ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

CLASS

2	**1**	**S**		

CHEMISTRY 9729/03

Paper 3 Free Response **14 September 2022**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.

Write in dark blue or black pen.

You may use a 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.

For Examiner’s Use		
Q1		**21**
Q2		**19**
Q3		**20**
Q4 or Q5		**20**
Total		**80**

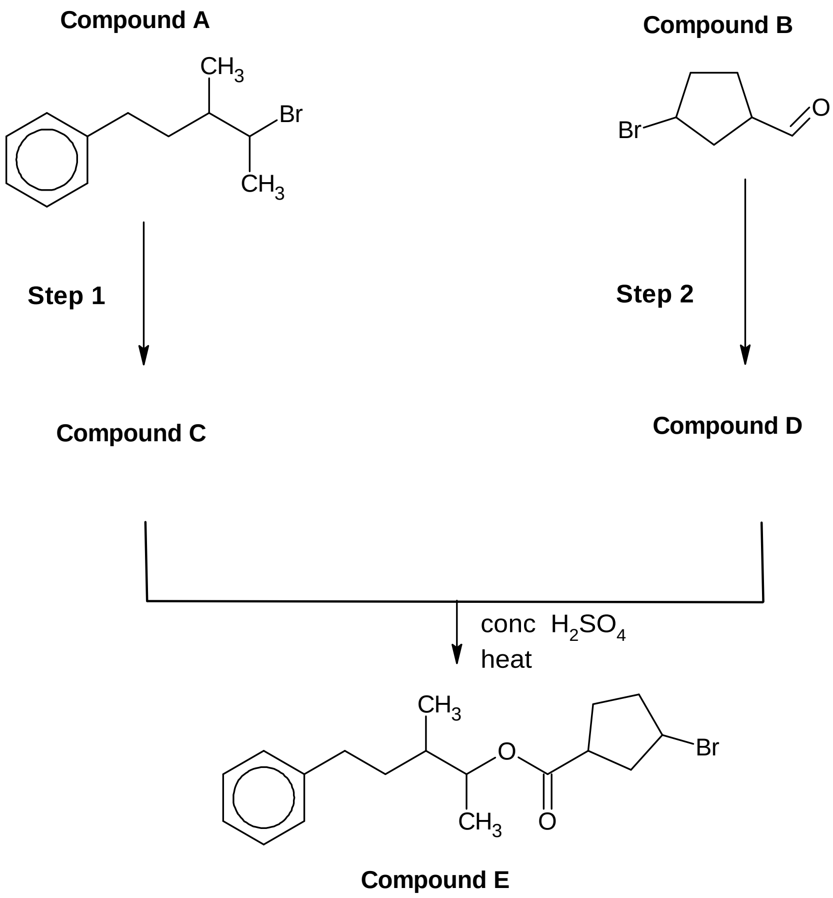
This document consists of **26** printed pages (including this cover page).

[TURN OVER

Section A

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

1 (a) The diagram below shows how compound **E** may be prepared.



(i) Draw the structural formulae for **C** and **D**. **[2]**

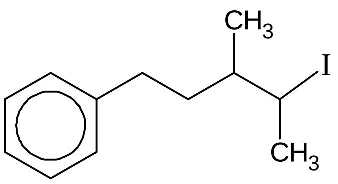
(ii) Suggest the reagents and conditions for steps **1** and **2**. **[2]**

(iii) Draw the structures of the products formed when **E** is reacted with hot aqueous sodium hydroxide. **[2]**

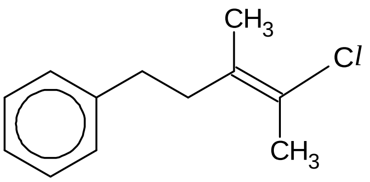
(iv) State the type of reaction when **C** and **D** react to form **E**. **[1]**

(v) Equal amounts of **A**, **F** and **G** are added separately to three test-tubes, which each contains equal concentration of ethanolic silver nitrate. The test-tubes are placed in a hot water bath. No precipitate is formed in one of the test-tubes. For the other two test-tubes, precipitates are formed at different rates.

