ST. ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

CLASS	2	4	S		

CHEMISTRY **9729/03**

Paper 3 Free Response **15 September 2025**

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.
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.

For Examiner's Use		
Q1		**22**
Q2		**18**
Q3		**20**
Q4 / Q5		**20**
Total		**80**

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.

This document consists of **35** printed pages (including this cover page).

Section A

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

1 **(a)** Calcium carbide, CaC_2, is an ionic compound primarily used in industry to generate acetylene gas, C_2H_2, which has numerous applications in welding, cutting and chemical synthesis.

reaction 1 $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

(i) The carbon atoms in CaC_2 and C_2H_2 have sp hybridisation and hence they have similar bonding between the two carbon atoms.

Explain what is meant by sp hybridisation with reference to the carbon atoms in C_2H_2. **[2]**

(ii) Suggest how the electrons are arranged in the second shell of sp carbon atom so that the bonding in the two carbon atoms in C_2H_2 can occur. **[2]**

(iii) Explain, in terms of structure and bonding, why CaC_2 is a solid at room temperature and pressure while C_2H_2 is a gas. **[2]**

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(b) Calcium carbide reacts vigorously and explosively with water.

Using the data in Table 1.1, calculate the standard enthalpy change of reaction for reaction 1.

Table 1.1

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$CaC_2(s)$	– 59.0
$H_2O(l)$	–285.8
$Ca(OH)_2(s)$	– 985.2
$C_2H_2(g)$	+226.6

[2]

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(c) Caution is required when handling calcium carbide to minimise its exposure to water. Flammable C_2H_2 gas is produced upon reaction of calcium carbide with water and poses explosion risks.

(i) Define the term *standard enthalpy change of combustion,* $\Delta H_c^{\ominus}$, *of* C_2H_2. **[1]**

(ii) Use bond energy values from the *Data Booklet* to calculate the standard enthalpy change of combustion of C_2H_2. **[2]**

(iii) The actual standard enthalpy change of combustion of C_2H_2 is -1300 kJ mol^{-1}.

Other than the use of average bond energies, suggest **one other reason** for the difference between the actual value and the value calculated in **(c)(ii)**. **[1]**

(iv) Suggest an appropriate storage method for calcium carbide to minimise explosion risks. **[1]**

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(d) C_2H_2 is a weak Brønsted-Lowry acid and reacts with sodium amide, $NaNH_2$, to form an equilibrium mixture containing two acid-base pairs.

equilibrium 2 $C_2H_2 + NaNH_2 \rightleftharpoons Na(C_2H) + NH_3$ $K_c = 1 \times 10^{13}$

(i) With reference to equilibrium 2, explain the terms *Brønsted-Lowry acid* and *conjugate acid-base pair*. **[2]**

(ii) Identify another acid in the mixture in equilibrium 2 and suggest whether the acid is a stronger or weaker acid than C_2H_2. Explain your answer. **[2]**

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(e) C_2H_2 can undergo polymerisation in the presence of suitable catalysts to form polyacetylene, an organic polymer with alternating single and double bonds. It is used in organic semiconductors and its reaction with iodine produces highly electrical conducting material.

$$n\ HC{\equiv}CH \rightarrow –[CH{=}CH]_n–$$

$–[CH{=}CH]_n–$ is known as a repeating unit in polyacetylene.

(i) Two isomers can be obtained when C_2H_2 undergoes polymerisation.
Draw the structures of the two isomers, showing at least **two** repeating units, and state their isomeric relationship. **[2]**

Polyacetylene ($–[CH{=}CH]_n–$) becomes highly conductive when doped with iodine. The reaction removes an electron from a double bond, creating a radical cation called polaron.

$$\underset{}{–[CH{=}CH]_n–} + \frac{3}{2}I_2 \rightarrow \underset{\text{polaron}}{–[CH{=}CH]_n^{\bullet +}} + I_3^-$$

(ii) State the role of iodine in the reaction. Explain your answer. **[2]**

(iii) Suggest why the doping process increases the electrical conductivity of polyacetylene. **[1]**

