ANDERSON SERANGOON JUNIOR COLLEGE

2024 JC 2 PRELIMINARY EXAMINATION

NAME:____________________________ (   ) **CLASS:** 24 / ____

CHEMISTRY **9729/02**

Paper 2 Structured Questions

11 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number 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.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 2	1	/15
	2	/13
	3	/11
	4	/16
	5	/20
Total		/ 75

This document consists of **21** printed pages and **3** blank pages.

Answer **all** the questions.

1 **(a)** Phosphorus, sulfur and chlorine are Period 3 elements of the Periodic Table.

Table 1.1 shows some properties of the three elements.

Table 1.1

	P	S	C*l*
number of electrons in 3p subshell			
number of unpaired electrons			

(i) Complete Table 1.1 to show the number of electrons in the 3p subshell and the number of unpaired electrons in an atom of P, S and C*l*. [2]

(ii) With reference to the *Data Booklet*, state and explain the trend of the ionic radius of P^{3-}, S^{2-} and Cl^{-}.

....

....

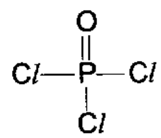
....

....

....

.... [2]

(b) Phosphoryl chloride, $POCl_3$, is a colourless liquid that is used to make phosphate esters.



$POCl_3$ has similar chemical properties as PCl_5. It has a melting point of 1 °C and a boiling point of 106 °C.

It also reacts vigorously with water, forming misty fumes and an acidic solution of H_3PO_4.

(i) Explain how the information in **(b)** suggests that the structure and bonding of $POCl_3$ is simple covalent.

....

....

....

....

.... [2]

(ii) Write a balanced equation for the reaction of $POCl_3$ with water.

.... [1]

(iii) In H_3PO_4, there is no hydrogen atom directly bonded to the phosphorus atom.

Draw the 'dot and cross' diagram of H_3PO_4 and state the shape of the molecule with respect to P.

shape: .... [2]

(c) Phosphoryl chloride, $POCl_3$, is manufactured industrially from phosphorus trichloride and oxygen as shown in equation 1.1.

equation 1.1 $$2PCl_3(g) + O_2(g) \longrightarrow 2POCl_3(g)$$

The standard enthalpy changes of formation for these species are shown in Table 1.2.

Table 1.2

Enthalpy change of formation of $PCl_3(g)$	-289 kJ mol^{-1}
Enthalpy change of formation of $POCl_3(g)$	-592 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation*.

....

.... [1]

(ii) Using the data from Table 1.2 and relevant data from the *Data Booklet*, calculate the bond energy of P=O in $POCl_3$.

[2]

(iii) Predict and explain the sign of the entropy change for the reaction in equation 1.1.

....

....

.... [1]

(iv) Comment on the effect of increasing temperature on the spontaneity of the reaction in equation 1.1.

....

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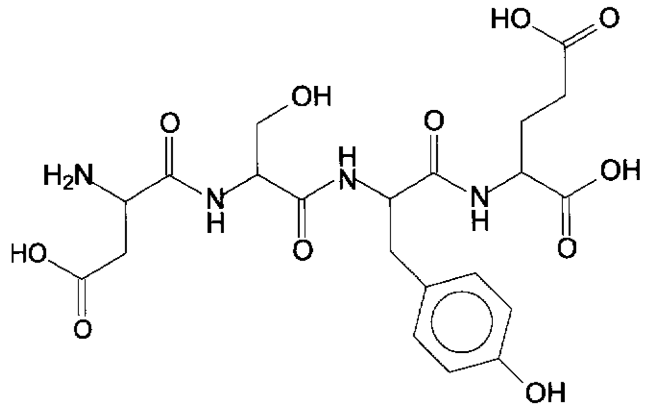
....

....

.... [2]

[Total: 15]

2 The structure of a tetrapeptide **T** is shown below.



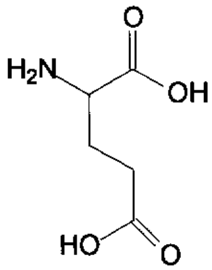
T

(a) Name the type of reaction to break **T** into its constituent amino acids.

.... [1]

(b) The four amino acids formed from the reaction in **(a)** are glutamic acid, tyrosine, **U** and **V**. The structures of glutamic acid and tyrosine are as shown.

glutamic acid



tyrosine

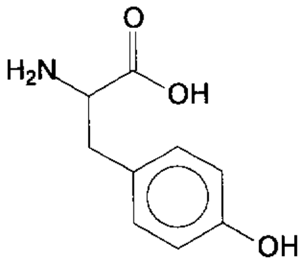
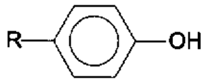


Table 2.1 lists the pK_a values of the different functional groups present on each of the four amino acids.

Table 2.1

Amino acid	pK_a		
	α-carboxyl group	α-amino group	side chain
glutamic acid	2.1	9.5	4.1
tyrosine	2.2	9.2	10.5
U	2.0	9.9	3.9
V	2.2	9.2	-

(i) Explain why the pK_a value of the side chain of glutamic acid is lower than that in tyrosine.

You may represent glutamic acid as $R-CO_2H$ and tyrosine as  .

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.... [3]

(ii) In the space below, draw the structures of the predominant species of **U** and **V** at pH 3.0.

U	V

[2]

(c) Solutions containing the zwitterions of **V** can act as buffers.

(i) State what is meant by the term *zwitterion*.

....

.... [1]

(ii) With the aid of appropriate equations, explain how a solution containing the zwitterions of **V** can resist pH changes. You may use $H_2NCHRCOOH$ to represent the structure of **V**.

....

....

....

.... [2]

(d) **(i)** Calculate the pH of 0.10 mol dm^{-3} solution of protonated **V**. Ignore the effect of pK_a of the α-amino group on the pH.

[2]

(ii) A student records the pH of the mixture when 20 cm^3 of 0.10 mol dm^{-3} NaOH(aq) was added to 10.0 cm^3 of 0.10 mol dm^{-3} solution of protonated **V**.

Sketch the shape of the pH curve on Fig. 2.1 using all relevant information given or calculated.

Your sketch should also clearly indicate the two points where the solution is most effective in resisting pH changes.

