F are octahedral in shape.
T

octahedral shape
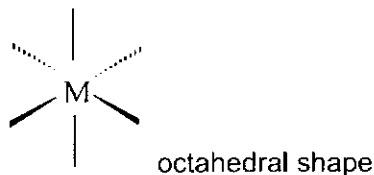
When excess aqueous $AgNO_3$ is added to 1 mole of F and 1 mole of G separately, 2 moles of a white precipitate is formed from F while 1 mole of the same white precipitate is formed from G.

(i) Deduce the structural formulae of complexes F and G. [2]

$$\frac{n(AgCl)}{n(complex\ F)} = \frac{2}{1}$$

$$\frac{n(AgCl)}{n(complex\ G)} = \frac{1}{1}$$

F has 2 moles of free Cl^- ion and one Cl^- ion datively bonded to the Co^{3+}.
G has 1 moles of free Cl^- ion and two Cl^- ion datively bonded to the Co^{3+}.

F: $[Co(NH_3)_5Cl]^{2+}$. $2Cl^-$ [1]
G: $[Co(NH_3)_4Cl_2]^+$. Cl^- [1]
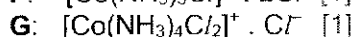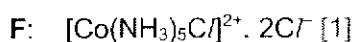
(ii) The Co^{3+} complex ion in G exhibits cis-trans isomerism like alkenes. Suggest the structure of the trans isomer, showing clearly how the ligands are bonded to the central metal ion. [2]

Complex G
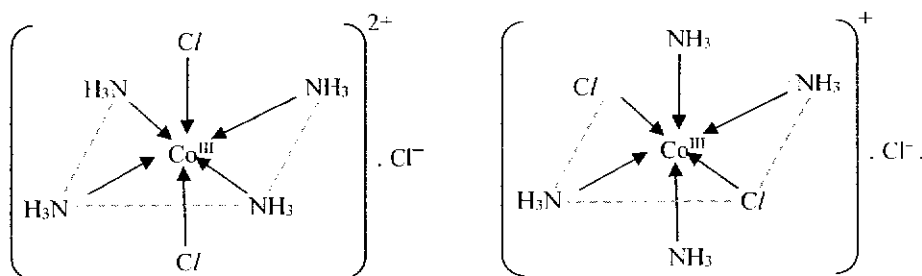
[1] Correct overall charge and dative bonds from nitrogen atom.
[1] Correct trans configuration (either structure)

[Total: 23]

2 Chlorine is a greenish yellow gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

(a) Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes.

As seen in Fig 2.1, a diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by-products.
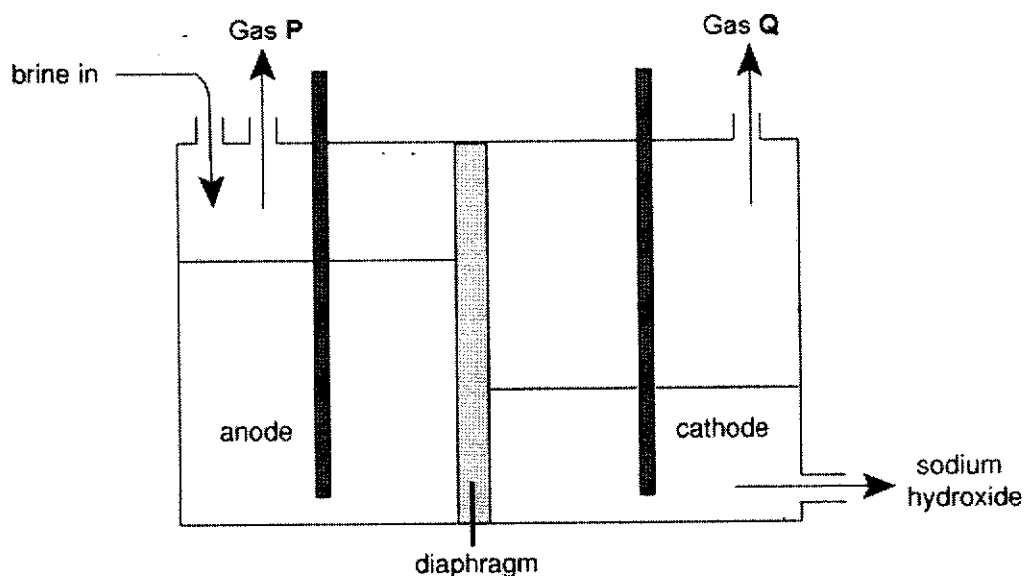
Fig 2.1

(i) Given the cathode reaction: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Write the ion-electron half-equation for the reactions taking place at the anode. Hence, construct the overall equation. You are to provide state symbols for all the equations. [2]

Cl^- (anion) would migrate to the anode and be oxidised to Cl_2 gas.
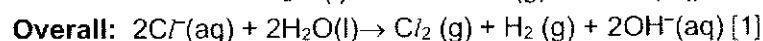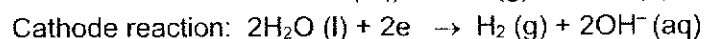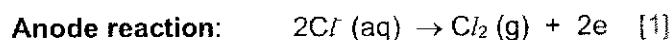
Anode reaction: $2Cl^-$ (aq) $\rightarrow Cl_2$ (g) + 2e [1]
Cathode reaction: $2H_2O$ (l) + 2e $\rightarrow H_2$ (g) + $2OH^-$ (aq)
Overall: $2Cl^-$(aq) + $2H_2O$(l)$\rightarrow Cl_2$ (g) + H_2 (g) + $2OH^-$(aq) [1]

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [3]

$Q = I \times t = 5 \times 7 \times 60 \times 60 = 1.26 \times 10^5$ C   [1]
$Q = n_e \times F$

Amount of electrons passed $= \dfrac{1.26 \times 10^5}{96500} = 1.306$ mol [1]

