RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

17 September 2024
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index 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. 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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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="7">For Examiner's Use</th></tr>
<tr><th colspan="2">Section A</th><th></th><th colspan="2">Section B</th><th></th><th>Total</th></tr>
<tr><td>1</td><td>/ 20</td><td></td><td colspan="2">(Circle the question you have answered)</td><td></td><td rowspan="3">/ 80</td></tr>
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This document consists of **29** printed pages and **3** blank pages.

Section A

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

1 Contrails are the visible clouds that form in a line behind an aircraft during its flight.

(a) One of the reactions involved in the formation of contrails is shown in equation 1.

equation 1 $2SO_2 + O_2 \rightleftharpoons 2SO_3$ $\Delta H_r < 0$

(i) Write the expression for the equilibrium constant, K_c, for equation 1, stating its units. [1]

(ii) At 450 °C, a sealed 1.00 dm^3 flask is found to contain an equilibrium mixture of gases as shown in Table 1.1.

Table 1.1

	SO_2	O_2	SO_3
amount / mol	0.500	0.100	4.60

Use these data to calculate K_c for the reaction in equation 1. [2]

(iii) Using information from **(a)(ii)**, calculate the total pressure, in MPa, of the gaseous mixture at equilibrium. Assume that the gases behave ideally.
[1 MPa = 10^6 Pa] [1]

(iv) Hence, calculate the equilibrium partial pressure, in MPa, of SO_3. [1]

(v) Calculate the amount of oxygen that must be added to the mixture to increase the amount of SO_3, at equilibrium, to 4.70 mol at the same temperature. [2]

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(b) Another sealed flask contains the same gaseous mixture in equation 1.

(i) Explain how an increase in temperature affects the equilibrium amount of SO_2. [2]

(ii) The system is initially at equilibrium at t = 0 s. At time = t_1, the temperature of the system increases sharply. Equilibrium is re-established at time = t_2.

Sketch a labelled graph of both the forward and backward rates of the reaction against time. You may use *f* and *b* to label the forward and backward rates respectively. [2]

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(c) Contrail formation depends on the proportion of H_2SO_4 produced in the exhaust gases of an airplane. The reactions to produce H_2SO_4 are shown below.

reaction 1 $SO_2(g) + {}^\bullet OH(g) \rightleftharpoons HO\overset{\bullet}{S}O_2(g)$

reaction 2 $HO\overset{\bullet}{S}O_2(g) + O_2(g) \rightleftharpoons H\overset{\bullet}{O}_2(g) + SO_3(g)$

reaction 3 $SO_3(g) + H_2O(g) \rightleftharpoons H_2SO_4(g)$

The higher the proportion of H_2SO_4, the more contrails are formed.

Fig. 1.1 shows how $\Delta G_r^\ominus$ for reaction 1 varies with temperature, T, of the exhaust gases.