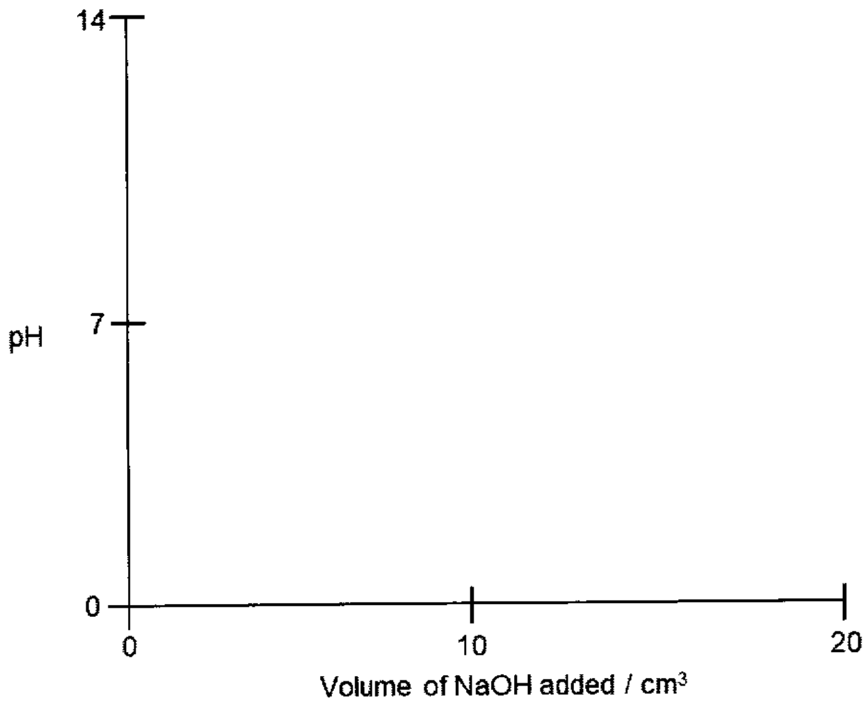


Fig. 2.1

[2]

[Total: 13]

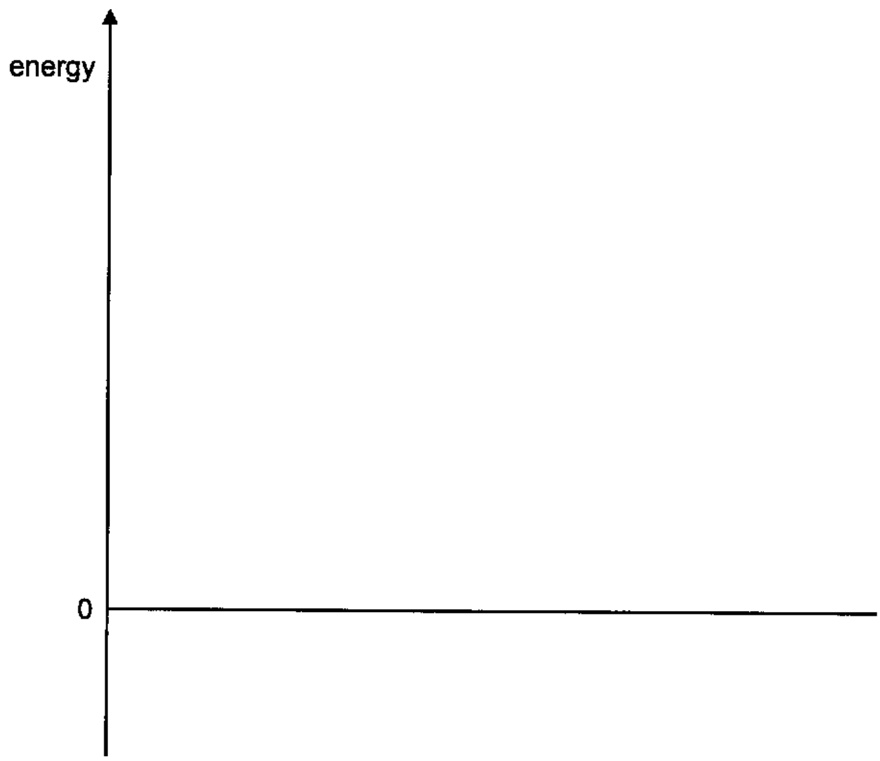
3 (a) (i) Write an equation to represent the lattice energy of magnesium bromide, $MgBr_2$.

.... [1]

(ii) Use the data in Table 3.1, together with data from the *Data Booklet*, to construct a Born–Haber cycle on the energy diagram below. Hence, calculate the lattice energy of magnesium bromide.

Table 3.1

	value / kJ mol^{-1}
enthalpy change of formation of magnesium bromide	–524
enthalpy change of atomisation of magnesium	+148
enthalpy change of vaporisation of bromine	+31
first electron affinity of bromine	–325



lattice energy of magnesium bromide = ... kJ mol^{-1} [3]

(iii) How would you expect the lattice energy of barium bromide to compare with that of magnesium bromide? Explain your answer.

....

....

....

.... [2]

(b) Barium compounds such as barium fluoride and barium hydroxide are sparingly soluble in water. The solubility product, K_{sp}, values for these compounds at 298 K, are listed in Table 3.2.

Table 3.2

compound	K_{sp}
BaF_2	1.0×10^{-6}
$Ba(OH)_2$	5.0×10^{-3}

(i) Calculate the solubility of barium fluoride in water at 298 K.

solubility of barium fluoride in water = ... [1]

(ii) A saturated solution **Q** containing barium fluoride and barium hydroxide has a pH of 13.

Calculate the solubility of barium fluoride in solution **Q**.

solubility of barium fluoride in solution **Q** = ...[2]

(iii) Comment and explain the difference in the solubilities of barium fluoride in water and in solution **Q**.

....

....

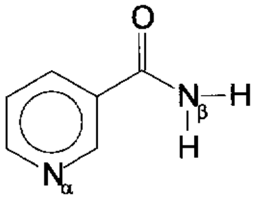
....

....

.... [2]

[Total: 11]

4 Nicotinamide is a water-soluble form of vitamin B3.



Nicotinamide

Structurally, nicotinamide has a 6-membered ring with π electron cloud that is similar to the benzene ring. This is part of a single delocalised system of electrons which includes the π bond of C=O and lone pair on NH_2.

(a) **(i)** State the number of delocalised electrons in one nicotinamide molecule.

.... [1]

(ii) N_α and N_β have the same type of hybridisation. State the hybridisation of the nitrogen atoms in nicotinamide.

.... [1]

(iii) The basicity of the two nitrogen atoms in nicotinamide are different. With reference to the orbitals that contains the lone pair of electrons, explain why N_α has a greater basicity than N_β.

....

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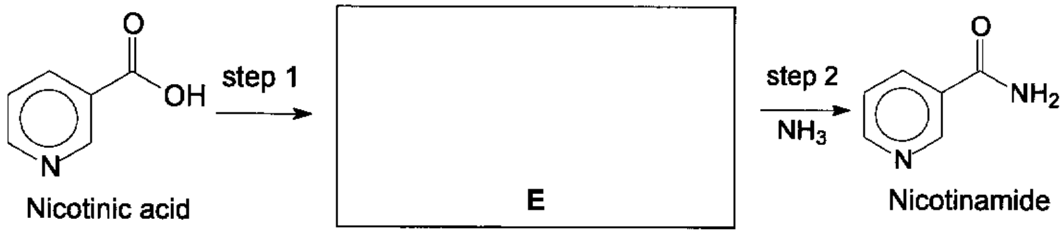
....