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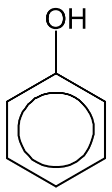
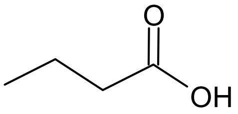
[Total: 22]

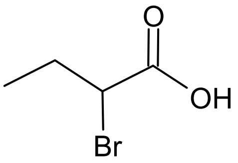
2 **(a)** Deduce the order of increasing acid strength of the following compounds. Explain your answer.



phenol



butanoic acid



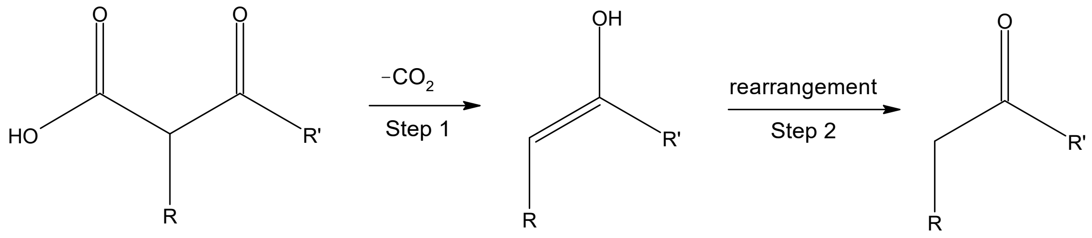
2-bromobutanoic acid

[3]

(b) Decarboxylation is the loss of carbon dioxide from a carboxylic acid group. It plays an important role in organic synthesis and occurs under specific thermal or catalytic conditions.

Two examples of decarboxylation are shown in Fig. 2.1.

Example 1:



Example 2:

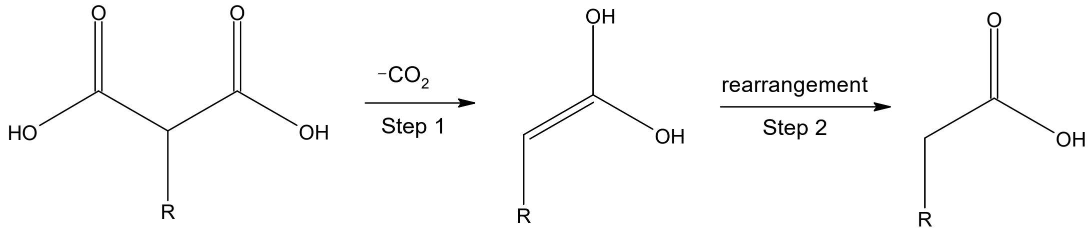
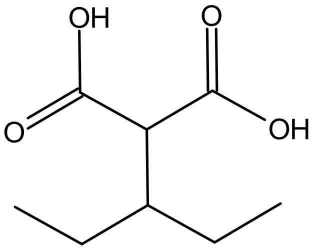


Fig. 2.1

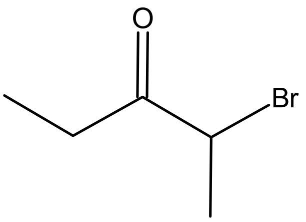
(i) Draw the structure of the organic product formed when compound **K** undergoes decarboxylation.



K

[1]

(ii) Two different acids, **M** and **N**, each can undergo decarboxylation to give **L**.



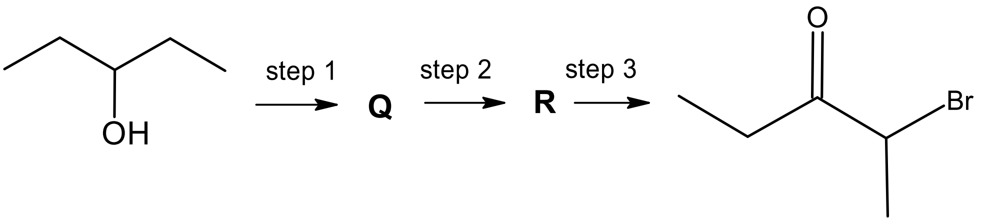
L

Suggest possible structures of **M** and **N**.