Explain these observations.



Compound F



Compound G

[3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(b) Copper is an important metal which can be used to catalyse many organic reactions. It exists naturally as an ore containing calcium and silver impurities. To obtain copper metal, the ore is purified using electrolysis.

(i) Draw a labelled diagram for the purification set-up. **[2]**

(ii) With reference to relevant data from the *Data Booklet*, explain what happens to the calcium and silver impurities during the purification. **[3]**

(iii) A current was passed through the set up in **(b)(i)** for 50 minutes and the electrodes were then removed, washed, dried and weighed. It was found that the cathode had gained 0.95 g in mass.
Calculate the current passing through the cell. **[2]**

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(c) Calcium phosphate, $Ca_3(PO_4)_2$, is used as a supplement for people who either do not get enough calcium from their diet or those who suffer from medical conditions like osteoporosis.

(i) With the aid of relevant data from the *Data Booklet*, deduce whether copper(II) phosphate or calcium phosphate will decompose at a lower temperature. Explain your answer. **[2]**

(ii) 50 cm^3 of 0.05 mol dm^{-3} sodium phosphate solution is mixed with 30 cm^3 of 0.05 mol dm^{-3} calcium nitrate solution.

Determine whether calcium phosphate precipitate is formed.

(K_{sp} of calcium phosphate = 2.07×10^{-33} $mol^5\,dm^{-15}$) **[2]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[Total: 21]

2 Chloric acid, $HClO$ is both a strong acid and an oxidising agent. It is corrosive and will accelerate the burning of combustible materials.

(a) When reacted with excess aqueous potassium hydroxide, $HClO$ is converted into water and two chloro-containing products, one of which is a chloro-oxo anion.

In an experiment, 0.5 mol of chloro-oxo anion was reacted with excess potassium iodide to form a brown solution and chloride ion. It was discovered that the brown solution required 3 moles of sodium thiosulfate for complete reaction.

(i) Calculate the number of moles of electrons gained by 1 mole of chloro-oxo anion in the reaction with potassium iodide. Hence, prove that the chloro-oxo anion is ClO_3^-. **[3]**

(ii) The other chloro-containing product formed a white precipitate with silver nitrate solution.
Identify this other chloro-containing product. Write an equation for the reaction between chloric acid and excess potassium hydroxide. **[2]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

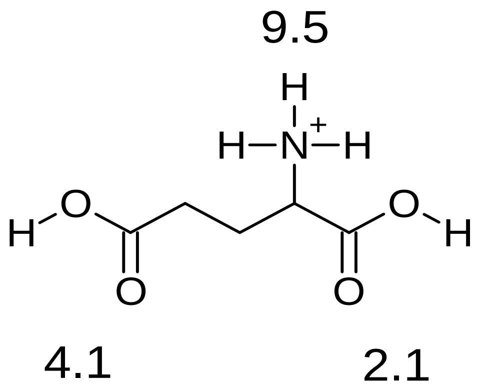
An experiment was carried out to determine the enthalpy change of neutralisation of chloric acid. 25 cm^3 of 1 mol dm^{-3} chloric acid was mixed with 25 cm^3 of 1.5 mol dm^{-3} potassium hydroxide and there was an increase in temperature by 8 ºC.

(i) Explain the term *standard enthalpy change of neutralisation*. **[1]**

(ii) Calculate the enthalpy change of neutralisation. Assume that the specific heat capacity of all solutions is the same as that of water. **[2]**

(iii) The enthalpy change of neutralisation between a strong acid and a strong base is -57.3 kJ mol^{-1}. Suggest a reason for the difference between this value and your answer in **b(ii)**. **[1]**

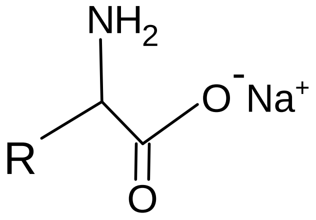
(c) Glutamic acid is often used as a food additive and a flavour enhancer. The structure of a fully protonated glutamic acid is as shown, with the pK_a values (2.1, 4.1 and 9.5) assigned.



