Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY 9729/03

Paper 3 Free Response **12 September 2023**

2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section B
Answer **one** question.

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

At the end of 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		
Section A	Q1	/23
	Q2	/17
	Q3	/20
Section B	Q4	/20
	OR	
	Q5	/20
TOTAL		80

Section A

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

1 The element lithium and its compounds have been pivotal in the area of development for clean automotive power, based on the use of lithium-ion batteries in electric vehicles and the potential use of lithium hydride and lithium aluminium hydride in hydrogen fuel cell vehicles.

(a) Lithium hydride can be prepared by passing hydrogen gas over heated lithium.

The following data will be useful in this question.

enthalpy change of formation of LiH(s)	= –90.5 kJ mol^{-1}
enthalpy change of atomisation of Li(s)	= +159.5 kJ mol^{-1}
electron affinity of hydrogen atoms	= –73.0 kJ mol^{-1}
enthalpy change of formation of A*l*C*l*$_3$(s)	= –704 kJ mol^{-1}
enthalpy change of formation of LiC*l*(s)	= –408.5 kJ mol^{-1}

(i) Calculate the lattice energy of LiH(s) using relevant data from the above list, together with relevant data from the *Data Booklet.* [2]

(ii) When heated with anhydrous aluminium chloride, lithium hydride forms lithium aluminium hydride, Li*Al*H$_4$. Lithium chloride is also produced. The enthalpy change for this reaction is –276 kJ per mole of Li*Al*H$_4$ formed.

Write an equation, with state symbols, for this reaction and use it together with the relevant data from the above list to calculate a value for the enthalpy change of formation of Li*Al*H$_4$. [3]

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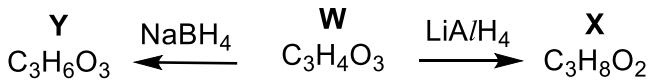
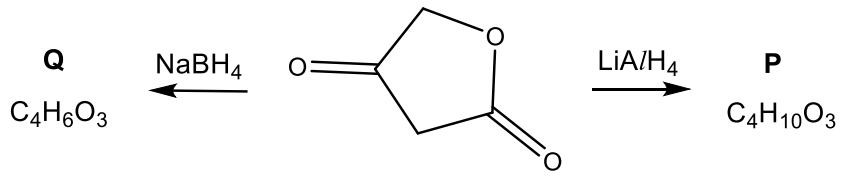
(b) $LiAlH_4$ and sodium borohydride, $NaBH_4$, are useful reducing agents in organic chemistry. An organic compound **W**, $C_3H_4O_3$, undergoes reduction to form **X**, $C_3H_8O_2$ and **Y**, $C_3H_6O_3$ via $LiAlH_4$ and $NaBH_4$ respectively. All three compounds **W**, **X** and **Y** form a yellow precipitate when reacted with alkaline aqueous iodine, and all three compounds react with sodium metal. Compounds **W** and **Y** also react with Na_2CO_3(aq), but compound **X** does not.



(i) Identify the structures for **W**, **X** and **Y**. [3]

(ii) Predict the structures of the products **P** and **Q** of the following reactions. [2]



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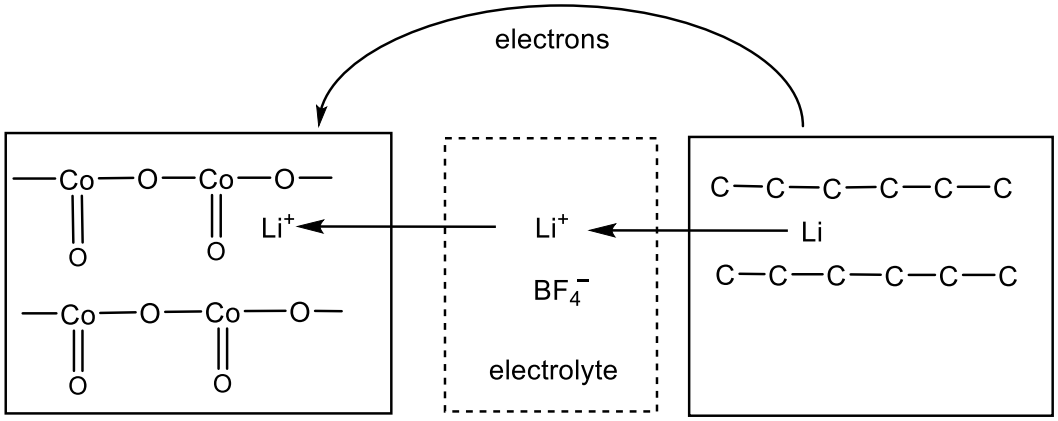
(c) Lithium-ion batteries work by the transfer of lithium ions and electrons from the anode to the cathode. At the anode, elemental lithium inserted between graphite layers is oxidised to Li^+. The Li^+ ions migrate to the cathode via the electrolyte $LiBF_4$, where they react with cobalt oxide, CoO_2, to form lithium cobalt oxide, $LiCoO_2$. This is illustrated in the following diagram in which C–C–C–C is a simplified representation of a layer of carbon atoms in graphite.