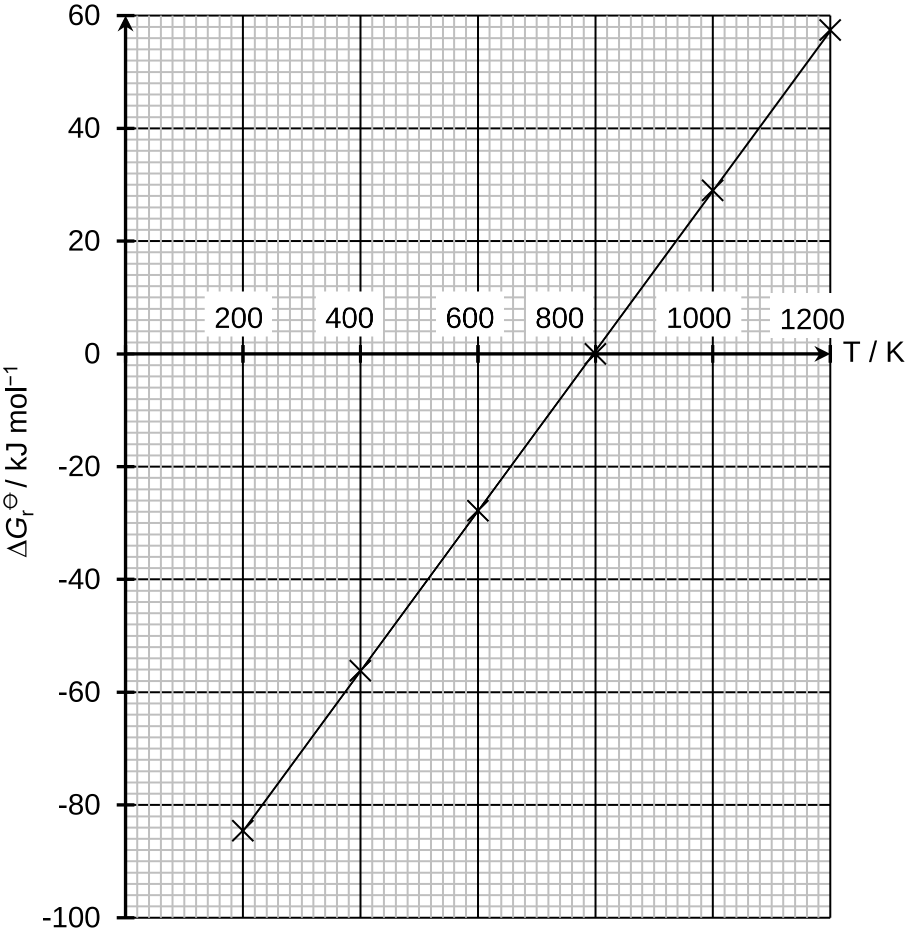

Fig. 1.1

(i) State the minimum temperature at which reaction 1 is no longer spontaneous. [1]

(ii) Explain, in terms of position of equilibrium, the effect of increasing temperature on the proportion of H_2SO_4 produced in the exhaust gases. [2]

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(d) **(i)** State two basic assumptions of the kinetic theory as applied to an ideal gas. [2]

(ii) Explain why a gas deviates from ideal behaviour at high pressure. [1]

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(e) Liquefaction is the process by which gases are converted to liquids. Some gases can be liquefied at a given temperature by applying a sufficiently high pressure.

However, when the temperature is higher than the critical temperature, T_c, gases cannot be liquefied regardless of the pressure applied.

The table below shows the value of T_c for some gases.

Table 1.2

gas	formula	T_c / °C
carbon dioxide	CO_2	31.0
steam	H_2O	374

(i) Explain why above T_c, gases cannot be liquefied regardless of the pressure applied. [1]

(ii) Explain why the critical temperature of steam is higher than that of carbon dioxide. [2]

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

(ii) Use the data from Table 2.1, together with data from the *Data Booklet*, to construct a Born-Haber cycle to calculate the standard enthalpy change of formation of solid sodium hydrogencarbonate, $NaHCO_3$.

Table 2.1

	value / kJ mol^{-1}
lattice energy of sodium hydrogencarbonate, $NaHCO_3(s)$	−656.0
standard enthalpy change of atomisation of Na(s)	+107.5
standard enthalpy change of formation of gaseous hydrogencarbonate ion, $HCO_3^-(g)$	−896.3

[4]

(iii) The standard enthalpy change of solution of sodium hydrogencarbonate, $NaHCO_3$, is +18.7 kJ mol^{-1}.

Calculate the temperature change when 11.2 g of sodium hydrogencarbonate (M_r = 84.0) is fully dissolved in 100 cm^3 of water. [2]

(iv) Given that the dissolution of sodium hydrogencarbonate is spontaneous at 298 K, state the sign of $\Delta S^\ominus$ for this reaction. Explain your reasoning without reference to any calculation. [1]

(v) Suggest whether hydrogencarbonate ion or hydroxide ion would have the more exothermic standard enthalpy change of hydration. Explain your answer. [1]

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(b) **(i)** Write an expression for the solubility product, K_{sp}, of copper(II) carbonate, stating its units. [1]

Equal volumes of 0.1 mol dm^{-3} lead(II) nitrate and 0.2 mol dm^{-3} copper(II) nitrate are mixed in a beaker.

