TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CIVICS GROUP	

H2 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

Write your name and Civics Group in the spaces at the top of the page.

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.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.

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

For Examiner's Use	
Section A	
1	**/ 15**
2	**/ 21**
3	**/ 24**
Section B	
4	**/ 20**
OR	
5	**/ 20**
Total	

Section A

Answer **all** questions from this section.

1 Ethanoic acid, CH_3COOH, is a common precursor used in industries to synthesise more complex compounds.

(a) Ethanoic acid has a K_a value of 1.74×10^{-5}.

(i) Calculate the pH of 0.200 mol dm^{-3} ethanoic acid to 1 decimal place. [1]

(ii) Write the K_a expression for ethanoic acid. [1]

(b) An aliquot of 25.0 cm^3 of 0.200 mol dm^{-3} of ethanoic acid is titrated with 25.0 cm^3 of 0.200 mol dm^{-3} NaOH solution.

(i) Explain, with the aid of a chemical equation, why the pH at equivalence point is alkaline. [2]

(ii) A buffer was formed during this titration. Write a chemical equation to show how the buffer solution resists pH change when a small amount of NaOH is added. [1]

(iii) By using the K_a value from **(a)**, calculate the pH of the solution to 2 decimal places when 15.0 cm^3 of NaOH was added. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(c) A sample of industrial waste contains only hydrochloric acid and ethanoic acid. 50.0 cm^3 of the industrial waste was collected in a volumetric flask and topped up to 250 cm^3. A 25.0 cm^3 sample of the resultant solution was then titrated using 0.200 mol dm^{-3} NaOH solution, giving two equivalence points at 12.40 cm^3 and 23.55 cm^3. The first equivalence point is for the neutralisation reaction with HC*l*.

(i) Both hydrochloric acid and ethanoic acid are Brønsted-Lowry acids. Define the term *Brønsted-Lowry acid.* [1]

(ii) Calculate the concentration of hydrochloric acid present in the 50.0 cm^3 sample of industrial waste. [3]

(iii) Hence, calculate an approximate value for the pH of the industrial waste. Give your answer to 1 decimal place. [1]

(iv) Sketch the shape of the titration curve and circle the portion that represents a buffer solution. No numerical pH values are needed. [2]

[Total: 15]

2 Cobalt is a critical component in lithium-ion batteries, which are essential for powering electric vehicles and portable electronics due to their high energy density and reliability.

(a) The following sequence of reactions in Fig. 2.1 involves cobalt and its complexes.

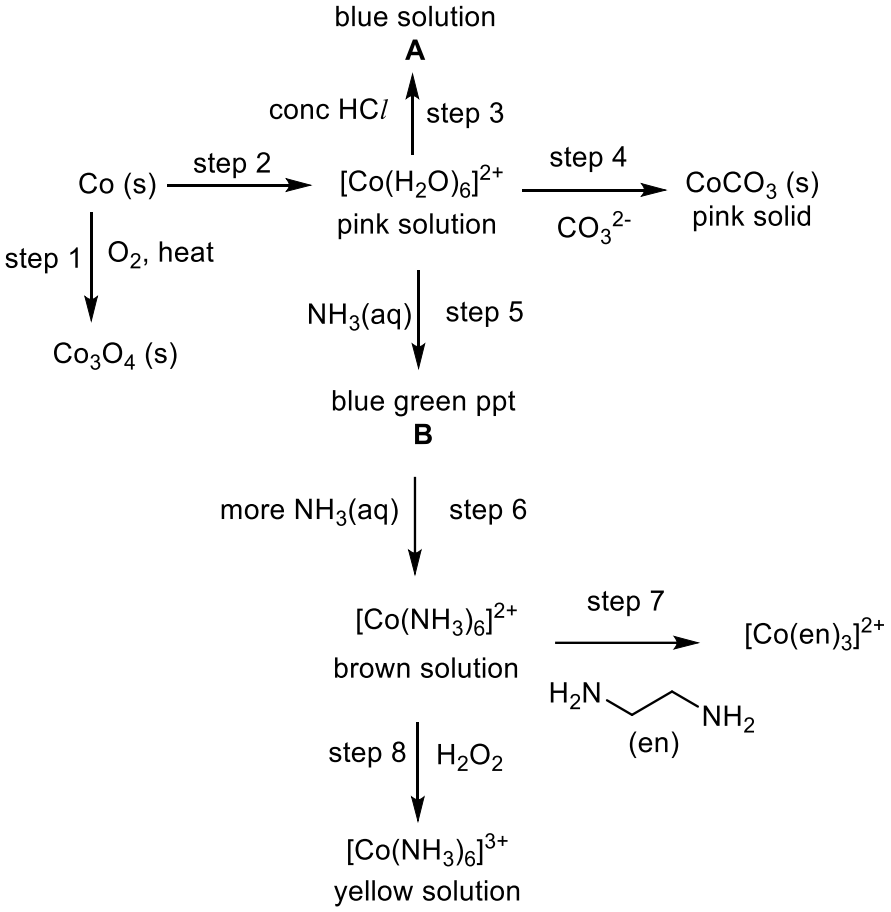


Fig. 2.1

(i) State the type of reaction that occurred in step 3 and the role of H_2O_2 in step 8. [2]

(ii) Given that complex **A** is square planar in shape, suggest the identities of complexes **A** and **B.** [2]

(iii) When solutions of $[Co(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ are each mixed with sodium carbonate solution, different reactions occur. $[Fe(H_2O)_6]^{3+}$ produces effervescence of CO_2 but not $[Co(H_2O)_6]^{2+}$.