[2]

(iii) Compound **L** can also be synthesised from pentan-3-ol by the three-step route shown in Fig. 2.2

State the reagents and conditions required for each step and suggest structures for the organic compounds **Q** and **R**.



L

Fig. 2.2 **[5]**

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(c) The Kolbe electrolysis reaction involves the decarboxylative dimerisation of carboxylate ions to form alkanes at the anode by the following reaction.

$$2R\text{–}CO_2^- \rightarrow R\text{–}R + 2CO_2 + 2e^-$$

$$R = \text{–}CH_3,\ \text{–}CH_2CH_3,\ \text{etc.}$$

For example, the electrolysis of sodium ethanoate solution produces ethane at the anode.

(i) Suggest the products of the reaction at the cathode and construct an equation for the electrolysis of sodium ethanoate. **[2]**

(ii) Calculate the mass of ethane, C_2H_6, produced when a current of 2.0 A is passed through a solution of sodium ethanoate for 55 minutes. **[2]**

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(d) Group 2 ethanoates decompose when heated to form carbonates and propanone.

(i) Write an equation for the thermal decomposition of $Ba(CH_3COO)_2$. **[1]**

(ii) The trend in the thermal stability of Group 2 ethanoates is similar to that of Group 2 carbonates.

Describe and explain the trend in the thermal stability of Group 2 ethanoates. **[2]**

[Total: 18]

3 **(a)** Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. **[3]**

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(b) To form concentrated solutions of hydroiodic acid, hydrogen iodide gas is first formed by reaction of hydrogen and iodine gas before being bubbled into water.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$

(i) State the conditions necessary for a gas to approach ideal behaviour. **[1]**

(ii) The graphs of *pV/RT* against *p* for HI gas and gas **J** are shown in Fig. 3.1.

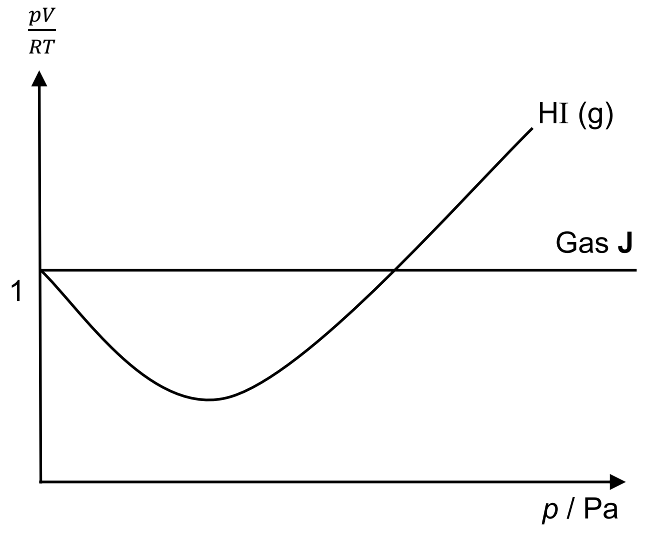
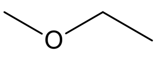


Fig. 3.1

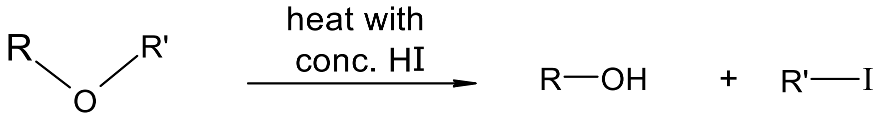
Explain the shape of the graph for HI gas and gas **J**. Your answer should include references to intermolecular forces. **[2]**

(c) Ethers have the general structure of $R_1–O–R_2$, where R_1 and R_2 are alkyl or aryl groups, for example, like methoxyethane.



methoxyethane

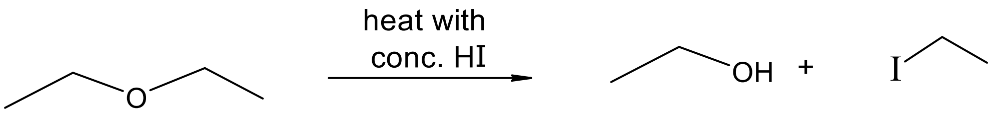
When reacted with hot concentrated solutions of hydroiodic acid, HI, ether can form an alkyl halide and an alcohol as shown in Fig. 3.2.