....

.... [2]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



(i) State the reagent for step 1.

.... [1]

(ii) Draw the structural formula of **E** in the box and write an equation to show the reaction which occurs in step 2.

[2]

(iii) Draw the **skeletal** formula of the product formed when nicotinamide is reacted with $LiAlH_4$. You may assume the six-membered ring remains unchanged.

[1]

(iv) Explain why $LiAlH_4$ cannot be used to react with C=C.

....

....

.... [1]

(c) A dipeptide **F** is synthesised from two amino acids as shown in Fig. 4.1.

$(C_6H_5)_3C—Cl$ + $H_2N—CH(CH_3)—COOH$

↓ step I

$(C_6H_5)_3C—NH—CH(CH_3)—COOH$

↓ step II and step III

$(C_6H_5)_3C—NH—CH(CH_3)—CO—NHCH_2COOH$

↓ step IV

$(C_6H_5)_3C—H$ + $NH_2—CH(CH_3)—CO—NHCH_2COOH$

dipeptide **F**

Fig. 4.1

(i) Step I is a S_N1 reaction between the amine group of $H_2N–CH(CH_3)–COOH$ and $(C_6H_5)_3C–Cl$.

Draw the mechanism for the reaction between an amine, $R–NH_2$, and $(C_6H_5)_3C–Cl$ to form $(C_6H_5)_3C–NH–R$ and any other products. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

[3]

(ii) Explain how the rate of step I will change if the following changes are made.

- $(C_6H_5)_3C{-}Br$ is used instead of $(C_6H_5)_3C{-}Cl$

....

....

- Higher concentration of $H_2N{-}CH(CH_3){-}COOH$

....

.... [2]

(iii) State the type of reaction in step IV.

.... [1]

(iv) Without step I, a mixture of two different dipeptides will be formed at the end of the synthesis in Fig. 4.1. Suggest the identity of the other dipeptide formed.

[1]

[Total: 16]

5 Ammonia is one of the most widely produced chemicals worldwide.

(a) The Haber-Bosch process accounts primarily for the world's ammonia production. This process involves gaseous hydrogen reacting with gaseous nitrogen using an iron catalyst at 150 – 250 bar and 400 – 500 °C to form ammonia.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

(i) Explain how iron acts as a *heterogeneous* catalyst in the Haber-Bosch process.

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.... [2]

(ii) Explain the conditions of temperature and pressure used in the Haber-Bosch process to produce ammonia.

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.... [2]

The hydrogen required for the Haber-Bosch process is produced from the steam reforming of methane gas as shown in equation 5.1.

equation 5.1 $$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

More hydrogen is formed from further reaction of the carbon monoxide produced with more steam as shown in equation 5.2.

equation 5.2 $$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

(iii) Prove that the overall mole ratio of CO_2 produced to H_2 produced during the steam reforming of methane gas is 1 : 4.

[1]

(iv) Using the information in **(a)(iii)**, calculate the mass of CO_2 produced as a by-product when methane is used to generate the hydrogen needed for the synthesis of 1.0 tonne of ammonia using the Haber-Bosch process.
(1 tonne = 1×10^6 g)

[2]

(b) The solid-state electrochemical synthesis of ammonia has the promise to produce ammonia in an environmentally more sustainable manner.

In this electrolytic cell, two metal electrodes are placed on both sides of a proton conductor solid electrolyte. Gaseous H_2, obtained from electrolysis of water, is passed over the anode and is converted to H^+. H^+ is then transported to the cathode where it is mixed with gaseous N_2 to form NH_3.

Fig. 5.1 shows the effect of applied current on the rate of ammonia production per unit area of electrode for this electrolytic cell. The rate of ammonia formation increased with increasing applied current up to 0.75 mA and remained almost constant by further increasing the current up to 2.0 mA.

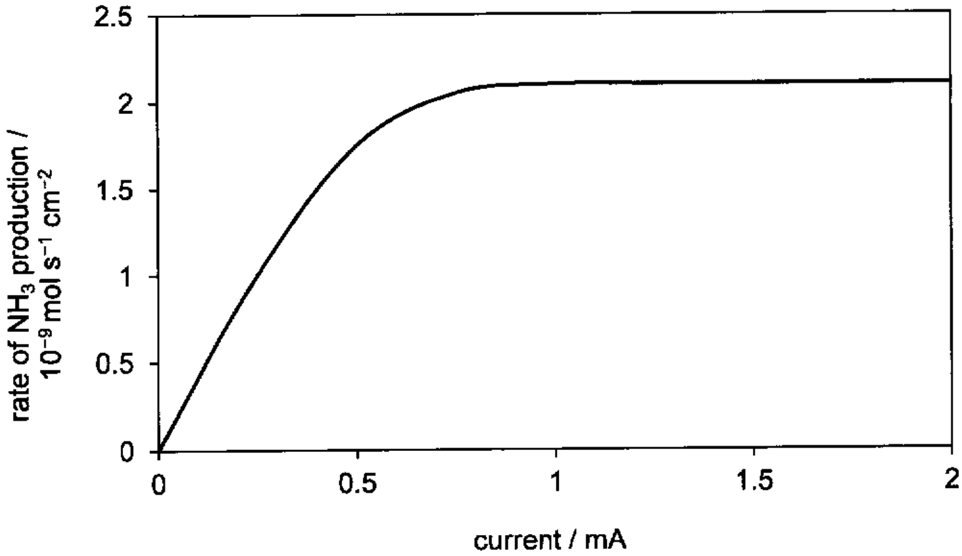

Fig. 5.1

(i) Write the half–equation for the reaction that takes place at the cathode.

.... [1]

(ii) Suggest why the rate of formation of ammonia remained almost constant when the current increased from 0.75 mA to 2.0 mA.

....

.... [1]

(iii) Suggest one advantage of the solid-state electrochemical synthesis of ammonia compared to the Haber-Bosch process.

....

.... [1]

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(c) Electrochemical lithium cycling process is another alternative pathway to sustainable ammonia production.