Explain why $[Fe(H_2O)_6]^{3+}$ results in the evolution of carbon dioxide gas when reacted with carbonate ions. [2]

.....

.....

.....

(b) Co_3O_4, also known as cobalt tetroxide, is a black ionic compound that contains both Co^{2+} and Co^{3+} ions.

(i) Suggest the ratio of the two different cobalt ions in Co_3O_4. [1]

Cobalt tetroxide can be reduced to cobalt oxide at 900 °C.

$$Co_3O_4(s) \rightleftharpoons 3\ CoO(s) + \tfrac{1}{2}\ O_2(g) \qquad \Delta H^{\ominus}_{rxn}\ 1$$

Some relevant thermochemical data is listed in the Table 2.1 below.

Table 2.1

enthalpy change	value / kJ mol^{-1}
$\Delta H^{\ominus}_{at}$ Co(s)	+426
$\Delta H^{\ominus}_{f}$ O^{2-}(g)	+850
Lattice energy of CoO(s)	–3910
$\Delta H^{\ominus}_{f}$ Co_3O_4(s)	–910

(ii) Using the data given in Table 2.1 and relevant information from the *Data Booklet*, show that the standard enthalpy change of formation of CoO, $\Delta H^{\ominus}_{f}$ CoO, is –237 kJ mol^{-1}. [3]

(iii) Hence, determine the enthalpy change of reaction, $\Delta H^{\ominus}_{rxn}$ 1. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(c) Cobalt oxide exhibits behaviour like aluminium oxide in its chemical properties and reactions, displaying both acidic and basic characteristics depending on the reaction environment.

(i) In your laboratory, you have three unidentified substances: magnesium oxide, silicon oxide and aluminium oxide. Describe a method to identify each substance based on their reactions with acids and bases. Provide relevant chemical equations for these reactions, describing the differences in their observable behaviours. [4]

(ii) Draw a melting point trend graph for period 3 oxides. Explain why MgO has a higher melting point than Na_2O. [3]

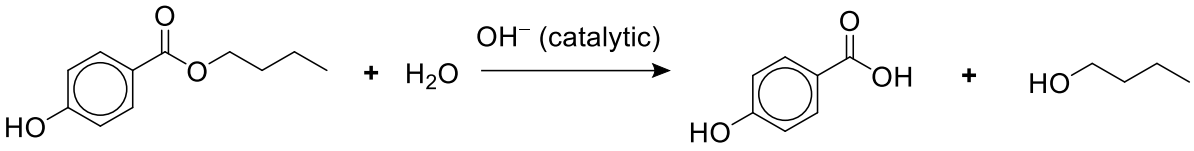
(d) **(i)** Describe the trend observed in the decomposition temperatures of Group 2 carbonates. [2]

(ii) Use relevant information from the Data Booklet, suggest which carbonate in Group 2 has a thermal decomposition temperature similar to that of $CoCO_3$. [1]

[Total: 21]

3 **(a)** Butylparaben (BP) is a member of the parabens family of organic compounds. Direct exposure to elevated levels of parabens is known to be harmful for human health.

