



ST ANDREW'S JUNIOR COLLEGE
 JC2 PRELIMINARY EXAMINATIONS
 HIGHER 2

CANDIDATE
 NAME

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CLASS

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CHEMISTRY

9729/02

Paper 2 Structured Questions

31 August 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.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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		12
Q2		14
Q3		14
Q4		10
Q5		25
Total		75

This document consists of **24** printed pages (including this cover page).

1 Hydrazine, N_2H_4 , is a colourless liquid with an ammonia-like odour. It is an important precursor in the pharmaceuticals industry.

(a) Hydrazine exists as a liquid while ammonia exists as a gas at room temperature and pressure. State two reasons to explain this difference in physical state. [2]

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(b) The K_b values of hydrazine, ethylamine, and phenylamine are shown in Table 1.1.

Table 1.1

base	$K_b / \text{mol dm}^{-3}$
Hydrazine	1.7×10^{-6} (for K_{b1})
Ethylamine	4.5×10^{-4}
Phenylamine	7.4×10^{-10}

(i) Explain what is meant by the term *Bronsted-Lowry base*. [1]

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(ii) Explain the relative magnitudes of the K_b values in Table 1.1. [2]

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- (iii) The K_b values of diethylamine and triethylamine are shown in **Table 1.2**.

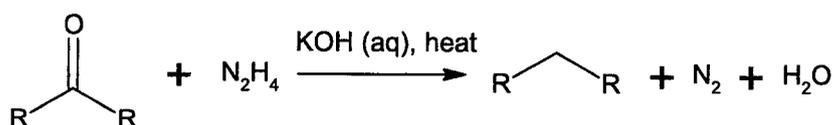
Table 1.2

base	$K_b / \text{mol dm}^{-3}$
Diethylamine	6.9×10^{-4}
Triethylamine	6.5×10^{-5}

Suggest why the K_b value of triethylamine is significantly smaller than the K_b values of ethylamine and diethylamine. [1]

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- (c) The Wolff-Kishner reaction is a valuable synthetic method to convert carbonyl compounds into alkanes. This is done by reacting a carbonyl compound with excess hydrazine in the presence of potassium hydroxide.

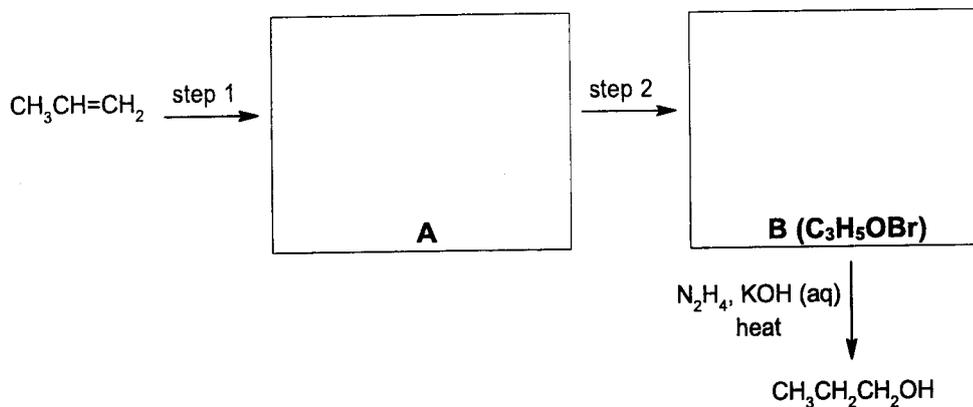


- (i) Suggest a simple chemical test to monitor the completion of the Wolff-Kishner reaction. [2]

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[TURN OVER

- (ii) Propan-1-ol can be synthesised from propene by the following 3-step route that incorporates the Wolff-Kishner reaction.



Suggest the structures of intermediate products **A** and **B** and state the reagents and conditions for each step.

Reagents and conditions

Step 1:

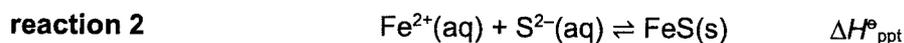
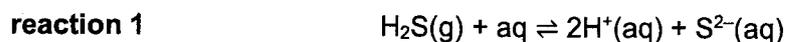
Step 2:

[4]

[Total: 12]

[TURN OVER

- 2 Organic matter is known to decay under low oxygen conditions, such as in swamps. The sulfate-reducing bacteria present in the organic matter will reduce the various sulfates into hydrogen sulfide, H_2S . Some of the hydrogen sulfide will react with Fe^{2+} present in swamp to produce insoluble FeS , which is responsible for the brown colour of sludge in the swamp.



- (a) (i) In a saturated solution of hydrogen sulfide, $[\text{H}^+]^2[\text{S}^{2-}]$ is $1.0 \times 10^{-23} \text{ mol}^3 \text{ dm}^{-9}$. Calculate the maximum concentration of sulfide ions present in the swamp, given that the pH of swamp water is 6.8. [1]

- (ii) Hence, calculate the minimum concentration of Fe^{2+} in the swamp required for the precipitation of FeS .
(K_{sp} of $\text{FeS} = 4.9 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$) [1]

[TURN OVER

- (iii) $\Delta G^\circ_{\text{ppt}}$, can be determined by using the following expression, where R is the molar gas constant and T is the temperature measured in K.

$$\Delta G^\circ_{\text{ppt}} = 2.303RT \lg K_{\text{sp}}$$

Using the K_{sp} in (a)(ii), calculate $\Delta G^\circ_{\text{ppt}}$ for the precipitation of FeS. Express your answer in kJ mol^{-1} . [2]

- (iv) Predict how the brown colour intensity of sludge will change when pH decreases. Explain your answer. [2]

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[TURN OVER

- (b) Using data from **Table 2** below, together with relevant data from the *Data Booklet*, draw an energy cycle and calculate $\Delta H^\ominus_{\text{ppt}}$ for **reaction 2**.

Table 2

standard enthalpy change of formation of FeS(s)	-102 kJ mol ⁻¹
standard enthalpy change of atomisation of Fe(s)	+415 kJ mol ⁻¹
standard enthalpy change of atomisation of S(s)	+279 kJ mol ⁻¹
sum of first and second electron affinity of sulfur	+337 kJ mol ⁻¹
standard enthalpy change of hydration of Fe ²⁺ (g)	-1970 kJ mol ⁻¹
standard enthalpy change of hydration of S ²⁻ (g)	-1372 kJ mol ⁻¹

[4]**[TURN OVER**

(c) (i) Use your answers in (a)(iii) and (b), calculate the $\Delta S_{\text{ppt}}^\circ$ for the formation of FeS precipitate. [1]

(ii) Hence, explain the significance of the sign of $\Delta S_{\text{ppt}}^\circ$ in (c)(i). [1]

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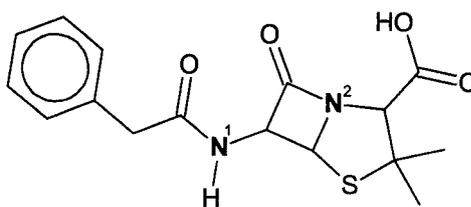
(d) Although hydrogen sulfide and water molecules have the same shape, they have slightly different bond angles. State and explain which species has a larger bond angle. [2]

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[Total: 14]

[TURN OVER

- 3 Ionisable drugs have acidic, basic or amphoteric properties. An example of an acidic drug is benzylpenicillin G, which is an antibiotic used to treat certain bacterial infection.



benzylpenicillin G

- (a) Both nitrogen atoms in benzylpenicillin G are sp^2 hybridised.