In this process, molten LiOH first undergoes electrolysis to produce molten lithium metal, oxygen, and steam.

stage 1 $$2LiOH \longrightarrow 2Li + \frac{1}{2}O_2 + H_2O$$

The next stage of the process involves gently heating all lithium metal from stage 1 in a stream of nitrogen to produce lithium nitride.

stage 2 $$6Li + N_2 \longrightarrow 2Li_3N$$

The last stage in the process involves reacting the lithium nitride with water to form a solution containing ammonia and lithium hydroxide.

stage 3 $$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$

The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(i) With reference to the *Data Booklet*, write the two half–equations for the electrolysis of molten LiOH.

Cathode: ....

Anode: .... [1]

(ii) Given that Li and Li_3N are intermediates in the three-stage process of electrochemical lithium cycling, construct an overall equation for the process.

[1]

The standard enthalpy change of reaction, ΔH° can be calculated from relevant standard enthalpy changes of formation, ΔH_f°. In the same way the standard Gibbs free energy change of reaction, ΔG° can be calculated from relevant standard Gibbs free energy changes of formation, ΔG_f°.

compound	ΔG_f° / kJ mol^{-1}
LiOH(s)	−439
Li_3N(s)	−137
H_2O(l)	−237
NH_3(g)	−17

(iii) Using the information given above, calculate the standard Gibbs free energy change ΔG°, for stage 3 of the electrochemical lithium cycling process. Hence, comment on the sign of ΔG°.

stage 3 $\quad$ $Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$

You should assume all species are in their standard states.

[2]

(iv) Using the equations in stages 2 and 3, calculate the amount of Li required to produce 1 kg of NH_3.

[1]

(v) Hence, calculate the current required to produce 1 kg of NH_3 in an hour.

[1]

(d) Efficient electrolysis of molten LiOH is challenging due to potential side reactions. One of the side reactions is the reverse reaction of stage 1 as shown in equation 5.3.

equation 5.3 $$Li + \frac{1}{4}O_2 + \frac{1}{2}H_2O \longrightarrow LiOH$$

(i) Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for equation 5.3.

[1]

(ii) Use your answer in **(d)(i)** to calculate the standard Gibbs free energy change for the reaction in equation 5.3.

[1]

It is suggested that a molten salt mixture consisting of LiOH and Li*Cl* could be used to mitigate the possible side reactions. To test for the possible formation of Cl_2 gas, potassium iodide starch paper was exposed to the anode throughout the electrolysis.

(iii) With the aid of an equation, suggest the role of potassium iodide and how the potassium iodide starch paper can test for the presence of Cl_2.

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.... [2]

[Total: 20]

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ANDERSON SERANGOON JUNIOR COLLEGE

2024 JC 2 PRELIMINARY EXAMINATION

CHEMISTRY **9729/02**

Paper 2 Structured Questions

SUGGESTED SOLUTIONS

Answer **all** the questions.

1 **(a)** Phosphorus, sulfur and chlorine are Period 3 elements of the Periodic Table.

Table 1.1 shows some properties of the three elements.

Table 1.1

	P	S	C*l*
number of electrons in 3p subshell			
number of unpaired electrons			

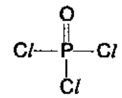
(i) Complete Table 1.1 to show the number of electrons in the 3p subshell and the number of unpaired electrons in an atom of P, S and Cl. [2]

	P [Ne]$3s^23p^3$	S [Ne]$3s^23p^4$	C*l* [Ne]$3s^23p^5$
number of electrons in 3p subshell	3	4	5
number of unpaired electrons	3	2	1

(ii) With reference to the *Data Booklet*, state and explain the trend of the ionic radius of P^{3-}, S^{2-} and Cl^-. [2]

- Ionic radius decreases from P^{3-} (0.212 nm), S^{2-} (0.184 nm) and Cl^- (0.181 nm)
- Nuclear charge increases from P^{3-} to Cl^-.
- Number of filled quantum (electron) shells and shielding effect remains the same since the anions (P^{3-} to Cl^-) are isoelectronic.
- Therefore, the stronger (electrostatic) forces of attraction between the nucleus and the outer electrons results in the decreasing ionic radius.

(b) Phosphoryl chloride, $POCl_3$, is a colourless liquid that is used to make phosphate esters.



$POCl_3$ has similar chemical properties as PCl_5. It has a melting point of 1 °C and a boiling point of 106 °C.

It also reacts vigorously with water, forming misty fumes and an acidic solution of H_3PO_4.

(i) Explain how the information in **(b)** suggests that the structure and bonding of $POCl_3$ is simple covalent. [2]

$POCl_3$ has low melting and boiling point suggests that it has weak instantaneous dipole-induced dipole attraction / permanent dipole-permanent dipole attraction between molecules that required low amount of energy to overcome. [1]

The vigorous reaction with water suggested that hydrolysis had taken place. [1]

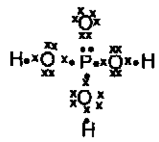
Thus, the structure and bonding of $POCl_3$ is likely to be simple covalent.

(ii) Write a balanced equation for the reaction of $POCl_3$ with water. [1]

$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$ [1]

(iii) In H_3PO_4, there is no hydrogen atom directly bonded to the phosphorus atom.

Draw the 'dot and cross' diagram of H_3PO_4 and state the shape of the molecule with respect to P. [2]



[1]

Shape: tetrahedral [1]

(c) Phosphoryl chloride, $POCl_3$, is manufactured industrially from phosphorus trichloride and oxygen as shown in equation 1.1.

equation 1.1 $2PCl_3(g) + O_2(g) \longrightarrow 2POCl_3(g)$

The standard enthalpy changes of formation for these species are shown in Table 1.2.

Table 1.2

Enthalpy change of formation of $PCl_3(g)$	–289 kJ mol^{-1}
Enthalpy change of formation of $POCl_3(g)$	–592 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation*. [1]

The amount of heat absorbed or evolved when one mole of a substance is formed from its constituent elements, all in their standard states at 298 K and 1 bar. [1]

(ii) Using the data from Table 1.2 and relevant data from the *Data Booklet*, calculate the bond energy of P=O in $POCl_3$. [2]

$\Delta H_r = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$
$= 2(-592) - 2(-289)$
$= -606 \text{ kJ mol}^{-1}$ [1]

$\Delta H_r^{\ominus} = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$

$\{[2\times3BE(P-Cl)] + BE(O=O)\} - \{[2\times3BE(P-Cl) + 2\times BE(P=O)\} = -606$
$\{(6 \times 330) + 496\} - \{(6 \times 330) + 2BE(P=O)\} = -606$
$496 - 2BE(P=O) = -606$
$BE(P=O) = +551 \text{ kJ mol}^{-1}$ [1]

(iii) Predict and explain the sign of the entropy change for the reaction in equation 1.1. [1]

ΔS is negative because there is a decrease in the number of gaseous particles. There are less ways to distribute the particles and the energies among these particles, resulting in less disorder in the system. Hence entropy of the system decreases. [1]