Amount of chlorine $= \dfrac{1.306}{2} = 0.653$ mol

Mass of chlorine produced = 0.653 x 2 x 35.5 = **46.4 g** [1]

With reference to the *Data Booklet*, explain why

(iii) Dilute aqueous sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36\ V$ ---(1)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\circ = +1.23V$ ---(2)
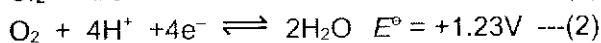
When dilute sodium chloride is used, the <u>E° (O_2/H_2O) is **less positive** than E° (Cl_2-/Cl^-)</u> and <u>H_2O is preferentially oxidised</u> at the anode to give O_2 gas, instead of chlorine gas. [1]

(iv) Unlike chlorine, fluorine gas cannot be manufactured in a similar way using concentrated sodium fluoride. [1]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36\ V$

$F_2 + 2e^- \rightleftharpoons 2F^-$ $E^\circ = +2.87\ V$

$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E^\circ = +1.23\ V$
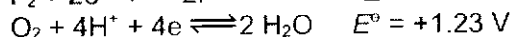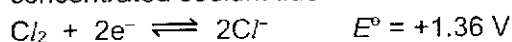
<u>E° (F_2/F^-)</u> is <u>much more positive</u> than E° (O_2/H_2O). <u>H_2O will always be preferentially oxidised</u> (rather than F_2 gas). OR

<u>E° (F_2/F^-)</u> is <u>much more positive</u> than <u>E° (Cl_2/Cl^-)</u>. <u>F^- will not be easily oxidised</u> even in high concentration of NaF. [1]

(accept explanation in terms of F_2, being strongly oxidising (link to E°) and if formed will react with water to form back F^-)

(b) When the diaphragm is removed the chlorine produced can react with the hydroxide ions to produce chloride and chlorate(V), ClO_3^-. Using oxidation number, construct a balanced equation for this reaction. Show your working. [2]

oxidation number of Cl = -1; oxidation number of ClO_3^- = +5

$Cl_2 + 2e^- \rightarrow 2Cl^-$ [each Cl atom gains 1 mol of e^-]

$Cl_2 \rightarrow 2ClO_3^- + 10e^-$ [each Cl atom loses 5 mol of e^-]

$5Cl_2 + 10e^- \rightarrow 10Cl^-$

$Cl_2 \rightarrow 2ClO_3^- + 10e^-$

$6Cl_2 + OH^- \rightarrow 10Cl^- + 2ClO_3^- + H_2O$ (balance charge)

$6Cl_2 + 12OH^- \rightarrow 10Cl^- + 2ClO_3^- + H_2O$ (balance H and O)

$6Cl_2 + 12OH^- \rightarrow 10Cl^- + 2ClO_3^- + 6H_2O$ (or $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$)
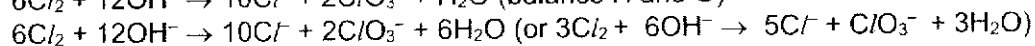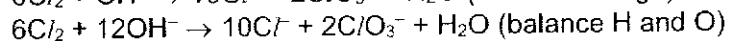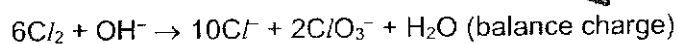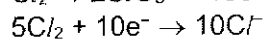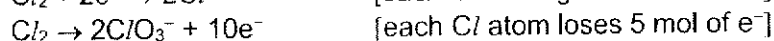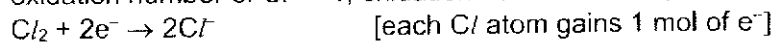
[1] relevant working

[1] final eqn

(c) The standard electrode potentials, $E^\ominus$, and standard Gibbs free energy changes, $\Delta G^\ominus$, of different chlorine-containing species and hydrogen peroxide are shown in Table 2.1.

Table 2.1

	Half-equation	$E^\ominus$ / V
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
4	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77

With reference to Table 2.1, predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-. [3]

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ (+1.77)

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ (+1.36)

$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$ (+1.47)

$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$ (+1.19)

$H_2O_2 (aq) + 2H^+ (aq) + 2Cl^- (aq) \rightarrow Cl_2 (aq) + 2H_2O(l)$
$E^\ominus_{cell} = (+1.77) - (1.36) = \underline{\textbf{+0.41 V}} > 0$ ∴reaction is feasible. [1]

$Cl_2 (aq) + 5H_2O_2 (aq) \rightarrow 2ClO_3^- (aq) + 4H_2O(l) + 2H^+ (aq)$
$E^\ominus_{cell} = (+1.77) - (+1.47) = \underline{\textbf{+0.30 V}} > 0$ ∴reaction is feasible. [1]

$H_2O_2 (aq) + ClO_3^- (aq) \rightarrow H_2O(l) + ClO_4^- (aq)$
$E^\ominus_{cell} = (+1.77) - (+1.19) = \underline{\textbf{+0.58 V}} > 0$ [1] ∴reaction is feasible.
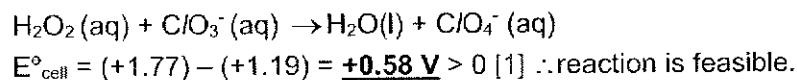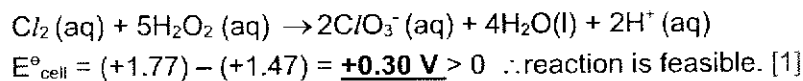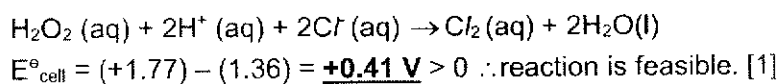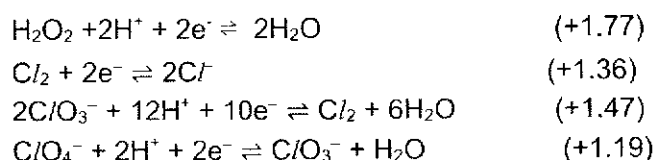
Cl^- will be oxidised to Cl_2, then to ClO_3^- and finally to ClO_4^- while H_2O_2 will be reduced to H_2O.

toxic and easy to produce. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set-up is illustrated in Fig. 2.2.