(i) Draw the shape of the hybrid orbitals around N^1 .

[1]

(ii) Suggest why sp^2 hybridisation at N^1 and N^2 will make benzylpenicillin G more stable.

[1]

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(iii) Suggest a reason why $C-N^2$ bond is weaker than $C-N^1$ bond.

[1]

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(b) The solubility of three different ionisable drugs is shown in Fig. 3.1.

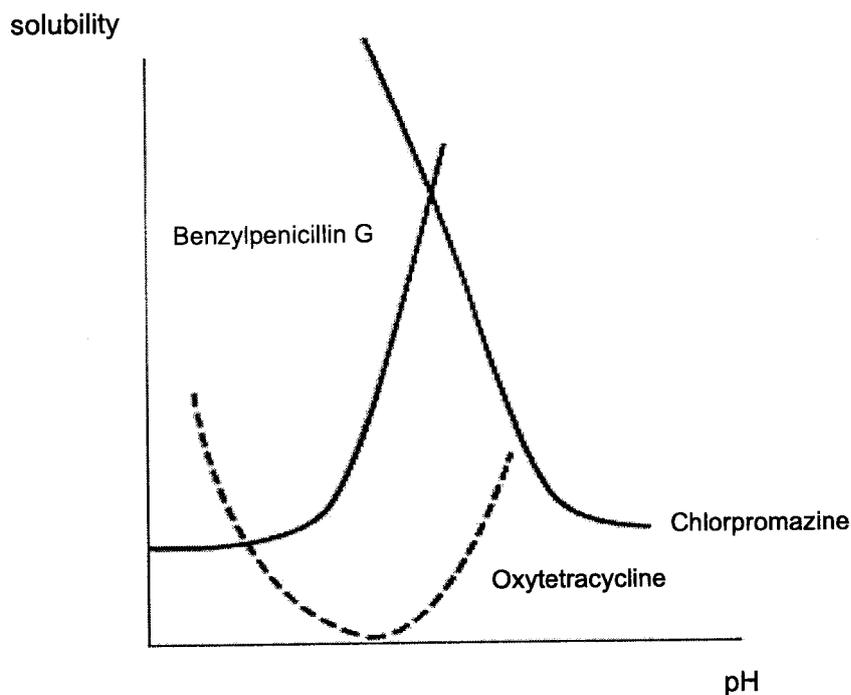


Fig. 3.1

(i) Explain why the solubility of benzylpenicillin G in aqueous increases from low to high pH. [2]

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(ii) Classify the following compounds according to the type of ionisable drug (acidic, basic and amphoteric). [1]

A) Chlorpromazine:

B) Oxytetracycline:

[TURN OVER

- (iii) The pH of blood containing benzylpenicillin G is 7.4.
Given that the pK_a of benzylpenicillin G is 2.76, calculate the concentration of the undissociated benzylpenicillin G. [2]

- (iv) The Henderson-Hasselbalch equation can be re-expressed to relate the solubility of a drug to the pH of the solution and its pK_a .

$$pH = pK_a + \log_{10} \left(\frac{S - S_0}{S_0} \right)$$

where S is the concentration of the dissolved drug and S_0 is the concentration of the undissociated drug.

The solubility of the undissociated benzylpenicillin G in blood with pH 7.4 is $9 \times 10^{-13} \text{ mol dm}^{-3}$. Using the information above and in (b)(iii), calculate the solubility of benzylpenicillin G in blood with pH 7.4. Express your answer in mol dm^{-3} . [2]

[TURN OVER

- (c) Benzylpenicillin G is administered intravenously as potassium benzylpenicillin G, which is an ionic compound.

The drug is prepared in a buffer solution made of citric acid, $C_5H_7O_5COOH$ and potassium citrate, $C_5H_7O_5COOK$ to maintain its solubility and stability.

- (i) Define the term *buffer*. [1]

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- (ii) Write an equation to show how the citric acid/citrate buffer maintains the pH of the solution when small amounts of alkali are added. [1]

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- (iii) Explain the difference between the ionic radius and atomic radius of potassium. [2]

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- 4 Compound X has the molecular formula $C_8H_8O_2$. It contains 2 different functional groups. Data about the reactions of X are given in the table below.

reaction	reagent	observations
1	alkaline aqueous iodine	yellow ppt
2	$Cr_2O_7^{2-}/H^+$, heat	orange solution
3	$Br_2(aq)$	white solid Y with $M_r = 293.8$

- (a) (i) Based on reaction 1 only, state all the deductions about X. [1]

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- (ii) Which deduction in (a)(i) is confirmed by reaction 2? Explain your answer. [2]

.....

- (iii) Based on your answer in (a)(ii), construct an equation to represent reaction 1. You may use R to represent part of compound X which does not react with alkaline aqueous iodine. [1]

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- (iv) State the type of reaction taking place in reaction 3. [1]

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[TURN OVER

- (v) Deduce the molecular formula of **Y**. State the identity of the other functional group found in **X** based on reaction 3. [3]

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- (b) Based on your answers in (a), draw the structural formulae of the 2 possible isomers of **X**. [2]

[Total: 10]

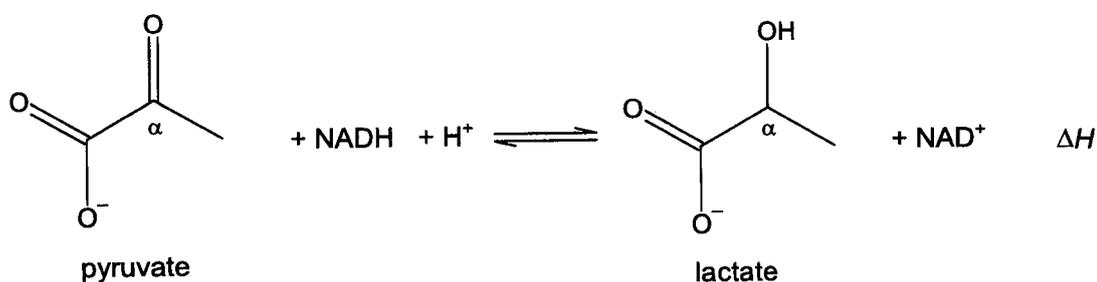
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- (ii) A normal person loses an average of 3.5 dm³ of sweat for every hour of exercise. Using the data in **Table 5.1**, calculate the mass of lactate lost in sweat after two hours of intense exercise. [2]

- (iii) 10 cm³ of blood was drawn from an individual and the mass of lactate was found to be 0.0027 g.

Determine the medical condition of this individual. [1]

The reduction of pyruvate to lactate involves a compound known as reduced nicotinamide adenine dinucleotide (NADH). The reduction is an equilibrium where all species are in aqueous state.



K_c value for this equilibrium at 298 K is 1.46×10^{11} .