(i) State the oxidation states of cobalt in CoO_2 and $LiCoO_2$. [1]

(ii) Construct an equation for the cathode reaction. [1]

(iii) Hence, construct the equation for the overall reaction. [1]

(iv) The lithium-ion battery is capable of producing an e.m.f. of 3.60V. By using suitable data from the *Data Booklet*, suggest a value for the $E^{\ominus}$ for the cathode reaction. [1]

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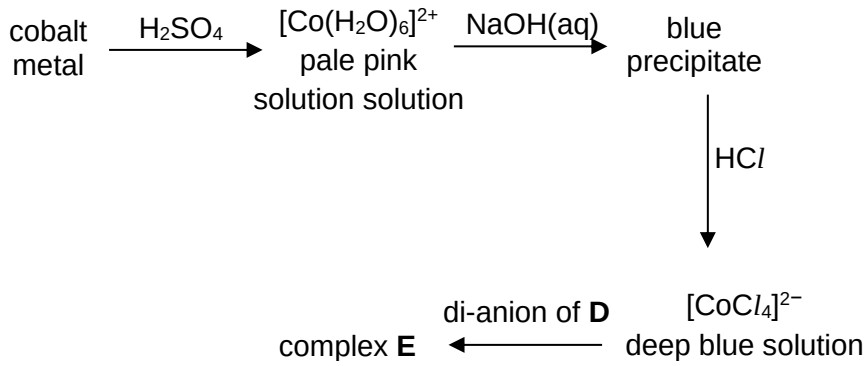
(d) Aside from its use in lithium-ion batteries, cobalt is also widely used in alloys in gas turbines and aircraft jet engines as these alloys are corrosion and wear resistant.

The following sequence of reactions are associated with cobalt complexes.



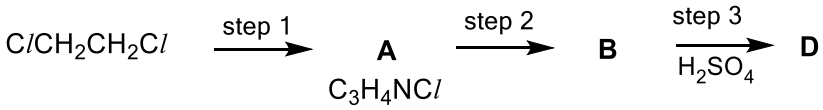
(i) State the electronic configuration of cobalt in $[CoCl_4]^{2-}$. [1]

(ii) Identify the species present in the blue precipitate. Hence, write an equation to show its formation from NaOH(aq) in the earlier step. [2]

(iii) The anion of compound **D** can act as a ligand for many transition metal ions.

$HO_2CCH_2CH_2NHCH_2CH_2CO_2H$
D

Compound **D** can be made by reacting dichloroethane by the following 3-step synthesis.



Suggest the structures of compounds **A** and **B** and the reagents and conditions for steps 1 and 2. [4]

(iv) Two molecules of **D** in basic solution bond to one Co^{2+} ion to form an octahedral complex **E**. Each molecule of **D** forms a di-anion in basic solution and forms three coordinate bonds to the Co^{2+} ion.

Draw a diagram of the structure of complex **E**, showing the 3-dimensional arrangement around the Co^{2+} ion. Indicate the overall charge on this complex. [2]

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[Total: 23]

2 (a) (i) Explain what is meant by the term *entropy* of a chemical system. [1]

(ii) Describe and explain how the entropy of a system will change when 1 mol of $H_2(g)$ at 298 K is added to 1 mol of $N_2(g)$ at 298 K. Assume the pressure of the system remains at 1 bar throughout. [1]

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(b) (i) In the Haber process, a mixture of H_2 and N_2 is added to a sealed vessel and heated. The gases react to form ammonia as shown:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

The entropy change, ΔS, for this reaction is $-99 \text{ J K}^{-1} \text{ mol}^{-1}$. Explain the significance of its sign with respect to the process that is occurring. [1]

(ii) Calculate the maximum temperature below which this reaction is spontaneous. Give your answer in degrees Celsius. [2]

(iii) The spontaneity of the reaction will be higher if the temperature is reduced. Yet the actual temperature range used in the Haber process is still fairly high between 400 to 500 ^{o}C.

