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**

Mark Scheme

This document consists of **28** printed pages

Section A

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

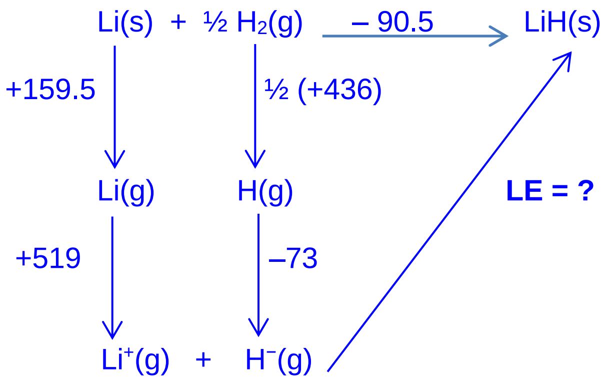
1 The element lithium and its compounds have been pivotal in the area of development for clean automotive power, based on the use of lithium-ion batteries in electric vehicles and the potential use of lithium hydride and lithium aluminium hydride in hydrogen fuel cell vehicles.

(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 $\mathrm{A}l\mathrm{C}l_3$(s)	= -704 kJ mol^{-1}
enthalpy change of formation of $\mathrm{LiC}l$(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]



Using Hess' Law,

$-90.5 = +159.5 + \frac{1}{2}(+436) + 519 + (-73.0) + \text{LE}$

LE = -914 kJ mol^{-1}

The relevant data from the Data Booklet include the **1st IE** of Li(g) (+519 kJ mol^{-1}) and the **BE** of H_2(g) (+436 kJ mol^{-1}).

This question was not well attempted despite it being a fairly straightforward Born Haber cycle for ionic compounds.

Common errors include:

- Not starting with ½ H_2 (g) for hydrogen element.
- Forgetting to include the enthalpy change of atomisation of H_2(g) or not dividing the BE of H_2(g) by 2 to obtain this enthalpy value.
- Attempting to use an energy level diagram but getting confused or unsure of the sign of the arrows and hence the sign of the enthalpy values in the calculations.

(ii) When heated with anhydrous aluminium chloride, lithium hydride forms lithium aluminium hydride, $LiAlH_4$. Lithium chloride is also produced. The enthalpy change for this reaction is –276kJ per mole of $LiAlH_4$ 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 $LiAlH_4$. [3]

$$\begin{array}{lllll} 4LiH(s) & + \; AlCl_3(s) & \longrightarrow & LiAlH_4(s) & + \; 3LiCl(s) \\ 4(-90.5) & \quad -704 & \quad -276 & \mathbf{\Delta H_f = ?} & \; 3(-408.5) \end{array}$$

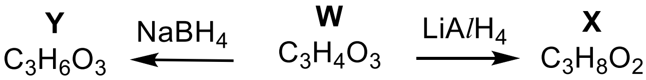
$$\Delta H_r = \sum \Delta Hf(products) - \sum \Delta Hf(reactants)$$

$$-276 = [\Delta H_f + 3(-408.5)] - [4(-90.5) + (-704)]$$

$$\mathbf{\Delta H_f = -116.5\ kJ\ mol^{-1}}$$

This question was also not well attempted.
Common errors include:
- Forgetting or giving the wrong state symbols for the chemical equation.
- Getting the formula for $\Delta H_r = \sum \Delta Hf(products) - \sum \Delta Hf(reactants)$ wrong.
- Forgetting to include factor 3 for $LiCl(s)$ (or 4 for $LiH(s)$) in calculation.

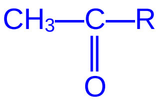
(b) $LiAlH_4$ and sodium borohydride, $NaBH_4$, are useful reducing agents in organic chemistry. An organic compound **W**, $C_3H_4O_3$, undergoes reduction to form **X**, $C_3H_8O_2$ and **Y**, $C_3H_6O_3$ via $LiAlH_4$ and $NaBH_4$ respectively. All three compounds **W**, **X** and **Y** form a yellow 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.



$$\overset{\mathbf{Y}}{C_3H_6O_3} \xleftarrow{NaBH_4} \overset{\mathbf{W}}{C_3H_4O_3} \xrightarrow{LiAlH_4} \overset{\mathbf{X}}{C_3H_8O_2}$$

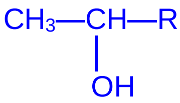
(i) Identify the structures for **W**, **X** and **Y**. [3]

Positive iodoform test suggests the group,



$$CH_3-\underset{\underset{O}{\|}}{C}-R$$

or

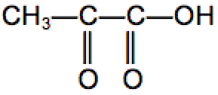


$$CH_3-\underset{\underset{OH}{|}}{CH}-R$$

present in **W**, **X** and **Y**

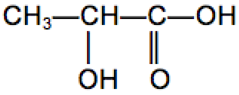
Reacts with Na suggests the alcohols or carboxylic acids functional groups present in **W**, **X** and **Y**.

Reacts with $Na_2CO_3(aq)$ suggests the presence of $-CO_2H$ in **W** and **Y only**.



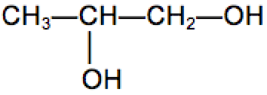
$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH$$

(W)



$$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH$$

(Y)

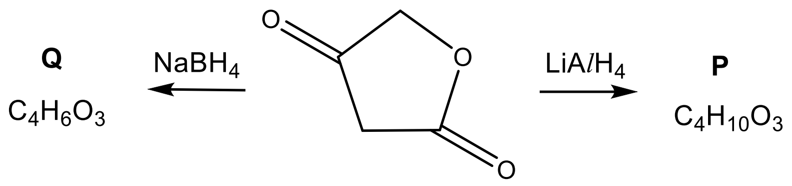


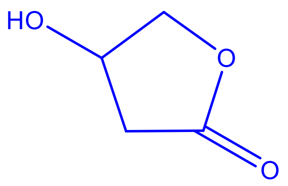
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-OH$$

(X)

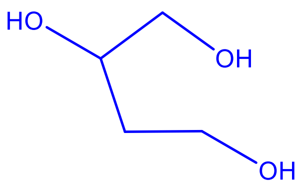
This question was fairly well attempted.
Common errors include:
- Wrongly deducing W contains an aldehyde. This would not be possible in this case as W undergoes a positive iodoform reaction. As a result of the wrong structure of W, the structures for X and Y were subsequently incorrect.