- (b) (i) State the change in oxidation number for carbon α . [1]

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[TURN OVER

- (ii) During an intense exercise, the pH of blood decreases from 7.4 to 7.1. Assuming that $[\text{NADH}]$ is equal to $[\text{NAD}^*]$, calculate the $[\text{lactate}] / [\text{pyruvate}]$ ratio at pH 7.1. [2]

- (iii) Fig. 5.2 shows the graph of $[\text{lactate}] / [\text{pyruvate}]$ against time. At time t_1 , the temperature of the reaction was increased.

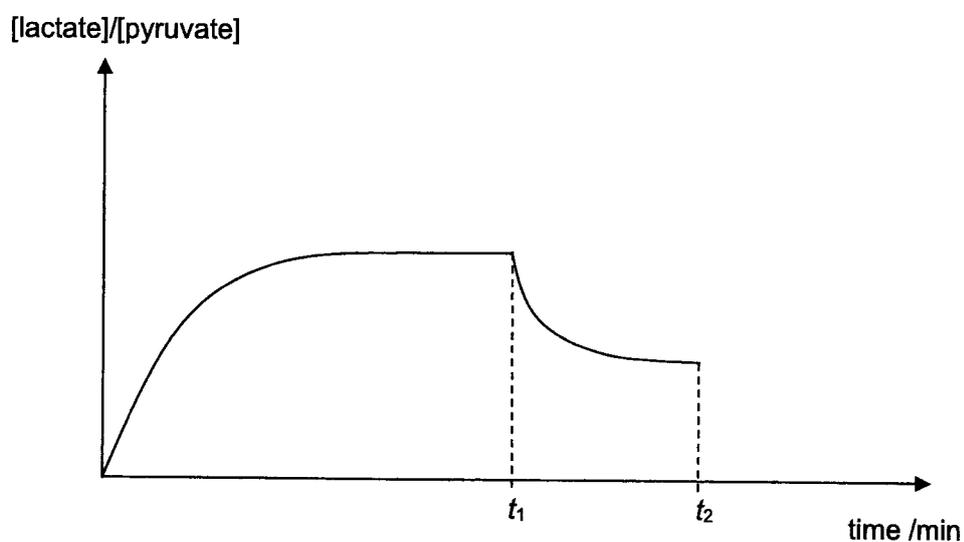


Fig. 5.2

Determine the sign of ΔH for this reaction. Explain your answer. [2]

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- (iv) On Fig. 5.2, complete the diagram to show the effect on $[\text{lactate}] / [\text{pyruvate}]$ when OH^- was added to the reaction mixture at time t_2 . [1]

[TURN OVER

Fig. 5.3 shows the reduction of pyruvate. This reaction happens in the following manner.

- The lone pair of electrons on N of NADH delocalises into a nearby alkene. This causes the π bond to be broken but a new one is subsequently formed.
- A C–H bond of NADH breaks and the two electrons form a σ bond with carbonyl carbon of pyruvate.
- The π bond of C=O breaks and a σ bond is formed with H^+ as shown.

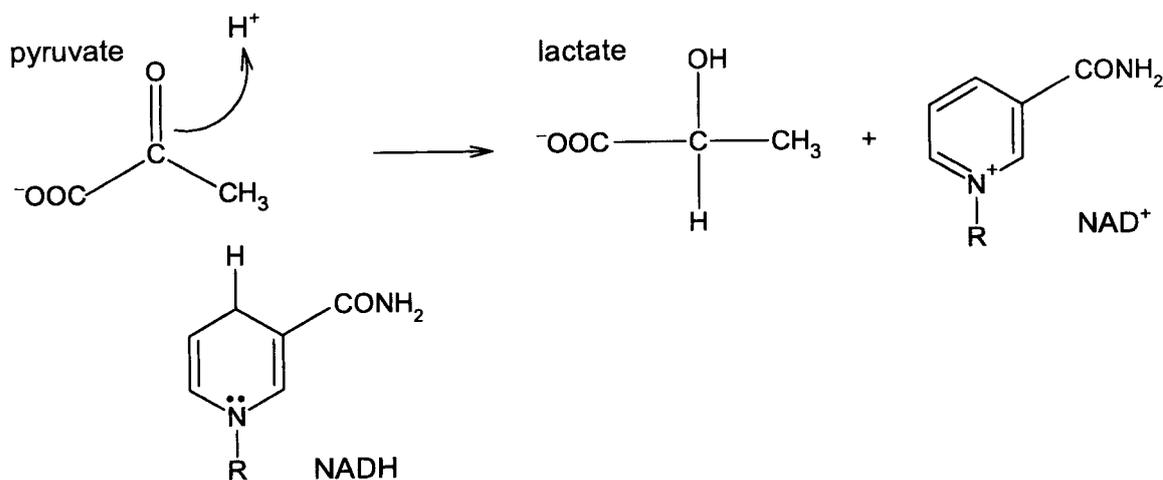


Fig. 5.3

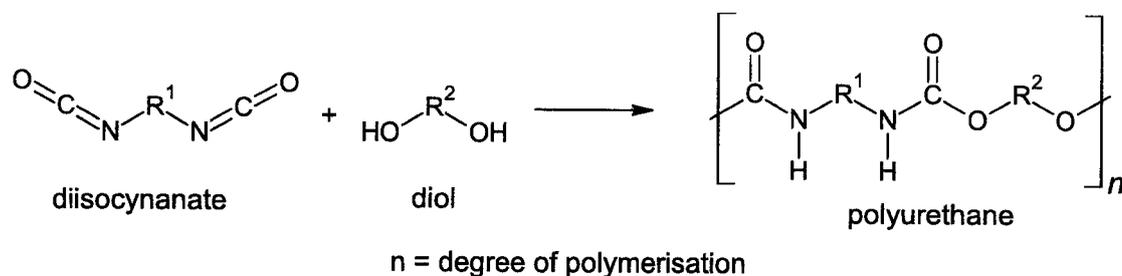
- (v) On **Fig. 5.3**, draw curly arrows to show the movement of electron pairs when NADH reduces pyruvate into lactate. [2]

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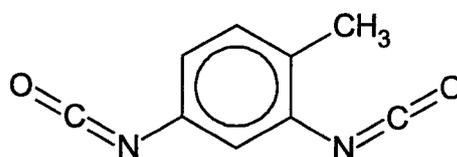
- (c) Polyurethane is a polymer used to make the straps of fitness bands and smartwatches as they have good resistance towards salt water and ultra-violet radiation. Hence, unlike cheaper plastic or resin straps, polyurethane straps are more suited for a wide range of sporting activities.

The reaction between diisocyanate and diol to form polyurethane is shown in **Equation 1**.