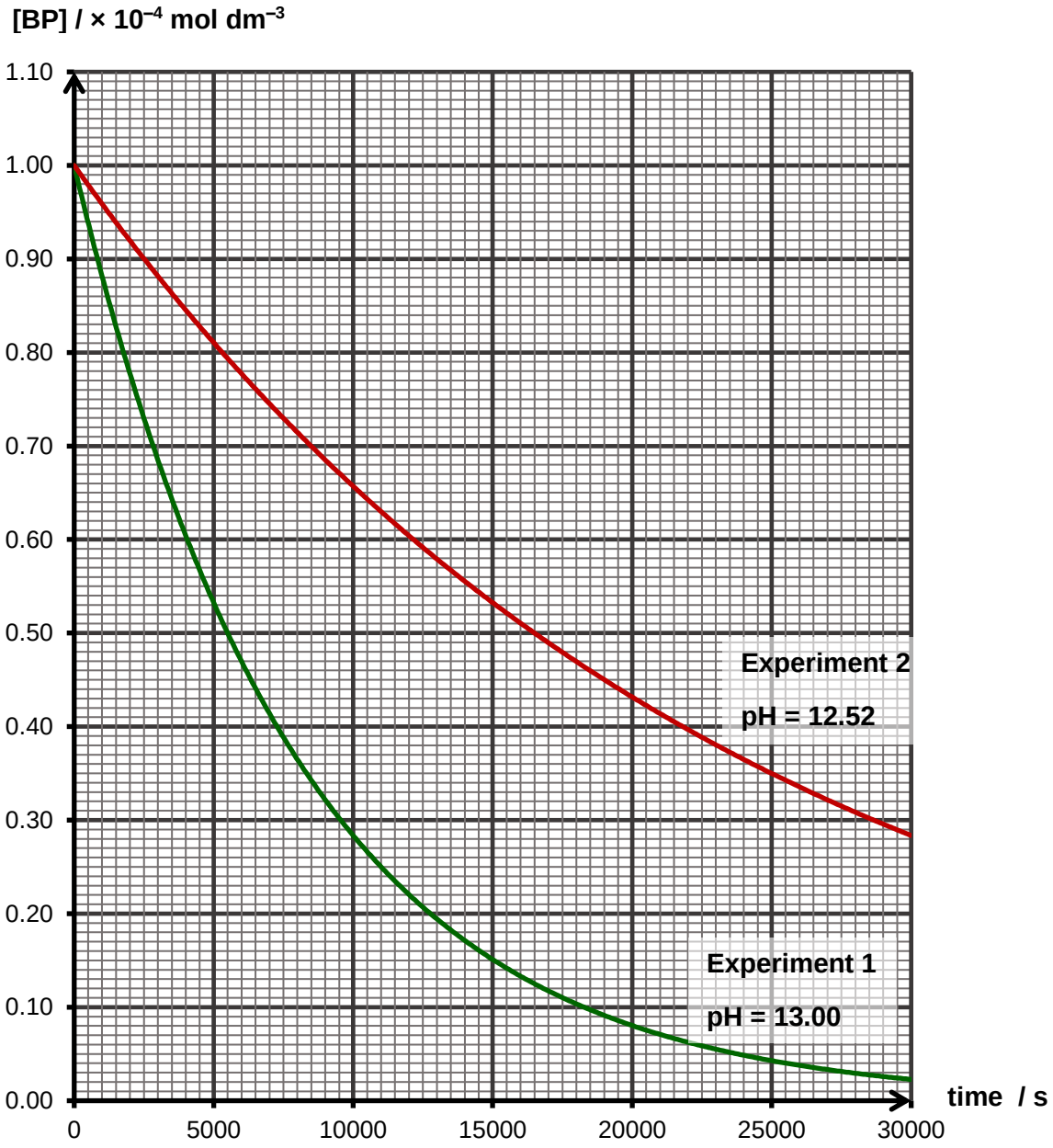
The kinetics of the hydrolysis of BP is investigated.



butylparaben (BP)

Two experiments at different pH levels were used to study the kinetics of the reaction. The pH of the reaction mixture was maintained throughout each experiment.

An [BP]–time graph was plotted using the results obtained from the experiments.

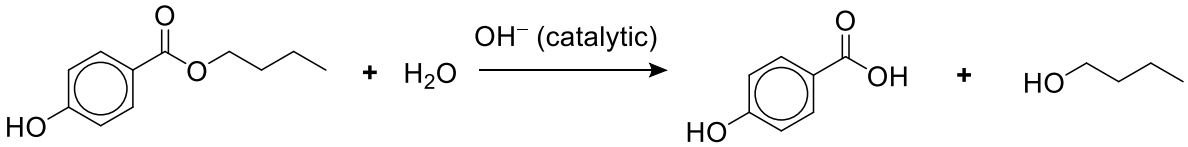


(i) Suggest why the pH of the reaction mixture was maintained throughout each experiment. [1]

(ii) Using the graph provided, show that the reaction is first order with respect to BP and first order with respect to hydroxide ion. Hence, write the rate equation for this reaction. [4]

(iii) Suggest how the half-life for Experiment 1 would change when the initial concentration of BP is increased to 2.00×10^{-4} mol dm^{-3}. Explain your answer. [1]

The basic hydrolysis of BP follows a nucleophilic acyl substitution mechanism.



butylparaben (BP)

This mechanism occurs via three steps.

Step 1: The hydroxide ion attacks the carbonyl carbon of the ester to form a tetrahedral intermediate.

Step 2: This is followed by the removal of an alkoxide, RO^- from the tetrahedral intermediate to give a carboxylic acid.

Step 3: The carboxylic acid is then quickly deprotonated by the alkoxide to give a carboxylate salt.