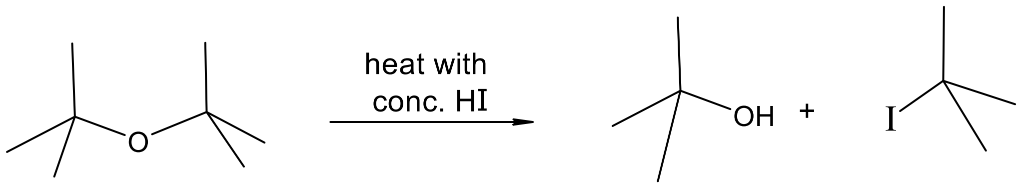
where R and R’ are different alkyl groups

Fig. 3.2

Two examples are shown below.



diethyl ether



di-tert-butyl ether

(i) It was found that primary or secondary ethers, like diethyl ether, reacts via S_N2 mechanism while tertiary ethers, like di-tert-butyl ether, reacts via S_N1 mechanism.

Explain why this reaction proceeds mainly via:

1. S_N2 mechanism for primary or secondary ethers
2. S_N1 mechanism for tertiary ethers **[2]**

(ii) Compound **A**, $C_7H_{16}O$, is an ether, and it reacts with hot concentrated solution of hydroiodic acid, HI, to form compound **B**, $C_6H_{14}O$, and compound **C**.

B is found to rotate plane-polarised light. **B** forms a yellow precipitate with alkaline aqueous iodine. When **B** reacts with hot concentrated H_2SO_4, only compound **D**, C_6H_{12}, is formed.

C reacts with hot ethanolic $AgNO_3$ to form yellow precipitate.

With reference to Fig. 3.2, deduce a possible structure for **A**. Hence, suggest the structures for **B**, **C** and **D**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. **[8]**

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(d) Crown ethers are a class of cyclic ethers that have garnered significant attention due to their unique ability to form complexes with cations.

An example of a crown ether is 12-Crown-4 in Fig. 3.3.

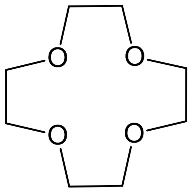

Fig. 3.3

12-Crown-4 forms complexes with various cations such as lithium ion, Li^+, in Fig. 3.4.

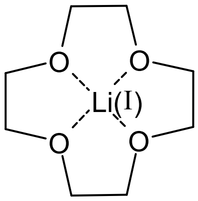

Fig. 3.4

(i) Suggest why 12-Crown-4 was found to be more selective in complexing with lithium ion, Li^+, than potassium ion, K^+. **[1]**

(ii) Suggest the type of interactions between 12-Crown-4 and Li^+. **[1]**

(iii) Crown ethers can be used to selectively remove caesium, a common component in nuclear waste, by complexing with caesium ions.

The radioactive decay of caesium-134 isotope is a first-order reaction with a half life of 2 years.

Use the following equations to calculate the percentage decrease of $^{134}Cs^+$ in a radioactive waste sample six months after it had been collected.

$$k = \frac{0.693}{t_{1/2}}$$

$$\frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_o} = 10^{-\frac{kt}{2.3}}$$

where k is the rate constant,
$(^{134}Cs^+)_t$ is the amount of $^{134}Cs^+$ collected in the sample at time = t,
$(^{134}Cs^+)_0$ is the amount of $^{134}Cs^+$ collected in the sample at time = 0,
t is the time elapsed after the sample was collected. **[2]**

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[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Manganese forms stable coloured ions in various oxidation states in aqueous solutions. Some of these manganese ions and their corresponding colours are shown in Table 4.1.

Table 4.1

formula of manganese ion	MnO_4^-	MnO_4^{2-}	Mn^{3+}	Mn^{2+}
colour of aqueous solution	purple	green	violet	pale pink

(i) Explain why manganese can form ions of variable oxidation states. **[1]**

(ii) Table 4.2 gives data about some physical properties of the elements, calcium, cobalt and manganese.