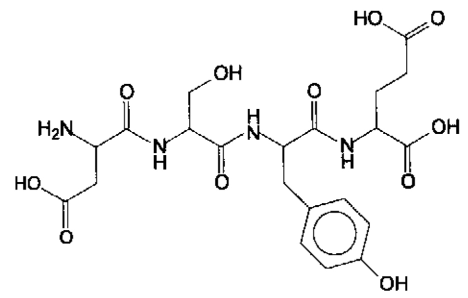
(iv) Comment on the effect of increasing temperature on the spontaneity of the reaction in equation 1.1. [2]

Since $\Delta H_r^{\ominus} < 0$ (negative) and $-T\Delta S_r^{\ominus} > 0$ (positive), $-T\Delta S_r^{\ominus}$ becomes more positive with increasing temperature. [1]

$\Delta G_r^{\ominus}$ becomes more positive and the reaction will become less spontaneous as the temperature of the reaction increases. [1]

[Total: 15]

2 The structure of a tetrapeptide **T** is shown below.



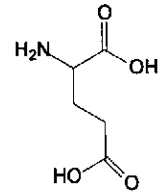
T

(a) Name the type of reaction to break **T** into its constituent amino acids. [1]

Hydrolysis [1]

(b) The four amino acids formed from the reaction in **(a)** are glutamic acid, tyrosine, **U** and **V**. The structures of glutamic acid and tyrosine are as shown.

glutamic acid



tyrosine

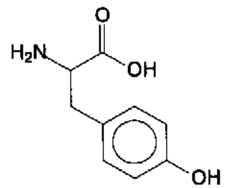
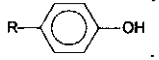


Table 2.1 lists the pK_a values of the different functional groups present on each of the four amino acids.

Table 2.1

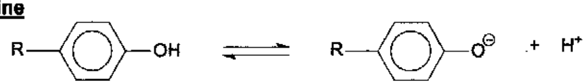
Amino acid	pK_a		
	α-carboxyl group	α-amino group	side chain
glutamic acid	2.1	9.5	4.1
tyrosine	2.2	9.2	10.5
U	2.0	9.9	3.9
V	2.2	9.2	-

(i) Explain why the pK_a value of the side chain of glutamic acid is lower than that in tyrosine.

You may represent glutamic acid as R–CO_2H and tyrosine as  .

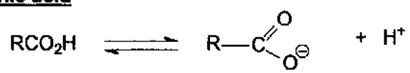
[3]

Tyrosine



In **phenoxide ion**, the lone pair of electrons on O atom can delocalise into the π electron cloud of the benzene ring, thus dispersing the negative charge, stabilising the phenoxide through resonance. [1]

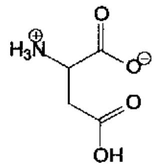
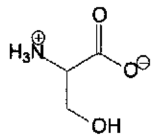
Glutamic acid



In **RCO_2^-**, the p-orbital on the C atom overlaps with the p-orbitals of the two neighbouring O atoms. Hence, the negative charge is more effectively dispersed between the two O atoms, [1] resulting in a more (resonance-) stabilised RCO_2^- as compared to the phenoxide ion.

Since the dissociation of RCOOH to release H^+ is more favoured, the side chain of glutamic acid is a stronger acid and has a lower pK_a value than that of tyrosine. [1]

(ii) In the space below, draw the structures of the predominant species of **U** and **V** at pH 3.0.

U	V
	

[2]

(c) Solutions containing the zwitterions of **V** can act as buffers.

(i) State what is meant by the term *zwitterion*.

[1]

A zwitterion is a species that carries both a positive charge and a negative charge but is electrically neutral. [1]

(ii) With the aid of appropriate equations, explain how a solution containing the zwitterions of **V** can resist pH changes. You may use $H_2NCHRCOOH$ to represent the structure of **V**.

[2]

When a small amount of acid is added:

$H_3N^+CHRCOO^- + H^+ \longrightarrow H_3N^+CHRCOOH$

When a small amount of base is added:

$H_3N^+CHRCOO^- + OH^- \longrightarrow H_2NCHRCOO^- + H_2O$

Since the acid or base added is removed, the pH is kept relatively constant.

(d) (i) Calculate the pH of 0.10 mol dm^{-3} solution of protonated **V**. Ignore the effect of pK_a of the α-amino group on the pH.

[2]

$H_3N^+CHRCOOH \rightleftharpoons H_3N^+CHRCOO^- + H^+$

$$K_a = \frac{[H_3N^+CHRCOO^-][H^+]}{[H_3N^+CHRCOOH]} \approx \frac{[H^+]^2}{[H_3N^+CHRCOOH]_i}$$

$$10^{-2.2} = \frac{[H^+]^2}{0.10}$$

$[H^+] = 0.02512$

[1]

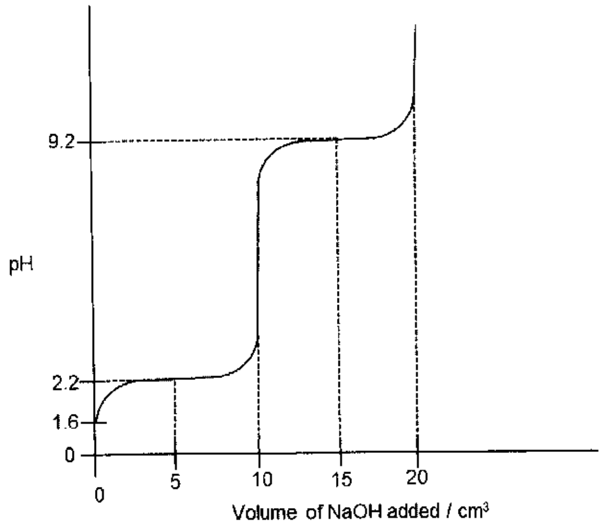
pH = 1.6 [1]

(ii) A student records the pH of the mixture when 20 cm^3 of 0.10 mol dm^{-3} NaOH(aq) was added to 10.0 cm^3 of 0.10 mol dm^{-3} solution of protonated **V**.

Sketch the shape of the pH curve on Fig. 2.1 using all relevant information given or calculated.

Your sketch should also clearly indicate the two points where the solution is most effective in resisting pH changes.

[2]



√ correct shape
√ initial pH
√ equivalence volumes
√ volumes and pH at MBC

[Total: 13]

3 (a) (i) Write an equation to represent the lattice energy of magnesium bromide, $MgBr_2$.

