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 XX 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]

The mixing/combining of one (2)s and one (2)p orbital of C to form (two) sp hybrid orbitals, which are arranged in a linear manner.

(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]**

There are two sp hybrid orbitals and two p orbitals with 1 electron each. C-C σ bond is formed from (head on) sp-sp overlap, when the sp hybrid orbital overlaps head-on with the sp hybrid orbital of C that also contains 1 electron. There is (unhybridised) p orbital with 1 electron. C-C π bond is formed when the p orbital of C overlaps side-on with the p orbtial of C that also contains 1 electron.

(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]**

CaC_2 has a giant ionic lattice structure with strong electrostatic attractions/ionic bond between oppositely charged ions.

C_2H_2 has a simple molecular structure with weak intermolecular instantaneous dipole - induced dipole attractions are easily broken.

More energy required to break the stronger ionic bonds, hence CaC_2 has higher melting point than C_2H_2 and is a solid.

(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]

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

$\Delta H_r^\ominus$ = $\Sigma\Delta H_f^\ominus$ (products) – $\Sigma\Delta H_f^\ominus$ (reactants)

= +226.6 – 985.2 – [–59.0 – (2 × 285.8)]

= $\underline{-128 \text{ kJ mol}^{-1}}$

(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]**

The standard enthalpy change of combustion, $\Delta H_c^\ominus$, is the enthalpy change/energy change/released when one mole of gaseous C_2H_2 is completely burnt in excess oxygen at standard conditions of 298 K and 1 bar.

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

$$\text{H–C}\equiv\text{C–H (g)} + \frac{5}{2}\text{O=O (g)} \rightarrow 2\ \text{O=C=O (g)} + \text{H–O–H }(l)$$

Bonds broken	**Bonds formed**
2 BE(C–H)	4 BE(C=O)
BE (C≡C)	2 BE(O–H)
$\frac{5}{2}$ BE(O=O)	

$\Delta H_c^\ominus$ = [2 BE(C–H) + BE (C≡C) + $\frac{5}{2}$ BE(O=O)] – [4 BE(C=O) + 2 BE(O–H)]

$$\Delta H_c^{\ominus} = [2 \times (410) + (840) + \frac{5}{2} \times (496)] - [4 \times (805) + 2 \times (460)]$$

$$= -1240 \text{ kJ mol}^{-1}$$

(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]**

Bond energy values are for gaseous compounds, whereas water is a liquid, hence the difference between the standard enthalpy changes of combustion.

OR

The value calculated in (c)(ii) did not take into account the standard enthalpy change of vapourisation/condensation of water.

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

*Condition must be dry, no water, no flame, no oxidiser

Use airtight, waterproof containers or

(Prevents contact with atmospheric humidity or accidental water exposure)

Store in a cool, dry, well-ventilated area away from water sources (e.g., sprinklers, pipes) or

No open flames/ignition sources in storage areas (acetylene is highly explosive) or

Store away from oxidisers (nitrates, chlorates, peroxides etc) and water or

For bulk storage, use nitrogen (N_2) or argon purging to displace oxygen and prevent acetylene accumulation / store in inert gas

Or

Store in anhydrous condition

(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]**

C_2H_2 is a Brønsted-Lowry acid as it donates proton to NH_2^-.

In the acid-base reaction, a H^+ is transferred from C_2H_2 to a NH_2^-.

C_2H_2 and C_2H^- is a conjugate acid-base pair, which differs by one H^+.

Or

NH_2^- and NH_3

(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]**

NH_3

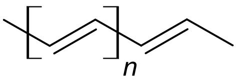
It is a weaker acid that C_2H_2 as the large K (>1) value implies that the position of equilibrium lies more on the right, favouring the donation of H^+ from C_2H_2.

(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.

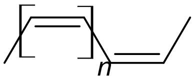
$$n\ HC{\equiv}CH \rightarrow -[CH{=}CH]_n-$$

$-[CH{=}CH]_n-$ 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]**



trans



cis

Cis-trans isomerism

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.

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

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

I_2 serves as the oxidising agent as it gains electron from polyacetylene. Or the oxidation number of iodine changes from 0 to -1 or -1/3, implying it is reduced.

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

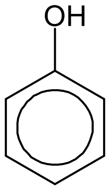
Polarons formed can act as mobile **charge carriers.**

Detailed reasons (not required)

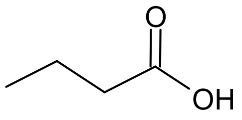
- I_2 oxidises polyacetylene, removing π-electrons to form I_3^- and leaving radical cations (polarons).
- Polarons delocalise over 4–6 CH units, creating mobile holes.
- These holes move under an electric field, enabling current flow.
- High doping fills the polymer with charge carriers, reducing resistance.