Give one advantage and one disadvantage of using a temperature that is much lower than this range. [2]

(iv) When the mixture of H_2 and N_2 in the molar ratio 3:1 is allowed to reach equilibrium, 45% of the hydrogen has reacted. The total pressure in the vessel is 3.00×10^4 kPa at equilibrium.

Write the expression for the equilibrium constant, K_p, for this reaction. Use your expression to calculate the value of K_p for this reaction. Include its units. [4]

(c) The ammonia molecule can react in various ways: as a base, as an acid and as a nucleophile.

This equation shows how ammonia acts as a base: $NH_3 + H_2O \rightleftharpoons NH_4OH$

(i) At –33°C, ammonia acts as an acid in its reaction with sodium hydride, NaH. Write a balanced equation for this reaction and explain how ammonia acts as an acid. [2]

(ii) Ammonia acts as a nucleophile when it reacts with an aldehyde, RCHO (R is an alkyl group) in a 1:1 ratio. This reaction produces water and an organic compound called an imine. An imine is a functional group containing a carbon-nitrogen double bond. This reaction is reversible and an equilibrium will be established between the reactants and products.

Suggest the structure of the imine, and write a balanced equation for the reaction between ammonia and RCHO. [2]

(iii) Describe a simple chemical test you could carry out to confirm the presence of the aldehyde in the equilibrium mixture in **(c)(ii)**.

State what you would observe. [2]

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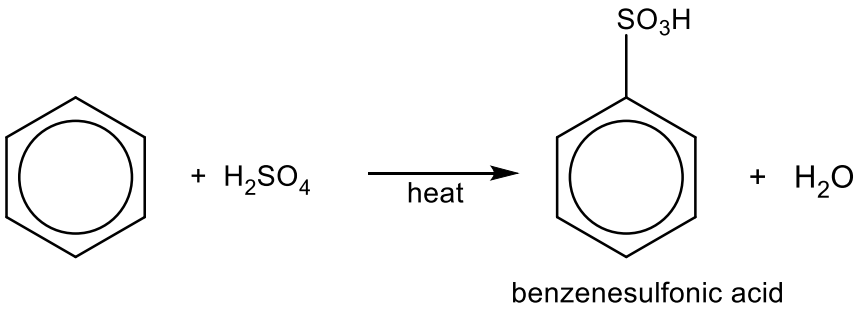
[Total: 17]

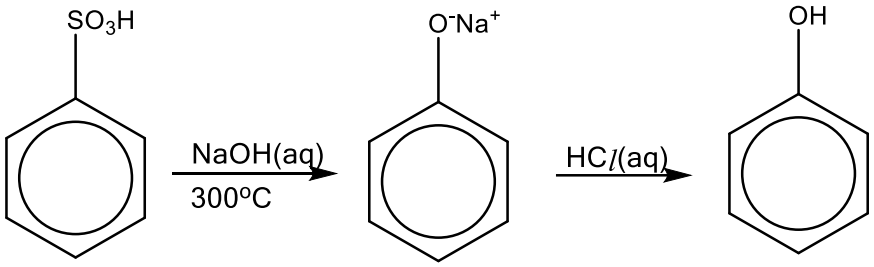
3 Benzenesulfonic acid is often used in the manufacture of surfactants in detergents, dyes and a variety of pharmaceutical drugs. It is produced by heating benzene under reflux with concentrated sulfuric acid for several hours.



benzenesulfonic acid

(a) Benzenesulfonic acid is a useful starting material as it can be easily converted to phenol by heating with NaOH(aq) at 300°C, followed by acidification as shown in reaction 1 below.

Reaction 1



Compound **V** can be synthesised from ethylbenzene in four steps as shown in Fig. 3.1.