Electron flow

) and CO_3^{2-}

Ni anode anion exchange membrane graphite cathode
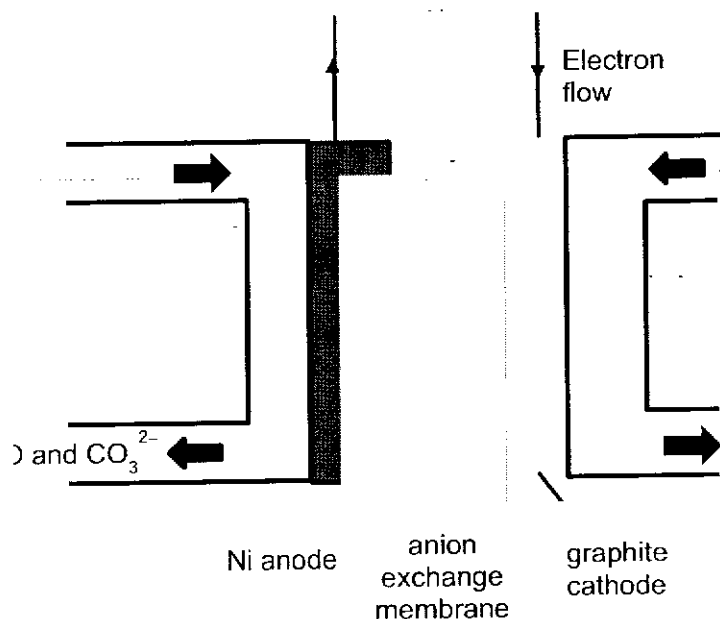
Fig. 2.2

At the anode, glucose is oxidised to carbonate ions, CO_3^{2-}, in an alkaline medium while at the cathode, oxygen gas is reduced. The value of $E^\ominus_{cell}$ is +0.85 V. The overall reaction occurring in the fuel cell is given below:

$$C_6H_{12}O_6 + 6O_2 + 12OH^- \rightarrow 6CO_3^{2-} + 12H_2O$$
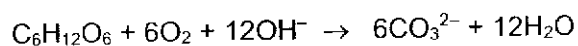
average O.N. of C in glucose = 0; O.N. of C in carbonate ions = +4
each mol of C loses 4 mol of e
6 mol of C loses 24 mol of e in this reaction

OR
O.N. of O in O_2 = 0; O.N. of O in H_2O = -2
each mol of O gains 2 mol of e
12 mol of O gains 24 mol of e

OR
Oxidation: $C_6H_{12}O_6 + 36OH^- \rightarrow 6CO_3^{2-} + 24H_2O + 24e$
Reduction: $2H_2O + 4e + O_2 \rightarrow 4OH^-$
[1] for correct value of n

No. of moles of electrons exchanged per mole of glucose: 24
$\Delta G^\ominus = -nFE^\ominus_{cell}$
$= -24(96500)(0.85)$
$= 1.97 \times 10^6 \text{ J mol}^{-1}$
[1] for use of correct expression to find $\Delta G^\ominus$ (ecf if n is wrong)

(ii) Calculate the standard electrode potential for the half-equation for the reduction of CO_3^{2-} to $C_6H_{12}O_6$, using appropriate $E^\ominus$ value from the *Data Booklet*.   [1]

$E^\ominus{}_{cell} = +0.40 - E^\ominus(CO_3^{2-}/C_6H_{12}O_6) = +0.85$

$E^\ominus(CO_3^{2-}/C_6H_{12}O_6) = 0.40 - 0.85 = -0.45$ V   [1]

(e) In the fuel cell, glucose molecules are adsorbed on the nickel anode surface prior to oxidation to carbonate ions. Fig. 2.3 shows how E_{cell} varies with the concentration of glucose.

Fig. 2.3

Explain the shape of the graph.   [2]

Oxidation: $C_6H_{12}O_6 + 36OH^- \rightarrow 6CO_3^{2-} + 24H_2O + 24e$
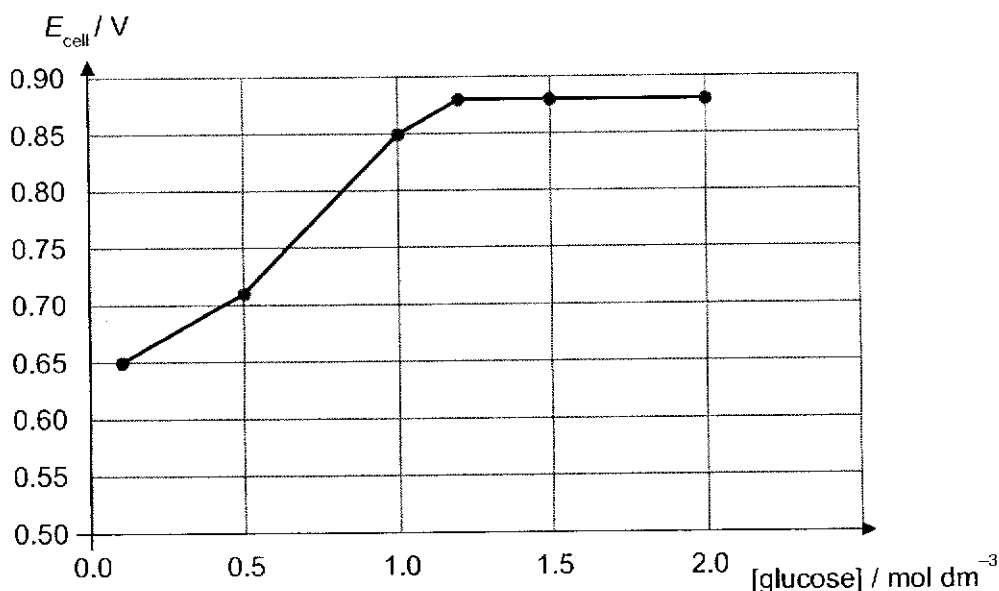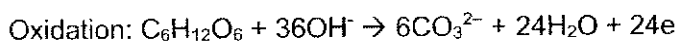
As concentration of glucose increases, $E(CO_3^{2-}/C_6H_{12}O_6)$ becomes **more negative** as **oxidation of glucose to CO_3^{2-} is favoured** so as to offset the increase in concentration of glucose, this results in the initial increase of E_{cell}. [1]