(iv) Draw the mechanism. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons by curly arrows. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

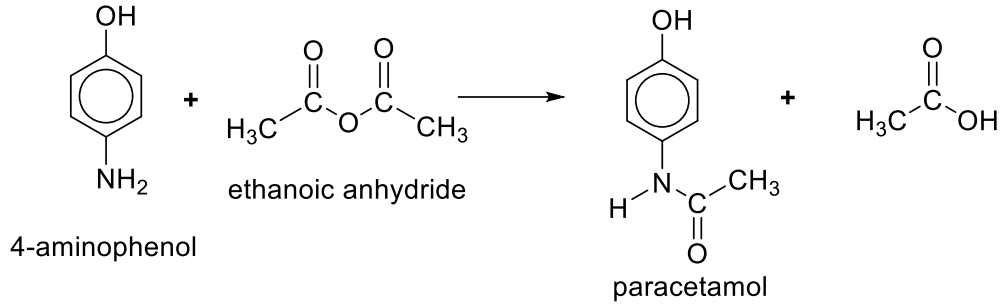
.....

.....

.....

.....

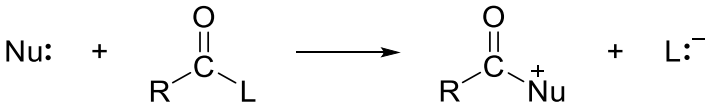
(b) Paracetamol can be synthesised by reacting ethanoic anhydride, $(CH_3CO)_2O$ and the amino group of 4-aminophenol to form an amide via a nucleophilic acyl substitution mechanism.



(i) Phenols can also react with ethanoic anhydride. However, the amino group of 4-aminophenol reacts faster with ethanoic anhydride than the hydroxy group, and the paracetamol product is isolated before the hydroxy group reacts.

Suggest a reason why the amino group reacts faster than the hydroxy group in the reaction between 4-aminophenol and ethanoic anhydride. [1]

(ii) One of the factors that affect the rate of nucleophilic acyl substitution is the nature of the leaving group, L.



Leaving groups that form more stable anions, L^-, can be substituted more easily, leading to faster reactions.

Suggest why the synthesis of paracetamol should be carried out using ethanoic anhydride, $(CH_3CO)_2O$ instead of ethyl ethanoate, $CH_3CO_2CH_2CH_3$. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

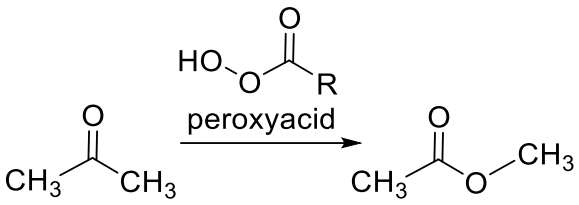
.....

.....

.....

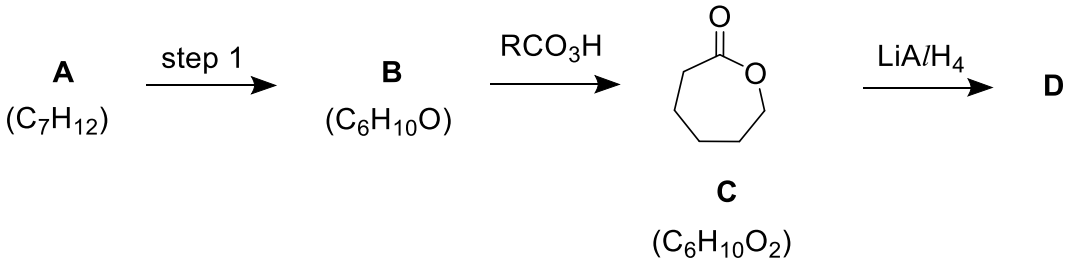
.....

(c) Esters can also be formed via Baeyer-Villiger reactions. A ketone is reacted with a peroxyacid, RCO_3H and this involves inserting an O atom into a C–C bond adjacent to a carbonyl group. For example, methyl ethanoate can be synthesised from propanone.



(i) Name an ester that can be formed by reacting pentan-2-one with peroxyacid, RCO_3H. [1]

(ii) The following reaction scheme involves using Baeyer-Villiger reaction to synthesise a cyclic ester, compound **C**.



State the reagents and conditions required for step 1 and suggest structures for the organic compounds **A**, **B** and **D**. [4]

.....

.....

.....

.....

.....

.....

.....

(d) Compound **E** has a molecular formula of $C_6H_9O_3Cl$ and is a neutral molecule. Compound **E** reacts with hot sodium hydroxide, followed by acidification to yield two organic compounds, **F** and **G** in a 1:1 ratio.

Compound **F,** $C_2H_2O_3$, gives an observation with Tollens' reagent. It also reacts with hot acidified $KMnO_4$ to form carbon dioxide gas only.

Compound **G** contains 2 chiral carbon atoms and has a molecular formula of $C_4H_{10}O_2$. Compound **G** gives a negative test with 2,4–dinitrophenylhydrazine but reacts with hot aluminium oxide to form **only** three isomers with the molecular formula of C_4H_8O. Only one of the three isomers, **H** exhibits enantiomerism.