[1]

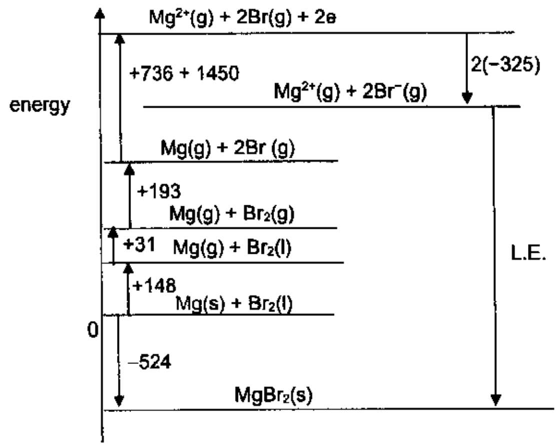
$Mg^{2+}(g) + 2Br^-(g) \longrightarrow MgBr_2(s)$ [1]

(ii) Use the data in Table 3.1, together with data from the *Data Booklet*, to construct a Born–Haber cycle on the energy diagram below. Hence, calculate the lattice energy of magnesium bromide.

Table 3.1

	value / kJ mol^{-1}
enthalpy change of formation of magnesium bromide	–524
enthalpy change of atomisation of magnesium	+148
enthalpy change of vaporisation of bromine	+31
first electron affinity of bromine	–325

[3]



$-524 = 148 + 31 + 193 + 736 + 1450 + 2(-325) + LE$

L.E. of CaF_2 = **<u>–2432 kJ mol⁻¹</u>**

= **<u>–2430 kJ mol⁻¹</u>** (3 sig fig)

(iii) How would you expect the lattice energy of barium bromide to compare with that of magnesium bromide? Explain your answer.

[2]

Lattice energy of $BaBr_2$ is <u>less exothermic</u> than that of $MgBr_2$. [1]

Since <u>ionic radius of Ba^{2+} is larger than that of Mg^{2+}</u>, the <u>inter–ionic distance between Ba^{2+} and Br^- will be larger</u>. This results in <u>weaker electrostatic forces of attraction between the Ba^{2+} and Br^-</u>. Hence lattice energy of $BaBr_2$ is less exothermic. [1]

(b) Barium compounds such as barium fluoride and barium hydroxide are sparingly soluble in water. The solubility product, K_{sp}, values for these compounds at 298 K, are listed in Table 3.2.

Table 3.2

Barium compound	numerical value of K_{sp}
BaF_2	1.0×10^{-6}
$Ba(OH)_2$	5.0×10^{-3}

(i) Calculate the solubility of barium fluoride in water at 298 K.

solubility of barium fluoride in water = ... [1]

Let x mol dm^{-3} be the solubility of BaF_2 in water.

$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$
x 2x

$K_{sp} = [Ba^{2+}][F^-]^2$
$1.0 \times 10^{-6} = (x)(2x)^2$
x = **6.30×10^{-3} mol dm^{-3}**[1]

(ii) A saturated solution **Q** containing barium fluoride and barium hydroxide has a pH of 13.

Calculate the solubility of barium fluoride in solution **Q**.

solubility of barium fluoride in solution **Q** = ... [2]

pH = 13 ⇒ pOH = 1
⇒ $[OH^-] = 10^{-1} = 1.00 \times 10^{-1}$ mol dm^{-3}

K_{sp} of $Ba(OH)_2 = [Ba^{2+}]_{total}[OH^-]^2$
$5.0 \times 10^{-3} = [Ba^{2+}]_{total}(1.00 \times 10^{-1})^2$
$[Ba^{2+}]_{total} = 0.500$ mol dm^{-3} [1]

Let y mol dm^{-3} be the solubility of BaF_2 in solution **Q**.

$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$
0.500 2y

$[Ba^{2+}]_{total}[F^-]^2 = 1.0 \times 10^{-6}$
$(0.500)(2y)^2 = 1.0 \times 10^{-6}$
y = **7.07×10^{-4} mol dm^{-3}** [1]

(iii) Comment and explain the difference in the solubilities of barium fluoride in water and in solution **Q**. [2]

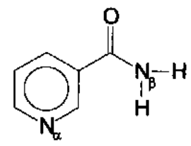
$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$

Solubility of BaF_2 in solution **Q** is lower than that in water.

The presence of Ba^{2+} from $Ba(OH)_2$ increases $[Ba^{2+}]$, which shifts the position of equilibrium to the left to decease the $[Ba^{2+}]$. This results in the precipitation of BaF_2 and decreases the solubility of BaF_2 in solution **Q**.

[Total: 11]

4 Nicotinamide is a water-soluble form of vitamin B3.



Nicotinamide

Structurally, nicotinamide has a 6-membered ring with π electron cloud that is similar to the benzene ring. This is part of a single delocalised system of electrons which includes the π bond of C=O and lone pair on NH_2.

(a) **(i)** State the number of delocalised electrons in one nicotinamide molecule. [1]

10 electrons [1]

(ii) N_α and N_β have the same type of hybridisation. State the hybridisation of the nitrogen atoms in nicotinamide. [1]

sp^2 [1]

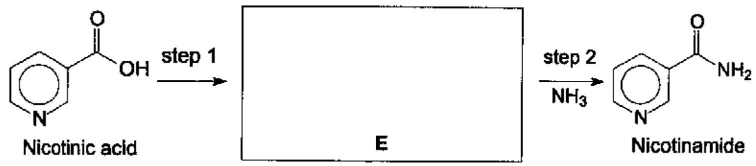
(iii) The basicity of the two nitrogen atoms in nicotinamide are different. With reference to the orbitals that contains the lone pair of electrons, explain why N_α has a greater basicity than N_β. [2]

Lone pair on N_β is in (unhybridised) p orbital. The lone pair is delocalised into the π bond of the adjacent C=O by resonance, hence the lone pair is not available to accept a proton. This makes the amide group containing N_β neutral. [1]

Lone pair on N_α is in sp^2 hybrid orbital. It is not delocalised and hence is available to accept a proton, making N_α more basic. [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

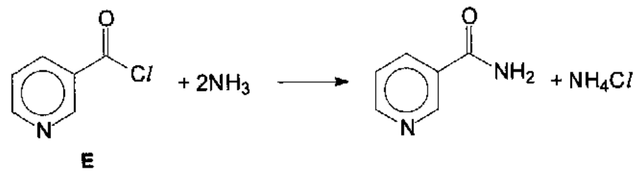
The synthesis involves two steps.