Beyond an optimum glucose concentration, the **active sites** on the **surface** of nickel anode becomes **saturated** and further increase in glucose concentration will not lead to a decrease in the value of $E(CO_3^{2-}/C_6H_{12}O_6)$. Hence, value of E_{cell} remains constant. [1]

(f) Beside the advantages mentioned in the question, suggest another possible advantage of using the glucose fuel cell compared to a hydrogen fuel cell.   [1]

Glucose is of liquid/aqueous form while H_2 is a gas. Hence glucose will occupy a smaller volume for the same mass. [1]
OR
There is a risk of explosion for hydrogen gas as it is highly flammable while glucose is not as flammable.
OR
Easy to transport/Ease of storage as glucose is a liquid while H_2 is a gas.
Note: Do not accept toxicity as answer

[Total: 18]

[Turn over

3 Succinic acid, $HOOCCH_2CH_2COOH$, (pK_{a1} is 4.2 ; pK_{a2} is 5.4) serves as the precursor of certain biodegradable polymers which are of interest in tissue engineering applications. It is commonly used as an acidity regulator in the food and beverage industry.

(a) **(i)** Butanoic acid, $CH_3CH_2CH_2COOH$ has a pK_{a1} of 4.8. With an aid of a diagram, explain why the pK_{a1} of succinic acid is lower. [2]
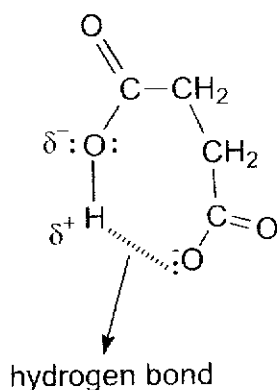
hydrogen bond

Conjugate base $HOOCCH_2CH_2COO^-$ is stabilised by hydrogen bonding.

[1] diagram showing H bonding, lone pair of electrons and partial charges
[1] stability of the conjugate base

(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of succinic acid (ignore the effect of pK_{a2} on pH). [1]

$[H^+]^2 = K_1[HA] = (10^{-4.2})(0.10) = 6.31 \times 10^{-6}$ mol^2 dm^{-6}

$[H^+] = 0.00251$ mol dm^{-3} pH = 2.60 [1]

(iii) Determine the pH of the solution when 30 cm^3 of 0.10 mol dm^{-3} KOH is added to 10 cm^3 of 0.10 mol dm^{-3} succinic acid. [2]

Let $HOOCCH_2CH_2COOH$ be H_2A
$H_2A + 2KOH \rightarrow K_2A + 2H_2O$
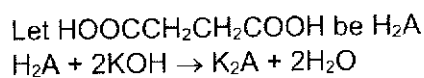
Amount of excess OH^- after 30 cm^3 of KOH added = 10/1000 x 0.10
                                                     = 0.001 mol

$[OH^-] = \dfrac{0.001}{\frac{40}{1000}} = 0.0250$ mol dm^{-3} [1]

pOH = 1.60
pH = 14-1.60 = 12.4 [1]

(iv) Hence, using the information provided and your answer from **(a)(ii)** and **(a)(iii)**, sketch the pH-volume curve you would expect to obtain when 30 cm³ of 0.10 mol dm⁻³ KOH is added to 10 cm³ of 0.10 mol dm⁻³ succinic acid. No additional calculation is required. [3]
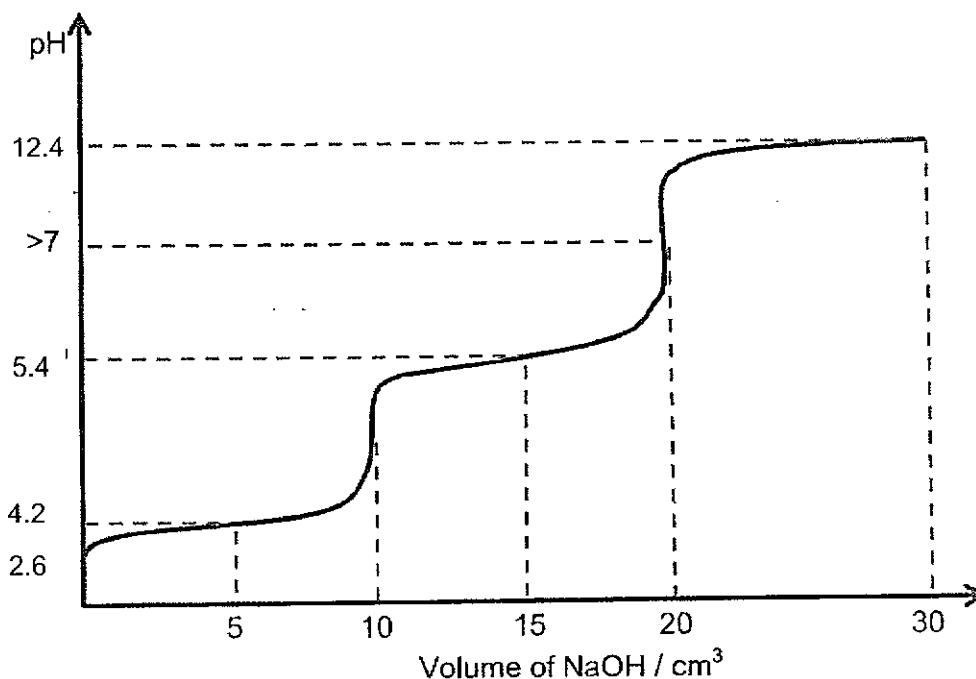
[1] for initial pH at 2.60 + final pH 12.4
[1] two neutralisation points at 10cm³ & 20cm³
[1] two buffer region centred at corresponding pH values to the two pK_a values

(b) Succinic acid can be synthesised from bromoethanal via a series of reaction.