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





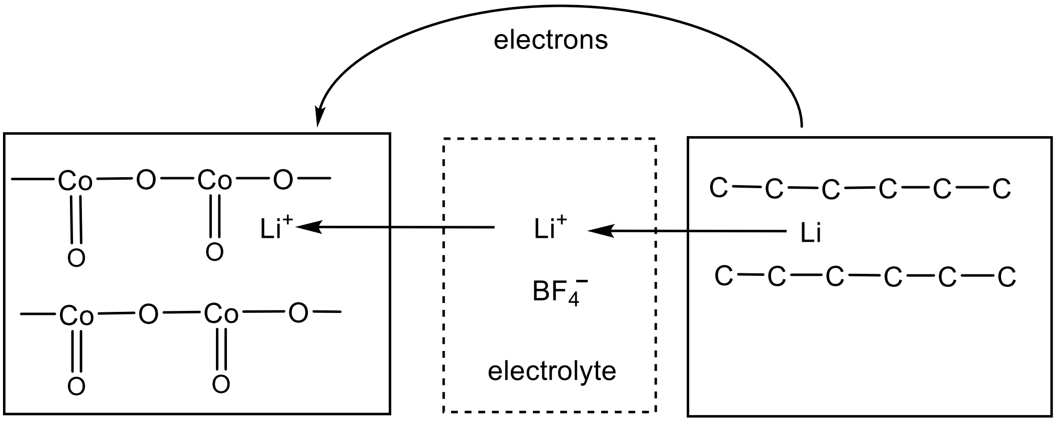
Q



P

This question was well attempted.
- Some candidates were unfamiliar with the reduction of esters to form alcohols.
- Some were also unfamiliar with the specificity of the effects of different reducing agents $NaBH_4$ and $LiAlH_4$ on different organic compound functional groups.

(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-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]

Oxidation state of Co is +4 in CoO_2 and decreases to +3 in $LiCoO_2$

Most candidates were able to score this mark.

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

$Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$

Common error involves using $\rightleftharpoons$ instead of single arrow → in the equation. Note that only reduction occurs at the cathode.
Some candidates missed out accounting for the electron gained in the equation (either not writing e- at all or writing e- on the right side, representing electron loss instead!)

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

$Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$ (reduction at cathode)

$Li \rightarrow Li^+ + e^-$ (oxidation at anode)

$Li + CoO_2 \rightarrow LiCoO_2$ (overall equation)

Some candidates wrongly wrote $\rightleftharpoons$ instead of → in the overall equation.
Some candidates also wrote $Li^+ + CoO_2^-$ as the products formed which is incorrect as the $LiCoO_2$ product mentioned in the question should be in the solid state (not aqueous ions).
Also please remember that the overall redox equation should not have any electron present!

(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]

$E_{cell}^\ominus = E_{red}^\ominus - E_{oxid}^\ominus$

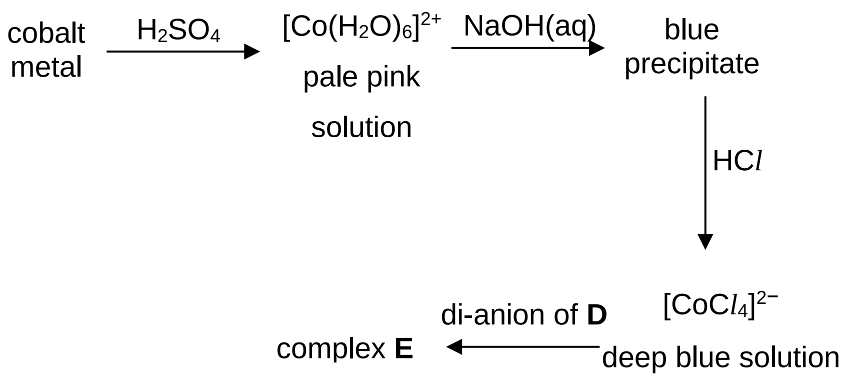
$3.60 = x - (-3.04)$

$x = +0.56$ V

Many candidates can score this mark.
The most common error was either identifying the wrong reduction potential value from the data booklet, as a result of identifying the wrong anode reaction or as a result of calculation error (i.e. adding +3.04 (instead of -3.04) to +3.60 instead).

(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]

Co^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Many candidates have forgotten how to write the electronic configuration of transition metal ions. Always make it a practice to write out the electronic configuration of the transition metal atom first, then figure out the electronic configuration of the metal ion by removing electrons sequentially from 4s subshell, followed by 3d subshell.

(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]

Species present in blue precipitate: **$Co(OH)_2$**

$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$

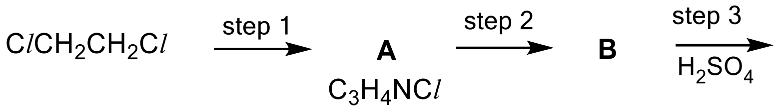
> Many candidates are unable to identify the blue ppt correctly. No credit was given for vague answers e.g. cobalt hydroxide (no oxidation state stated); it is best to write out the formula instead.
> In many answers, the formula of the ppt included the water ligands i.e. $Cu(H_2O)_4(OH)_2$ is the most common wrong answer given.
> As for the equation accounting for the formation of the blue ppt, the answers given were often not balanced either in terms of charge or elements.

(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]

Step 1: (limited) KCN (alcoholic) Heat under reflux

Step 2: NH_3 (alcoholic) heat in sealed tube

A

$Cl-CH_2CH_2-CN$

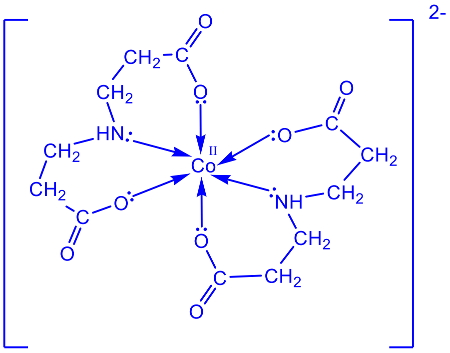
B

$NC-CH_2CH_2-NH-CH_2CH_2-CN$

> While most candidates were able to score 1 mark for the correct structure of A. However much fewer candidates could figure out the correct structure of B.
> Candidates also need to memorise the reagents and conditions of the reactions properly as many answers were not credited due to a lack of correct details (e.g. wrong reagent and/ or solvent, heat under wrong condition etc.)

(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]



Dative bonds to Co, lone pair of electrons on O and N, dicarboxylate anions

Octahedral shape, overall charge of anion is –2

Legend can also be accepted to represent ligand used.

[Total: 23]

Many candidates scored at least 1 mark for this question. However quite a sizeable number of candidates left this part blank.
Often, marks were lost when candidates did not read the question carefully and missed out the information: '*a di-anion in basic solution and forms three coordinate bonds to the Co^{2+} ion*'.
Hence common errors involved the following:

- octahedral geometry about the central metal ion was not properly or correctly represented,
- the -2 charge on the complex ion was either missing or wrongly represented as +2,
- misrepresenting the ligands as bidentate (instead of tridentate) ligands in the answer even though this information was already given in the question,
- missing out drawing lone electron pairs on the N and/or O atoms,
- drawing dative bond formation from the wrong O atom of the $-CO_2^-$ group to the central Co^{2+} ion.
- drawing the ligands in the molecular form instead of the di-anion form.
- In some answers, the N and O atoms (of the same ligand) are drawn bonded to the central metal ion at positions 180° apart (when they should be 90° apart only).

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

Entropy of a system measures its amount of disorder, and it gives a **measure of the extent of which particles and energy are distributed within the chemical system**. **[2010 P3Q1]**

JC1 Chemical Energetics notes p4-42.

Majority of candidates had incomplete explanations and hence earned no credit.

(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]

By adding 1 mol of H_2(g) to 1 mol of N_2(g), both at 298 K, the **entropy of the system will increase** ($\Delta S > 0$), as this is the process of **mixing**. This results in **more ways of arranging the particles** within the system.

[modified from 2010 P3 Q1]

JC1 Chemical Energetics tutorial Q16(b)(i).