Table 4.2

	Calcium	Cobalt	Manganese
relative atomic mass	40.1	58.9	54.9
atomic radius (metallic) /nm	0.197	0.125	0.132
density / g cm^{-3}	1.53	8.83	*x*

Using the data provided in Table 4.2, suggest a value for *x*, the density of manganese. Explain your answer. (No calculations are required.) **[2]**

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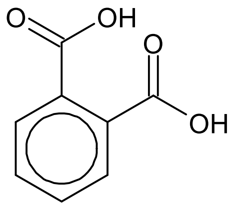
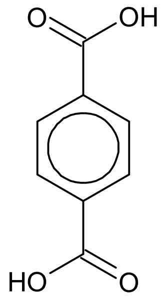
(b) 2-(hydroxymethyl)benzoic acid acts as a bidentate ligand and forms complexes with transition metal ions such as Fe^{3+}.

(i) 2-(hydroxymethyl)benzoic acid can be formed from phthalic acid. Explain the difference in boiling point between phthalic acid and its isomer, terephthalic acid.

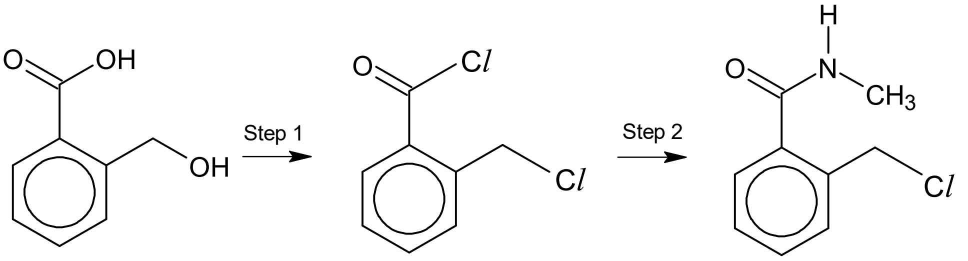


phthalic acid



terephthalic acid **[2]**

Compound **Y** can be made from 2-(hydroxymethyl)benzoic acid in the following two steps.



2-(hydroxymethyl)benzoic acid **X** **Y**

(ii) Explain the different reactivities of the two chlorine atoms in compound **X**. **[2]**

(iii) Suggest reagents and conditions for step 1 and step 2. **[2]**

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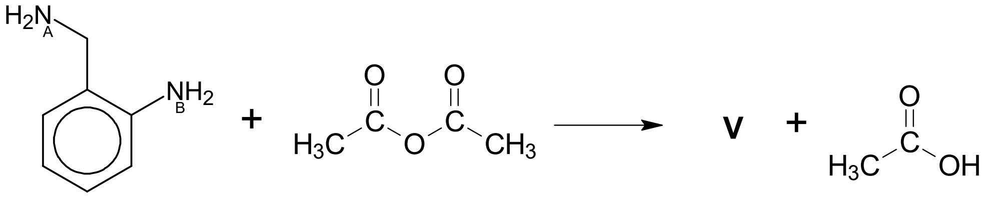
(c) Ethanoic anhydride, $(CH_3CO)_2O$, reacts in a similar way with amines as acyl chlorides. The following reaction is a nucleophilic acyl substitution between $(CH_3CO)_2O$ and compound **U**.



U

ethanoic anhydride
1 mole

Fig. 4.1

(i) Explain the relative basicity of N_A and N_B atom in compound **U**. **[2]**

(ii) In nucleophilic substitution reactions, stronger bases tend to be stronger nucleophiles.