Table 2.2 shows the numerical values of the solubility products, K_{sp}, of lead(II) carbonate and copper(II) carbonate at 298 K.

Table 2.2

substance	numerical value of K_{sp}
lead(II) carbonate	7.40×10^{-14}
copper(II) carbonate	1.40×10^{-10}

Solid sodium carbonate is gradually added into the beaker until the first precipitate is seen.

(ii) With relevant calculations, show that lead(II) carbonate is the first precipitate to form. [2]

(iii) Describe and explain what you would see when NH_3(aq) is added slowly to a solution containing Cu^{2+}(aq) ions, until NH_3(aq) is in excess.

Write equations for any reactions that occur. [4]

(c) The continual increase in carbon dioxide emission has caused changes to marine ecosystems in the ocean.

Carbonic acid is formed when carbon dioxide is dissolved in water. The carbonic acid formed can further dissociate to give hydrogencarbonate ions and carbonate ions.

The mole fractions of H_2CO_3, HCO_3^- and CO_3^{2-} are dependent on the pH of the solution, as shown in Fig. 2.1.

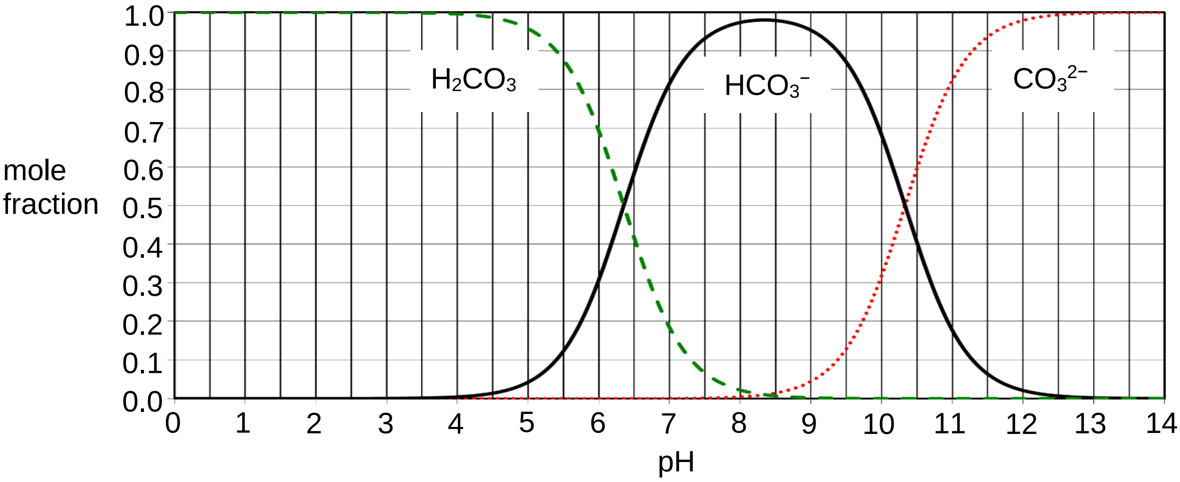

Fig. 2.1

(i) A sample of water was analysed and the mole fraction of carbonate ion, CO_3^{2-}, was determined to be 0.05.

Use Fig. 2.1 to estimate the concentration of hydrogen ions present in the sample. [1]

(ii) On Fig. 2.1, indicate with an ‘x’, the pK_a of HCO_3^-. Draw a construction line to show how you obtained your answer. [1]

(iii) The composition of the shells of crustaceans is mainly made up of calcium carbonate.