[Total: 22]

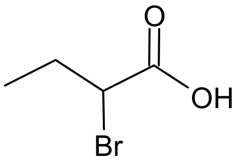
2 **(a)** Deduce the order of increasing acid strength of the following compounds. Explain your answer.



phenol



butanoic acid



2-bromobutanoic acid

[3]

Acidity : phenol < butanoic acid < 2-bromobutanoic acid

$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$

$RCO_2H \rightleftharpoons H^+ + RCO_2^-$

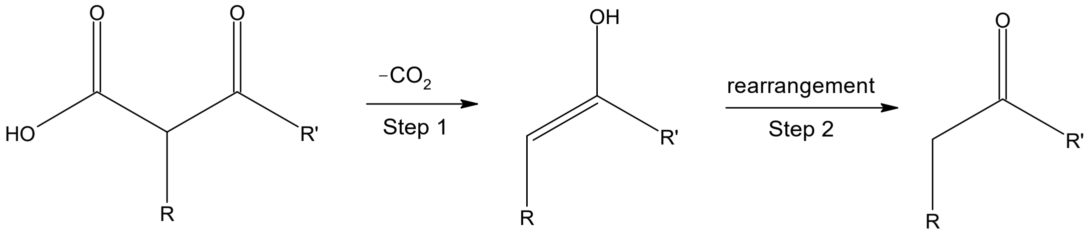
In the phenoxide ion of phenol, $C_6H_5O^-$, the negative charge / lone pair of electrons on O delocalises into the benzene ring. This extent of charge dispersal / stabilisation is less that in the $CH_3CH_2CH_2COO^-$ ion in which the negative charge / lone pair of electrons is delocalised over the O-C-O bond / delocalised over the C=O bond / delocalised over the two O atoms, hence less H^+ donated.

2-bromobutanoic acid is the strongest acid. Bromine is electron withdrawing / electronegative and would disperse the negative charge on O to greater extent. Hence, its anion/conjugate base is most stable and donates H^+ most readily than butanoic acid.

(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:

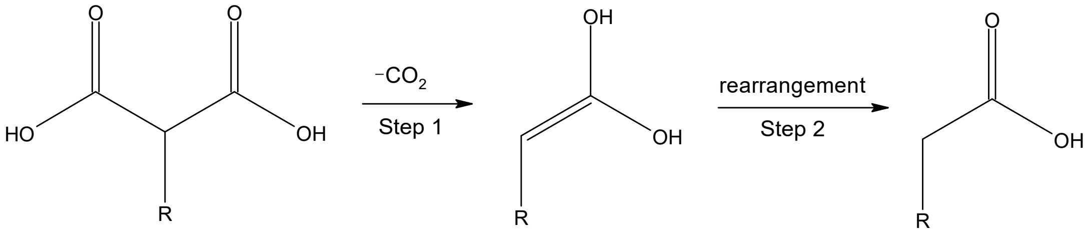
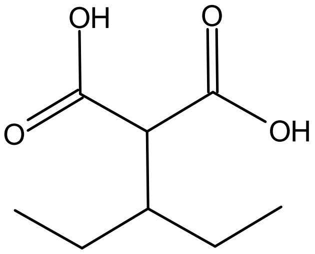


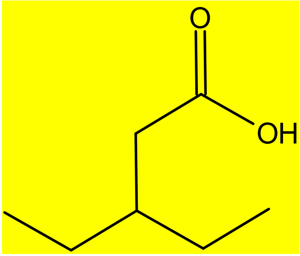
Fig. 2.1

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

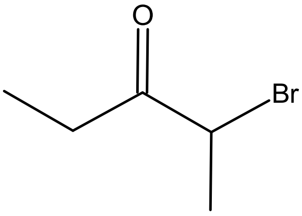


K

[1]



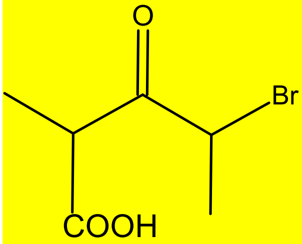
(ii) Two different acids, **M** and **N**, each can undergo decarboxylation to give **L**.

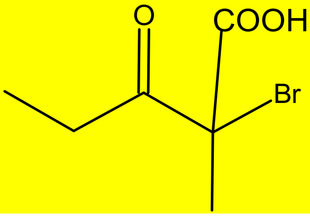


L

[2]

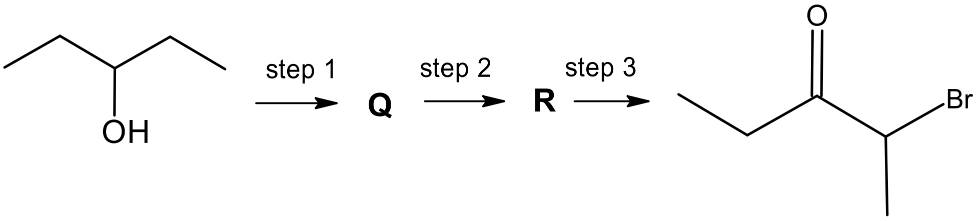
Suggest possible structures of **M** and **N**.