Report by the 'A' level examiner: A positive ΔS is achieved simply **by the process of mixing**. There is no increase in the total number of molecules in the system as a whole.
Most candidates were unable to attain this mark as many stated that the number of particles increased.

(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 J K^{-1} mol^{-1}. Explain the significance of its sign with respect to the process that is occurring. [1]

The sign of ΔS is negative since there is a **decrease in the number of gaseous molecules** (4 moles to 2 moles), hence there is a decrease in the disorder of the system. **[modified from 2015 P3 Q2f(i)]**

Majority of candidates were able to achieve the mark for this.
A few were confused and thought negative ΔS means that the reaction is spontaneous (that is negative ΔG.)

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

For spontaneous reaction, $\Delta G = \Delta H - T\Delta S < 0$

$T < \frac{\Delta H}{\Delta S} = \frac{92\times10^3}{99}$ = 929 K = 656 °C (to 3 s.f.) **[modified from 2015 P2Q2d(ii)]**

Majority of candidates were able to achieve the marks for this.
Common errors were:

- Stating $\Delta G \leq 0$ rather than just $\Delta G < 0$
- Forgetting to convert either the ΔH into J mol^{-1} **OR** convert the ΔS into kJ mol^{-1} K^{-1}.
- Forgetting to give the answer to °C as requested by the question.
- Converting K to °C wrongly.

(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 °C.

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

Advantage: *Le Chatelier's Principle* predicts that a lower temperature **favours the forward exothermic reaction and hence the yield will increase**.

Disadvantage: However, if the temperature is too low, the **reaction is too slow**.

JC1 Chemical Equilibria notes p6-37 under point #2 about moderate temperature.

Common errors were:

- (Advantage) Not explaining why the yield is higher (due to LCP)
- (Advantage) Giving the wrong reason or no reason why the yield is higher.
- (Disadvantage) Stating that high cost is required. (That is more for high pressure which is not asked in the question.)

(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]

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}$$

Let initial no. of moles of H_2 and N_2 gases be 3 and 1 mol respectively.

	$3\ H_2(g)$	$N_2(g)$	$\rightleftharpoons$	$2\ NH_3(g)$
Initial amt / mol	3	1		0
Change	**– 3(0.45)**	**– 0.45**		**+ 2(0.45)**
Equilibrium amt / mol	3 – 1.35 = 1.65	1 – 0.45 = 0.55		0.90

Total number of molecules at equilibrium = 1.65 + 0.55 + 0.9 = 3.10 mol

$$P_{NH_3} = \frac{0.9}{3.10} \times 3.00 \times 10^4 = 8710 \text{ kPa}$$

$$P_{H_2} = \frac{1.65}{3.10} \times 3.00 \times 10^4 = 15968 \text{ kPa}$$

$$P_{N_2} = \frac{0.55}{3.10} \times 3.00 \times 10^4 = 5323 \text{ kPa}$$

$$K_p = \frac{(8710)^2}{(15968)^3(5323)} = \underline{\mathbf{3.50 \times 10^{-9}\ kPa^{-2}}}$$

[modified from 2022 P2Q2c(i)]

Many candidates managed to get 1 mark for K_p expression. Those who gave K_c expression OR K_p expression with square brackets did not get credit.

While the ICE table was fairly straightforward, candidates still **lost marks** because:

- They did not have headers hence resulted in improper presentation and no credit
- Candidates did not read the question and started with a 1:1 ratio of reactants.
- Candidates assumed that since 45% of H_2 reacted, it means that 15% of N_2 reacted which is wrong.
- Giving wrong units for K_p.

(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]

$NH_3 + NaH \rightarrow NaNH_2 + H_2$

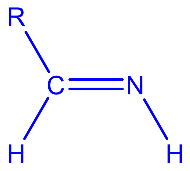
It **donates a proton** to NaH to give H_2.

[modified from 2013 P3Q2b]

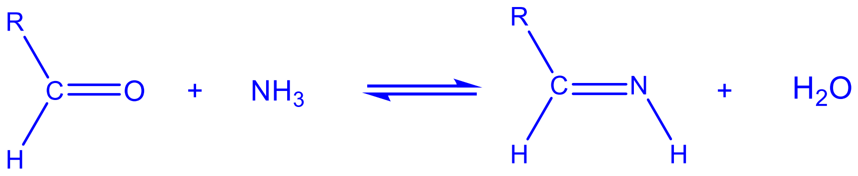
Many candidates were unable to give the equation, but many who hazarded a guess managed to get one mark for 'proton donor'.

(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]



The most common errors were not respecting that C needs 4 bonds and N needs 3 bonds. Hence a variety of illogical molecules were given. Some candidates did not read the question and had H_2 gas produced too.



(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]

Add Fehling's solution and heat. Red precipitate (of copper (I) oxide) formed. OR

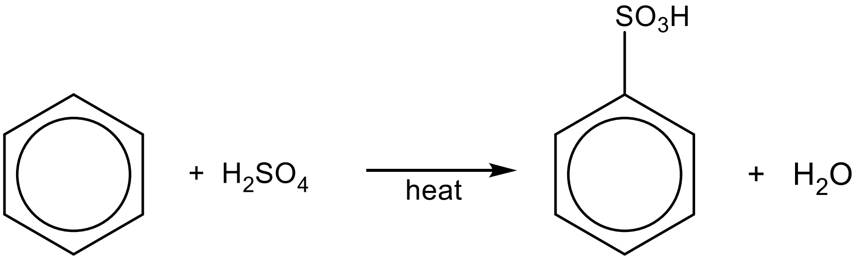
Add Tollens' reagent and heat. Silver mirror formed.

[phrasing of Q taken from 2014 P2Q5d]

[Total: 17]

The most common error was to use 2,4-DNPH (and candidates often forgot to put the hyphen between 4 and D.) But this tests for ketones too and hence not conclusive for aldehydes.

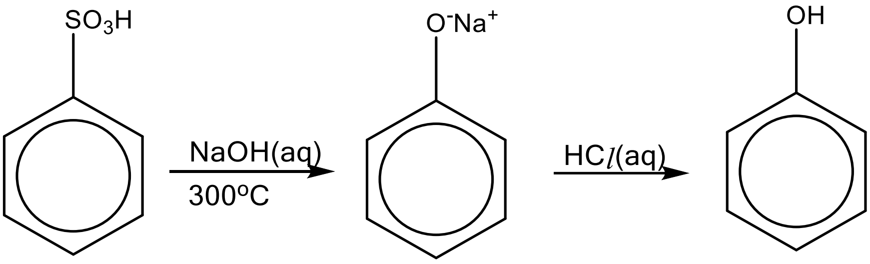
3 Benzenesulfonic acid is often used in the manufacture of surfactants in detergents, dyes and a variety of pharmaceutical drugs. It is produced by heating benzene under reflux with concentrated sulfuric acid for several hours.