Using the information in **(c)**, suggest why it is increasingly difficult for crustaceans to build their shells as the emission of carbon dioxide increases. [2]

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3 **(a)** Explain why 2-chloropropanoic acid is more acidic than 2-iodopropanoic acid. [2]

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(b) Compound **R** can be synthesised from cyclohexanol in three steps as shown in Fig. 3.1.

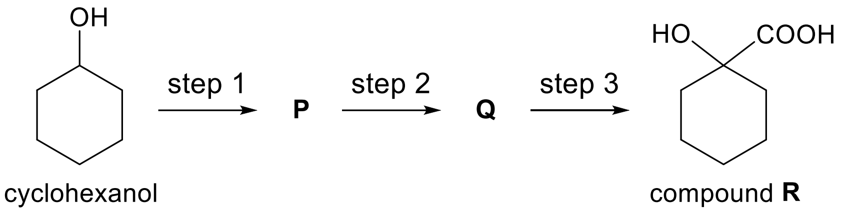

Fig. 3.1

(i) Suggest structures for the organic compounds **P** and **Q.** [2]

(ii) Suggest reagents and conditions for each of the steps 1, 2 and 3. [3]

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(c) Compound **S**, $C_8H_{12}O_4$, is a neutral, sweet-smelling oil. It does not give any orange precipitate with 2,4-DNPH.

Samples of compound **S** are reacted separately with

- cold alkaline $KMnO_4$ forming an organic compound **T**, $C_8H_{14}O_6$
- hot acidic $KMnO_4$ forming **U**, $C_2H_4O_2$, as the only organic product
- hot aqueous KOH forming organic compound **V**, C_2H_6O, and salt **W**, $C_4O_4H_2K_2$.

Compound **V** gives a yellow precipitate with alkaline aqueous iodine.

Suggest possible structures for **S**, **T**, **U**, **V** and **W**. [5]

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(d) The cycloaddition of azides, R−N_3, to alkynes, compounds with a C≡C group, requires prolonged heating to form triazole. The mechanism of this cycloaddition reaction is shown in Fig. 3.2.

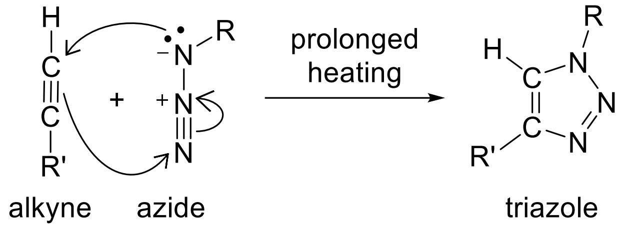

Fig. 3.2

Suggest why the alkyne requires prolonged heating to react with an azide which is a nucleophilic reagent. [1]

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(e) Unlike straight-chain alkynes, cyclooctynes undergo cycloaddition with azides under mild conditions. This is useful in applications involving the tagging of living cells with fluorescent molecules as shown in Fig. 3.3.

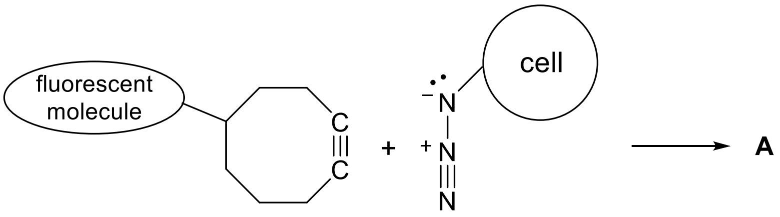

Fig. 3.3

(i) Suggest the structure of product **A**. [1]

(ii) Suggest a reason why cycloaddition can take place under mild conditions when cyclooctyne is used. [1]

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(f) Cu(I) complexes were discovered to catalyse the cycloaddition reaction in Fig. 3.2, leading to the 2022 Nobel Prize for Chemistry.

Some steps of the copper-catalysed cycloaddition are shown in Fig. 3.4, where [Cu] represents a Cu-complex.