(i) Explain the assignment of pK_a values to the respective acidic groups. **[3]**

(ii) Suggest the structural formulae of the major species present in solutions of glutamic acid with the pH values of 3.0, 6.0, and 10.0. **[3]**

(iii) The structure of compound **H** is as shown.



H has 2 pK_b values.

- pK_{b1} = 4.5
- pK_{b2} = 11.9

Calculate the pH of a 0.50 mol dm^{-3} solution of **H**. Ignore the effect of pK_{b2} on pH. **[1]**

(iv) Sketch the pH-volume curve that you would expect to obtain when 25 cm^3 of 0.50 mol dm^{-3} compound **H** is titrated with 60 cm^3 of 0.50 mol dm^{-3} chloric acid. Briefly describe how you have calculated the various key points on the curve. **[3]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[TURN OVER

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

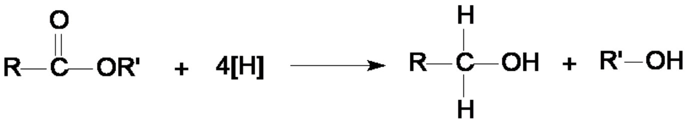
....

....

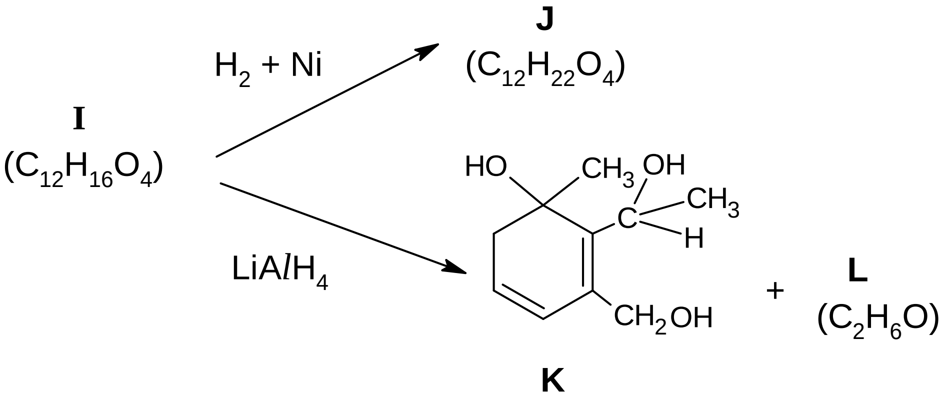
[Total: 19]

[TURN OVER

3 **(a)** LiA*l*H_4 and H_2 are useful reducing agents in organic chemistry. Esters are reduced by LiA*l*H_4 and the equation is as shown.



Compound **I** contains an ester functional group and undergoes the following reactions with LiA*l*H_4 and H_2.



(i) Compounds **I**, **J**, **K** and **L** react with Na, as well as with alkaline aqueous iodine. Suggest the structures for **I**, **J** and **L.** **[3]**

(ii) Sodium boron hydride, $NaBH_4$, is used in the reduction of compound **M** to form compound **K**. Given that **M** reacts with 2,4-DNPH but not Fehling's solution, suggest the structure for **M**. **[1]**

....

....

....

....

....

....

....

....

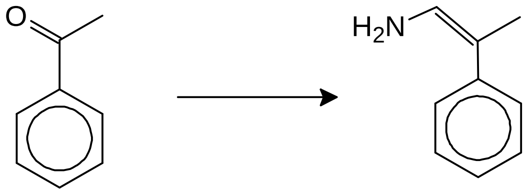
(b) Both $NaBH_4$ and $LiAlH_4$ produce the hydride ion, H^-, as the reacting species during reduction.

(i) Explain why $LiAlH_4$ is a stronger reducing agent than $NaBH_4$. **[1]**

(ii) When $NaBH_4$ is added to propanal and propanone separately, it was found that propanal reacts faster than propanone.