Equation 1



(i)



toluene diisocyanate (M_r : 174)

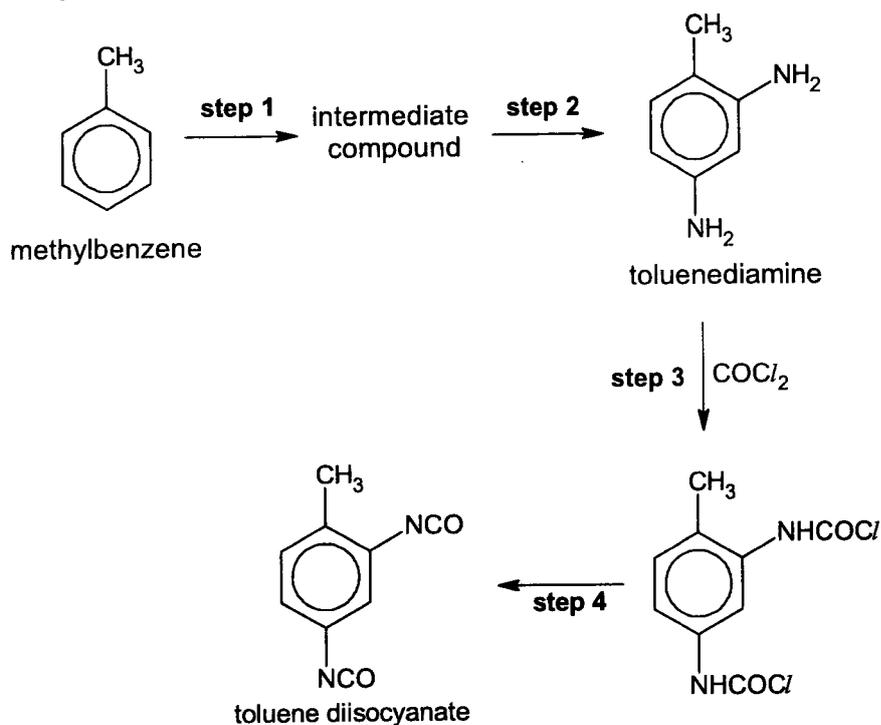
Suggest the structure of the polyurethane polymer formed when toluene diisocyanate is reacted with ethane-1,2-diol.

[1]

- (ii) The average molar mass of the polyurethane polymer formed in (c)(i) is $1.3688 \times 10^4 \text{ g mol}^{-1}$. Calculate the degree of polymerisation, n , for this polymer. [1]

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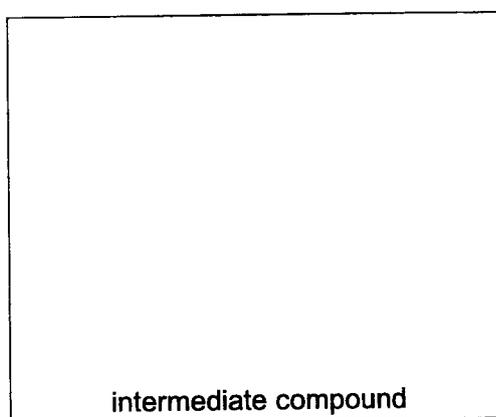
(d) Toluene diisocyanate is synthesised from methylbenzene by the following route.



(i) Complete the reaction scheme to show how toluenediamine could be synthesised from methylbenzene in two steps. Show the structure of the intermediate product and state the reagents and conditions for each step. [3]

Step 1

Step 2



[TURN OVER

- (ii) Suggest the type of reaction in **step 4**. [1]

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- (iii) The reaction between toluenediamine and phosgene gas, COCl_2 , in **step 3** is carried out at a temperature of 500 °C and 400 kPa. Assuming the process is 100% efficient, calculate the volume of phosgene required to produce 1 kg of toluene diisocyanate.

[2]

- (iv) Phosgene gas is known to exhibit non-ideal gas behaviour. State a reason for this observation. [1]

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- (v) Toluene diisocyanate must be stored in an anhydrous condition. In the presence of water, toluene diisocyanate will react to form toluenediamine and an acidic gas.

Suggest the identity of the acidic gas. [1]

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- (e) The production of polyurethane occurs in the presence of diethyltin dichloride catalyst. Tin atoms are capable of undergoing ligand exchange with ethane-1,2-diol as shown in Fig. 5.4.

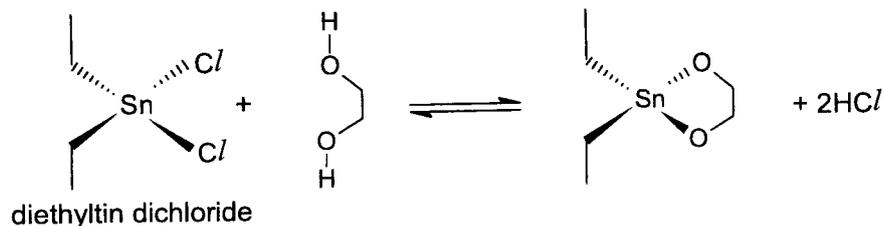


Fig. 5.4

- (i) Suggest how the presence of a catalyst would affect the magnitudes of the rate constant, k , and activation energy, E_a , of the reaction in Fig. 5.4. [1]

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- (ii) Suggest a chemical test to show that ligand exchange has occurred according to Fig. 5.4. Include the expected observations in your answers. [2]

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[Total: 25]

END OF PAPER

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CANDIDATE
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CLASS

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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

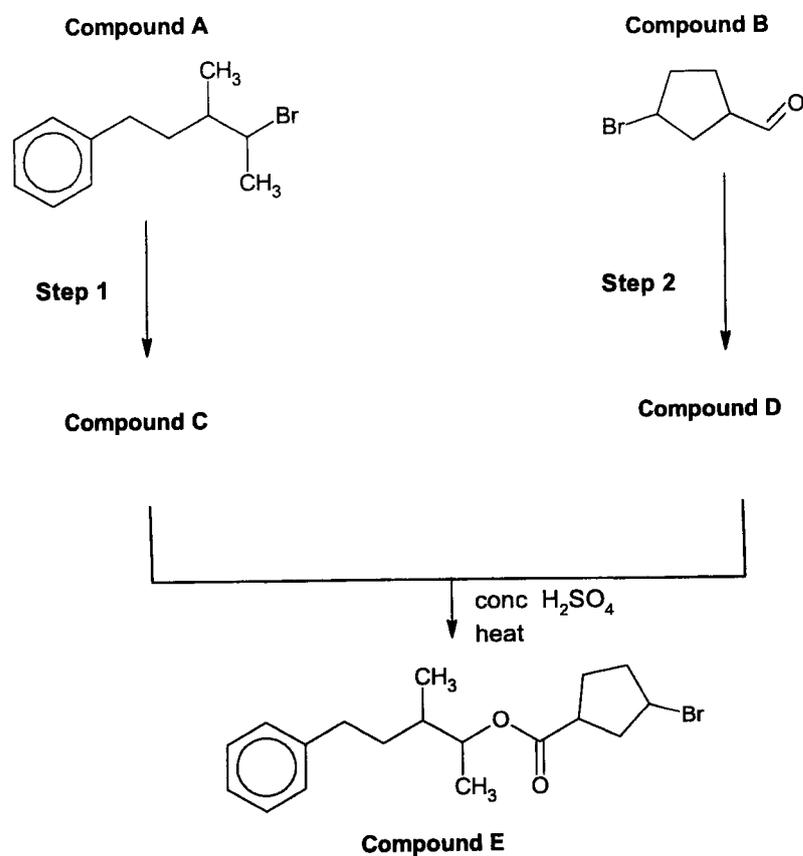
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Section A

Answer all the questions in this section.