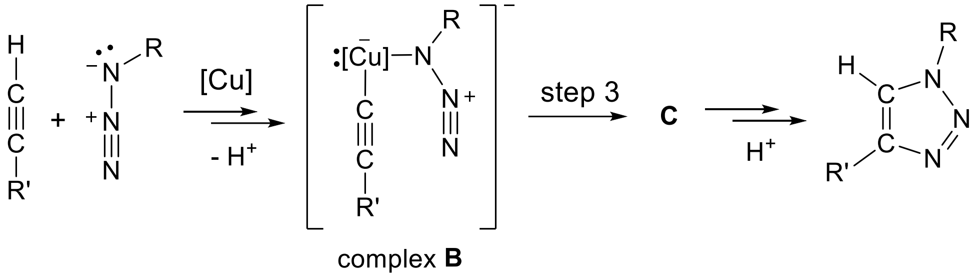

Fig. 3.4

(i) The alkyne and azide are coordinated to Cu in complex **B**.

Explain why in complex **B**,

① the azide becomes a stronger electrophile;
② the alkyne is more susceptible to electrophilic attack. [2]

(ii) In step 3, the formation of compound **C** from complex **B** takes place in a single step.

- An electron pair moves from Cu to form a Cu−C π bond.
- An electron pair moves from the alkyne C≡C to the azide to form a new C−N bond.
- A strained 6-membered ring is formed.

On Fig. 3.4, draw three curly arrows on complex **B** to show the mechanism of step 3. [2]

(iii) Suggest the structure of compound **C**. [1]

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Section B

Answer **one** question from this section.

4 **(a)** Explain why an aqueous solution of Cu^{2+} ions is coloured while an aqueous solution of Zn^{2+} ions is colourless. [4]

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(b) Bromine is a stronger oxidising agent than iodine.

Suggest a simple chemical reaction that can be carried out to support this statement. Write relevant equations for the reactions that occur. [3]

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(c) Fig. 4.1 shows a voltaic cell made up of Cu^{2+} / Cu and VO_2^+ / VO^{2+} half-cells.

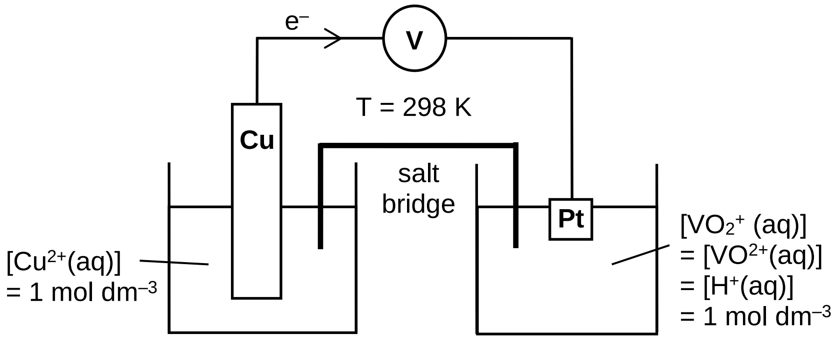

Fig. 4.1

(i) Define the term standard cell potential, $E^\ominus_{cell}$. [1]

(ii) Write the overall equation and calculate $\Delta G^\ominus$ for this voltaic cell. [2]

(iii) Use of the *Data Booklet* is relevant to this question.

Suggest the effect on E_{cell} if the following changes are imposed:

① Solid sodium carbonate is added to the Cu^{2+} / Cu half-cell.
② Water is added to the VO_2^+ / VO^{2+} half-cell. [4]

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Redox flow batteries are rechargeable devices which are used for energy storage and the electrolytes are pumped through an electrochemical cell to transform chemical energy into electrical energy.

The zinc-bromine flow battery (ZBFB) is a widely used redox flow battery where the electrolyte containing aqueous zinc bromide is continuously pumped through.

Fig. 4.2 shows the schematic diagram of a ZBFB.