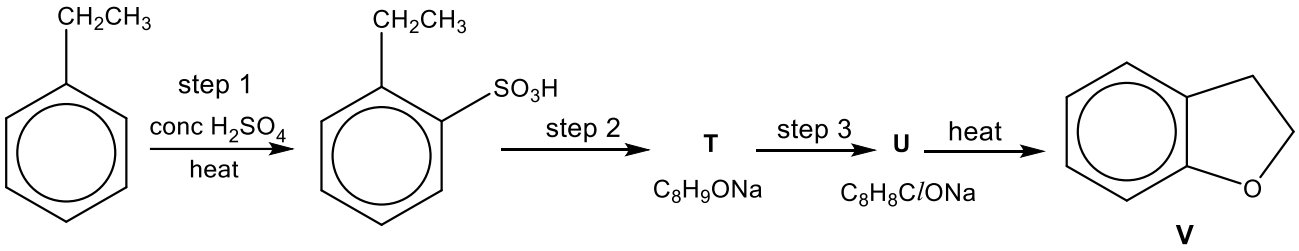


Fig. 3.1.

(i) Deduce the structures of the intermediate organic products **T** and **U**. [2]

(ii) Suggest reagents and conditions for step 2 and step 3. [2]

(iii) When fuming sulfuric acid reacts with alkenes, addition reactions occur. Explain why benzene does **not** undergo addition reactions with fuming sulfuric acid. [2]

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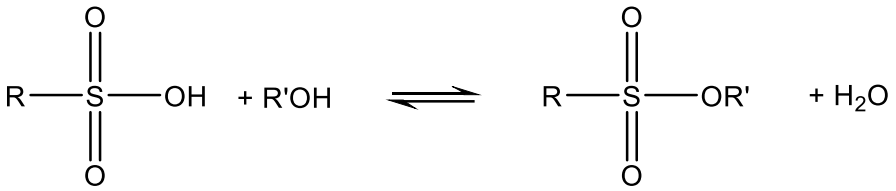
(b) Benzenesulfonic acid is a white crystalline solid and can undergo esterification process with alcohols under anhydrous conditions, to form sulfonate esters, similar to how benzoic acids undergo esterification reactions.



X, $C_{10}H_{14}SO_3$, is a neutral compound. Hydrolysis of **X** gives **Y**, $C_6H_6SO_3$, which is a white solid and **Z**, $C_4H_{10}O$, which does not decolourise acidified $KMnO_4$ on heating.

Identify the structures of **X** to **Z** and write a balanced equation for the hydrolysis reaction involved. [4]

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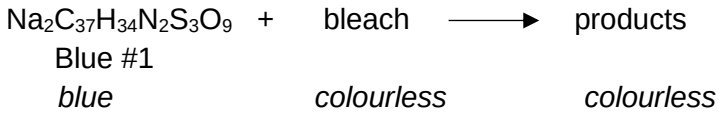
(c) Benzenesulfonic acid is also used in the synthesis of Blue #1, a synthetic organic compound used primarily as a blue colorant for processed foods, medication and cosmetics. It can be oxidised by household bleach to form colourless products, as represented by the equation below.



To study the kinetics of the reaction, a student used a UV spectrophotometer to study the absorbance of Blue #1 at a particular wavelength over time during the bleaching process.

The absorbance of Blue #1 at a particular wavelength is proportional to the concentration of Blue #1 in the solution.

In experiment 1, the student mixes 3.0 cm^3 of 0.1 mol dm^{-3} Blue #1, 1.0 cm^3 of water and 0.5 cm^3 of 3.5 mol dm^{-3} bleach together. The results of experiment 1 are as shown below.

Table 3.1

time (s)	15	30	45	60	75	90	105	120	135
absorbance	0.495	0.424	0.371	0.328	0.285	0.251	0.218	0.191	0.170

(i) Explain why bleach is used in large excess as compared to that of Blue #1. [1]

(ii) Define the term *order of reaction*. [1]

(iii) Given that absorbance measured varies linearly with the concentration of Blue #1, using the data in Table 3.1, but without plotting of any graph, determine the order of reaction with respect to the blue food colouring, Blue #1. [2]

(iv) The student subsequently conducted a few more experiments at 25°C using other volumes of Blue #1 and bleach. The table below shows the results obtained.