Suggest two reasons for this observation. **[2]**

(iii) $LiAlH_4$ is used in the following synthesis.



Suggest a 3-stage synthesis for the above conversion. You should state the reagents and conditions needed for each step and show clearly the structures of any intermediate compounds. **[4]**

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

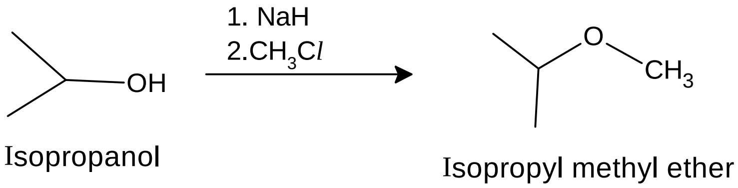
………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

(c) Sodium hydride is a strong base commonly used in the Williamson Ether Synthesis. An example is the synthesis of isopropyl methyl ether from isopropanol.



The mechanism is as follows:

Step 1: Hydride ion removes a H^+ from isopropanol to form an alkoxide, $CH(CH_3)_2O^-$ and hydrogen gas.

Step 2: The alkoxide acts attacks the electron deficient carbon atom of chloromethane to form the ether and Cl^-.

(i) Outline the mechanism for **step 2** of the Williamson Ether Synthesis of isopropyl methyl ether. Label the partial charges on the reacting species and use curly arrows to show the flow of electrons during the reaction. **[2]**

(ii) CH_2ClCH_2OH reacts with sodium hydride via the Williamson Ether Synthesis to form an ether with the molecular formula C_2H_4O. Draw the structure of this ether. **[1]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

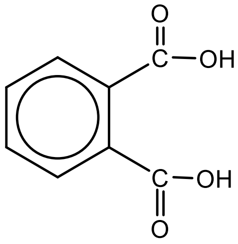
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

(d) Compound **Q**, $C_{11}H_{14}$, exists as a mixture of two stereoisomers but it contains no chiral centre. **Q** decolourises hot acidified potassium manganate(VII) to give **R**, $C_9H_8O_3$, as one of the organic products. **R** reacts with alkaline aqueous iodine to give a yellow precipitate and a soluble salt. Upon acidification, the soluble salt forms aqueous benzene-1,2-dicarboxylic acid as shown.



Q also reacts with cold concentrated sulfuric acid followed by steam to give **S**, $C_{11}H_{16}O$. **S** is able to rotate plane-polarised light but does not react with aqueous alkaline iodine.

Deduce the structures of **Q**, **R** and **S**, explaining the reactions described. **[6]**

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

[TURN OVER

Section B

Answer **one** question from this section.

4 Nitrogen is a critical nutrient for the survival of all living organisms, as it is a necessary component of many biomolecules, such as proteins. Although nitrogen is very abundant in the atmosphere, it needs to be converted into ammonia for it to be available to primary producers, such as plants. This process is called nitrogen fixation. Only a select group of bacteria can carry out this energetically demanding process. The equation for nitrogen fixation is as shown.

$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$$

(a) By using appropriate data from the *Data Booklet*, explain why nitrogen fixation is an energetically demanding process. **[1]**

…………………………………………………………………...……………………………...

…………………………………………………………………...……………………………...

(b) Bacteria that carry out nitrogen fixation have an enzyme called nitrogenase. Nitrogenase contains an iron-sulfur-molybdenum metal cluster, as shown in **Fig. 4.1**. Histidine (His) and cysteine (Cys) are two important amino acids present in the active site of nitrogenase.