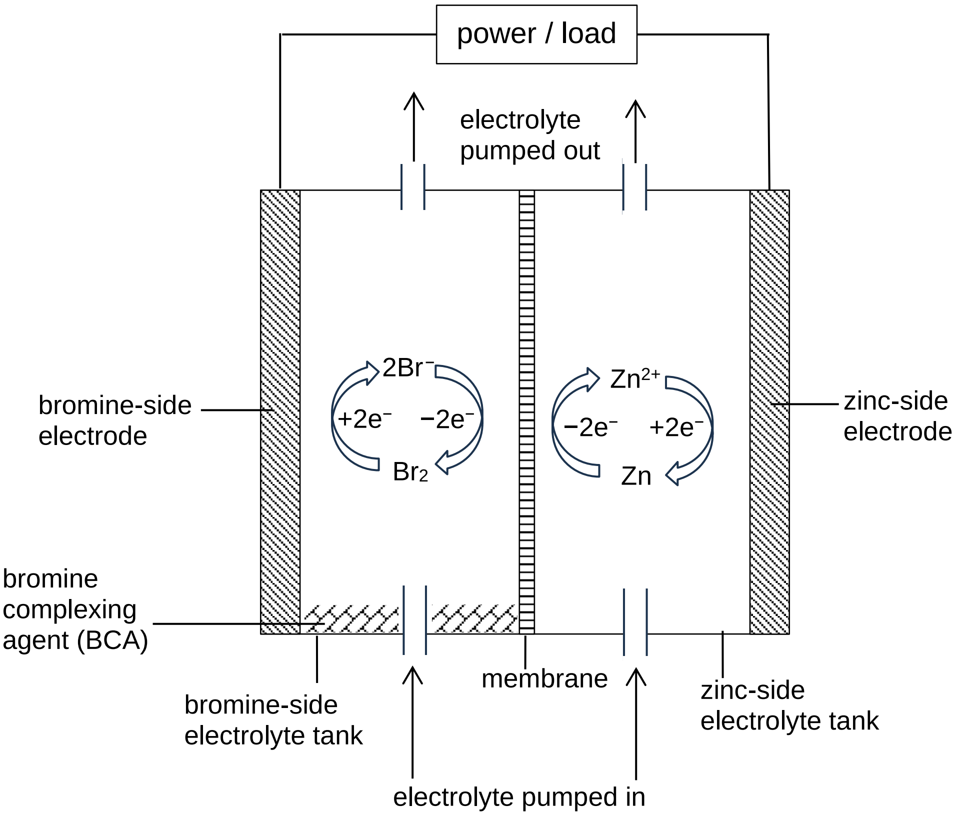

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Fig. 4.2

(d) The membrane serves to keep the two electrolytes separate. Explain why the membrane needs to allow selected ions to flow through. [1]

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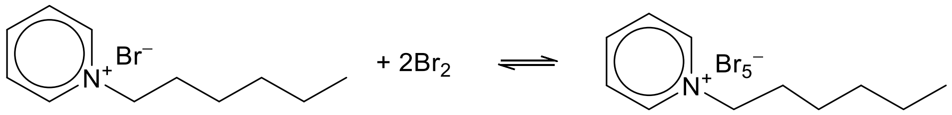
(e) During the charging process, bromine is produced at the positive electrode.

A bromine complexing agent (BCA) is added to the bromine-side electrolyte tank.

BCA reacts with bromine as shown in the following equation.



BCA

complex **A**

(i) Suggest why it is necessary to add BCA to the bromine-side electrolyte tank. [1]

(ii) Explain why complex **A** is immiscible with the aqueous electrolyte. [2]

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(f) During the charging process, zinc is deposited on the negative electrode.

Calculate the time, in hours, needed to deposit 1.00 kg of zinc on the electrode given that the charging current is 32.0 A and the charging process has an efficiency of 80.0%. [2]

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5 This question is about nickel and its complexes.

(a) Briefly explain why the electrical conductivity of Ni is higher than that of s-block elements. [1]

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(b) Nickel is widely used as a heterogenous catalyst in the reduction of alkenes.