Suggest structures for compounds **E**, **F**, **G** and **H**, showing your reasoning clearly.

[7]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 24]

Section B

Answer **one** question from this section.

4 Ethanol has numerous important applications across various industries, making it a vital compound in our daily lives.

(a) Ethanol was electrolysed at different voltages in one research experiment. To achieve high energy efficiencies in cells, the yield of carbon dioxide in Equation 1 must be high.

Equation 1: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12e + 12H^+$

However, in practice, low yields of CO_2 have generally been reported, with the major products being ethanal and ethanoic acid. The three products at the anode, ethanoic acid, ethanal and carbon dioxide, were collected and analysed.

The amounts of ethanol consumed, and products were determined by proton nuclear magnetic resonance (NMR) spectroscopy while CO_2 was measured with a non-dispersive infrared CO_2 monitor.

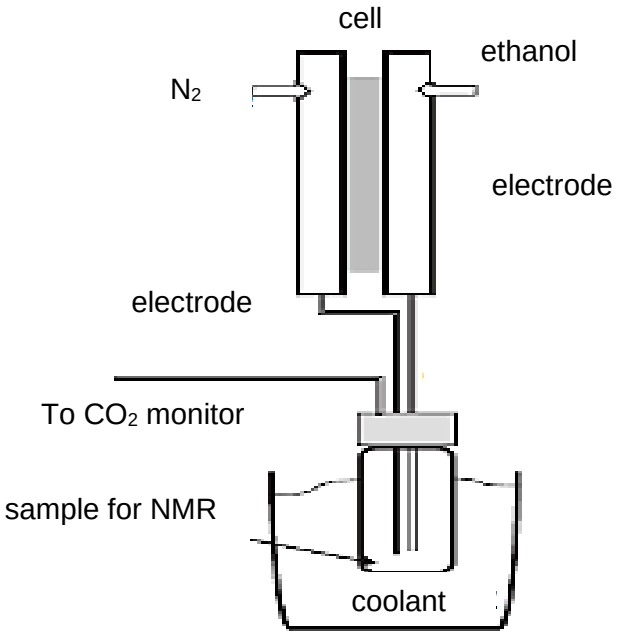


Fig. 4.1

(i) Write the two half-equations, for the reactions involving ethanol occurring at the anode to account for the two major products, ethanoic acid, ethanal. [2]

(ii) Draw and label the direction of electron flow in the cell on Fig. 4.1. [1]

.....

.....

.....

.....

BLANK PAGE

The percentages of products (ethanoic acid, ethanal and carbon dioxide) using catalyst mounted on a carbon anode, platinum (Pt/C) are shown in Fig. 4.2.

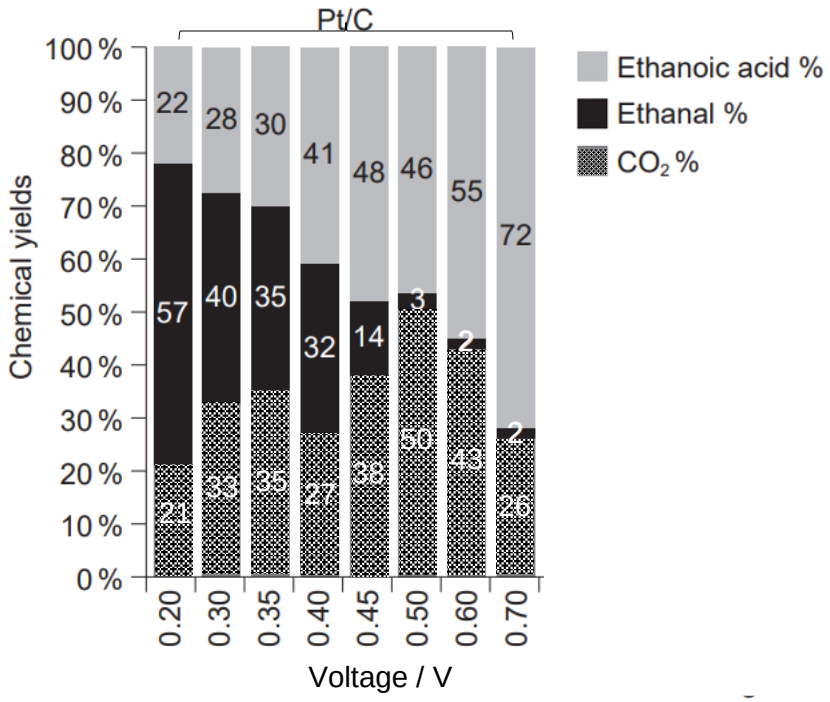


Fig. 4.2

[Source: Product Distributions and Efficiencies for Ethanol Oxidation in a Proton Exchange Membrane Electrolysis Cell, Rakan M. Altarawneh and Peter G. Pickup, Journal of the Electrochemical Society, 2017, volume 164, issue 7, http://jes.ecsdl.org/]

(iii) Describe what happens to the chemical yield of ethanal using Pt/C as a catalyst when the voltage increases. [1]

(iv) With reference to Fig. 4.2 and Equation 1, calculate the rate of reaction of carbon dioxide, in molecules per minute, that produces a current of 1.00 A at 0.50 V using Pt/C as a catalyst. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(b) Ethanol is also being investigated as a fuel in fuel cells.