Table 3.2

Experiment	Volume of Blue #1 / cm^3	Volume of bleach / cm^3	Volume of distilled water / cm^3	Initial rate of reaction/ mol dm^{-3} min^{-1}
2	4.0	0.5	0.0	0.00882
3	3.0	1.0	0.5	0.01323

Using results from **(c)(iii)** and the data in Table 3.2, deduce the order of reaction with respect to bleach, showing how you arrive at your answers.
Hence write a rate equation for the reaction. [3]

(v) Explain why the total volumes of reactions 2 and 3 must be kept constant. [1]

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(d) Chlorine dioxide, ClO_2 is used for bleaching paper pulp and for some water treatment. It is manufactured from ClO_3^- ions in acid solution.

$$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2 + H_2O$$

(i) This reaction may be carried out by using aqueous hydrogen peroxide, H_2O_2. Use the *Data Booklet* to identify the half-equation for H_2O_2 in this reaction. [1]

(ii) Use your answer to **(d)(i)** to construct the overall equation for the reaction of ClO_3^- ions with H_2O_2 in acid solution. [1]

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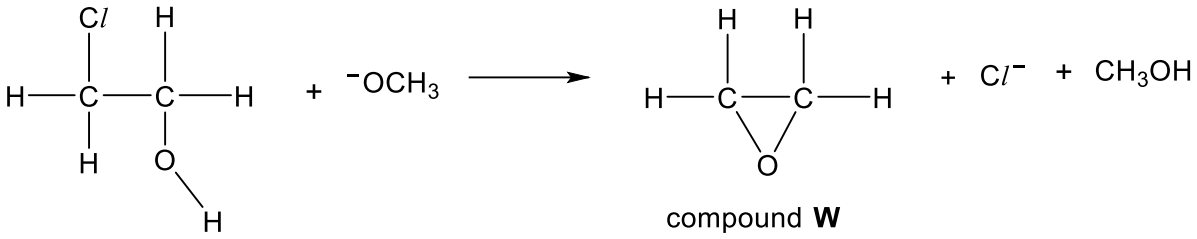
[Total: 20]

Section B

Answer **one** question from this section.

4 (a) (i) 2–chloroethanol, CH_2ClCH_2OH, reacts with sodium methoxide, $CH_3O^-Na^+$, to give compound **W**, which is an epoxide. Epoxides are cyclic ethers which have a 3–membered ring.



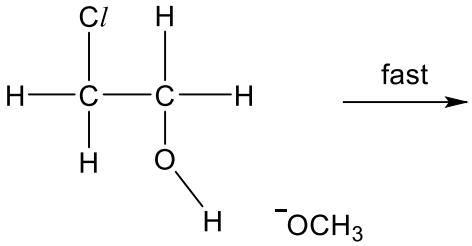
compound **W**

The reaction between CH_3O^- and CH_2ClCH_2OH occurs in two steps.

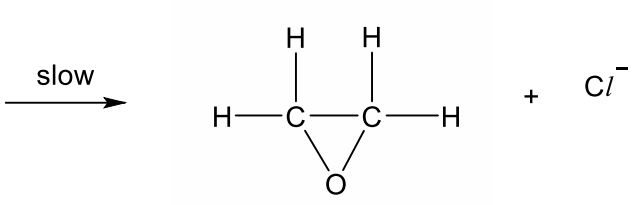
- The first step involves an acid-base reaction.
- The second step involves an intramolecular reaction and it is rate-determining.

Complete the diagram to suggest a mechanism to show how compound **W** is formed. Show all charges and relevant lone pairs, and show the movement of electron pairs using curly arrows. [2]

Step 1



Step 2



compound **W**

(ii) With reference to Step 1 in the mechanism, suggest why 2-chloroethanol is unlikely to undergo the intramolecular reaction in the absence of the methoxide ion. [1]

(iii) The rate of the synthesis increases when CH_2BrCH_2OH is used in place of CH_2ClCH_2OH. Suggest an explanation for this difference in the rate of reaction. [1]