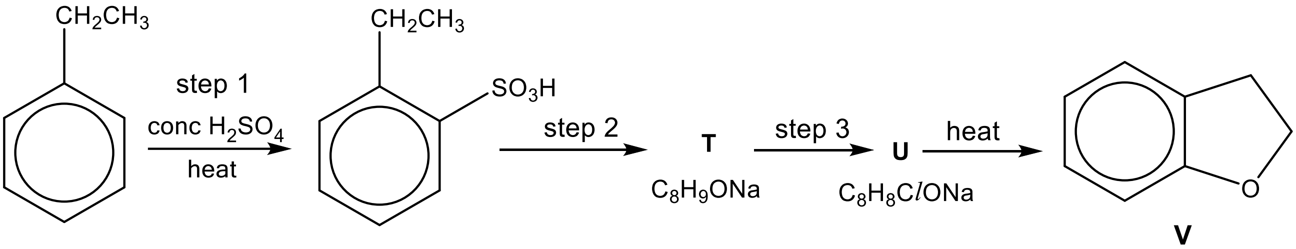
benzenesulfonic acid

(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.

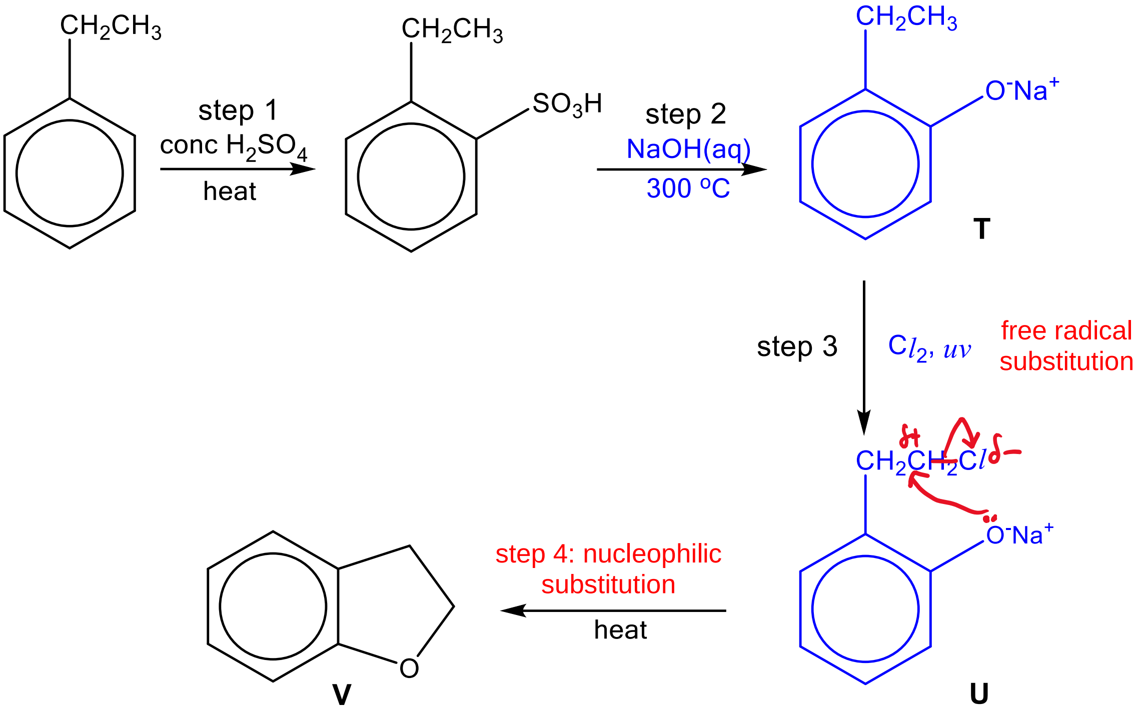


V

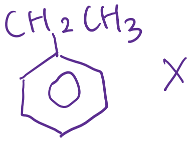
Fig. 3.1.

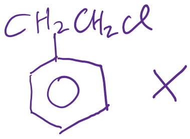
(i) Deduce the structures of the intermediate organic products **T** and **U**. [2]

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

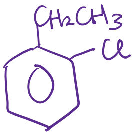


Most candidates were able to get the structures of **T** and **U** as the molecular formula is given. However, there were still several candidates who drew the structures without showing clearly C bonded to the benzene ring. i.e.





Quite a handful of candidates also gave the following structure,



as the answer, showing clearly that they did not understand how compound **V** is formed. The p–p orbital overlap results in the delocalisation of the lone pair of electrons on C*l* into the π electron system of the benzene ring, leading to the formation of partial double bond character in C–C*l*, strengthening the C–C*l* bond, and the bond does not break, and nucleophilic substitution cannot take place.

Phenols are poor nucleophiles and thus must be converted to phenoxides before nucleophilic substitution in step 4 can take place. Thus, reagents and conditions for step 2 only involves NaOH(aq), <300°C, to get to only phenoxide. It should not be protonated to form phenol.

Common mistakes for the reagents and conditions include stating the wrong phase for Cl_2 i.e. Cl_2 in CCl_4 or Cl_2(aq)

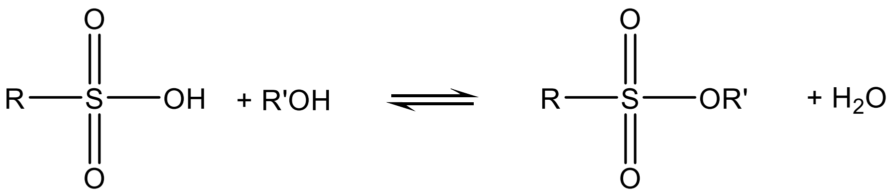
(iii) When fuming sulfuric acid reacts with alkenes, addition reactions occur. Explain why benzene does **not** undergo addition reactions with fuming sulfuric acid. [2]

Benzene contains a ring of delocalised π electrons which leads to extra stability (resonance stability), hence to maintain the stability of benzene, it would not undergo addition reaction which will lead to breaking the ring of delocalised π electrons and giving less stable products due to loss of resonance stability.

[Q taken from 2018 P2 Q2cii]

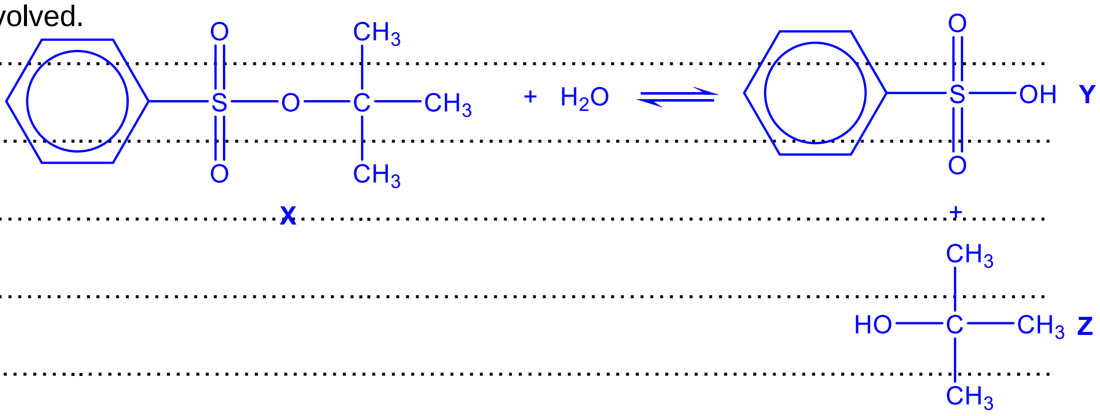
Only a handful of candidates were able to get the full credit for this question. Many candidates were unable to recognise that benzene undergoes electrophilic substitution reactions instead of electrophilic addition reactions so as to maintain its resonance stability.