Bromoethanal was reacted with HCN in the presence of KCN to form **W**, C_3H_4BrNO. **W** was then reacted with reagent **U** under appropriate condition to form **X**, $C_4H_4N_2O$.

Upon heating **X** with dilute hydrochloric acid, **Y**, $C_4H_6O_5$ was generated.

Y was then heated with concentrated sulfuric acid to form **Z** which is a dicarboxylic acid with molecular formula $C_4H_4O_4$. Subsequent introduction of $H_2(g)$ in the present of platinum catalyst will convert **Z** to succinic acid.

It is also known that when hot acidified $KMnO_4$ was added to **Z**, only an acidic gas was produced.

(i) State reagent **U** and the conditions required to convert **W** to **X**. [1]

alcoholic NaCN, heat [1]

(ii) Deduce the structures of **W**, **X**, **Y** and **Z**, explaining the reactions described.[7]

$\begin{array}{c}\text{H}\quad\text{OH}\\|\quad\;|\\ \text{Br—C—C—CN}\\|\quad\;|\\ \text{H}\quad\text{H}\end{array}$ **W** [1]	$\begin{array}{c}\text{H}\quad\text{OH}\\|\quad\;|\\ \text{NC—C—C—CN}\\|\quad\;|\\ \text{H}\quad\text{H}\end{array}$ **X** [1]
$\begin{array}{c}\text{H}\quad\text{OH}\\|\quad\;|\\ \text{HOOC—C—C—COOH}\\|\quad\;|\\ \text{H}\quad\text{H}\end{array}$ **Y** [1]	$\begin{array}{c}\text{HOOC}\qquad\text{COOH}\\ \diagdown\qquad\diagup\\ \text{C=C}\\ \diagup\qquad\diagdown\\ \text{H}\qquad\quad\text{H}\end{array}$ **Z** [1]
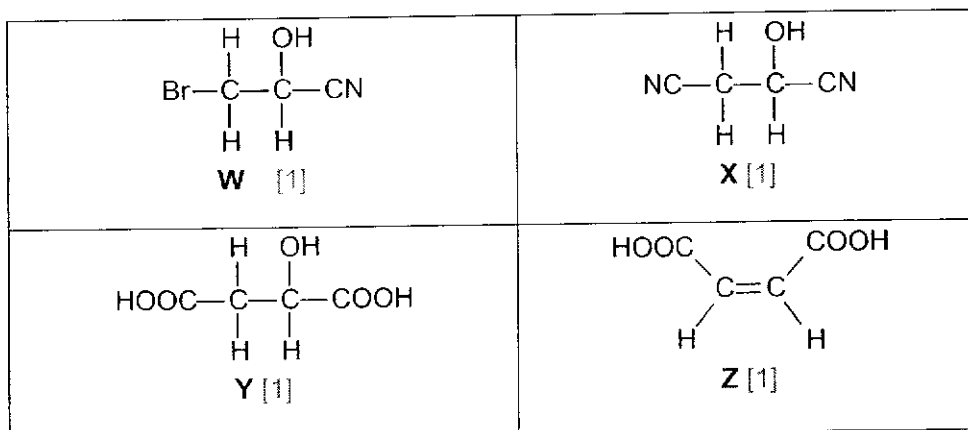
Statement	Deduction (type of reaction & functional group)	
Bromoethanal was reacted with HCN in the presence of KCN to form compound **W**, C_3H_4BrNO	*(gain of HCN in M.F.)* Nucleophilic addition occur. **W** contains cyanohydrin	✓ ✓
W was then reacted with reagent U under appropriate condition to form compound **X**, $C_4H_4N_2O$.	*(loss of Br; gain of CN in M.F.)* Nucleophilic substitution **X** contains nitrile	✓ ✓
heating **X** with hot hydrochloric acid forms compound **Y**, $C_4H_6O_5$	(acid-catalysed) hydrolysis of (both) CN group occurs, **Y** contains (di)carboxylic acid.	✓ ✓
Y was then heated with concentrated sulfuric acid to form **Z**, $C_4H_4O_4$	*(loss of H_2O in M.F.)* Elimination occur **Z** contains C=C	✓ ✓
$H_2(g)$ in the present of platinum catalyst will convert **Z** to succinic acid	Reduction of (C=C in **Z**) occur (**Z** contains C=C: marked once only)	✓
acidified $KMnO_4$ was added to **Z**, only an acidic gas was produced	Oxidation (CO_2 is released)	✓ ✓

8 or more ✓ ➔ [3]
6 ✓ ➔ [2]
4 ✓ ➔ [1]

(iii) **Z** is known to exhibit stereoisomerism. Draw and label the **skeletal** formula of the stereoisomers of **Z**. [2]
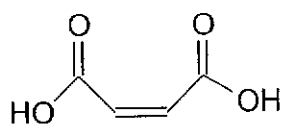
cis
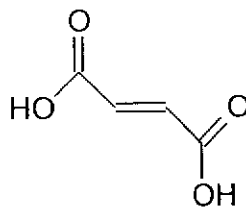
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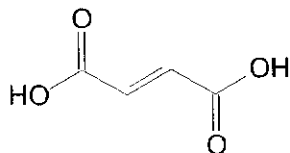
trans
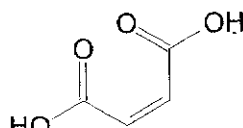
cis

[1] correct label (must show 120° configuration)
[1] correct skeletal structures

(iii) Write a chemical equation to show the reaction between **Z** and hot acidified $KMnO_4$. [1]

$+ 6[O] \rightarrow 4CO_2 + 2H_2O$

[1] (can make use of molecular formula)
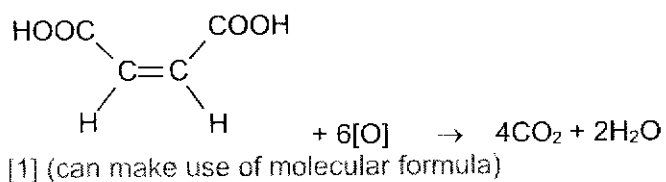
[Total: 20]

Section B
Answer **one** question from this section.