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

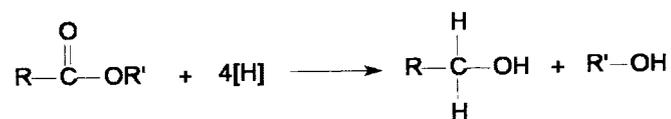


- (i) Draw the structural formulae for C and D. [2]
- (ii) Suggest the reagents and conditions for steps 1 and 2. [2]
- (iii) Draw the structures of the products formed when E is reacted with hot aqueous sodium hydroxide. [2]
- (iv) State the type of reaction when C and D react to form E. [1]
- (v) Equal 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.

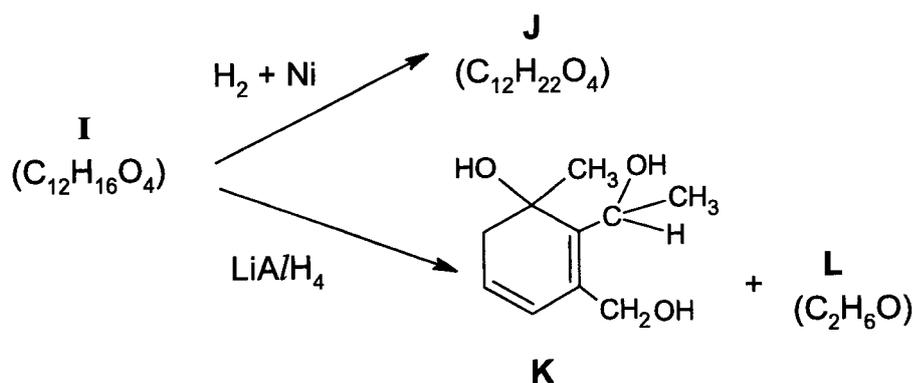
Explain these observations.

[TURN OVER

- 3 (a) LiAlH_4 and H_2 are useful reducing agents in organic chemistry. Esters are reduced by LiAlH_4 and the equation is as shown.



Compound **I** contains an ester functional group and undergoes the following reactions with LiAlH_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]

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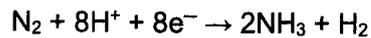
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Section B

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.



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

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- (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.

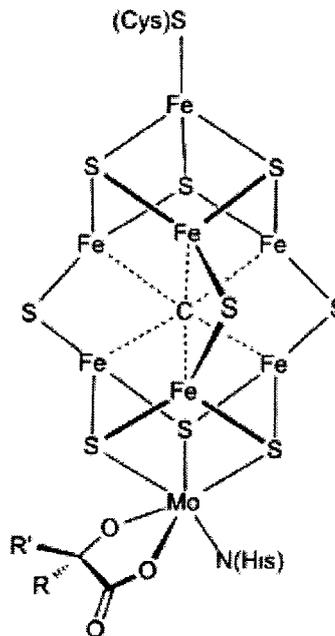


Fig. 4.1

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- (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]

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- (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} .

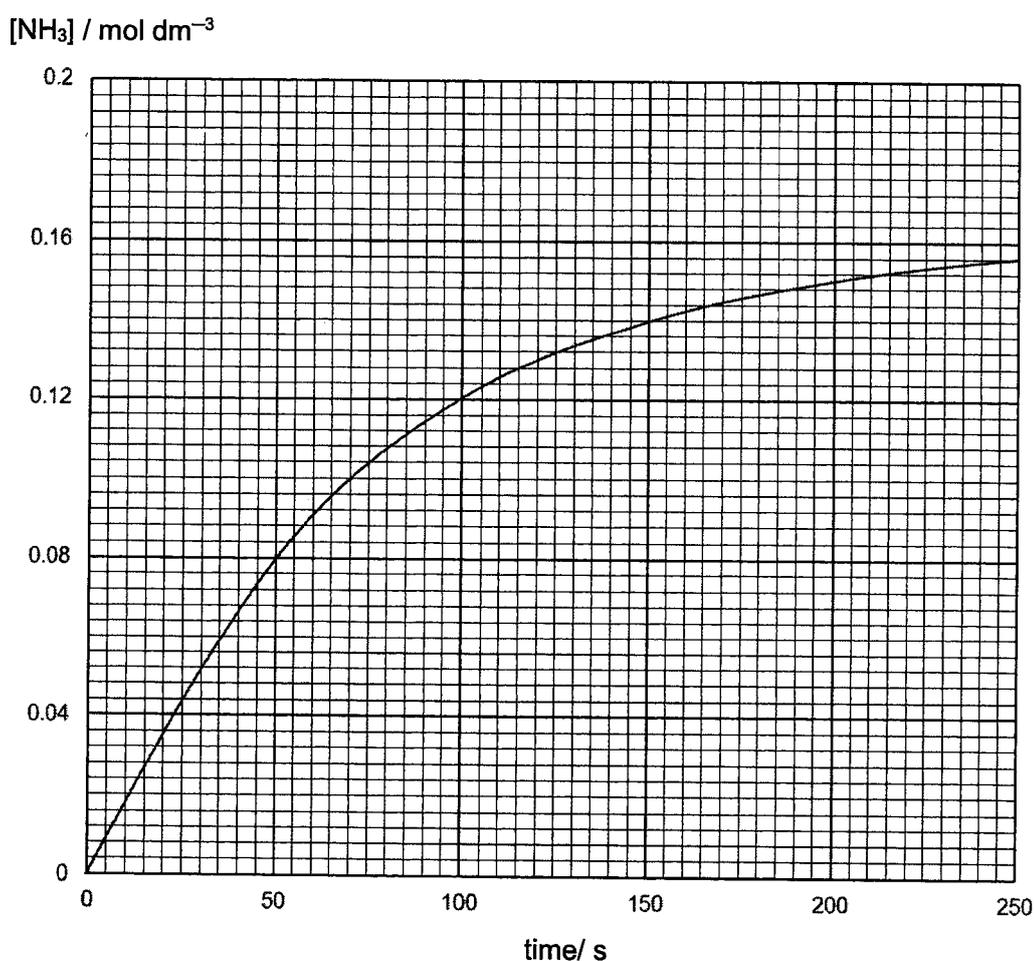


Fig. 4.2

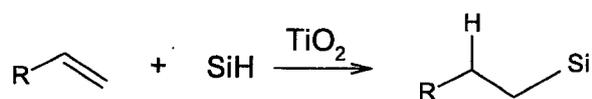
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5 This question is about the chemistry of titanium and its ions.

- (a) Titanium (II) oxide, TiO, and titanium (IV) dioxide, TiO₂, 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 Ti²⁺ ion. [1]
- (ii) Explain, in terms of structure and bonding, the difference in melting point between TiO and TiO₂. [2]
- (iii) TiO₂ is a catalyst used in the anti-Markovnikov hydrosilylation of gaseous alkenes with gaseous silane, SiH₄.



Outline the mode of action of TiO₂ 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 hydrosilylation with TiO₂.



[1]

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- (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 $\text{Mn}^{2+}/\text{Mn}^{3+}$ in one electrolyte tank and $\text{Ti}^{3+}/\text{TiO}^{2+}$ in another. Sulfuric acid is the electrolyte in both tanks.