The equation for the complete combustion of 1 mol of ethanol is shown below.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

(i) The standard enthalpy change of combustion of ethanol, $\Delta H^{\ominus}_c$, has a value of –1367 kJ mol^{-1}, and the entropy change for the same process is –140 J mol^{-1} K^{-1}.

Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the combustion of ethanol at 298K. [1]

(ii) Account for the negative sign of ΔS for the complete combustion reaction of ethanol. [1]

(iii) Hence, comment on the effect of decreasing temperature on the spontaneity of the reaction. State any assumption that must be made for your comment to be valid. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(c) The mechanism for the reaction of ethanol with $SOCl_2$ in the presence of base is shown in Fig. 4.3.

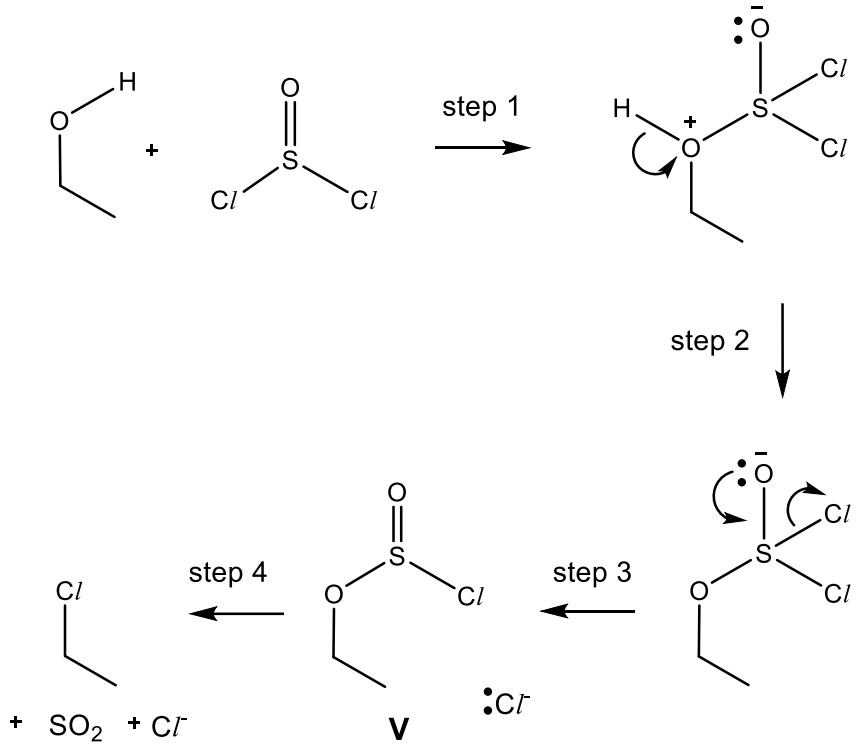


Fig. 4.3

The reaction of **V** with Cl^- ions in step 4 proceeds via an S_N2 mechanism. Sulfur dioxide is a by-product of this reaction.

(i) Complete the mechanism for step 1 on Fig. 4.3 by adding a lone pair, curly arrows and a dipole. [2]

(ii) Complete the mechanism for step 4 on Fig. 4.3 by adding **three** curly arrows. [2]

(d) Compound **W** can be used to synthesise compound **Z** by the four–step route shown in Fig. 4.4.