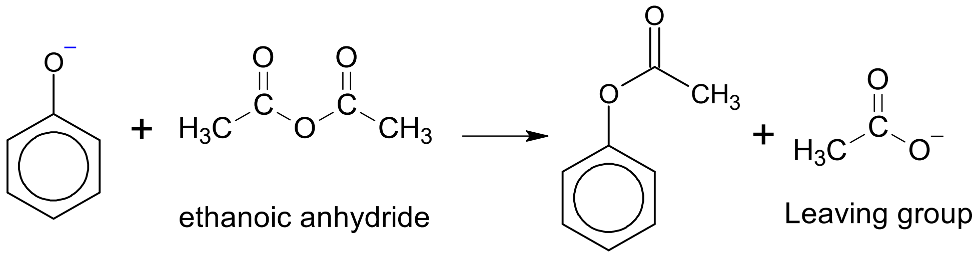
Suggest the structure of compound **V**, $C_9H_{12}N_2O$. **[1]**

(iii) One of the factors that affects the rate of nucleophilic acyl substitution is the nature of the leaving group on the acid anhydride or acyl chloride.

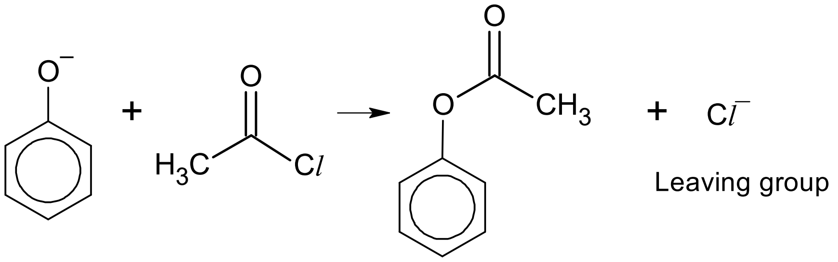
Leaving groups (e.g. Cl^-, CH_3COO^-) that give rise to more stable anions are more readily substituted, therefore increasing the rate of the reaction.

A student proposed two reactions to synthesise phenyl ethanoate using phenoxide ions.

Reaction **1**



Reaction **2**



Explain why reaction **1** is a better method to synthesise phenyl ethanoate than reaction **2**. **[1]**

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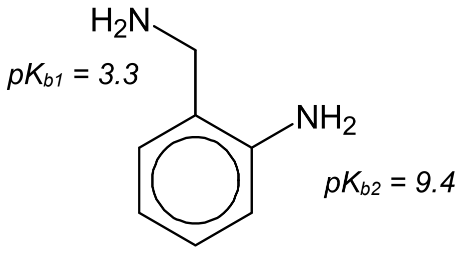
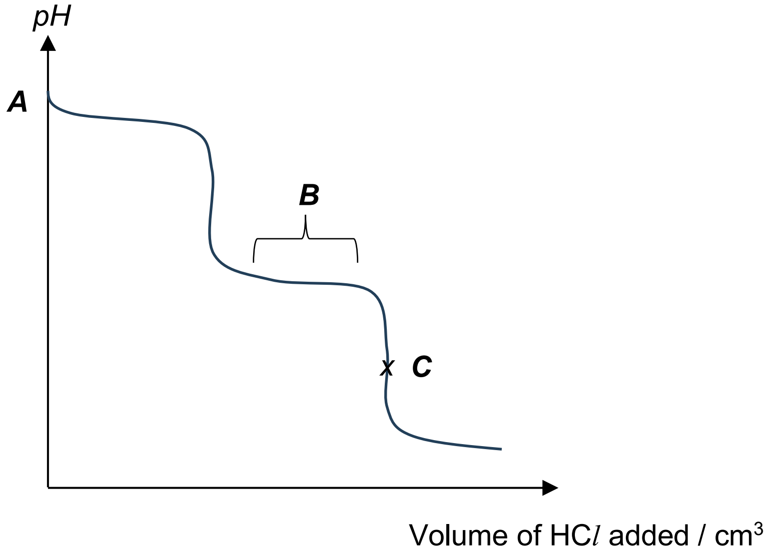
(d) The two pK_b values for each amine groups in **U** is shown below.



U

The pH curve below shows the addition of 0.010 mol dm^{-3} HC*l* to 10.0 cm^3 of 0.020 mol dm^{-3} compound **U**.