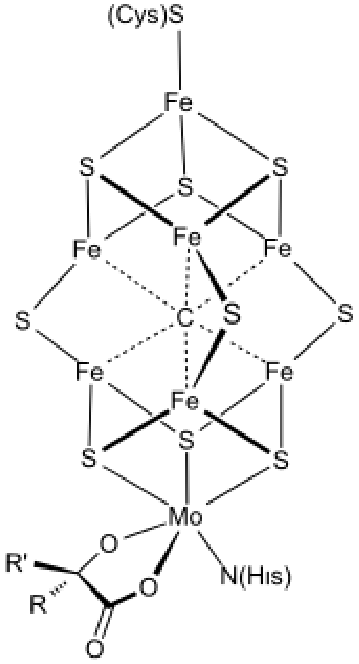
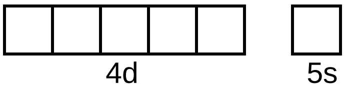


Fig. 4.1

(i) Molybdenium, ^{42}Mo, is in the same group as chromium and has a similar electronic configuration as chromium.

In the diagram below, show how the electrons are arranged in the 4d and 5s orbitals of Mo atom.

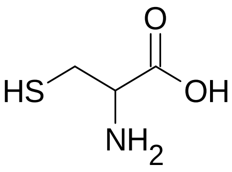


[1]

(ii) Draw a fully labelled diagram of a 4d orbital that lies along both the x and y axis. **[1]**

(iii) State the shape about Mo in **Fig. 4.1**. **[1]**

(iv) The structure of cysteine (Cys) amino acid is given below.



Cys

Draw the stereoisomers of Cys. **[1]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

(c) Nitrogenase are deactivated in the presence of oxygen, as oxygen and nitrogen can compete for binding to iron in the active site of the enzyme.

Explain how oxygen is able to interact with nitrogenase in a similar manner as nitrogen. **[1]**

……………………………………………………………………..……………………………...

……………………………………………………………………..……………………………...

(d) Nitrogenase is stable when the temperature is between 20 °C to 40 °C.

The kinetics of nitrogen fixation by nitrogenase was studied at 20 °C. The final concentration of NH_3 formed was found to be 0.16 mol dm^{-3}.