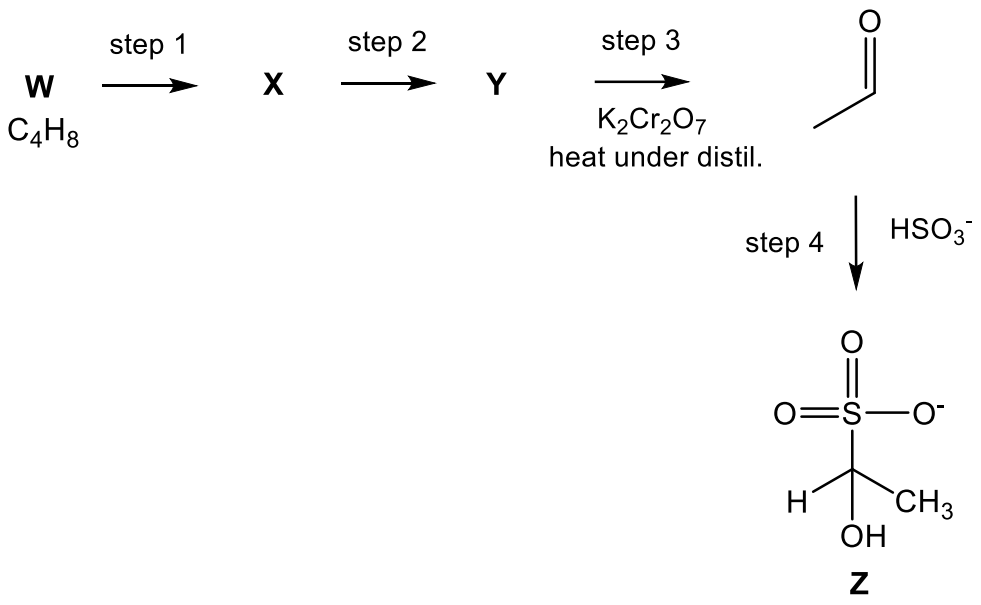


Fig. 4.4

(i) State the reagents and conditions required for each of the step from steps 1–2 and suggest structures for the organic compounds **W**, **X**, and **Y**. [3]

(ii) Oxygen was accidentally added to **step 4** in Fig. 4.4.

Table 4.1

Electrode reaction	$E^{\ominus}$/ V
$HSO_3^- + 5H^+ + 4e^- \rightleftharpoons HS^- + 3H_2O$	–0.11
$SO_4^{2-} + 3H^+ + 2e^- \rightleftharpoons HSO_3^- + H_2O$	+0.54

Use data from the *Data Booklet* and Table 4.1 to predict whether a side reaction between oxygen and HSO_3^- can occur. Explain your reasoning. [2]

.....

.....

.....

.....

.....

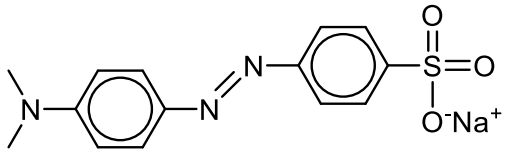
.....

.....

.....

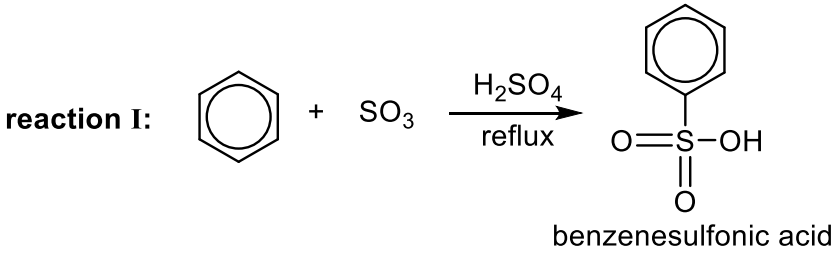
[Total: 20]

5 **(a)** Methyl orange is an azo dye which is commonly used as a pH indicator in titrations because of its clear and distinct colour change at different pH values and its structure is given below.



methyl orange

A precursor compound used in the synthesis of methyl orange is benzenesulfonic acid, which is produced by heating benzene with fuming sulfuric acid under reflux in **reaction I** shown in Fig. 5.1. Fuming sulfuric acid is a concentrated solution of sulfur trioxide, SO_3, in sulfuric acid, H_2SO_4.

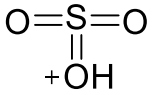


benzenesulfonic acid

Fig. 5.1

Reaction I is an electrophilic substitution reaction which involves the following steps.

- The first step involves the protonation of SO_3 by H_2SO_4 to form HSO_3^+. The structure of HSO_3^+ is shown.



- In the second step, benzene reacts with HSO_3^+ to form an intermediate.
- In the last step, the stable benzene ring is restored to form benzenesulfonic acid and H_2SO_4 is regenerated at the end of the reaction.

(i) Outline the mechanism occurring in **reaction I** to form benzenesulfonic acid. Include all relevant charges, lone pairs of electrons and curly arrows. [3]

Diazotization is the process of converting primary aromatic amines into its diazonium salts. Diazonium salts are important synthetic intermediates that can undergo "coupling reactions" to form azo dyes.

Fig. 5.2 shows the reaction scheme of how methyl orange can be formed from a primary aromatic amine.