(i) State the reagent for step 1. [1]

anhydrous PCl_3 / PCl_5 / $SOCl_2$ [1]

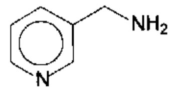
(II) Draw the structural formula of **E** in the box and write an equation to show the reaction which occurs in step 2. [2]



E

[1] Structure of **E**
[1] Balanced equation

(III) Draw the skeletal formula of the product when nicotinamide is reacted with $LiAlH_4$. You may assume the six-membered ring remains unchanged. [1]



[1]

(iv) Explain why $LiAlH_4$ cannot be used to react with C=C. [1]

C=C is non-polar and is not susceptible to nucleophilic attack by negatively charged hydride ions from $LiAlH_4$. [1]

(c) A dipeptide **F** is synthesised from two amino acids as shown in Fig. 4.1.

$(C_6H_5)_3C$—C*l* + H_2N—CH(CH_3)—COOH

↓ step I

$(C_6H_5)_3C$—NH—CH(CH_3)—COOH

↓ step II and step III

$(C_6H_5)_3C$—NH—CH(CH_3)—CO—$NHCH_2COOH$

↓ step IV

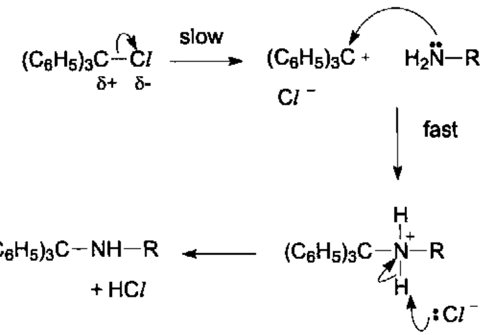
$(C_6H_5)_3C$—H + NH_2—CH(CH_3)—CO—$NHCH_2COOH$

dipeptide **F**

Fig. 4.1

(i) Step I is a S_N1 reaction between the amine group of H_2N–CH(CH_3)–COOH and $(C_6H_5)_3C$–C*l*.

Draw the mechanism for the reaction between an amine, R–NH_2, and $(C_6H_5)_3C$–C*l* to form $(C_6H_5)_3C$–NH–R and any other products. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs. [3]



[2]

- $(C_6H_5)_3C$–Br is used instead of $(C_6H_5)_3C$–C*l*

The C–Br bond is weaker than C–C*l* bond, making it easier to break and increase the rate of nucleophilic substitution. [1]

- Higher concentration of H_2N–CH(CH_3)–COOH

There will be no change in the rate of reaction as H_2N–CH(CH_3)–COOH is not in the slow step/rate equation. [1]

(iii) State the type of reaction in step IV. [1]

Reduction [1]

(iv) Without step I, a mixture of two different dipeptides will be formed at the end of the synthesis in Fig. 4.1. Suggest the identity of the other dipeptide formed. [1]

H_2N–CH_2–CO–NHCH(CH_3)COOH [1]

[Total: 16]

5 Ammonia is one of the most widely produced chemicals worldwide.

(a) The Haber-Bosch process accounts primarily for the world's ammonia production. This process involves gaseous hydrogen reacting with gaseous nitrogen using an iron catalyst at 150 – 250 bar and 400 – 500 °C to form ammonia.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\ \text{kJ mol}^{-1}$$

(i) Explain how iron acts as a ***heterogeneous*** catalyst in the Haber-Bosch process. [2]

- Iron is in solid phase, different from the gaseous H_2 and N_2 molecules.
- H_2 and N_2 molecules form weak temporary bonds with the iron catalyst due to the presence of partially filled 3d subshells.
- This results in the weakening of existing bonds within H_2 and N_2 molecules, thus lowering the activation energy of the reaction.
- H_2 and N_2 molecules are also brought closer together at the active sites, thus resulting in higher concentration of these molecules at the surface of the iron catalyst and increase in rate of reaction.

(ii) Explain the conditions of temperature and pressure used in the Haber-Bosch process to produce ammonia. [2]

(1) Moderately high temperature of 450°C.
The forward exothermic reaction is favoured by a low temperature as position of equilibrium (POE) shifts to the right to produce more heat and more NH_3. However, the temperature cannot be too low, as the rate of reaction will be too slow making the process uneconomical. [1]

(2) Moderately high pressure of 250 atm.
The production of NH_3 is favoured by a high pressure as POE shifts to the right to produce fewer gas particles and more NH_3. However, very high pressure demands higher costs of construction and maintenance since more expensive and thicker vessels have to be employed in order to withstand high pressures. [1]

The hydrogen required for the Haber-Bosch process is produced from the steam reforming of methane gas as shown in equation 5.1.

equation 5.1 $\qquad CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$

More hydrogen is formed from further reaction of the carbon monoxide produced with more steam as shown in equation 5.2.

equation 5.2 $\qquad CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$

(iii) Prove that the overall mole ratio of CO_2 produced to H_2 produced during the steam reforming of methane gas is 1 : 4. [1]

Method 1
$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$ -----(2)
$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$-----(3)

From equation 2, 1 mol of CH_4 produces 1 mol of CO and 3 mol of H_2
From equation 3, 1 mol of CO produces 1 mol of CO_2 and 1 mol of H_2.

Therefore, 1 mol of CH_4 would give 1 mol CO_2 and 4 mol of H_2.

Method 2
$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$ -----(2)
$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$-----(3)

(2) + (3):
Overall: $CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$

Therefore, from the overall equation, the mole ratio of CO_2 produced to H_2 produced is 1 : 4.

[1] for explanation

(iv) Using the information in **(a)(iii)**, calculate the mass of CO_2 produced as a by-product when methane is used to generate the hydrogen needed for the synthesis of 1.0 tonne of ammonia using the Haber-Bosch process.
(1 tonne = 1×10^6 g) [2]

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

n(NH_3) produced = $(\frac{10^6}{17.0}) = 5.882 \times 10^4$ mol

n(H_2) needed = $58824 \times \frac{3}{2} = 8.824 \times 10^4$ mol [1]

n(CO_2) produced = ¼ × $8.824 \times 10^4 = 2.206 \times 10^4$ mol

mass of CO_2 produced = $2.206 \times 10^4 \times [12.0 + 2(16.0)]$
= **971000 g** or
= **971 kg** or
= **0.971 tonne** [1]

(b) The solid-state electrochemical synthesis of ammonia has the promise to produce ammonia in environmentally more sustainable manner.

In this electrolytic cell, two metal electrodes are placed on both sides of a proton conductor solid electrolyte. Gaseous H_2, obtained from electrolysis of water, is passed over the anode and is converted to H^+. H^+ is then transported to the cathode where it is mixed with gaseous N_2 to form NH_3.

Fig. 5.1 shows the effect of applied current on the rate of ammonia production per unit area of electrode for this electrolytic cell. The rate of ammonia formation increased with increasing applied current up to 0.75 mA and remained almost constant by further increasing the current up to 2.0 mA.