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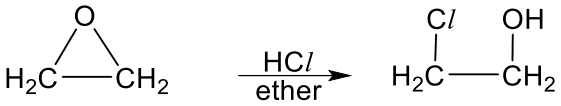
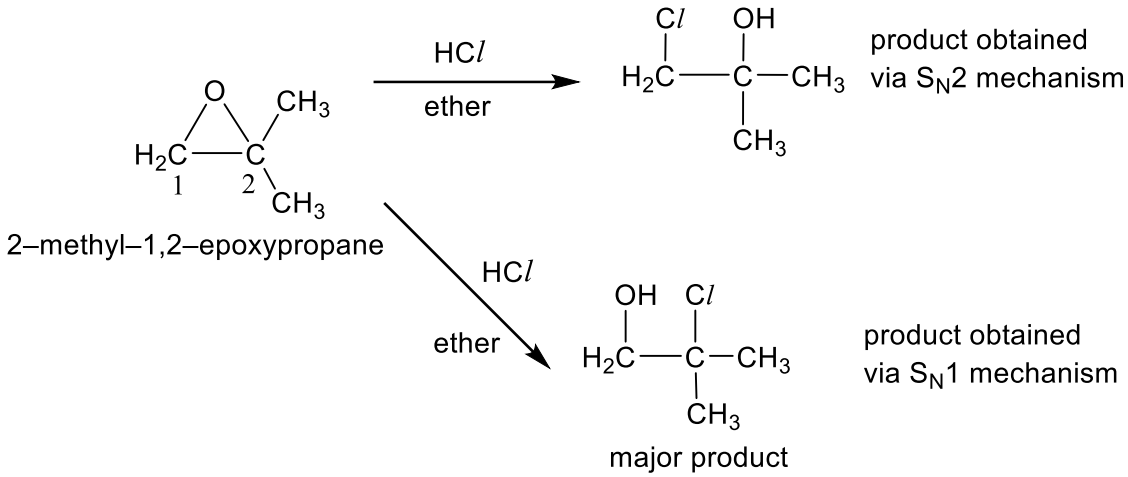
(b) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HC*l* is used in a solvent like ether, the epoxide forms a halohydrin.



The ring–opening reaction of epoxides can proceed via S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetrical, the structure of the product will vary according to which mechanism predominates.

For example, 2–methyl–1,2–epoxypropane reacts with HC*l* via different mechanisms to give the following products.

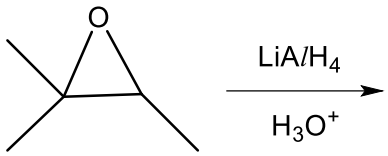


(i) Suggest why the reaction involving the carbon labelled 2 proceeds predominantly via S_N1 mechanism and not S_N2 mechanism. [2]

(ii) Apply your knowledge of VSEPR theory and considering the bond angles within the ring, suggest a reason for the high reactivity of epoxide. [2]

(iii) Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides to form alcohols. S_N2 mechanism usually predominates with these reagents.

Draw the structural formula of the major product formed when the following epoxide reacts with $LiAlH_4$. [1]



(c) Thiols are a class of organosulfur compounds known to have strong unpleasant odours. Data concerning methanethiol, CH_3SH, and two of its analogues are given in Table 4.1 below.

Table 4.1

compound	M_r	atomic radius of atom **Z** in CH_3**Z**H / nm	boiling point / °C	pK_a
CH_3OH	32.0	0.073	65	15.5
CH_3SH	48.1	0.102	6	10.4
CH_3SeH	95.0	0.116	25	≈ 5

(i) Explain the differences in boiling points of the three compounds in Table 4.1. [2]

(ii) Arrange the three compounds in order of **decreasing** acidity and suggest a reason for this trend. [2]

(iii) When each of the three compounds has dissolved, each molecule is surrounded by water molecules. Draw simple diagrams to show how a water molecule interacts with a CH_3SH molecule and with a CH_3OH molecule. Label each diagram to show the type of interaction involved. [2]

(iv) As thiols are the sulfur analogue of alcohols, their relative acidities are often compared. One notable difference is the ability of thiols to react with aqueous alkalis.

Methanethiol reacts with aqueous NaOH according to the following equation:

$$CH_3SH + NaOH \longrightarrow CH_3S^-Na^+ + H_2O$$

Calculate the pH of the solution when 15 cm^3 of 0.10 mol dm^{-3} NaOH is added to 25 cm^3 of 0.10 mol dm^{-3} CH_3SH. [2]

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(d) **X**, **Y** and **Z** are Period 3 elements.

Element **X** forms a white oxide that is insoluble in water.
Element **Y** forms an acidic oxide which produces a white precipitate when shaken with excess aqueous $Ba(NO_3)_2$ solution.
Element **Z** forms a basic oxide that dissolves readily in water.

The oxide of element **X** dissolves when a solution of oxide of element **Y** or **Z** is added to it.