4 **(a)** Cyanogen iodide, ICN exists as white crystals that react slowly with water to form hydrogen cyanide and one other acidic by-product where the oxidation number of iodine is +1.

   (i) State the molecular formula of the by-product. [1]
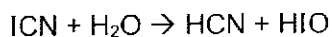
   ICN + H_2O → HCN + HIO
   by-product : HIO   [1] (accept HOI, OHI, OIH)

   (ii) Draw the displayed structure of this by-product. [1]
   I-O-H [1]   X: H-I=O

   (iii) Cyanogen iodide, ICN, undergoes addition reactions with alkenes.
   With but-1-ene, isomer **D** is produced rather than isomer **E**.
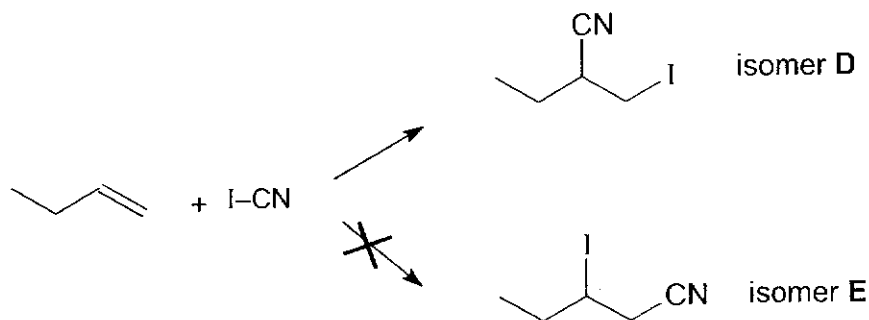
Fig. 4.1

Suggest a mechanism for the production of isomer **D** shown in Fig 4.1. [2]

Electrophilic addition
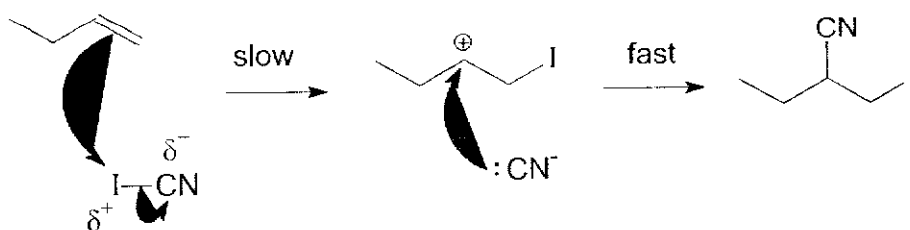
[1]: partial charges + structure of carbocation intermediate
[1]: lone pair + curly arrows

[Turn over

(iv) With reference to the mechanism and carbocation intermediate formed explain the preferential production of isomer **D** shown in Fig 4.1. [1]

Electrophilic attack on C by $^{\delta+}$I yields a <u>more substituted</u> (secondary) <u>carbocation</u> intermediate, which is <u>more stable</u> (than a primary carbocation since 2° C$^+$ has more electron donating alkyl groups bonded to the C$^+$ to disperse the positive charge). [1]

Hence, **D** is formed preferentially over **E**.

(b) State how the reactivity of the halogens as oxidising agents varies down the group and relate these variation to relevant $E°$ value. Hence, deduce the products when F_2 and Br_2 is added separately to $NaCl$ (aq). [2]

Down the group, <u>oxidising power of halogens decreases</u> (or reactivity of halogens as oxidising agents decreases) down the group from F_2 to I_2 since $E°_{(X_2/X^-)}$ values become <u>less positive</u> [1]

$Br_2 + 2NaCl \longrightarrow$ **No reaction**
$F_2 + 2NaCl \longrightarrow Cl_2 + 2NaF$ [1] equation not required
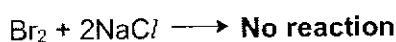
(c) Sodium, aluminium and sulfur are elements in Period 3 in the Periodic Table.

Use the oxides of these three elements to describe reactions that illustrate the variation in their acid–base behaviour. Write equations for all the reactions you describe. [5]

Sodium oxide, a **basic oxide**, undergoes acid-base reaction with HCl
$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$ [1]

Aluminium oxide, an **amphoteric oxide**, undergoes acid-base reaction with both HCl and NaOH
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ [1]
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ [1] for both
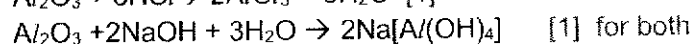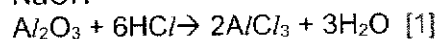
Oxides of sulfur are **acidic oxide** and will undergo acid-base reaction with NaOH.
$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ [1]

accept: $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$

[1] correctly identify nature of all oxides
(need to account for Na and Cl if NaOH or HCl is used)

(d) The boiling points of some Period 3 oxides is shown in Table 4.1.