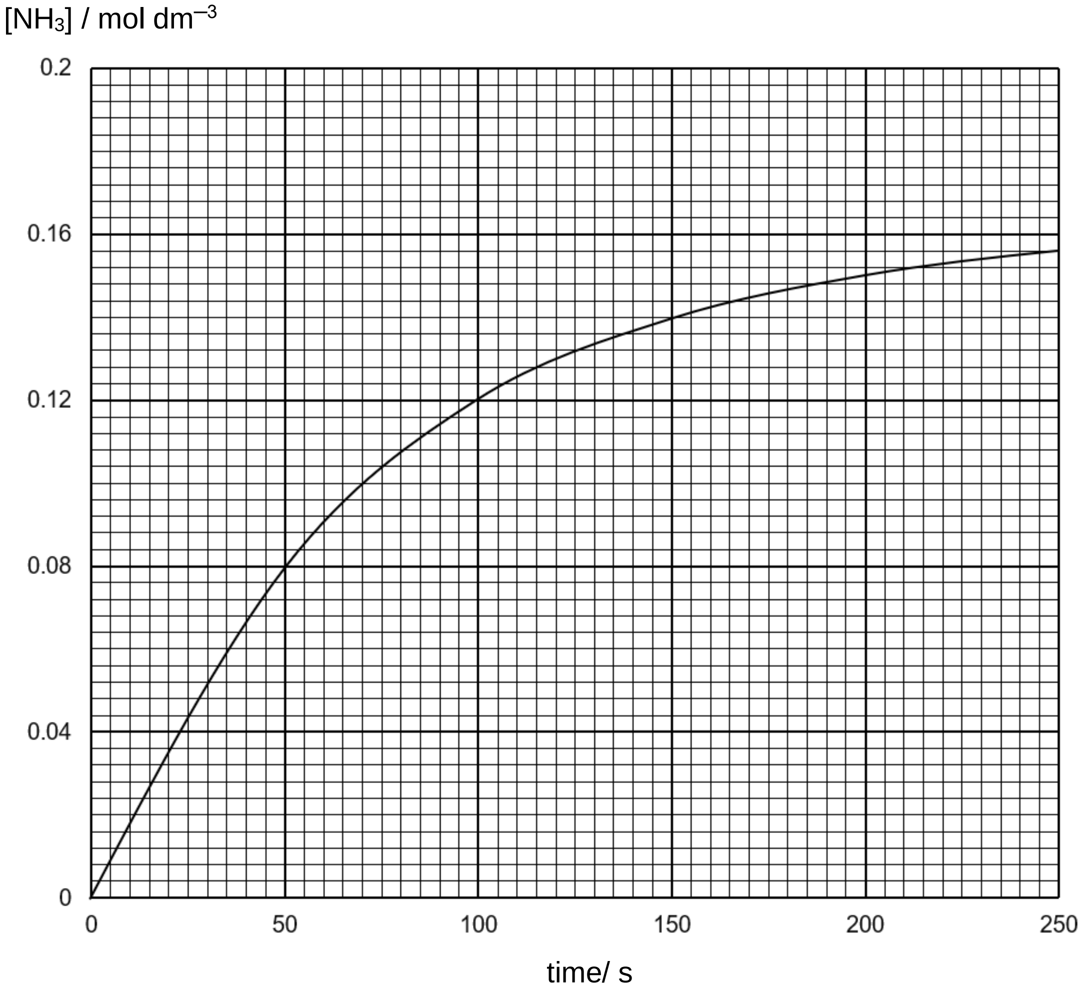


Fig. 4.2

(i) Explain the term *rate of reaction*. **[1]**

(ii) Using **Fig. 4.2**, calculate the initial rate of reaction. **[1]**

(iii) Use **Fig. 4.2** to determine the order of reaction with respect to [N_2]. Hence, sketch a graph of rate against initial [N_2]. **[3]**

(iv) On **Fig. 4.2**, sketch how the graph would look like when the experiment is carried out at 40 °C. Label this new graph as **Y**.
Explain your answer using the Collision Theory. **[3]**

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

(e) Denitrification is an important process because it converts nitrate back into nitrogen gas. A Latimer diagram shows the standard electrode potentials connecting various oxidation states of an element. The sum of the standard electrode potential for each reduction is the same as the standard electrode potential for the overall reduction.

The Latimer diagram for some nitrogen-containing species in acidic medium is as shown below.

$$NO_3^- \xrightarrow[\text{Step 1}]{+0.42\text{V}} NO_2^- \xrightarrow[\text{Step 2}]{+0.34\text{V}} NO \xrightarrow[\text{Step 3}]{+1.18\text{V}} \tfrac{1}{2}N_2O \xrightarrow[\text{Step 4}]{+1.35\text{V}} \tfrac{1}{2}N_2$$

(i) Draw a dot-and-cross diagram of NO_2^-. State the bond angle of the ion. **[2]**

(ii) Explain how the Latimer diagram shows that NO is an intermediate in the denitrification process. **[1]**

(iii) Write a half equation for the reduction of NO_3^- to N_2 in acidic medium. **[1]**

(iv) Use the Latimer diagram to calculate the standard electrode potential for the reduction of NO_3^- to N_2. Hence, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, per mole of N_2 formed. **[2]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[TURN OVER

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

[TURN OVER

5 This question is about the chemistry of titanium and its ions.

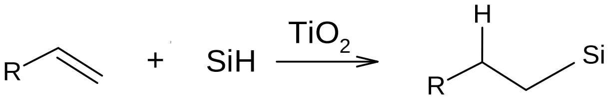
(a) Titanium (II) oxide, TiO, and titanium (IV) dioxide, TiO_2, are common sources of titanium ions with different oxidation states.

compound	melting point / °C
TiO	1750
TiO_2	1843

(i) State the electronic configuration of a Ti^{2+} ion. **[1]**

(ii) Explain, in terms of structure and bonding, the difference in melting point between TiO and TiO_2. **[2]**

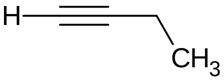
(iii) TiO_2 is a catalyst used in the anti-Markvonikov hydrosilyation of gaseous alkenes with gaseous silane, SiH.