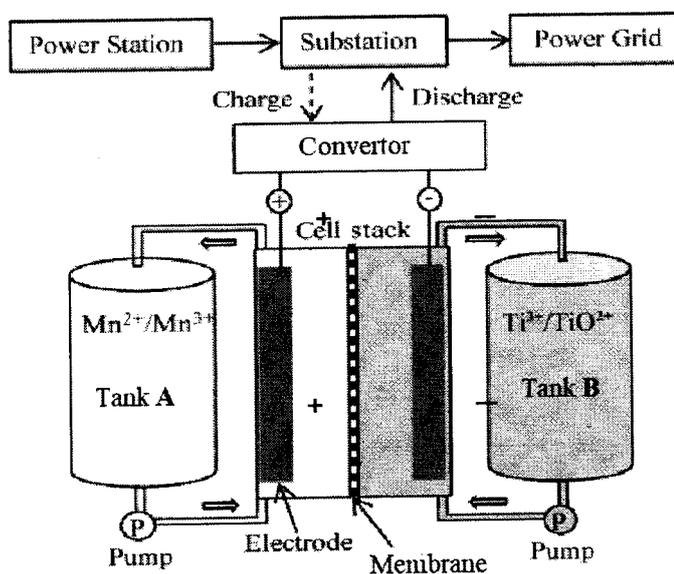
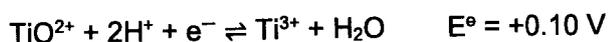


Fig. 5.1

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



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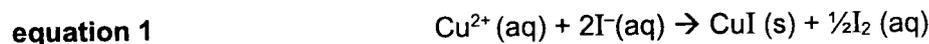
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ST ANDREW'S JUNIOR COLLEGE  JC2 PRELIMINARY EXAMINATION															
CHEMISTRY		9729/04													
Paper 4 Practical		18 Aug 2022													
		2 hours 30 minutes													
Additional Materials: Qualitative Analysis Notes															
<p>READ THESE INSTRUCTIONS FIRST.</p> <p>Write your name and class on all the work you hand in.</p> <p>Give details of the practical shift and laboratory in the boxes provided above.</p> <p>Write in dark blue or black pen.</p> <p>You may use a soft pencil for any diagrams or graphs.</p> <p>Do not use staples, paper clips, highlighters, glue or correction fluid.</p> <p>Answer all questions in the spaces provided on the Question Paper.</p> <p>The use of an approved scientific calculator is expected, where appropriate.</p> <p>You may lose marks if you do not show your working or if you do not use appropriate units.</p> <p>The number of marks is given in the brackets [] at the end of each question or part question.</p>															
		<table border="1"> <thead> <tr> <th colspan="2">For Examiner's Use</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">1</td> <td style="text-align: center;">19</td> </tr> <tr> <td style="text-align: center;">2</td> <td style="text-align: center;">14</td> </tr> <tr> <td style="text-align: center;">3</td> <td style="text-align: center;">14</td> </tr> <tr> <td style="text-align: center;">4</td> <td style="text-align: center;">8</td> </tr> <tr> <td style="text-align: center;">Total</td> <td style="text-align: center;">55</td> </tr> </tbody> </table>		For Examiner's Use		1	19	2	14	3	14	4	8	Total	55
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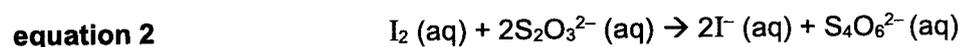
1 Determination of water of crystallisation in a sample of hydrated copper(II) sulfate

The formula of hydrated copper(II) sulfate is $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, where x refers to the number of moles of water of crystallisation. In 1(a)(i), you will perform titration to determine the value of x .

Excess aqueous KI is first added to copper(II) sulfate solution. This will produce a white precipitate in a brown solution of I_2 .



The liberated iodine is then titrated against sodium thiosulfate.



You are provided with:

- solid **FA 1**, hydrated copper(II) sulfate
- **FA 2**, $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- **FA 3**, potassium iodide solution, KI
- **Solution S**, starch solution.

Note: *Solution S will also be used in Question 2.*

(a) (i) Procedure

1. Fill a burette with **FA 2**.
2. Weigh accurately about 5 g of **FA 1**. Record the mass on page 3. Transfer all the solids into a 100 cm^3 beaker. Add about 75 cm^3 of deionised water and stir with a glass rod to dissolve them.
3. Transfer the solution into a 250 cm^3 volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.
4. Make up to the 250 cm^3 mark with deionised water. Stopper the volumetric flask and shake well to mix. Label this solution as **FA 4**.
5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and use a measuring cylinder to add 15 cm^3 of **FA 3** into the same conical flask.
6. Titrate this solution with **FA 2** until the mixture becomes pale brown. An off-white precipitate is also present in the conical flask.

3

7. Add approximately 1 cm³ of **solution S** to the conical flask and continue titration until the blue-black colour just disappears, with the off-white precipitate remaining in the conical flask.
8. Discard the contents and rinse the conical flask with water.
9. Repeat the titration to obtain consistent results. Record your titration results in the space below.

Results**[4]****[Turn Over**

4

- (ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 2** = cm³ [1]

- (b) (i) Calculate the amount, in moles, of Cu²⁺ present in 25.0 cm³ of **FA 4**.

Amount of Cu²⁺ = mol [1]

- (ii) Calculate the concentration of Cu²⁺ in **FA 4**.

Concentration of Cu²⁺ = mol dm⁻³ [1]

- (iii) Given that the concentration of CuSO₄·xH₂O in **FA 4** is 20.00 g dm⁻³, use your answer in (b)(ii) to determine the value of **x**.

[A: H, 1.0 Cu, 63.5 S, 32.1 O, 16.0]

x = [4]

- (iv) In step 5, **FA 3** was added using a 25 cm³ measuring cylinder. Calculate the percentage error in the measurement of the specified volume in step 5.

Percentage error = % [1]

- (c) (i) A student conducted the experiment as mentioned in (a)(i). After carrying out step 5, he left the conical flask containing **FA 3** and **FA 4** to stand for 30 minutes, before continuing with steps 6 to 8. It was noted that his titre volume was less than expected. Suggest a reason for this observation.

.....
 [1]

- (ii) Two other students conducted the same experiment in (a)(i) but with the following modifications to the procedures.

Student 2: In Step 5, add 30 cm³ of **FA 3** instead of 15 cm³.

Student 3: In Step 7, omit the use of **solution S**.

Explain how each of these modifications will affect the accuracy of the results.

Student 2

.....

Student 3

.....
 [2]

[Turn Over

(iii) Another student proposed the following modification.

- Filtering the contents in the conical flask after step 5, before carrying out the titration in step 6.

State an advantage and a disadvantage of this modification.

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.....

.....

[2]

(d) Table 1.1 shows some standard electrode potential values.

Table 1.1

electrode reaction	E^\ominus / V
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.15
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54

The E^\ominus_{cell} for equation 1 is -0.39 V . Explain why the reaction occurred in (a)(i) despite the negative E^\ominus_{cell} value.

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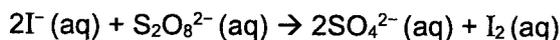
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[2]

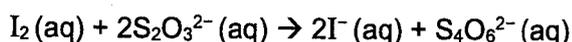
[Total: 19]

2 Determination of the kinetics of the iodide-peroxodisulfate redox reaction

This question seeks to investigate the kinetics of the redox reaction between iodide ions, I^- , and peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$. The redox reaction may be represented by the equation below.