(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]



Observation	**Type of reaction**	**Deduction (Functional group)**
X is neutral **X** undergoes hydrolysis to give **Y** and **Z**		**X** has no phenol and carboxylic acid **X** is an ester
Z does not decolourise acidified $KMnO_4$	Oxidation	**Z** is a tertiary alcohol
Y is a white solid		**Y** is benzene sulfonic acid

This question was poorly attempted. Although most candidates were able to get the structures for **Y** correct, only a handful of candidates managed to get the structures of **X**, **Z** and the hydrolysis equation correct. Many candidates failed to see that the backward reaction of the equation given is the hydrolysis reaction and gave the equation for the forward reaction. **Like hydrolysis of esters,** (clue given in the question) the hydrolysis of sulfonate esters is a reversible one and does not go to completion. Hence the reversible arrow must be used in the hydrolysis equation.

(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.

$$\underset{\substack{\text{Blue \#1} \\ \textit{blue}}}{Na_2C_{37}H_{34}N_2S_3O_9} \quad + \quad \underset{\textit{colourless}}{\text{bleach}} \quad \longrightarrow \quad \underset{\textit{colourless}}{\text{products}}$$

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]

To ensure that [bleach] remains almost constant throughout the reaction (so it is pseudo zero-order), so that the rate of reaction can be measured with respect to Blue #1.

This question was quite well done. Since [bleach] remains almost constant, it is pseudo zero order and not pseudo first order with respect to bleach.

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

The order of reaction with respect to a reactant is defined as the power to which the concentration of a reactant is raised to in the experimentally – determined rate equation.

This question was poorly done. Most candidates do not have the underlined key words and phrases in the answer.

(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]

When absorbance decreases from 0.424 to 0.218, $t_{½} \approx$ 75s.

When absorbance decreases from 0.495 to 0.251, $t_{½} \approx$ 75s

[states 2 $t_{½}$ values]

Since almost constant $t_{½} \approx$ 75s is observed, the order of reaction wrt to Blue#1 is 1.

This question was poorly done. Many candidates do not understand the definition of half-life. The half-life of a reaction, $t_{½}$, is the time taken for the concentration of reactant to fall to half its original value. Candidates must state the original absorbance values (eg 0.424) and approximately half of the absorbance value (eg. 0.218). Because question states that no graph to be plotted, candidates must state the value given in the table. No estimation of the half-life is accepted. Candidates must show clear understanding of constant half-life and correct conclusion of the order for full credit to be awarded.

(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]

Using data from experiment 2 and 3,

$$\frac{0.01323}{0.00882} = \frac{k\,(3.0)\,(1.0^n)}{k\,(4.0)(0.5^n)}$$

$$\frac{3}{2} \times \frac{4}{3} = 2^n$$

$$2 = 2^n$$

$$\therefore n = 1$$

Rate = k [Blue #1] [bleach]

This question was poorly done. Candidates who answered by inspection method, must show how BOTH Blue #1 and bleach affects the initial reaction rate. Candidates who answered by mathematical method must show clear substitution of values into the equation. Some candidates could not write the correct rate equation (ie. k must be present; the word ‘equation’ should not be present.)

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

As the total volume of the reaction mixture is kept constant, the volume of the bleach in the reaction mixture is directly proportional to the concentration of bleach solution used; i.e. $V_{bleach} \propto [bleach]$

This question was quite well done. Candidates must state the volume of bleach is proportional to the volume of bleach, not total volume of reaction mixture.

(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]

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

This question was quite well done. Take note that since ClO_3^- is being reduced, H_2O_2 must be oxidised. So, the oxidation equation must be used.

(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]

$2ClO_3^- + 2H^+ + H_2O_2 \rightarrow 2ClO_2 + 2H_2O + O_2$ **must be single arrow**

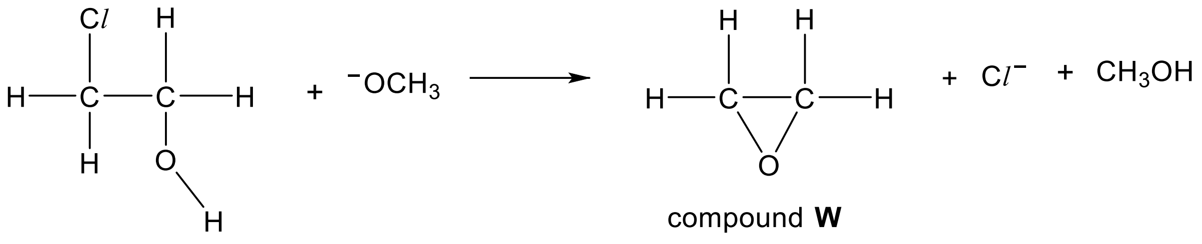
[Total: 20]

This question was poorly done. Single arrow must be used in the overall equation. The question has stated that ClO_3^- ions reacts with H_2O_2. So only the forward reaction will occur. There should be no electrons present in overall equation. The H^+ should also be simplified in the overall equation.

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.



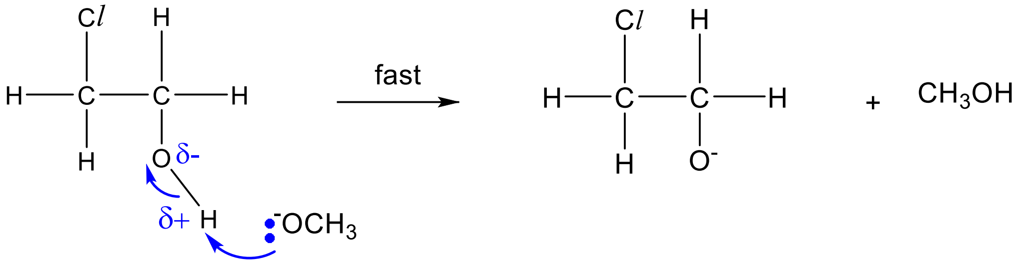
compound **W**

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

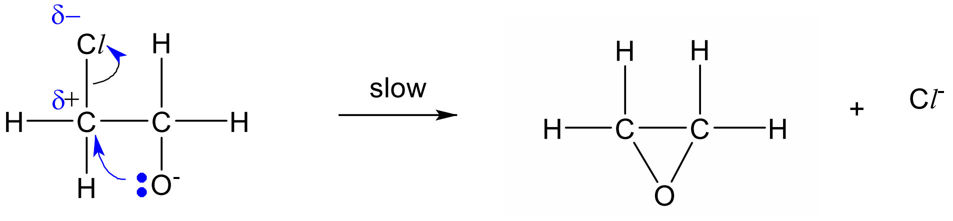
- The first step involves an acid-base reaction.
- The second step involves an intramolecular reaction and it is rate-determining.

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**

Common mistakes included omitting partial charges or lone pair of electrons. Step 1 (acid-base reaction) was a novel context and few candidates managed to get full credit.

(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]

CH_3O^- removes H^+ from 2-chloroethanol to generate the alkoxide, with higher electron density on O, which is **a stronger nucleophile**.