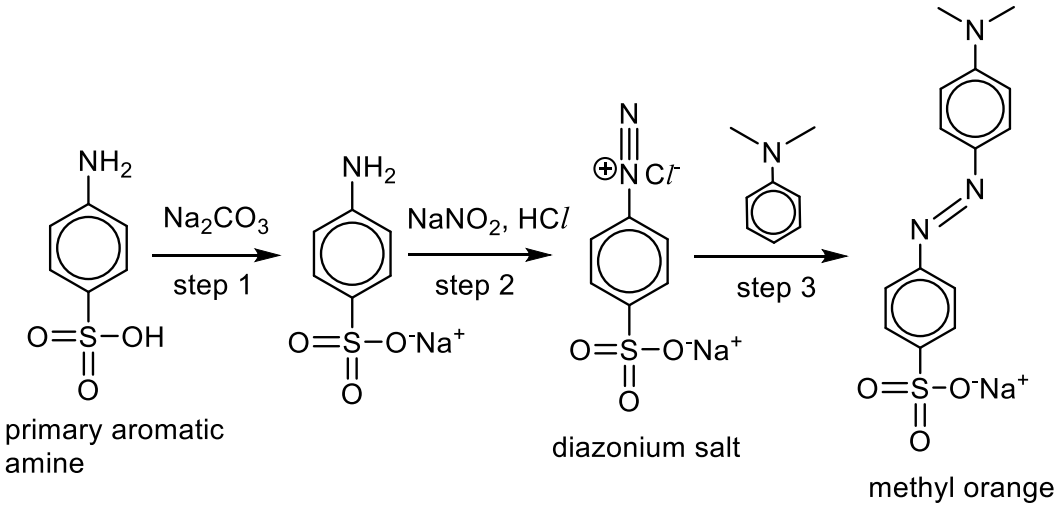


Fig. 5.2

(ii) Suggest the type of reaction for step 1 and step 3. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

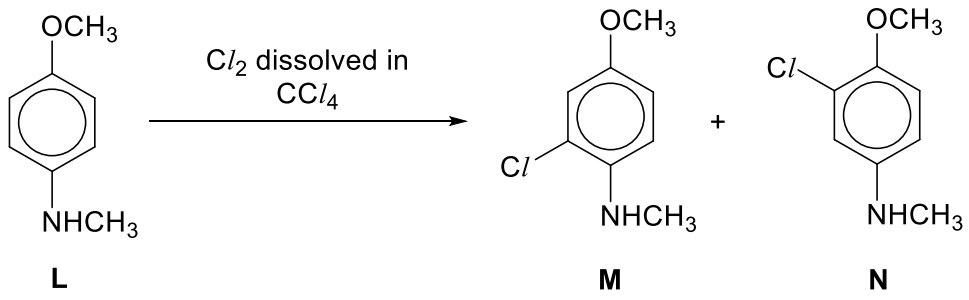
.....

.....

.....

.....

(b) When compound **L** is reacted with Cl_2 dissolved in CCl_4, compounds **M** and **N** are two of the products formed, as shown in Fig. 5.3.



L **M** **N**

Fig. 5.3

Suggest why compound **M** will be formed in a greater proportion.

[1]

(c) Fig. 5.4 shows the synthesis of compound **Q** from but-2-ene.

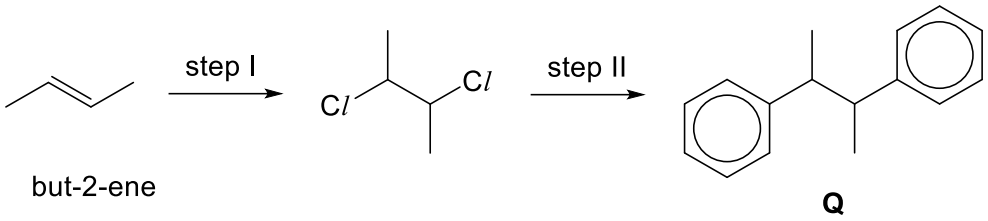


Fig. 5.4

(i) Describe the C=C bond in but-2-ene with reference to the hybridisation of the carbon atoms and orbital overlap. [2]

(ii) Suggest the reagents and conditions required for step II. [1]

There are three different types of compound **Q** molecules, namely **R**, **S** and **T** molecules.

- molecule **R** has no effect on plane-polarised light
- molecule **S** rotates plane-polarised light by 15° to the left
- molecule **T** rotates plane-polarised light by 15° to the right

(iii) Explain why molecule **R** has no effect on plane-polarised light. [1]

(iv) Draw the structures of molecules **S** and **T**. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(d) **(i)** Describe the reactions, if any, of the chlorides NaC*l*, A*l*C*l*$_3$, and PC*l*$_5$, with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. Relate the reactivity of these chlorides to their structure and bonding.

[5]

(ii) Table 5.1 gives the melting points, in °C, of the fluorides and chlorides of three elements in Period 3.

Table 5.1

	sodium	magnesium	silicon
fluoride	993	1261	−90
chloride	801	714	−70

Explain the differences in melting points between

- NaC*l* and MgC*l*$_2$ [1]

- MgF$_2$ and SiF$_4$, [2]

(iii) Unlike magnesium fluoride which is highly insoluble in water, magnesium sulfate exhibits high solubility in water. When magnesium sulfate dissolves, the anions and cations are each surrounded by water molecules.

Draw a simple diagram to show how a water molecule can be attached to a sulfate anion. Label the diagram to show the type of interaction involved.

[1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

Additional answer space

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