Outline the mode of action of TiO_2 catalyst in this reaction. **[2]**

(iv) Alkynes can react with silane in a similar way as alkenes.

Suggest the alkene formed when the following alkyne undergoes hydrosilyation with TiO_2.



[1]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………..…………………………

……………………………………………………………………..…………………………

……………………………………………………………………..…………………………

……………………………………………………………………..…………………………

……………………………………………………………………..…………………………

……………………………………………………………………..…………………………

(b) The use of renewable energy sources, such as solar energy, has been gaining momentum around the world with the aim of realising a carbon-zero society. However, climate change can affect the power output and therefore, there is a need to use large-scale batteries to store the power harnessed.

One such example is shown in **Fig. 5.1**. The battery uses the redox couple Mn^{2+}/Mn^{3+} in one electrolyte tank and Ti^{3+}/TiO^{2+} in another. Sulfuric acid is the electrolyte in both tanks.

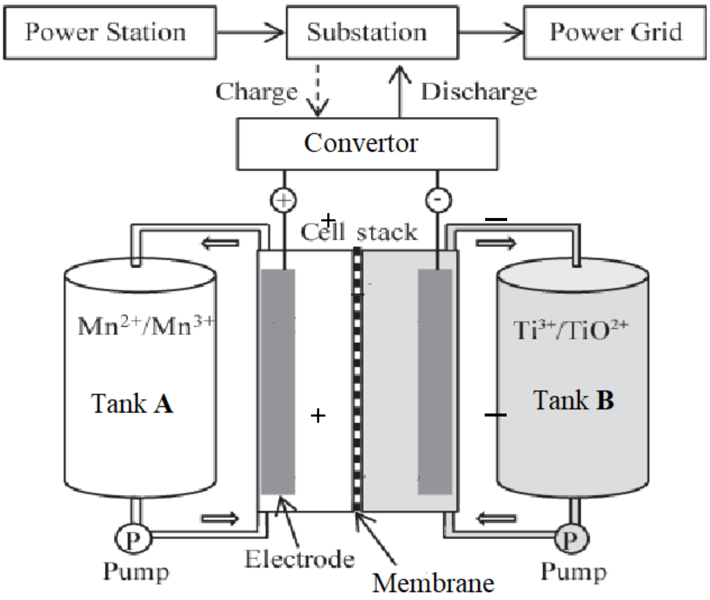


Fig. 5.1

The standard electrode potential for the reduction of TiO^{2+} is as given.

$$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O \qquad E^\ominus = +0.10\text{ V}$$

(i) Write an equation to represent the discharging of this battery. **[1]**

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ when the battery is discharged.

Hence, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, per mole of Mn^{3+} used in the discharging process. **[2]**

(iii) Suggest and explain the effect on E_{cell} if an electrolyte of lower pH was used. **[2]**

(iv) Sulfuric acid, which is a source of H^+, will flow through the exchange membrane as the battery discharges.

Suggest the direction of flow of H^+ through the membrane. Explain your answer. **[2]**

(v) Suggest an advantage of using *porous* carbon electrodes. **[1]**

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

(c) **(i)** With reference to the table below, suggest the colour change in Tank **B** when the battery is charging.

Species	Colour
Ti^{3+} (aq)	violet
TiO^{2+} (aq)	colourless

[1]

(ii) Explain what is meant by the term *transition element*. **[1]**

(iii) Explain why Ti^{3+}(aq) ions are coloured, but TiO^{2+}(aq) ions are not. **[3]**

(iv) Two separate solutions of Ti^{3+} and $\mathrm{A}l^{3+}$ are acidic.

Using relevant data from the *Data Booklet,* predict which solution of equal concentration, Ti^{3+} or $\mathrm{A}l^{3+}$, will give a lower pH. **[1]**

…………………………………………………………………………………………..

…………………………………………………………………………………………

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

[Total: 20]

END OF PAPER

Additional Answer Space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……
..