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

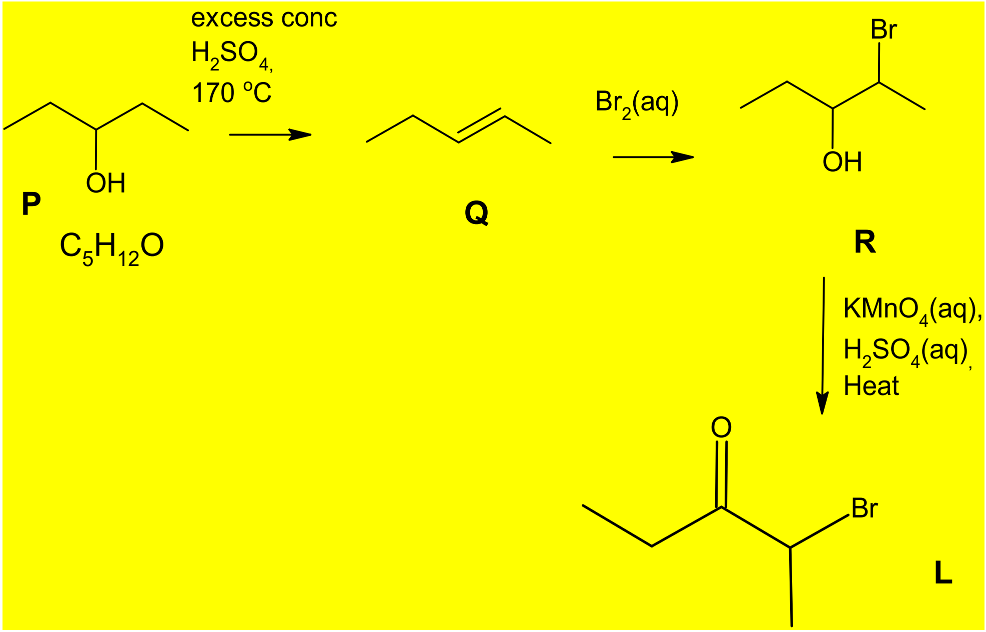
State the reagents and conditions required for each step and suggest structures for the organic compounds **Q** and **R**.



L

Fig. 2.2

[5]



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

$$2R–CO_2^- \rightarrow R–R + 2CO_2 + 2e^-$$

$R = –CH_3, –CH_2CH_3$, 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]**

Products at the cathode: $NaOH(aq)$ and $H_2(g)$

Anode: $2CH_3CO_2^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^-$

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Overall: $2CH_3CO_2^- + 2H_2O \rightarrow CH_3CH_3 + 2CO_2 + 2OH^- + H_2$

(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]**

$Q = I \times t = (2.0)(55 \times 60) = 6600$ C

$2CH_3CO_2^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^-$

$Q = n_eF$

Amt of e^- = 6600/96500 = 0.06839 mol

Amt of ethane = 0.5 x 0.06839 = 0.03420 mol

Mass of ethane = 0.03420 x 30.0 = 1.03 g

(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]**

$Ba(CH_3COO)_2 \rightarrow BaCO_3 + (CH_3)_2CO$

(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]**

Down the group, the ionic radius of M^{2+} increases, the charge density decreases, the polarising power of M^{2+} decreases OR the extent of the polarisation of the electron cloud of the anion, $CH_3CO_2^-$ decreases, hence, the C-O bond in the anion is weakened to a lesser extent. More energy is required to decompose MO_2. Hence, the thermal stability of Group 2 ethanoates increases down the group.

[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]

$2HX \rightleftharpoons X_2 + H_2$

Thermal stability decreases from HC*l* to HBr and to HI.

Atomic radius / size of halogen atom increases from C*l* to Br and to I. Hence, the extent of effective orbital overlap between valence orbital of the halogen and 1s of H becomes poorer down the group.

The strength of H-X decreases from HC*l* to HBr and to HI.

OR

Thermal stability decreases from HCl to HBr and to HI.

Electronegativity decreases from Cl to Br and to I.

The smaller the electronegativity difference between the H and X, the less polar the bond, the weaker the bond down the group.

(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]

High temperature, low pressure

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

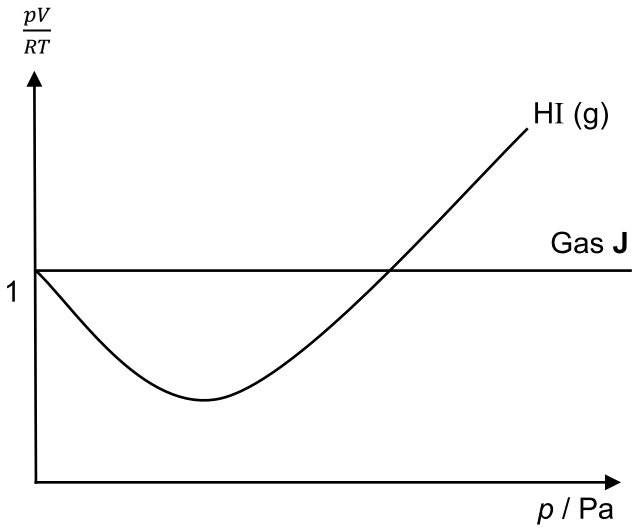


Fig. 3.1

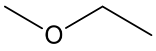
Explain the shape of the graph for HI gas and gas **J**. Your answer should include references to intermolecular forces.