(i) Calculate the pH at point **A**. **[2]**

(ii) Draw the two organic structures at region **B** and explain how these species help to maintain the pH of the solution when a small amount of H^+ or OH^- is added. **[3]**

(iii) Calculate the concentration of the salt at point **C**. **[2]**

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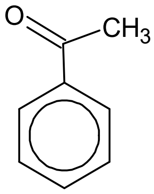
5 **(a)** Aluminium is a lightweight, strong and corrosion-resistant metal, widely used in aerospace, construction, packaging and electrical transmission. Its compounds are important in manufacturing, water treatment and pharmaceuticals. One such compound is anhydrous aluminium chloride which catalyses the synthesis of acetophenone from benzene, which is similar to Friedel-Crafts alkylation.



Acetophenone

(i) Write an equation to show how aluminium chloride functions as a Lewis acid catalyst in the synthesis of acetophenone by using a suitable acyl chloride. **[1]**

(ii) Explain, with the aid of an equation, why aluminium chloride must be anhydrous in order for it to function as a Lewis acid catalyst during the synthesis of acetophenone from benzene. **[2]**

(iii) Describe the mechanism for the synthesis of acetophenone from benzene, showing curly arrows, charges and any relevant lone pairs. **[2]**

(iv) Suggest a simple chemical test to confirm the presence of acetophenone. **[2]**

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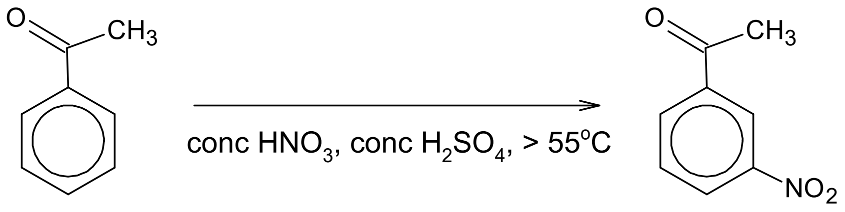
(b) **(i)** Both acetophenone and benzene react with nitric acid, but under different conditions to form compounds **S** and **T** respectively.



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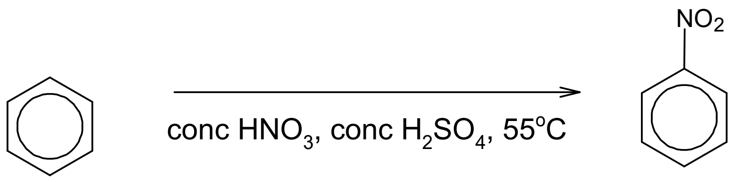

T

Explain why different conditions are needed for these two reactions. **[2]**

(ii) The solubility of **S** and **T** in water are shown in Table 5.1.

Table 5.1

Compound	Solubility in water / mg dm^{-3}
S	108
T	80

Explain, in terms of structure and bonding, the difference in solubility between **S** and **T**. **[2]**

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(c) **E**, **F** and **G** are three elements in Period 3 of the Periodic Table. The pH of the solutions of their oxides and chlorides are as shown in Table 5.2.

Table 5.2

	E	**F**	**G**
pH of oxides	9	7	2
pH of chlorides	6	3	2

(i) Identify the elements **E**, **F** and **G**. **[1]**

(ii) Explain your choice of the elements in **(c)(i)** **[3]**

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(d) In the gaseous phase, aluminium chloride dimerises to form Al_2Cl_6, as shown in the equation below.

$$2\ AlCl_3\ (g) \rightarrow Al_2Cl_6\ (g) \qquad \Delta H_{dimerisation} = -158.8\ kJ\ mol^{-1}$$

(i) Draw the structure of the dimer, Al_2Cl_6 and state the shapes around Al and Cl atom. **[2]**

(ii) The average bond energy for the $Al–Cl$ bond in Al_2Cl_6 can be determined using the relevant data in the *Data Booklet* and the following data.

Enthalpy change of dimerisation of Al_2Cl_6 (g) = –158.8 kJ mol^{-1}
Enthalpy change of formation of $AlCl_3$ (g) = – 248.6 kJ mol^{-1}
Enthalpy change of atomisation of Al (s) = + 326 kJ mol^{-1}

Construct an energy cycle to calculate the average bond energy for the $Al–Cl$ bond in Al_2Cl_6. **[3]**

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Additional Answer Space

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

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