(i) Identify the elements **Y**, **Z** and the oxide of **X** in the above reactions. [1]

(ii) Write two equations to account for the dissolution of the oxide of **X** in the solutions of oxides of **Y** and **Z** above. [2]

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[Total: 20]

5 **(a)** The melting points of pentane, diethylamine and glycine are shown in the table below.

compound	formula	M_r	melting point/ °C
pentane	$CH_3(CH_2)_3CH_3$	72.0	–130
diethylamine	$(CH_3CH_2)_2NH$	73.0	–50
glycine	$H_2NCH(CH_3)CO_2H$	75.0	290

Explain the differences in melting points in terms of the structure and bonding of the compounds. [3]

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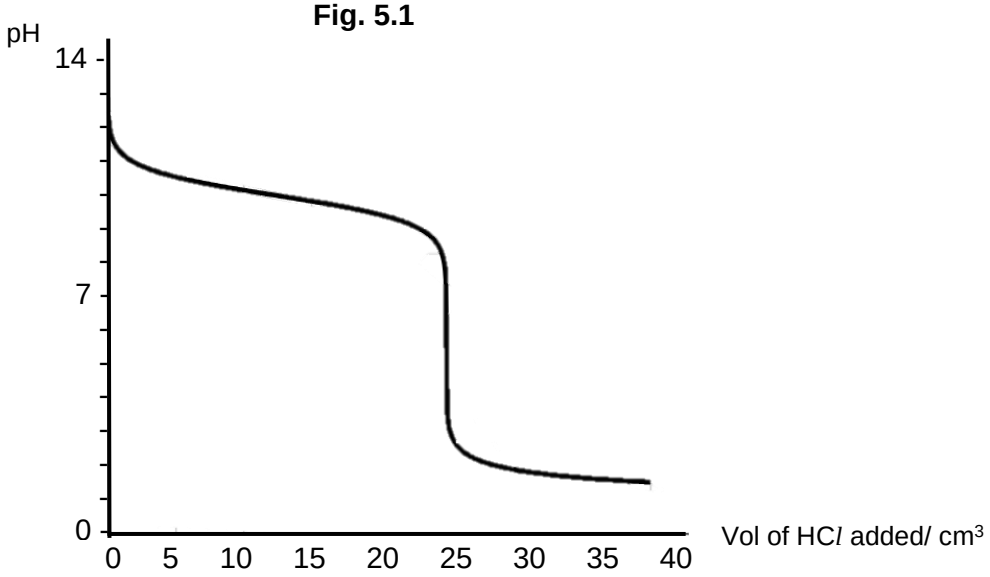
(b) Diethylamine, $(CH_3CH_2)_2NH$, is a weak base, and its K_b is 6.9×10^{-4} mol dm^{-3}.

(i) Describe and explain how the basicity of diethylamine compares to that of ethylamine, $CH_3CH_2NH_2$. [2]

Fig. 5.1 shows the titration curve when 25.0 cm^3 of 0.10 mol dm^{-3} of aqueous diethylamine is titrated with HC*l*(aq).

Fig. 5.1



(ii) Calculate the initial pH of the aqueous diethylamine solution. [1]

(iii) Identify the two major organic species present in this solution over the pH range 10.0-11.0. Explain, with the aid of an equation, why the slope only changes gradually in this region. [2]

(iv) Calculate the pH at the equivalence point. [2]

(c) A breathalyzer is a device that can measure alcohol vapour in a person's breath, enabling the police to tackle drink-driving.

To detect alcohol, a person breathes into the breathalyzer. The breath sample is bubbled through a mixture of sulfuric acid, potassium dichromate(VI) and water. The following chemical reactions take place:

Reaction 1 The sulfuric acid removes the alcohol from the air into aqueous solution.
Reaction 2 The alcohol reacts with potassium dichromate(VI) to produce chromium(III) sulfate, potassium sulfate, ethanoic acid and water.

(i) Suggest another role of sulfuric acid in the breathalyzer. [1]

(ii) Using relevant half-equations from the *Data Booklet* or otherwise, construct a balanced ionic equation for reaction 2, using ethanol as the alcohol. [2]

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(d) The concentration of alcohol in a person's exhaled air is related proportionally to the concentration of alcohol in their blood in a ratio of 1 : 2100. The legal drink-driving limit in Singapore and many other countries is 80 milligrams per 100cm^3 of blood, or 0.08% blood alcohol content.

(i) Calculate the concentration of ethanol, in mg per 100cm^3 of breath, that would correspond to a blood alcohol content of 0.08%. [1]

(ii) Given that the average M_r of air is 28.96, calculate the density of air at room temperature and pressure. [2]

(iii) Hence, given that an average human exhales 500cm^3 of air per breath, calculate the percentage by mass of ethanol vapour in a breath (at room temperature and pressure) that corresponds to a blood alcohol content of 0.08%. [1]

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(e) Upon reaction with potassium dichromate(VI), apart from forming a carboxylic acid, an alcohol can also be oxidised to an aldehyde.