Table 4.1

compound	formula	boiling point / °C
sodium oxide	Na_2O	1950
silicon oxide	SiO_2	2230
sulfur dioxide	SO_2	−10
sulfur trioxide	SO_3	45

(i) Using structure and bonding, suggest the differences between the boiling points of Na_2O, SiO_2 and SO_2. [3]

Sodium oxide has a giant ionic structure with strong electrostatic forces of attractions between oppositely charge ions. Thus, large amount of energy is required to overcome the strong ionic bonds resulting in a high boiling point.   [1]

Silicon oxide has a giant covalent structure. Largest amount of energy is required to overcome the strong and extensive covalent bonds between the atoms in a 3-D network, resulting in the highest boiling point. [1]

Sulfur dioxide has a simple molecular structure. Least amount of energy is required to overcome the weakest permanent dipole-permanent dipole attractions between the molecules [1]

Energy must mention once

(ii) Account for the difference in boiling points between SO_2 and SO_3.   [1]

SO_3 has a larger electron cloud size than SO_2 which leads to greater polarisability / ease of distortion. More energy is required to overcome the stronger instantaneous dipole–induced dipole attractions between SO_3 molecules than that between SO_2 molecules. Hence higher boiling point for SO_3. [1]
(do not accept extensiveness of id-id)

(iii) With reference to Table 4.1, SO_2 and SO_3 are sealed in separate containers and heated from room temperature to a temperature of 100 °C. Suggest an explanation which compound will have a greater change in the entropy of the system.
                                                                                      [1]

From room temperature to 100 °C
SO_2 (g) → SO_2 (g)   change in no. of gaseous particles = 0
SO_3(l) → SO_3 (g)   change in no. of gaseous particles = +1

Since SO_3 is a liquid at room temperature there will be a change of state from liquid to gas. Thus, there will be more ways to distribute the particle and their energies, hence resulting in greater disorder of the system. [1]

Or
When SO_3(l) changes to SO_3(g) there are more ways to distribute the particles and their energies since there are more gas particles moving randomly. The greater disorder in the system results in an greater change in entropy of the system.

(iv) When reacted with SO_3, PCl_3 produces a compound **J** with M_r = 153.5 and a by–product **K**. **J** is also produced when PCl_5 is reacted with a small amount of H_2O.

Suggest the identity of **J** and **K** and construct equations for the production of **J** from PCl_3 and PCl_5.   [3]
J: $POCl_3$ [check: Mr of $POCl_3$ = 31.0 + 16.0 + 3 (35.5) =153.5]

K: sulfur dioxide   [1]

PCl_3 + SO_3 → $POCl_3$ + SO_2 [1]

When small amount of water react with PCl_5
PCl_5 + H_2O → $POCl_3$ + 2HCl   [1]

[Total: 20]

5 (a) The Strecker Synthesis is a preparation method for α-amino acids using aldehydes. In the process, α-aminonitriles, which are versatile intermediates form α-amino acids via hydrolysis of the nitrile group.
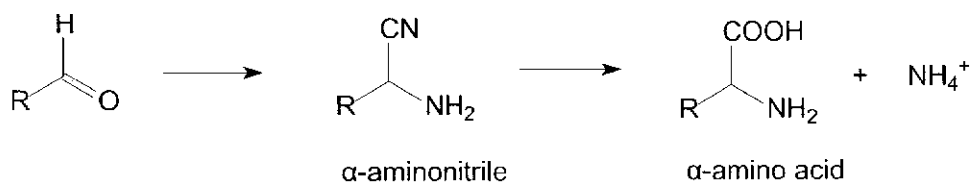
Alanine, 2-aminopropanoic acid, can be prepared from ethanal via Strecker Synthesis as shown below.
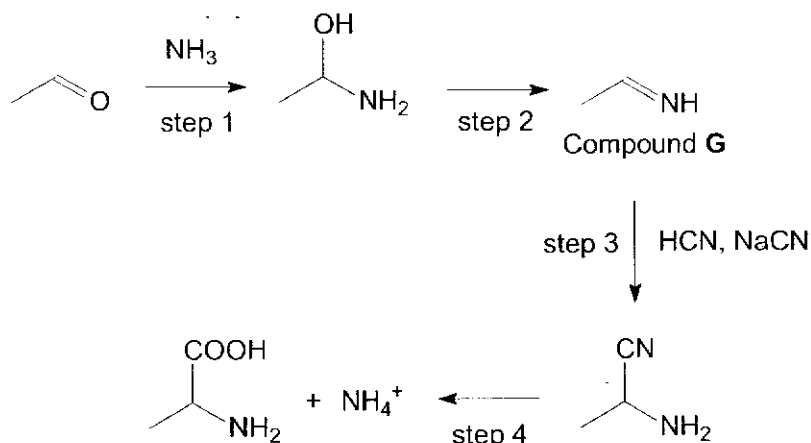
Fig 5.1

(i) Alanine has a melting point of 213 °C while ethanal has a melting point of −124 °C. Suggest the difference in their melting point. [2]

Alanine exists as zwitterions with strong ionic bonds between oppositely charged end of the neighboring zwitterions which require larger amount of energy [1] to overcome while ethanal exists as simple molecular structure with weaker permanent dipole-permanent dipole attraction between the molecules thus requiring lesser amount of energy. Thus, alanine has a higher melting point. [1]

(Do not accept if students wrote cations/anions)

(ii) Imines are the nitrogen analogues of aldehydes and ketones, containing a C=N bond instead of a C=O bond. Compound **G** Fig 5.1 is one example of an imine.

Assuming the C=N bond of imines has the same reactivity as the C=O bond of carbonyl compounds, name and describe a mechanism for step 3 shown in Fig 5.1.