(i) State the feature of Ni that allows it to act as a heterogenous catalyst. [1]

(ii) Explain clearly how Ni increases the rate of the reaction. [3]

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(c) Nickel forms many complexes. Fig. 5.1 shows a sequence of reactions involving nickel. Compound **B** contains Ni^{2+} with a co-ordination number of 6.

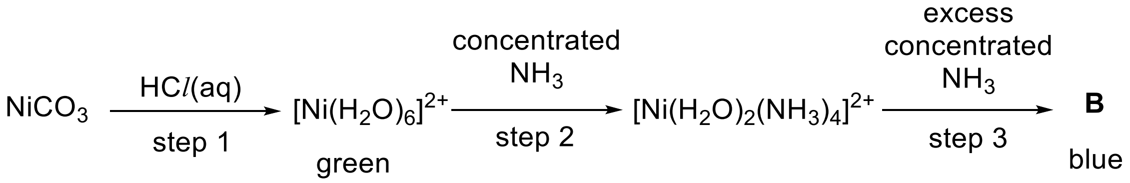

Fig. 5.1

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

(ii) $NiCO_3$ undergoes thermal decomposition to give similar products as Group 2 carbonates. Describe and explain the trend in the thermal stabilities of Group 2 carbonates. [3]

(iii) Draw and label the 3-dimensional structures of the stereoisomers of $[Ni(H_2O)_2(NH_3)_4]^{2+}$. [2]

(iv) Suggest why NH_3 must be added in excess in step 3 and identify **B**. [1]

(v) Explain why $[Ni(H_2O)_6]^{2+}$ and **B** are coloured, with **B** having a different colour from $[Ni(H_2O)_6]^{2+}$. [4]

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(d) Nickel forms many complexes with a co–ordination number of 4 and 6 which exist in either tetrahedral, square planar or octahedral geometry. Fig. 5.2 shows the relative energy levels of d–orbitals in octahedral and square planar geometry.

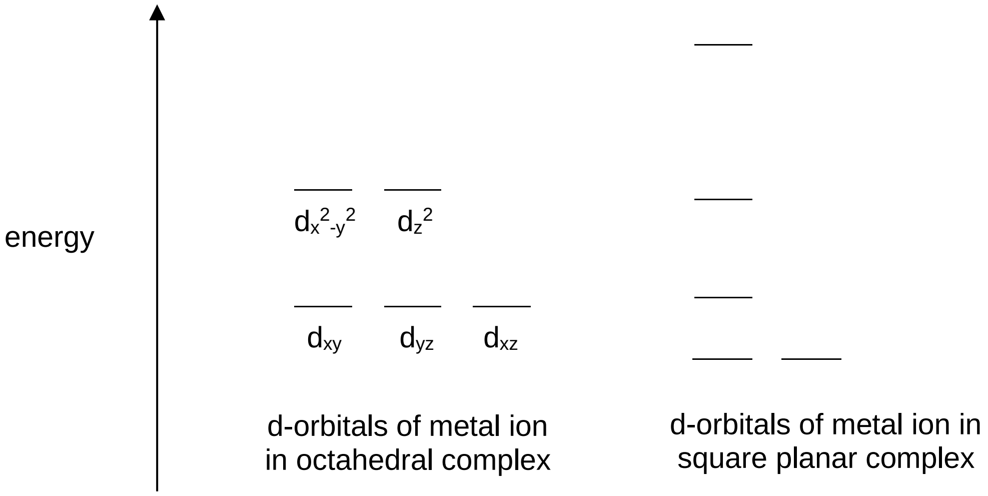

Fig. 5.2

(i) Write the electronic configuration of Ni^{2+} ion. [1]

(ii) With reference to Fig. 5.2, explain the relative energy levels of the d-orbitals in an octahedral complex. [2]

(iii) By considering your answer in **(d)(ii)**, state which 3d-orbital has the highest energy level in a square planar complex. [1]

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