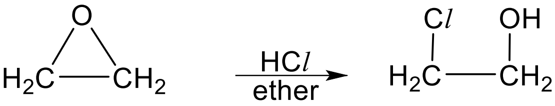
Few candidates managed to answer this correctly. A common misconception was mistaking the methoxide ion as the nucleophile.

(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]

The rate-determining step involves breaking of the C-X bond in step 2. **Less energy** is required to overcome the **weaker C-Br bond** in CH_2BrCH_2OH, leading to a faster rate of reaction.

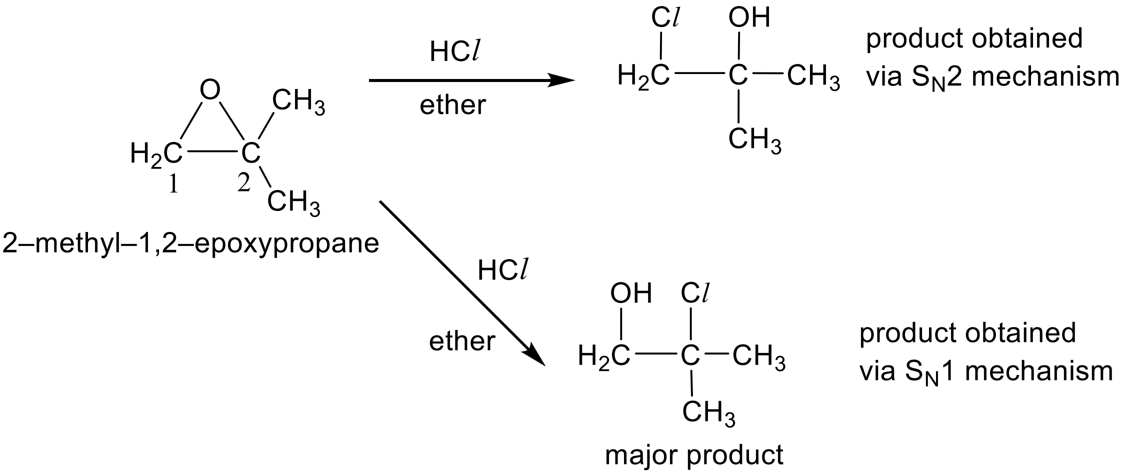
> This is a typical explanation question and was well done by most candidates.

(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]

S_N1 mechanism is favoured as there are 3 electron donating alkyl groups to the electron deficient carbon in 2-methyl-1,2-epoxypropane that help to disperse the positive charge, hence making it a stable carbocation.

- The 3 bulky alkyl groups on the C atom (C with 2 $-CH_3$ groups) also cause steric hindrance to the attacking Cl^- nucleophile making it impossible to form the pentavalent transition state in the S_N2 mechanism

> There are 2 parts to this question. Most candidates failed to address both reasons adequately. Keywords were often missing.

(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]

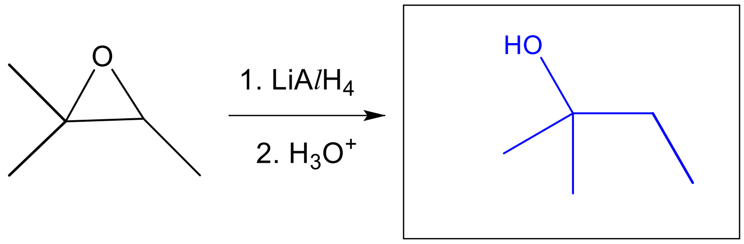
Based on VSEPR theory, the C (or O atoms) in epoxide should have a bond angle of **109.5°(105° for O)** respectively to minimise electron pair repulsion.

However, in the three-atom ring of epoxide, the **bond angle of 60° is smaller** than predicted by VSEPR, which causes **significant bond pair-bond pair repulsion** (or ring strain), the C−O bonds are easier to break / unstable.

> Candidates were expected to state the predicted angle by VSEPR and also actual angle based on the given context that it's a 3-membered ring. Most common incorrect answer was taking the shape around C or O to be trigonal planar. Candidates are reminded to interpret the skeletal structure carefully and also identify any lone pairs which may not be shown.

(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]



> Few candidates managed to get the correct answer.

(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]

All three substances have simple covalent structures.

A larger amount of energy is needed overcome **stronger hydrogen bonds between CH_3OH molecules** than the weaker permanent dipole-permanent dipole forces of attraction between CH_3SH or CH_3SeH molecules.

Thus CH_3OH has the highest boiling point.

Number of electrons in CH_3SeH is larger than that in CH_3SH. A larger amount of energy is needed to overcome **stronger instantaneous dipole-induced dipole forces of attraction** between CH_3SeH molecules.

Thus CH_3SeH has a higher boiling point than CH_3SH.

There is a handful of candidates who had misconceptions and talked about breaking of covalent bonds. As these are simple covalent molecules, the intermolecular forces are overcome and not covalent bonds.

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

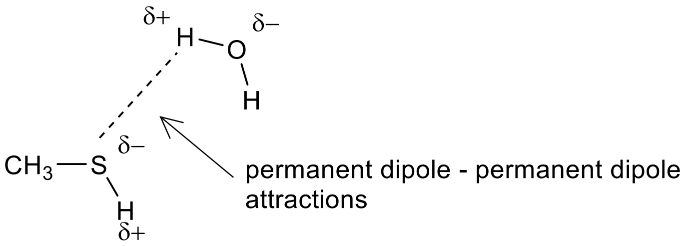
Strongest $CH_3SeH > CH_3SH > CH_3OH$ *Weakest*

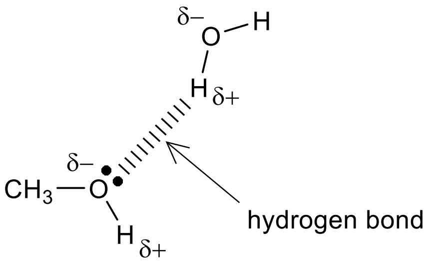
Size of atom decreases from Se to O.
Z–H bond length decreases from Se–H to O–H.
Bond strength increases from Se–H to O–H.
Ease of breaking **Z**–H bond decreases from Se to O.

Or CH_3Se^- is more stable than CH_3O^- because the negative charge is dispersed over a larger size. Consequently, CH_3SeH is more acidic, and has a smaller pK_a value, than methanol.

Most were able to give the correct trend based on the data given. Candidates were expected to utilise the data given regarding the atomic size and relate to the **Z**-H bond strength.

(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]





Very few candidates managed to recognise that CH_3SH would only form permanent dipole-permanent dipole forces of attraction with water. Common wrong answers include hydrogen bonding and id-id. Candidates are reminded that they have to show the lone pairs of electrons and 2 pairs of partial charges in the diagram.

(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]

Amt of NaOH = $\frac{15}{1000}$ x 0.10 = 0.0015 mol
Amt of CH_3SH = $\frac{25}{1000}$ x 0.10 = 0.0025 mol

Since CH_3SH (weak acid) is in excess, a buffer solution is formed.
Amt of excess CH_3SH = 0.0025 – 0.0015 = 0.0010 mol

$$pH = pK_a + \lg\frac{[salt]}{[acid]} = 10.4 + \lg\frac{\frac{0.0015}{40}}{\frac{0.0010}{40}} = \underline{\mathbf{10.6}}$$

Very few candidates managed to get the correct answer. It is important to first identify what is in the resulting solution, i.e. buffer solution. There were many attempts to calculate but candidates were observed to be randomly substituting the values into formulae without first recognising the type of solution formed.