[2]

pV/RT is constant for gas J as pressure increases. This is because gas J is an ideal gas with negligible intermolecular forces of attraction.

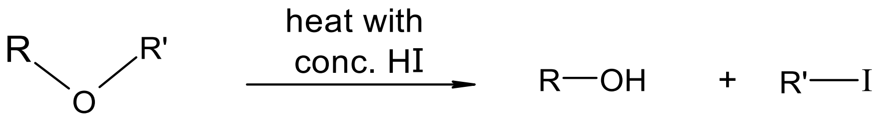
HI gas is a non-ideal gas/real gas with significant intermolecular forces of attraction / permanent dipole-permanent dipole interactions. As the pressure increase, the gas molecules are packed more closely together and intermolecular forces between gas molecules become significant. Hence, HI gas deviates from ideality.

I 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

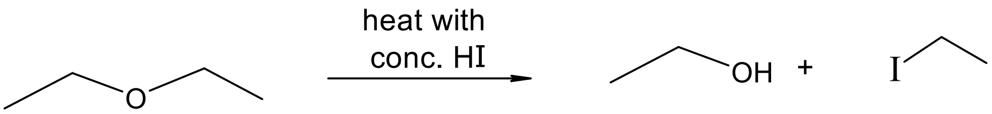
When reacted with hot concentrated solutions of hydroiodic acid, HI, ether can form an alkyl halide and an alcohol as shown in Fig. 3.2.



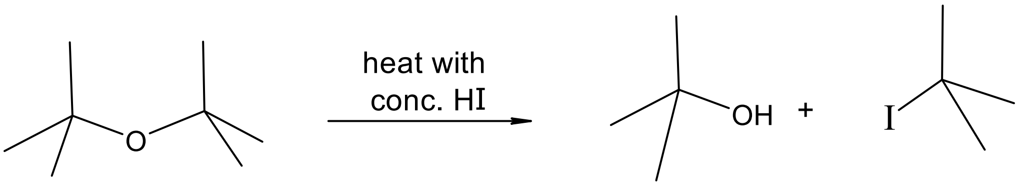
where R and R' are different alkyl groups

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]

In primary/secondary ethers, the reactive C does not have many bulky groups around it / experiences least steric hindrance. Hence, I^- can attack the carbon from the back of the C-O bond easily through S_N2. This was not possible for tertiary ethers as it has 3 bulky groups ($–CH_3$) attached to that carbon atom.

For tertiary ethers, a tertiary carbocation is formed when it undergoes S_N1. The electron donating alkyl groups ($-CH_3$) disperse the positive charge and increase the stability of the tertiary carbocation. This was not possible for primary or secondary ethers as the primary/secondary carbocation formed is not as stable.

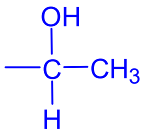
(ii) Compound **A**, $C_7H_{16}O$, is an ether, and it reacts with hot concentrated solution of hydroiodic acid, HI, to form compound **B**, $C_6H_{14}O$, and compound **C**.

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.

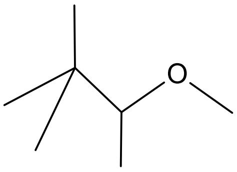
With reference to Fig. 3.2, deduce a possible structure for **A**. Hence, suggest the structures for **B**, **C** and **D**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound.

[8]

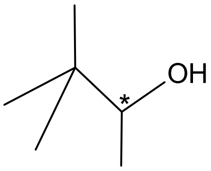
Observations	***Deductions***
Compounds **A**, $C_7H_{16}O$, reacts with hot concentrated solution of hydroiodic acid to form compound **B**, $C_6H_{14}O$ and compound **C.**	Given the molecular formula and the reaction of ether with HI, Compound **B** is an **alcohol / ROH / -OH**. Hence, Compound **C** is an **alkyl halide / RX**
B is found to rotate plane-polarised light.	B contains a **chiral C** that is attached to 4 different groups.
B forms a yellow precipitate with alkaline aqueous iodine.	**B** undergoes **oxidation** with alkaline aqueous iodine **B** contains a  $-CH(OH)CH_3$.

When **B** reacts with hot concentrated H_2SO_4, only compound **D**, C_6H_{12}, is formed.	**B** undergoes **elimination** to form **D only.** **D** is an **alkene** / **C=C** This implies that there is only 1 way of eliminating -H and -OH from **B** OR There are no H attached to adjacent C.
C reacts with hot ethanolic $AgNO_3$ to form yellow precipitate.	**C** undergoes **nucleophilic substitution** to form yellow precipitate, **AgI** . **C** is confirmed an **alkyl iodide /iodoalkane/alkyl halide/halogenoalkane**

A:

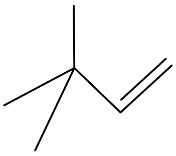


B:



C: CH_3I

D:



(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.