(i) State the conditions required to oxidise an alcohol to an aldehyde. [1]

(ii) The oxidation of an alcohol to an aldehyde can also be carried out using chromic acid via a 3-step mechanism.

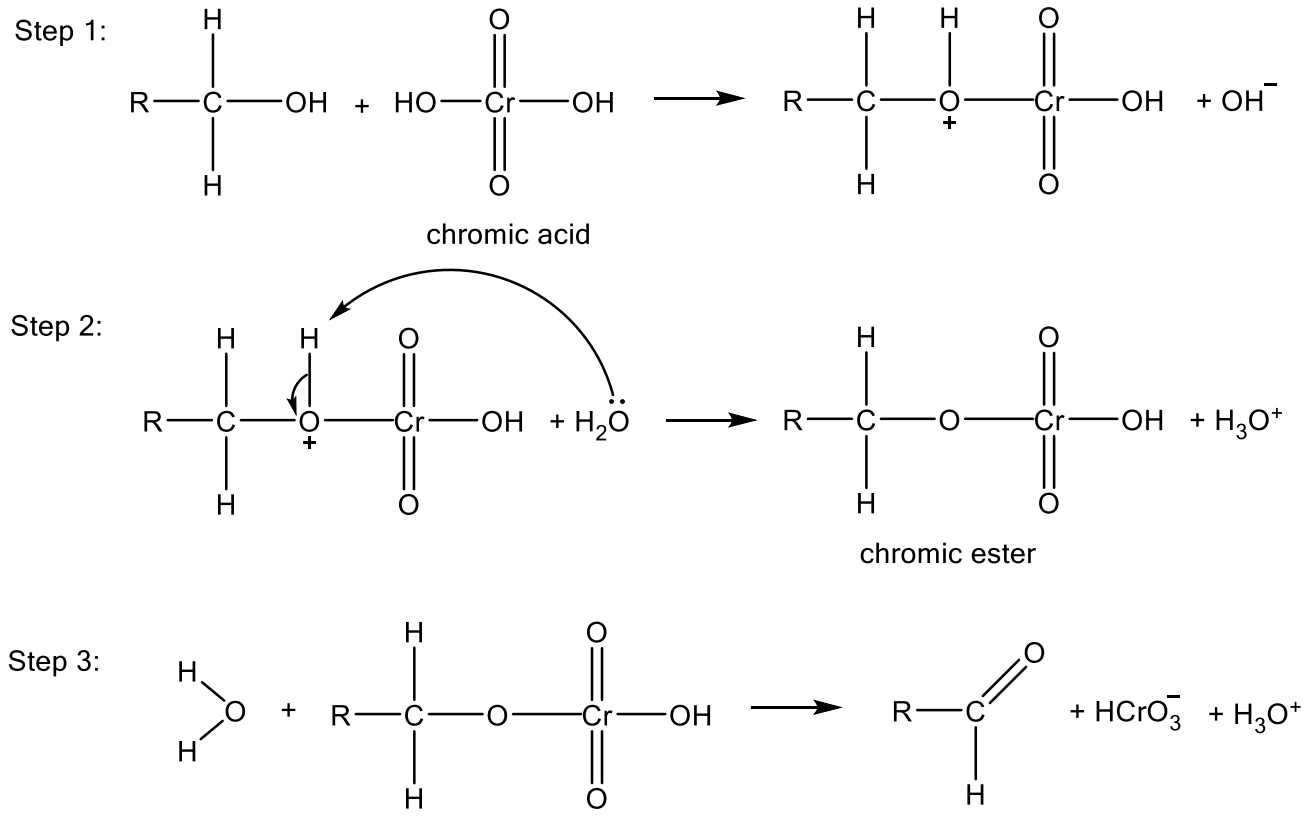
In step 1, the oxygen atom of the alcohol acts as a nucleophile and attacks the chromium atom. This step is analogous to an S_N2 reaction with a –OH group of chromic acid as the leaving group.

In step 2, the oxygen loses a proton and a chromic ester is formed.

In step 3, water extracts a hydrogen atom from the alcohol carbon, and a carbon-oxygen double bond is formed while the O–Cr bond in the chromic ester breaks.

Complete steps 1 and 3 of the mechanism in Fig. 5.2 by drawing curly arrows. Show all relevant dipoles and lone pair electrons in your answer. [2]

Fig. 5.2



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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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