(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]

- Element Y: Sulfur
- Element Z: Sodium
- Oxide of Element X : Aluminium oxide or Al_2O_3

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

$$H_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow \underset{\text{White ppt}}{BaSO_4(s)} + 2HNO_3(aq)$$

(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]

$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$

State symbols not required, accept ionic equations.

Very few candidates managed to get marks for this part, probably due to lack of time. A common wrong answer for element Z was Mg, but MgO would be sparingly souble in water.

The equation for aluminium oxide with an acid or base proved to be challenging for most candidates. It is important to note that is one of the learning outcomes.

[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]

Melting points increase in the order: pentane < diethylamine < glycine.

Both pentane and diethylamine have simple molecular structures, but pentane is non-polar and forms intermolecular instantaneous dipole-induced dipole attractions, while diethylamine can form stronger intermolecular hydrogen bonding. Glycine is an amino acid which has a giant ionic structure with strong electrostatic forces of attraction between zwitterions in solid state. Hence energy required to overcome the attractions increases in the order pentane < diethylamine < glycine, hence melting points increase in the same order.

This question was mostly well attempted, with many candidates scoring at least 2 marks for identifying the correct type of structure and intermolecular forces in pentane and diethylamine, and linking it to the melting points.
Many candidates thought that glycine had intermolecular hydrogen bonding which was more extensive than diethylamine, and forgot that amino acids exist as zwitterions, hence form giant ionic lattices in solid state, with strong electrostatic forces of attraction between the charged $-NH_3^+$ and $-COO^-$ groups.
Some candidates also failed to mention the structures, or gave ambiguous answers that did not clearly state that the id-id forces and hydrogen bonding are intermolecular, or between molecules. Not within molecules/ between atoms.

(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]

Diethylamine is a stronger base than that of ethylamine.

Diethylamine has 2 electron-donating ethyl groups while ethylamine only has 1 alkyl group. Hence, the lone pair of electrons on N of diethylamine is more available to accept a proton and act as a base.

Thus, diethylamine is a stronger base than ethylamine.

This question was well attempted, with most candidates correctly identifying that diethylamine is a stronger base than ethylamine. A number of candidates mentioned a charge on N, or mixed up the explanation for basicity with acidity.

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).

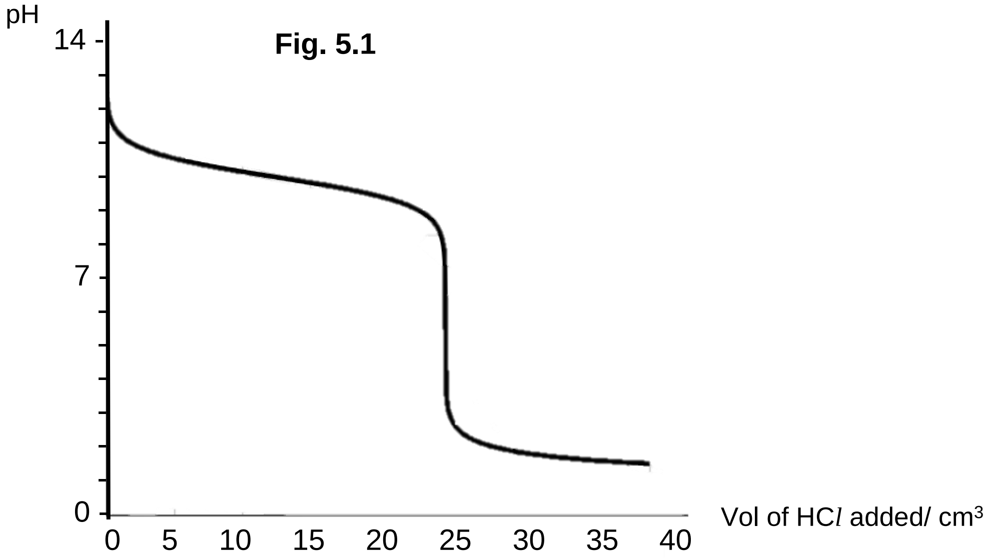


Fig. 5.1

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

$[OH^-] = \sqrt{K_b \times [base]} = \sqrt{6.9 \times 10^{-4} \times 0.10}$ = 0.00831 mol dm^{-3}
pH = 14 – pOH
= 14 + lg(0.00831)
= 11.9

This question was mostly well attempted. The most common mistakes were remembering the formula wrongly eg. pOH = $\sqrt{K_b \times [base]}$, or multiplying the concentration of the base by its volume.

(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]

$(CH_3CH_2)_2NH$ and $(CH_3CH_2)_2NH_2^+Cl^-$

This region is a buffer region. When small amounts of HC*l* are added to the mixture, the large reservoir of base present removes the small amount of H^+ ions added.

$$(CH_3CH_2)_2NH + HCl \rightarrow (CH_3CH_2)_2NH_2^+Cl^-$$

Therefore, pH changes gradually in this region, resulting in gradual changes in the slope.

Quite a few candidates made mistakes in the formula of the two major organic species (the weak base and its salt), although they should simply differ by 1 H^+, as a base accepts a proton to form the salt.

Many students gave incomplete explanations, missing the equation and/or keywords to describe the buffer, or describing both cases when some H^+ OR OH^- is added to the reaction mixture, although in this titration that is being plotted as a graph, only H^+ is being added to the reaction mixture. Note that the solution is **not** at **maximum buffer capacity (MBC)** over the entire pH range 10-11, but only at one particular point when pOH = pK_b. (At pH 10.8, although this question did not require this calculation).

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

K_a of conjugate acid = K_w/K_b = $\frac{10^{-14}}{6.9\times10^{-4}}$ = 1.45×10^{-11} mol dm^{-3}

[conjugate acid] = $\frac{mol\ of\ salt\ formed}{total\ volume}$ = $\frac{\frac{25.0}{1000}\times 0.10}{\frac{50}{1000}}$ = 0.05 mol dm^{-3}

$[H^+] = \sqrt{K_a \times [conjugate\ acid]}$

$= \sqrt{1.45 \times 10^{-11} \times 0.05}$ = 8.51×10^{-7} mol dm^{-3}

pH = –lg(8.51×10^{-7})

= 6.07

This question was not very well attempted. Candidates should be familiar with this calculation of pH at equivalence point, where the salt of the weak base is a **conjugate acid** that can hydrolyse in water and release H^+, causing pH to be <7.

(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]

To provide an acidic medium for the oxidation of alcohol to carboxylic acid.

This question was poorly attempted. Candidates often did not read the information provided carefully, and many suggested that sulfuric acid was either a dehydrating agent or a catalyst for the reaction. The most obvious role is to provide an acidic medium for the redox reaction (reaction 2). If there is water in the mixture, the acid is not concentrated enough to act as a dehydrating agent.