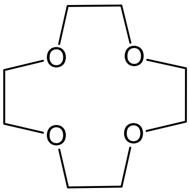


Fig. 3.3

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

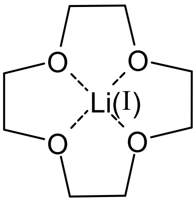


Fig. 3.4

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

Li^+ is <u>smaller</u> than K^+ and can fit the size of the cavity/hole in 12-Crown-4 better.

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

<u>Ion-dipole interaction</u> OR <u>dative bond</u>

(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]

$$\frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_0} = 10^{-\frac{kt}{2.3}} = 10^{-\frac{\frac{0.693}{2}\times 0.5}{2.3}} = 0.8408$$

Time can be in years or months

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Percentage decrease

$= \left(1 - \frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_0}\right) \times 100\%$

= 15.9%

[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]**

Due to the close similarity in energies of the 3d and 4s subshells/orbitals, both 3d and 4s electrons can be removed from manganese or shared to form stable ions of different oxidation states

(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]**

Density = mass/volume (not marking point)

Accept density values above 1.53 but less than 8.83

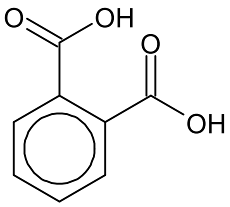
Manganese has a larger relative atomic mass than calcium but smaller relative atomic mass than cobalt.

Manganese has a smaller atomic radius than calcium but bigger atomic radius than cobalt.

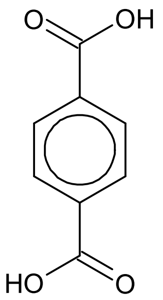
This results in a more closely packed metallic lattice / closer packing in manganese compared to calcium.
OR
This results in a less closely packed metallic lattice / poorer packing in manganese compared to cobalt.

(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.



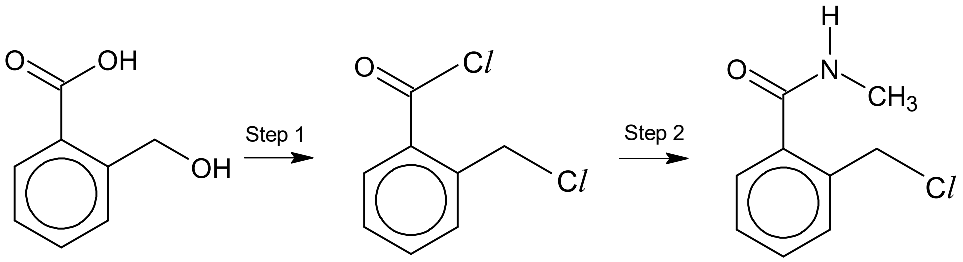
phthalic acid



terephthalic acid **[2]**

Phthalic acid and terephthalic acid are both polar simple covalent molecules with hydrogen bonding. However, phthalic acid can form intra-molecular hydrogen bond, resulting in less extensive / weaker intermolecular hydrogen bonding. Lesser energy is required to overcome the hydrogen bond OR Phthalic acid has a lower boiling point.

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]**

The C atom of C=O is more electron deficient or more $\delta+$ as it is connected to two / more electronegative atoms, C*l* and O. Hence, the electron deficient C is more readily attacked by nucleophiles.

For the other Cl atom, the carbon is only bonded to one / less electronegative C*l* atom and is less electron deficient or less $\delta+$, so it is less readily attacked by nucleophiles.

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

Step 1: $SOCl_2$ or PCl_5 or PCl_3, heat

Step 2: CH_3NH_2

(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**.

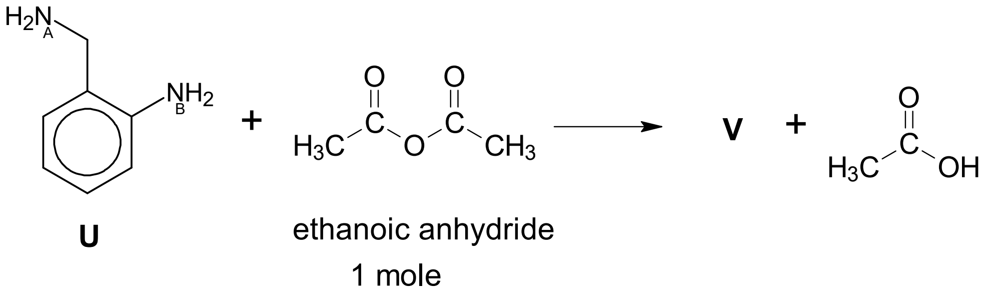


Fig. 4.1

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

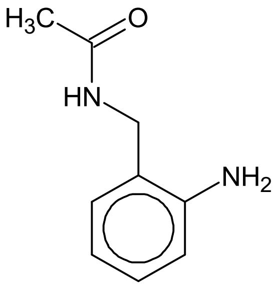
The phenylamine, N_B has the lone pair of electrons on N delocalises into the benzene ring and decreases its availability for donation to H^+, making phenylamine less basic.