In order to measure the rate of this reaction, a fixed volume of aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to the reaction mixture. Starch is also added to the reaction mixture. When the sodium thiosulfate completely reacts with the iodine produced, the remaining iodine reacts with starch to form a dark blue complex.



The rate of reaction is studied by measuring the time taken for the solution to turn dark blue, t , in a series of five experiments. You will then graphically analyse your results to determine the order of reaction with respect to $[\text{I}^-]$.

FA 5 is $0.100 \text{ mol dm}^{-3}$ potassium iodide, KI.

FA 6 is $0.500 \text{ mol dm}^{-3}$ sodium peroxodisulfate, $\text{Na}_2\text{S}_2\text{O}_8$.

FA 7 is $0.00500 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

You will also need **Solution S** from **Question 1**.

(a) Prepare a table in the space provided on page 9 to record, to an appropriate level of precision:

- volume of **FA 5**, $V_{\text{FA 5}}$
- volume of deionised water,
- all values of t ,
- all calculated values of $1/t$, $\lg(1/t)$ and $\lg(V_{\text{FA 5}})$.

Experiment 1

1. Fill the burette with **FA 5**.
2. Transfer 20.00 cm^3 of **FA 5** into a 250 cm^3 conical flask.
3. Using separate 10 cm^3 measuring cylinders, add 10.0 cm^3 of **FA 7** and 1.0 cm^3 of **Solution S** into the same conical flask.
4. Using a 25 cm^3 measuring cylinder, measure 20.0 cm^3 of **FA 6**.
5. Start the stopwatch upon adding **FA 6** into the conical flask. Swirl the reaction mixture and place the conical flask on a white tile.

[Turn Over

6. Stop the stopwatch when the solution first turns dark blue.
7. Record the time taken, t , to the nearest second in your table.
8. Discard the reaction mixture and wash out the conical flask. Stand it upside down on a paper towel to drain.

Experiments 2 to 5

Repeat experiment 1 four times, using 18.00 cm³, 16.00 cm³, 14.00 cm³ and 12.00 cm³ of FA 5 respectively at step 2.

In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding appropriate volumes of deionised water.

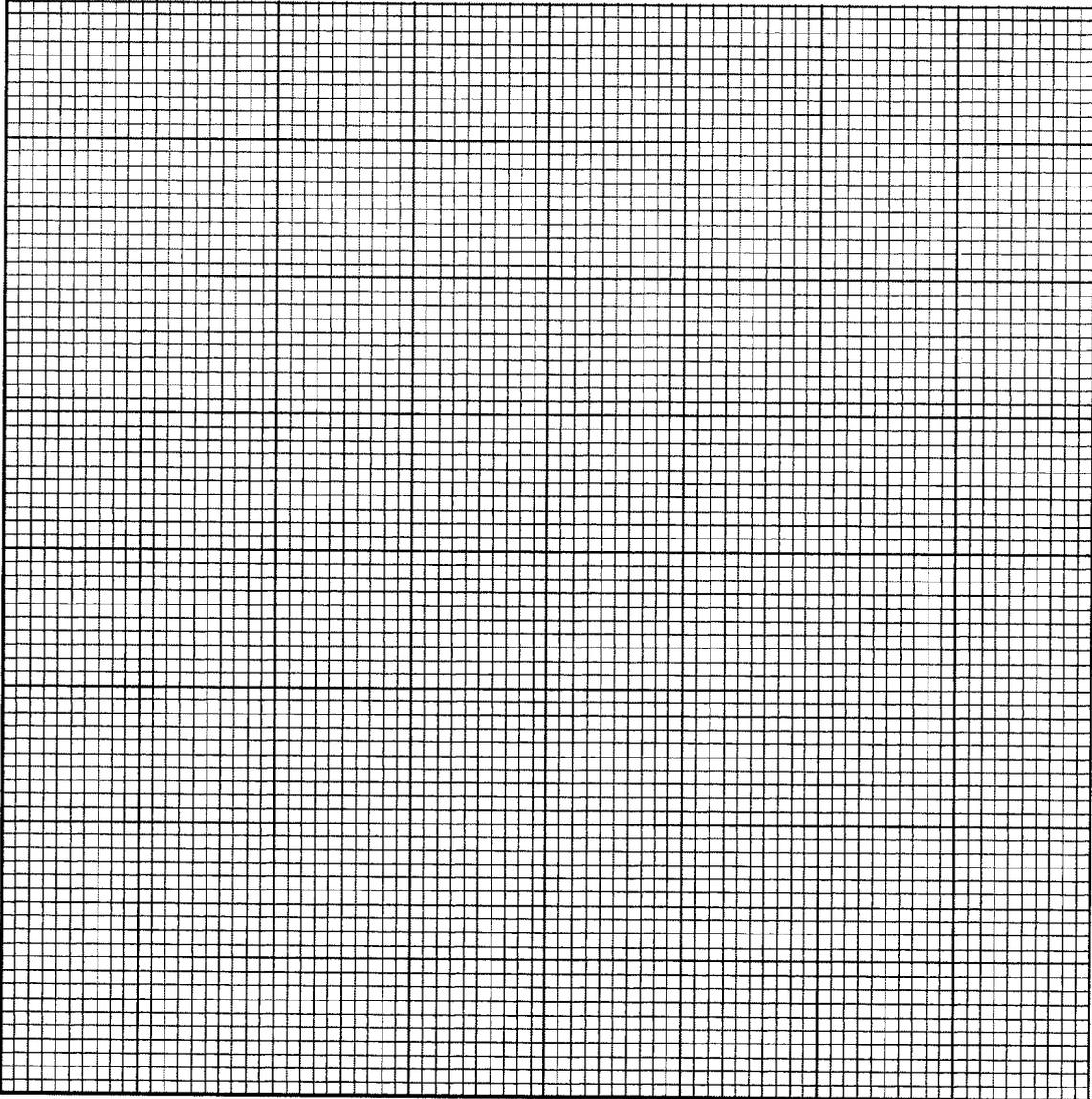
You should alternate the use of the two conical flasks.

Results

[4]

- (b) (i) Plot a graph of $\lg(1/f)$ on the y-axis against $\lg(V_{FA5})$ on the x-axis.
Draw a best-fit straight line through your plotted points.

[3]



[Turn Over

- (ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of reaction with respect to $[I^-]$.

Gradient =

Order of reaction with respect to $[I^-]$ =

[3]

- (iii) Explain why the total volume of the reaction mixture needs to be kept constant in all five experiments in (a).

.....
.....

[1]

- (c) (i) Iron(III) salts are sometimes used as a catalyst for the reaction you performed in (a). Suggest why there is a need for a catalyst.

.....
.....

[1]

- (ii) Using data from **Table 2.1** below, show how iron(III) ions can perform this role and write relevant equation(s).

Table 2.1

electrode reaction	E°/V
$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$	-0.04
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01

[2]

[Total: 14]

[Turn Over

3 Investigation of some inorganic reactions

- (a) **FA 8** is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**.

Perform the tests described in **Table 3.1**. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

Tests		Observations for FA 8
1.	Place a spatula of FA 8 in a dry boiling tube and heat.	
2.	Add a spatula of FA 8 in a test-tube. Add 1 cm depth of H_2O_2 , followed by 1 cm depth of aqueous sodium hydroxide.	
3.	Add half a spatula of FA 8 into a test-tube. Add aqueous ammonia dropwise until it is in excess.	