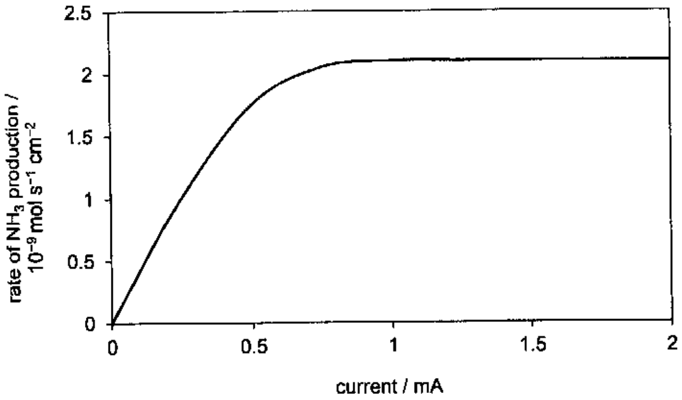


Fig. 5.1

(i) Write the half–equation for the reaction that take place at the cathode. [1]

$N_2 + 6H^+ + 6e \longrightarrow 2NH_3$ [1]

(ii) Suggest why the rate of formation of ammonia remained almost constant when the current increased from 0.75 mA to 2.0 mA. [1]

At higher potential, rate is independent of current since all the surface area for reaction on the electrodes are fully occupied. [1]

(iii) Suggest one advantage of the solid-state electrochemical synthesis of ammonia compared to the Haber-Bosch process. [1]

- It does not produce CO_2 which is a greenhouse gas (a gas that causes global warming);
- It does not produce toxic CO;
- It does not need to the gases to be at high pressure.

[1] for any of the above reason

(c) Electrochemical lithium cycling process is another alternative pathway to sustainable ammonia production.

In this process, molten LiOH first undergoes electrolysis to produce molten lithium metal, oxygen, and steam.

stage 1 $\quad 2LiOH \longrightarrow 2Li + \frac{1}{2}O_2 + H_2O$

The next stage of the process involves gently heating all lithium metal from stage 1 in a stream of nitrogen to produce lithium nitride.

stage 2 $\quad 6Li + N_2 \longrightarrow 2Li_3N$

The last stage in the process involves reacting the lithium nitride with water to form a solution containing ammonia and lithium hydroxide.

stage 3 $\quad Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$

The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(i) With reference to the *Data Booklet*, write the two half–equations for the electrolysis of molten LiOH. [1]

Cathode: $Li^+ + e \longrightarrow Li$

Anode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e$

[1] for both equations

(ii) Given that Li and Li_3N are intermediates in the three-stage process of electrochemical lithium cycling, construct an overall equation for the process. [1]

$2LiOH \longrightarrow 2Li + \frac{1}{2}O_2 + H_2O$ ----(4)
$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$ -------(5)
$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$ ---(6)

④ x 3: $\cancel{6LiOH} \rightarrow \cancel{6Li} + \frac{3}{2}O_2 + 3H_2O$
⑤: $\cancel{6Li} + N_2 \rightarrow \cancel{2Li_3N}$
⑥ x 2: $\cancel{2Li_3N} + 6H_2O \rightarrow \cancel{6LiOH} + 2NH_3$

Overall equation: $\mathbf{N_2 + 3H_2O \rightarrow \frac{3}{2}O_2 + 2NH_3}$ [1]

The standard enthalpy change of reaction, ΔH° can be calculated from relevant standard enthalpy changes of formation, ΔH_f°. In the same way the standard Gibbs free energy change of reaction, ΔG° can be calculated from relevant standard Gibbs free energy changes of formation, ΔG_f°.

compound	ΔG_f° / kJ mol^{-1}
LiOH(s)	−439
Li_3N(s)	−137
H_2O(l)	−237
NH_3(g)	−17

(iii) Using the information given above, calculate the standard Gibbs free energy change ΔG°, for stage 3 of the electrochemical lithium cycling process. Hence, comment on the sign of ΔG°.

stage 3 $Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$

You should assume all species are in their standard states. [2]

$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$

$\Delta G^\ominus$ stage 3 = $\Sigma n\Delta G_f^\ominus$ (products) – $\Sigma n\Delta G_f^\ominus$ (reactants)
= (3 × –439) + (–17) – [(–137) + (3 × –237)]
= <u>–486 kJ mol⁻¹</u> [1]

Since <u>$\Delta G^\ominus < 0$</u>, the reaction is <u>spontaneous</u>. [1]

(iv) Using the equations in stages 2 and 3, calculate the amount of Li required to produce 1 kg of NH_3. [1]

$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$
$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$

$n(NH_3)$ = 1000 / 17 = 58.824 mol
$n(Li_3N)$ required = 58.824 mol
n(Li) required = 3 × 58.824 = 176.47 mol
= <u>176 mol</u> [1]

(v) Hence, calculate the current required to produce 1 kg of NH_3 in an hour. [1]

$Li^+ + e \longrightarrow Li$

n(Li) required = 176.47 mol

n(e) = 176.47 mol

$I \times t = n_e \times F$
I × (60 × 60) = 176.47 × 96500
I = <u>4730 A</u> [1]

(d) Efficient electrolysis of molten LiOH is challenging due to potential side reactions. One of the side reactions is the reverse reaction of stage 1 as shown in equation 5.3.

equation 5.3 $Li + \frac{1}{4}O_2 + \frac{1}{2}H_2O \longrightarrow LiOH$

(i) Use data from the *Data Booklet* to calculate the E°_{cell} for equation 5.3. [1]

$Li^+ + e \rightleftharpoons Li$ –3.04 V
$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$ +0.40 V

$E^\circ_{cell} = E^\circ(R) - E^\circ(O)$
= +0.40 – (–3.04)
= **<u>+3.44 V</u>** [1]

(ii) Use your value in **(d)(i)** to calculate the standard Gibbs free energy change for the reaction. [1]

For 1 mol of Li, no of mol of e = 1

$\Delta G^\ominus = -nFE^\circ_{cell}$
= – 1 × 96500 × (+3.44)
= –331960
= **<u>–332000 J mol⁻¹</u>** [1] including sign and unit

It is suggested that a molten salt mixture consisting of LiOH and LiCl could be used to mitigate the possible side reactions. To test for the possible formation of Cl_2 gas, potassium iodide starch paper was exposed to the anode throughout the electrolysis.

(iii) With the aid of an equation, suggest the role of potassium iodide and how the potassium iodide starch paper can test for the presence of Cl_2. [2]

$Cl_2 + I^- \longrightarrow 2Cl^- + I_2$ [1]

Since Cl_2 is reduced to Cl^- and I^- is oxidised to I_2. KI is a <u>reducing agent</u> and the <u>I_2 produced will react with starch to form a blue-black complex</u> which will indicate that Cl_2 is produced. [1]

[Total: 20]