The aliphatic amine, N_A has the electron donating group that increases the availability of lone pair of electrons on N for donation to H^+, making the aliphatic amine more basic.

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

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

Compound V:



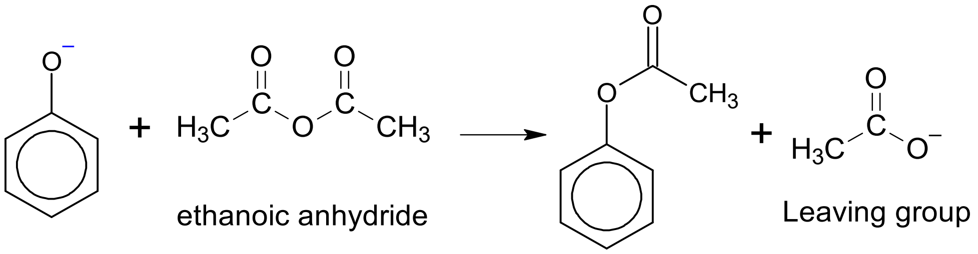
Note: Aliphatic amine is stronger nucleophile than phenylamines. The lone pair of electrons on N of phenylamine is delocalised into the benzene ring, hence it is less available to act as a nucleophile.

(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.

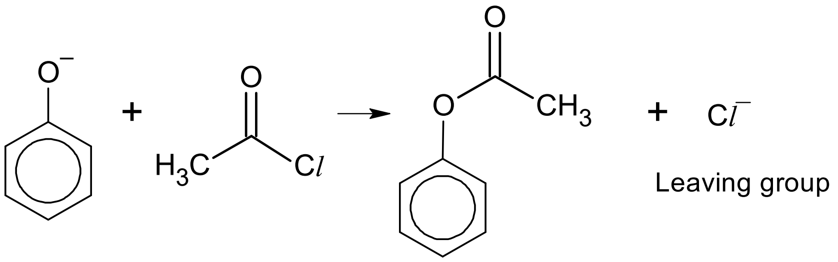
Leaving groups (e.g. Cl^-, CH_3COO^-) that give rise to more stable anions are more readily substituted, therefore increasing the rate of the reaction.

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

Reaction **1**



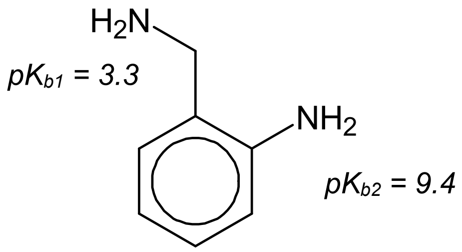
Reaction **2**



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

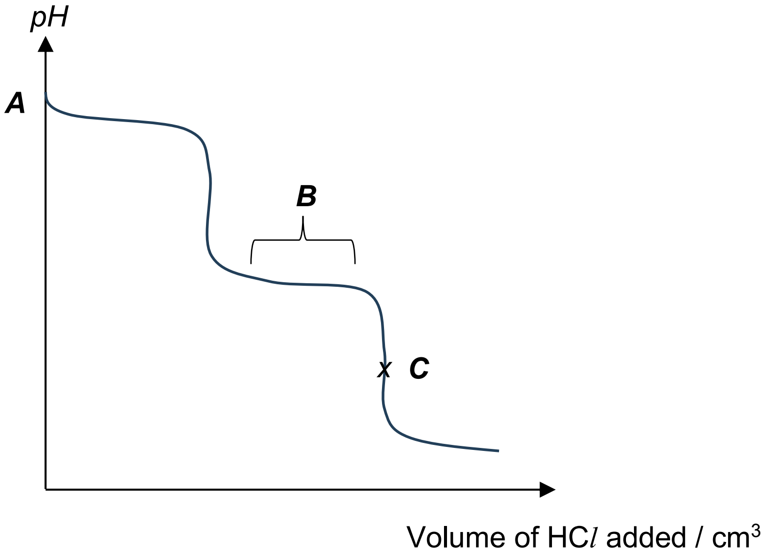
The lone pair of electrons / negative charge on the leaving group, $CH_3CO_2^-$ is delocalised over two highly electronegative oxygen atoms / delocalised over O-C-O . Hence, $CH_3CO_2^-$ is more stable, making it a better leaving group.

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

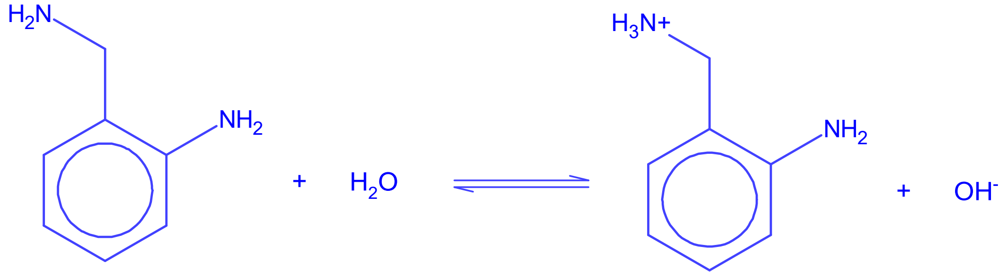


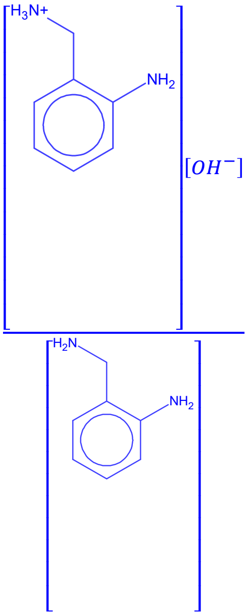
U

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]**



$K_b =$  $= \frac{[OH^-]^2}{0.02}$

(formula not required)

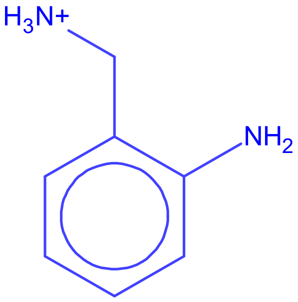
$10^{-3.3} = \frac{[OH^-]^2}{0.02}$

$[OH^-] = 3.166 \times 10^{-3}$ mol dm^{-3}

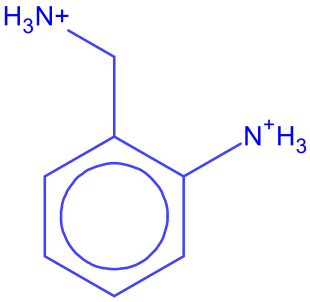
pOH = $-\lg 3.166 \times 10^{-3} = 2.50$

pH = $14 - 2.50 = 11.5$

(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]**

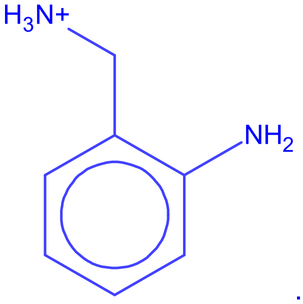


Base



Conjugate acid

Small amount of H^+ ions are removed by the large amount of



Small amount of OH^- ions are removed by the large amount of.

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

No of moles of the salt formed = $\frac{10}{1000}$ x 0.02 = 2×10^{-4} mol

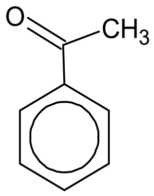
Volume of HC*l* at second equivalence point

= $\frac{\frac{10}{1000} x\ 0.02}{0.01}$ x 1000 x 2 = 40 cm^3

Concentration of the salt = $\frac{2\ x\ 10^{-4}}{\frac{10+40}{1000}}$ = 4×10^{-3} mol dm^{-3}

[Total: 20]

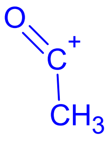
5 **(a)** Aluminium is a lightweight, strong and corrosion-resistant metal, widely used in aerospace, construction, packaging and electrical transmission. Its compounds are important in manufacturing, water treatment and pharmaceuticals. One such compound is anhydrous aluminium chloride which catalyses 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]**

$AlCl_3 + CH_3COCl \rightarrow AlCl_4^- +$



$CH_3C^+{=}O$

(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]**

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

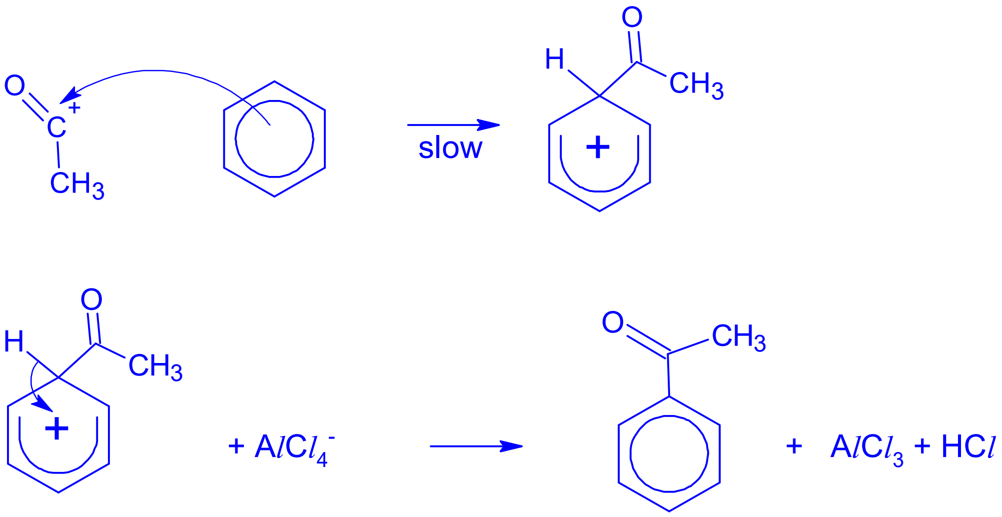
OR

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

In the presence of water, Al^{3+} no longer has empty orbitals as $AlCl_3$ forms the octahedral complex, $[Al(H_2O)_6]^{3+}$.

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

Electrophilic Substitution



- Name of mechaniam
- 1st curly arrow in first step
- Slow
- Structure of intermediate
- 2nd curly arrow in second step
- Regeneration of catalyst and side pdt

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

Reagents and Conditions: I_2 (aq), NaOH (aq), warm

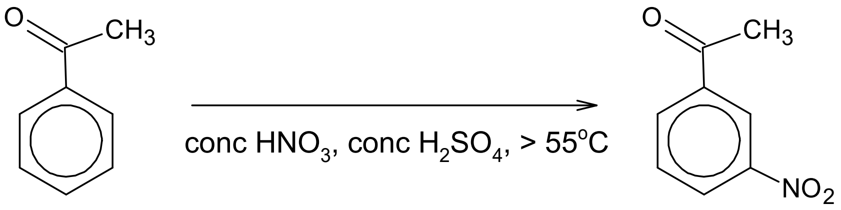
Observations: Yellow ppt formed indicates the presence of acetophenone.

OR

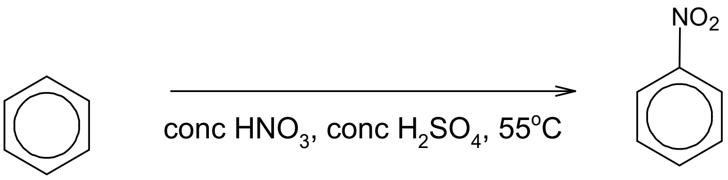
Reagents and Conditions: 2,4-DNPH

Observations: Orange ppt formed indicates the presence of acetophenone.

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

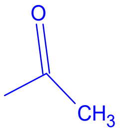


S



T

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



is a deactivating / electron withdrawing group, reducing the electron density in the benzene ring / less susceptible / less reactive to electrophilic attack. Hence, a harsher condition of a higher temperature is needed.

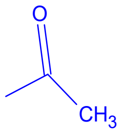
(ii) The solubility of **S** and **T** in water are shown in Table 5.1.

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]**

Both S and T are polar simple covalent molecules with permanent dipole – permanent dipole (pd – pd) between molecules.

S is more soluble because the extra  results in a more extensive / stronger hydrogen bonding√ formed with water molecules which releases more energy to overcome the pd-pd between molecules of S/T and hydrogen bonding between water.

(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]**

E is Mg

F is A*l*

G is P or S

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

E is Mg. From the pH of it's oxide, it is a basic oxide. Given that it's chloride is slightly acidic, partial hydrolysis must have occurred due to the more polarising Mg^{2+} as compared to Na^{+}.

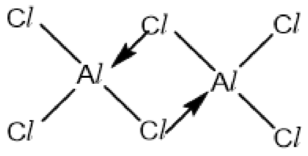
F is A*l*. pH of it's oxide is 7 because it is insoluble in water due to its high lattice energy or strong ionic bonds. It's chloride is more acidic because $A\mathit{l}^{3+}$ is more polarising than Mg^{2+}, increasing the extent of hydrolysis.

G is P. From the pH of it's oxide, it is an acidic oxide. The low pH of it's chloride suggests that complete hydrolysis have occurred, resulting in the formation of HC*l*, a strong acid.

(d) In the gaseous phase, aluminium chloride dimerises to form $A\mathit{l}_2C\mathit{l}_6$, as shown in the equation below.

$$2\ A\mathit{l}C\mathit{l}_3\ (g) \rightarrow A\mathit{l}_2C\mathit{l}_6\ (g) \qquad \Delta H_{dimerisation} = -158.8\ kJ\ mol^{-1}$$

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



Around Al: tetrahedral

Around Cl: bent

(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]**

$$\begin{tikzcd}
2\,AlCl_3\,(g) \arrow[rr, "-158.8\ kJ\,mol^{-1}"] & & Al_2Cl_6\,(g) \arrow[d, "+8\ BE(Al-Cl)"] \\
2Al\,(s) + 3Cl_2(g) \arrow[u, "2(-248.6)\ kJ\,mol^{-1}"'] \arrow[dr, "2(+326)\ kJ\,mol^{-1}"'] & & 2\,Al(g) + 6\,Cl(g) \\
 & 2Al\,(g) + 3Cl_2(g) \arrow[ur, "3(+244)\ kJ\,mol^{-1}"'] &
\end{tikzcd}$$

2(–248.6) + (–158.8) + 8 BE(Al – Cl) = 2(+326) + 3(+244)

BE(Al – Cl) = + 255 kJ mol^{-1}

[Total: 20]

END OF PAPER

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