4.	<p>Add half a spatula of FA 8 into a test-tube and dissolve with 1 cm depth deionised water. Use a glass rod to stir if necessary.</p> <p>Add aqueous sodium carbonate dropwise to the resultant solution until it is in excess.</p>	
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[4]

(b) Consider your observations in **Table 3.1**.

(i) Based on your observations for test 2, suggest the role of **FA 8**.

.....

[1]

(ii) **Table 3.2** shows the K_{sp} values for both copper(II) carbonate and copper(II) hydroxide.

Table 3.2

	K_{sp}
CuCO_3	$1.4 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
Cu(OH)_2	$4.8 \times 10^{-20} \text{ mol}^3 \text{ dm}^{-9}$

Calculate the solubility of each salt. Hence, suggest the identity of the species responsible for the observations seen in test 4.

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.....

.....

[3]

[Turn Over

(c) To determine the identity of anion in **FA 8**, a student added barium nitrate solution to a solution of **FA 8**. A white ppt is formed.

(i) Based on the observations given, state the possible identities of the anions.

..... [1]

(ii) Suggest a test to confirm the identity of the anion in **FA 8**. **DO NOT** carry out the test.

Test: [1]

(d) **Note: You are NOT given FA 9.**

FA 9 is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**. **Table 3.3** shows a test which is performed on **FA 9** and the corresponding observations.

Table 3.3

Test	Observations for FA 9
To 1 cm depth of a solution of FA 9 , add aqueous ammonia dropwise until it is in excess.	A white ppt is formed. It dissolves in excess aqueous ammonia to give a colourless solution.

(i) Suggest the identity of the cation present in **FA 9**.

..... [1]

(ii) Suggest an explanation for the observations in **Table 3.3** in terms of the species present.

.....

[1]

(iii) **Assuming** you have an aqueous solution of **FA 9**.

There is no observable change when barium nitrate solution is added to **FA 9** solution.

Devise a series of simple tests to identify the anion in **FA 9**. Your tests should be based on the Qualitative Analysis Notes and should use only the bench reagents provided. Record your tests in the space below.

[2]

[Total: 14]

[Turn Over

4 Planning

The labels for a bottle of carbonic acid and a bottle of citric acid were mixed up. Both acids have the same concentration of 1.00 mol dm^{-3} . Carbonic acid is dibasic and citric acid is tribasic. In order to identify the correct acids, a series of six experiments will be performed, where different volumes of the acid from one of the bottles and sodium hydroxide are chosen to ensure there are sufficient points before and after the equivalence point. The total volume for each experiment should be kept constant at 60.0 cm^3 .

The temperature change, ΔT , for each neutralisation is calculated using the formula below:

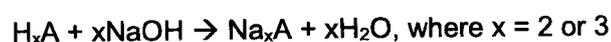
$$\Delta T = T_{\text{final}} - T_{\text{average}},$$

where T_{average} is the weighted average of the initial temperatures of the acid and sodium hydroxide:

$$T_{\text{average}} = \frac{(V_{\text{acid}} \times T_{\text{acid}}) + (V_{\text{NaOH}} \times T_{\text{NaOH}})}{V_{\text{acid}} + V_{\text{NaOH}}}$$

A suitable graph can then be plotted to determine the basicity of the acid.

Let the unknown acid be H_xA . The neutralisation reaction is shown below.



You are provided with:

- 1.00 mol dm^{-3} sodium hydroxide, NaOH
- 1.00 mol dm^{-3} acid from one of the bottles, H_xA
- the equipment normally found in a school or college laboratory.

- (a) (i) Calculate the volumes of acid required for complete reaction if the acid is dibasic and tribasic respectively.

[1]

(ii) Using your answers in (i), fill in the volumes of acid and NaOH in the table below.

Experiment	Volume of acid / cm ³	Volume of NaOH / cm ³
1		
2		
3		
4		
5		
6		

[1]

(b) In your plan to determine the basicity of H_xA, you should include brief details of:

- the apparatus you would use;
- the procedure you would follow;
- the measurements you would make.

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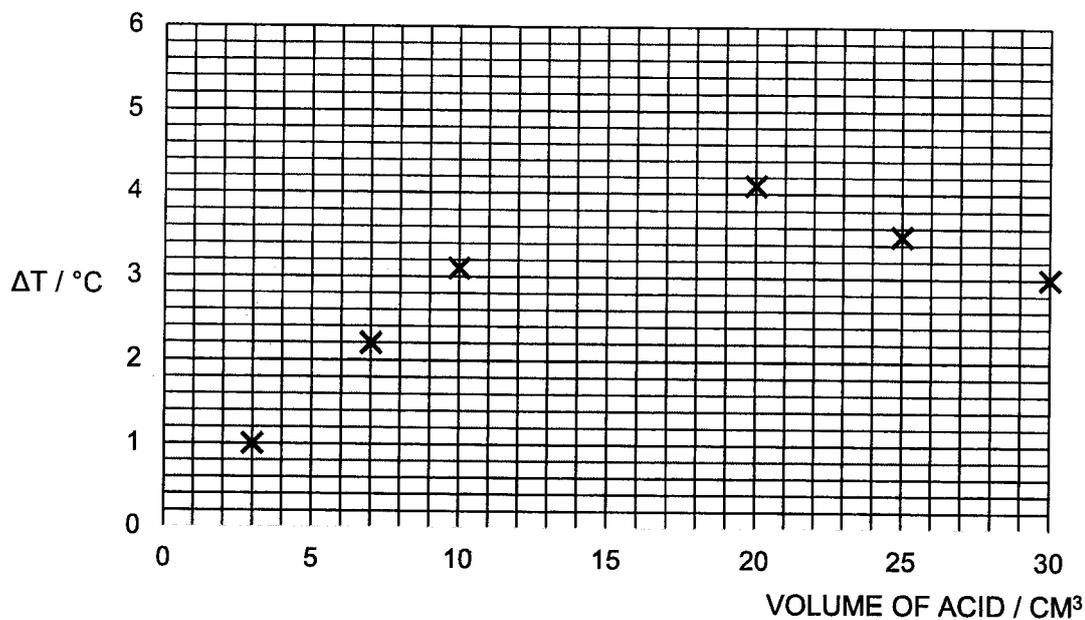
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[Turn Over

- (b) A student conducted the experiment and obtained the following graph of ΔT against volume of acid.



Draw 2 best-fit straight lines and extrapolate both lines to find volume of acid required to completely react with NaOH.

Hence, deduce the identity of the acid.

[2]

[Total: 8]

[Turn Over

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

Cation	reaction with	
	NaOH(aq)	NH ₃ (aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	–
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.
chromium(III), Cr ³⁺ (aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off–white ppt. rapidly turning brown on contact with air insoluble in excess	off–white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn Over

(b) Reactions of anions

<i>ion</i>	<i>reaction</i>
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$)
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$)
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$)
nitrate, $\text{NO}_3^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and <i>A/</i> foil
nitrite, $\text{NO}_2^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and <i>A/</i> foil NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown NO_2 in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	SO_2 liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

(c) Tests for gases

<i>gas</i>	<i>test and test result</i>
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

<i>Halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple