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^{-}.

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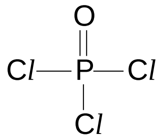
(b) Phosphoryl chloride, $POCl_3$, is a colourless liquid that is used to make phosphate esters.



$POCl_3$ 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.

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

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(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*.

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(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.

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

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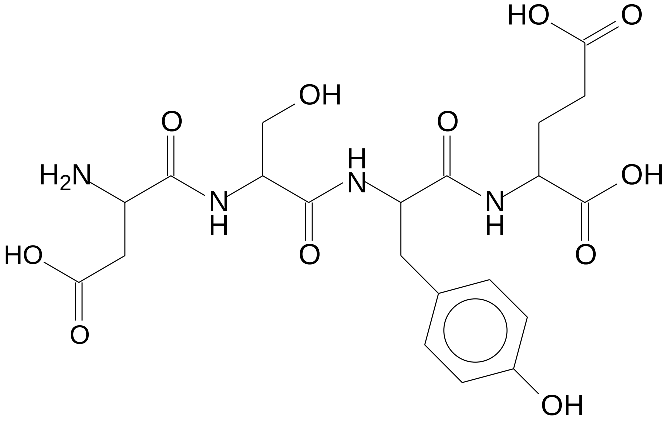
[Total: 15]

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



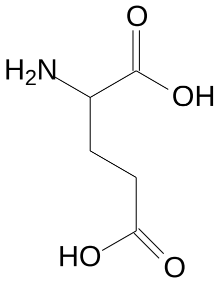
T

(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

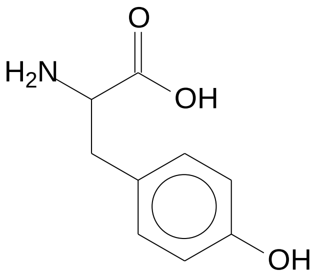
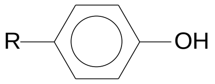


Table 2.1 lists the pK_a values of the different functional groups present on each of the four amino acids.

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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(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*.

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…………………………………………………………………………………………….. [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**.

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(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.

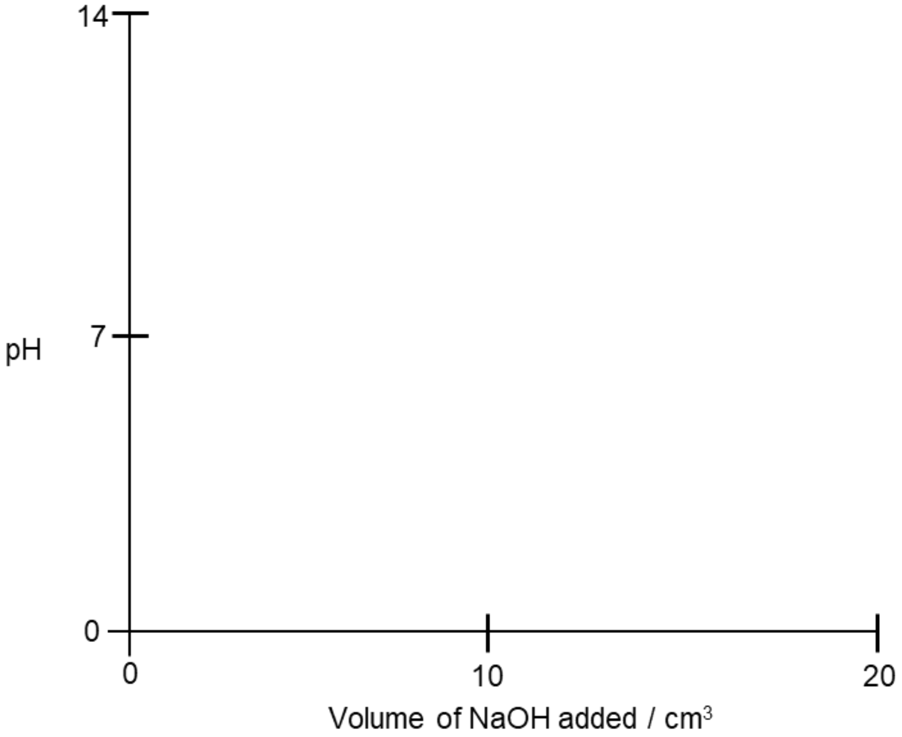


Fig. 2.1

[2]

[Total: 13]

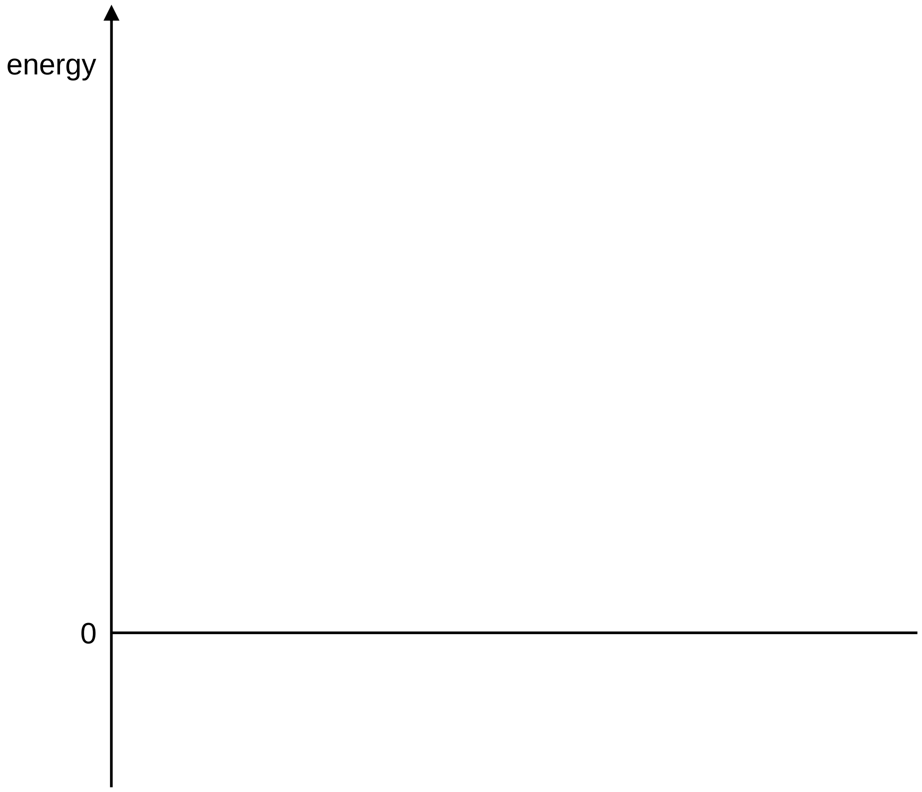
3 **(a)** **(i)** Write an equation to represent the lattice energy of magnesium bromide, $MgBr_2$.

.... [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.

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………………………………………………………………………………………………. [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**.

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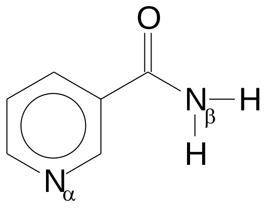
[Total: 11]

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.

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(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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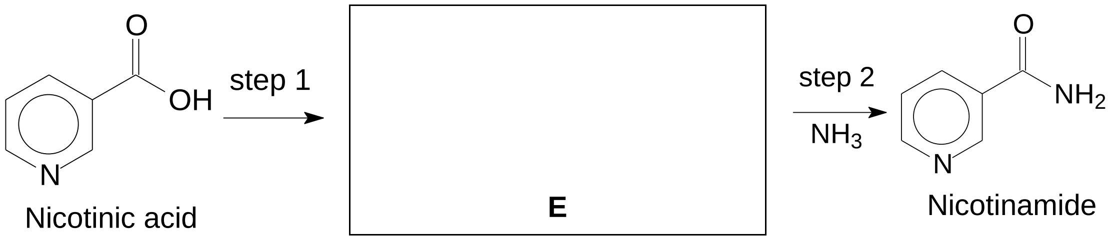
(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



(i) State the reagent for step 1.

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(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.

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

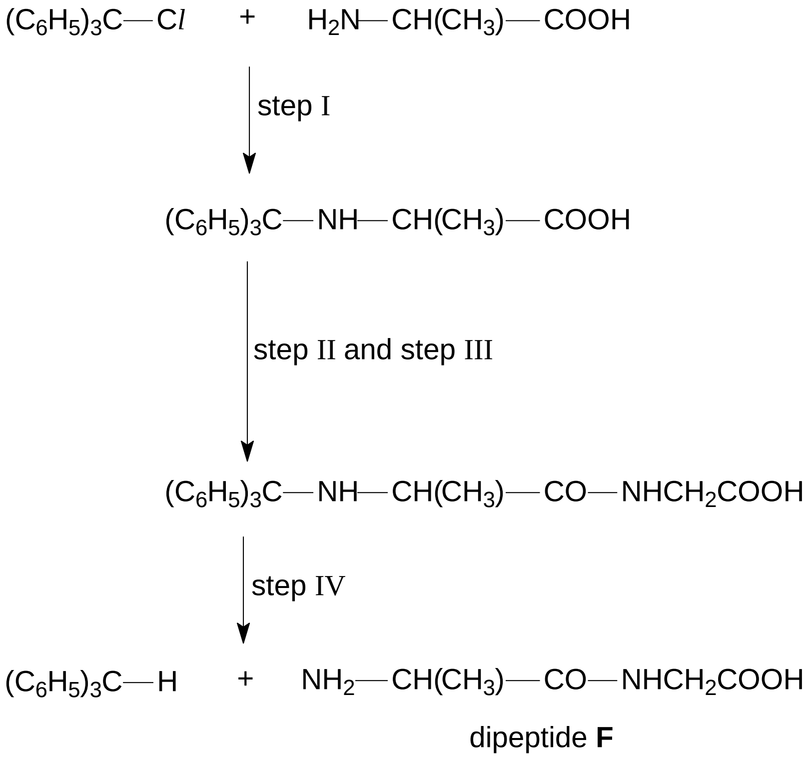

Fig. 4.1

(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 $(C_6H_5)_3C{-}Cl$

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

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

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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.

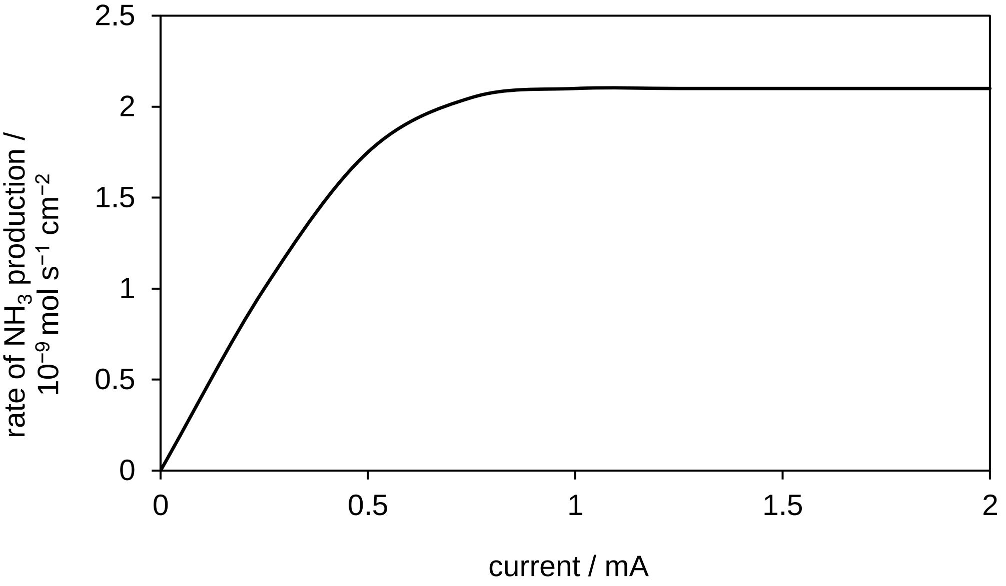

Fig. 5.1

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

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

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

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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 $2LiOH \longrightarrow 2Li + ½O_2 + H_2O$

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, $\Delta H^{\ominus}$ can be calculated from relevant standard enthalpy changes of formation, $\Delta H_f^{\ominus}$. In the same way the standard Gibbs free energy change of reaction, $\Delta G^{\ominus}$ can be calculated from relevant standard Gibbs free energy changes of formation, $\Delta G_f^{\ominus}$.

compound	$\Delta G_f^{\ominus}$ / 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 $\Delta G^{\ominus}$, for stage 3 of the electrochemical lithium cycling process. Hence, comment on the sign of $\Delta G^{\ominus}$.

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

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 LiC*l* 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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