[3]

Nucleophilic Addition [1] name of mechanism
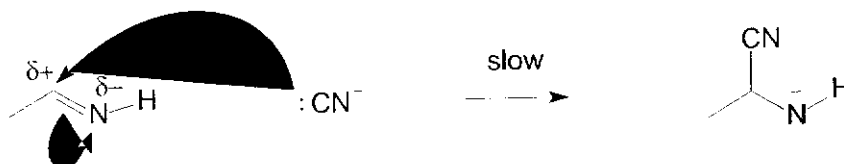
[1] for correct curly arrows, partial charges, lone pair and negative charge on CN and labelling "slow" step
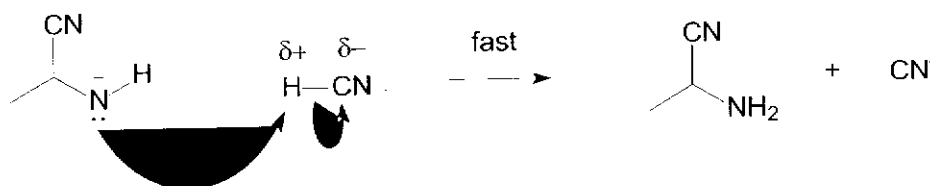
[1] for correct curly arrows, lone pair and negative charge on N atom of intermediate and balanced equation

(iii) Explain why step 3 produces an equimolar mixture of stereoisomers. [2]

The geometry about the carbonyl C is <u>trigonal planar</u> [1].

Hence, there is <u>equal probability for the CN⁻ ion to attack from either side of the plane</u> [1], giving rise to an equimolar mixture of two stereoisomers.

(iv) Draw the stereoisomers formed in step 3. [1]
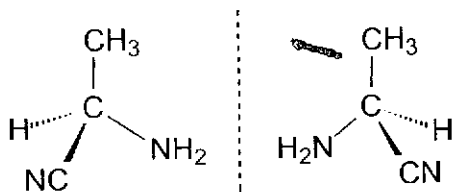
[1] correct 3-D diagrams about chiral C, displayed formula drawn with correct structure.

(b) Protonated alanine can be produced in the laboratory from ethanol using five-step synthesis reaction scheme shown below.
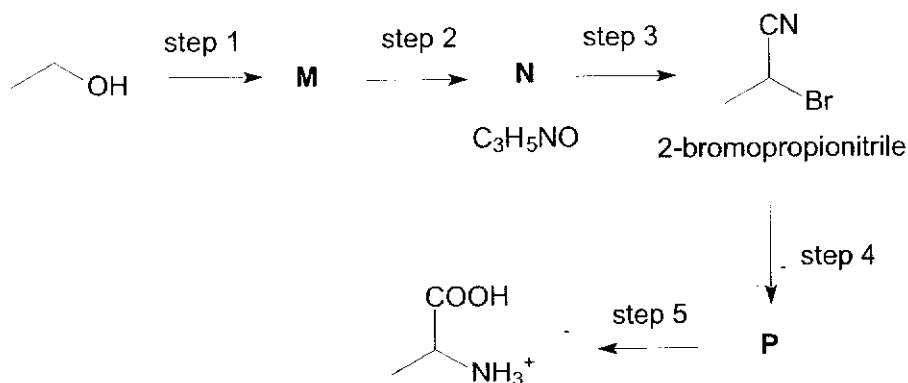
Identifying the intermediates **M**, **N** and **Q**. Suggest the reagents and conditions for step 1,and 4. [5]

Step 1: $K_2Cr_2O_7$, dilute H_2SO_4, warm with distillation [1]
Step 4: (excess) concentrated NH_3 in ethanol, heat in a sealed tube [1]
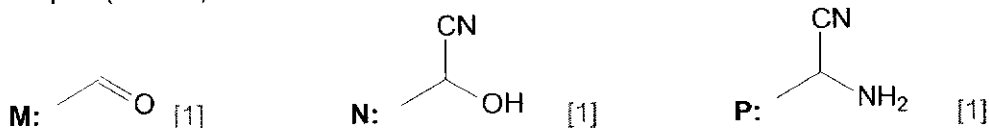
M: [1]   **N:** [1]   **P:** [1]

(c) Ethanol can be synthesised from bromoethene with bromoethane as an intermediate.

The bromine atom in bromoethane is very reactive while the bromine atom in bromoethene is unreactive.

Suggest two reasons for the unreactivity of the bromine atom in bromoethene. [2]

Any two:
• p-orbitals of Br and C=C overlap and the electrons of the Br atom is delocalised into the adjacent pi bond, resulting in <u>partial double bond</u> to the C-X bond (and <u>reduced partial positive charge</u> on C of C-X bond)

• The <u>electrons of the pi bond repel the attacking nucleophile</u> (steric hindrance)

• The <u>sp² hybridised</u> carbon in C-X bond of bromoethene contains <u>more s-character</u> than the sp³ hybridised carbon in the C-X bond of brormoethane. The <u>bonding electrons</u> in its sp² C-X bond in bromoethene are <u>held more closely to the nucleus</u>, resulting in it being <u>stronger</u> and more difficult to cleave.
(similar question in N2012/P1/39)

(d) Oxides of sodium and sulfur both react with water. Write equations with state symbols for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

$Na_2O + H_2O \rightarrow 2NaOH$ Universal Indicator turns from green to violet (blue)
$SO_3 + H_2O \rightarrow H_2SO_4$ Universal Indicator turns from green to red (orange)
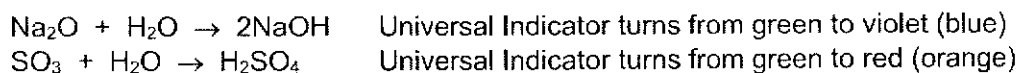
[1] Both equations correct   [1] Both UI colours correct

(e) Describe and explain how the thermal stability of hydrogen halides varies down Group 17.
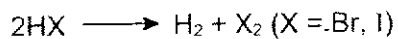
[3]

Thermal stability decreases down the group. [1]

HCl does not decompose.
HBr decomposes slightly to give some (brown) fumes of Br_2.
HI decomposes readily to give (purple) fumes of I_2 on gentle heating.

[1]

$2HX \longrightarrow H_2 + X_2$ (X = Br, I)

This is due to the decrease in H-X bond energy and less energy is required to break the weaker H-X bond down the group. [1]

FYI: This is because the size of valence orbitals increases down Grp 17 and become more diffused. This causes less effective overlap between the valence orbital of halogen and s-orbital of hydrogen.

END

9729/03/H2

[Turn over