(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]

R: $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ (from Data booklet) } x2

O: $C_2H_5OH + H_2O \rightarrow CH_3COOH + 4\ H^+ + 4\ e^-$ } x3

Overall: $2\ Cr_2O_7^{2-} + 3\ C_2H_5OH + 16\ H^+ \rightarrow 4\ Cr^{3+} + 3\ CH_3COOH + 11\ H_2O$

This question was poorly attempted. Many candidates were able to identify the correct half-equation for $Cr_2O_7^{2-}$ being reduced from the Data booklet, but were unable to construct the half equation for oxidation of ethanol to ethanoic acid. Some chose other half equations involving eg. SO_4^{2-}, K^+, or H_2O. As a result, many of the overall equations were not balanced, or did not have ethanol in it, or had electrons in it.

(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]

Mass of ethanol per 100ml of breath = 80 / 2100 = 0.038 mg

Most candidates were able to score this mark. Those who had different answers most likely did not read the information given and the units required by the question.

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

At r.t.p., T = 293 K, p = 1 atm = 101325 Pa

pV= nRT = (m/M_r)RT
density, $\rho = m/v = pM_r/RT$

Density of air at r.t.p. = 101325 x 28.96 / 8.31 x 293
= 1210 g m^{-3}
= 1.21 kg m^{-3}

OR density = $\frac{\text{mass}}{\text{volume}}$

For 1 mole,
density = $\frac{28.96}{24}$
= 1.21 g dm^{-3}
= 1.21 kg m^{-3}

Some candidates were able to get the answer easily using either the ideal gas equation, or the molar volume of air at r.t.p. being 24 dm^3. Some candidates got mixed up with the units, or manipulated the equation wrongly, or used the wrong values of p or T. SI units for density are kg m^{-3}, but since the question did not specify units for density, other sensible units were accepted eg. g m^{-3}, g cm^{-3}, or g dm^{-3}.

(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]

Mass of air in a breath = 1205 x 500 / 10^6
= 0.6025 g

Percentage by mass of ethanol vapour = $\frac{0.038 \text{ x } 10^{-3} \times \frac{500}{100}}{0.6025} \times 100\%$
= 0.0315%

The most common mistakes here were in converting units of masses or volumes.

(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]
Heat with immediate distillation (Reagents: $K_2Cr_2O_7$, H_2SO_4 (aq), and primary alcohol)

Many candidates gave the correct reaction conditions, while a number also gave the reagents which was unnecessary. A few candidates gave $KMnO_4$, which is more likely to produce the carboxylic acid than the aldehyde. A small handful stated the "*condition*" that a primary alcohol must be used – candidates should be familiar with the meaning of common terms used in Chemistry eg. Reagents and conditions etc.

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

Curly arrow should originate from lone pair on O and point to Cr atom.

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 S_N2 mechanism, as nucleophile attacks the δ+ atom, another curly arrow is drawn to show the bond breaking and the δ– leaving group leaving. It is fine to show either one of the -OH groups leaving.

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

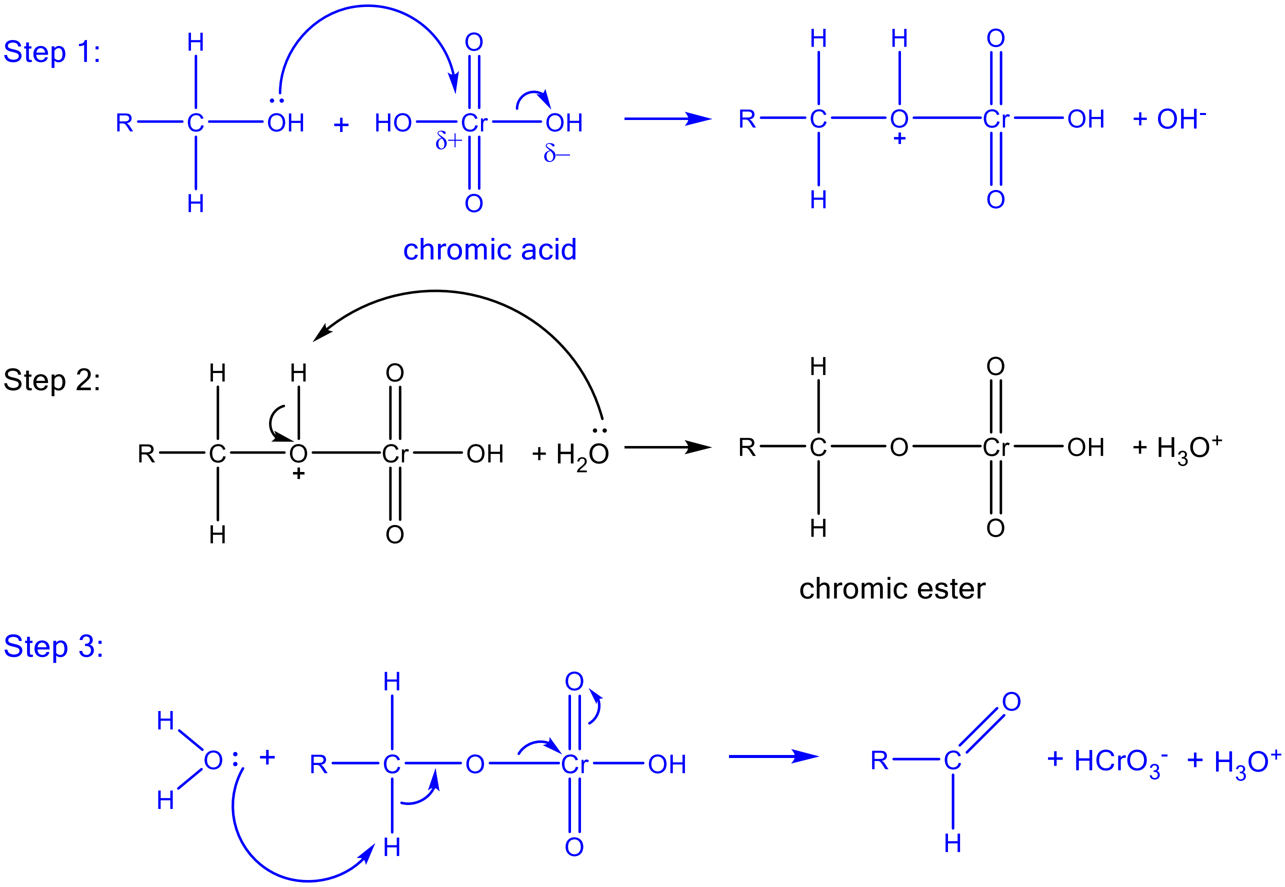
In step 3, water extracts a hydrogen atom from the alcohol carbon, and a carbon-oxygen double bond is formed while the O—Cr bond in the chromic ester breaks.

For water to remove H^+ from the C, a curly arrow must point from a lone pair on O to the H. (again, either H is acceptable)

The electrons of the C—H bond move to form the C=O bond, and for the O—Cr bond to break, the bonding electrons must move to form the CrO_3^- ion.

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



[Total: 20]

Not many candidates gained full credit for this question, possibly partly due to lack of time. Some candidates did not show a lone pair on O although that should be familiar from the known mechanisms. Also, some curly arrows pointed from other atoms without lone pairs to the O atoms, showing a lack of understanding that the arrows must originate from an electron source.