RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME										
CLASS	2	1	J							
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY
9729/02

Paper 2 Structured Questions

14 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on all the work that 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.
DO **NOT** WRITE IN ANY BARCODES.

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.

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

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

For Examiner's Use								
Question Number	**1**	**2**	**3**	**4**	**5**			
Marks	**9**	**17**	**14**	**14**	**21**			
significant figures			**units**				**Total**	**75**

This document consists of **20** printed pages.

1 Ammonium salts are typically used in instant cold packs. The cold pack contains water and an inner pouch containing an ammonium salt. A crushing action causes the inner pouch to break and release the salt, which quickly dissolves to lower the pack's temperature.

To determine whether ammonium nitrate or ammonium chloride is more effective as the cold pack ingredient, a student decided to conduct an experiment to find out the enthalpy changes of solution of the two salts.

He first added ammonium nitrate to water and determined the temperature change by plotting a suitable graph to correct for heat transfer.

In a preliminary investigation, the enthalpy change of solution of ammonium nitrate was found to be approximately +26.0 kJ mol^{-1}.

(a) Define the term *enthalpy change of solution*.

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(b) **(i)** The student was told to use 50.0 cm^3 of water to conduct the experiment. Suggest a minimum mass of ammonium nitrate that could be used to effect a temperature change of 5.0 °C. Justify your choice with relevant calculations.

You should assume that 4.18 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.

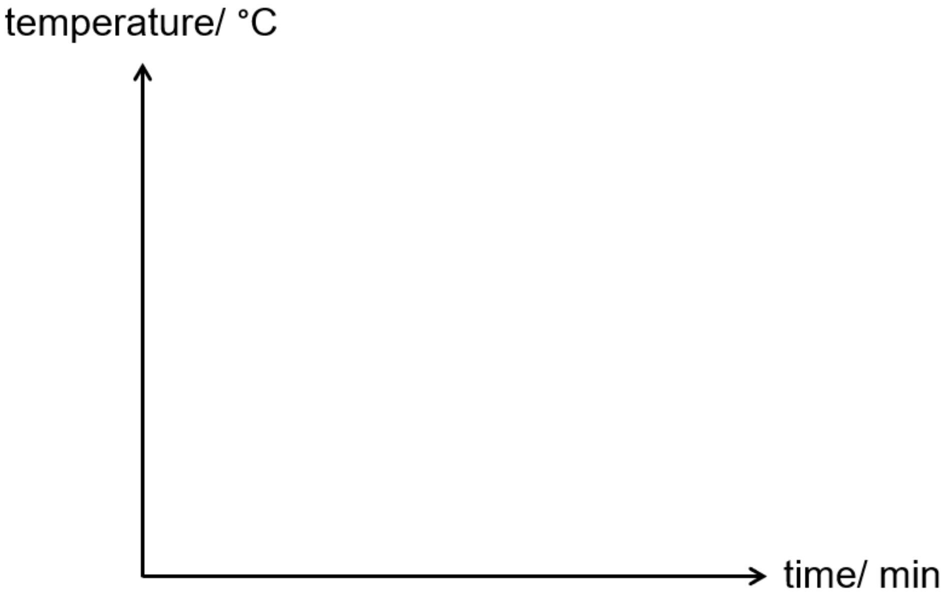
[1]

(ii) The student carried out the following procedure to find the enthalpy change of solution of ammonium nitrate.

1. Weigh accurately about 4.00 g of ammonium nitrate in a weighing bottle.
2. Using a 50 cm^3 measuring cylinder, add 50.0 cm^3 of deionised water into a polystyrene cup.
3. Stir the contents in the polystyrene cup gently with the thermometer and record the temperature every 0.5 minute.
4. At exactly 3.0 minutes, add the ammonium nitrate into the water. Do not read the temperature at this time.
5. Stir the mixture thoroughly and continue to record the temperature every 0.5 minute from 3.5 minutes to 9.0 minutes until constant temperature is reached.
6. Reweigh the weighing bottle with the residual ammonium nitrate.

Sketch the graph of temperature against time that you expect to obtain from the experiment.

Indicate clearly on the graph how the temperature change, ΔT, can be determined.



[2]

(c) Given the following data, draw an energy level diagram to determine the standard enthalpy change of solution of ammonium chloride.

Lattice energy of ammonium chloride = –705 kJ mol^{-1}

Enthalpy change of hydration of NH_4^+ = –307 kJ mol^{-1}

Enthalpy change of hydration of Cl^- = –381 kJ mol^{-1}

[3]

(d) Explain how the magnitude of enthalpy change of hydration of chloride ions differs from that of bromide ions.

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[Total: 9]

2 Use of the *Data Booklet* is relevant to this question.

Cobalt is a transition element that is used in the manufacture of magnetic alloys and catalysts.

(a) Define the term *transition element*.

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………………………………………………………………………………………… [1]

(b) The melting point of cobalt is 1495 °C while the melting point of calcium is 843 °C.

Explain this in terms of structure and bonding of both elements.

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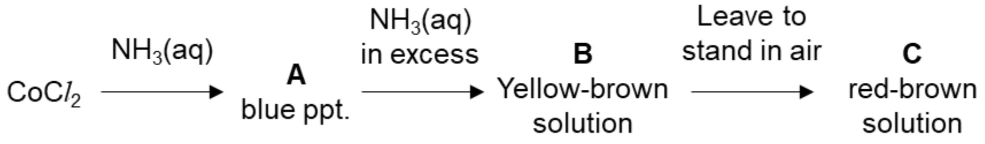
(c) Aqueous cobalt(II) chloride, $CoCl_2$, is a pink solution which gives the following reactions:



(i) State the electronic configuration of the cobalt species in compound **A**.

………………………………………………………………………………… [1]

(ii) Given the following information:

$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$ $E^\ominus = +0.11$ V

By using relevant $E^\ominus$ values, account for the observation when solution **B** is left to stand in air.

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(iii) Construct a labelled diagram to describe how the $E^\ominus$ value of the equation $[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$ can be measured.

[3]

(iv) Indicate the direction of electron flow in your diagram above.

[1]

(d) **D** is a cobalt(III) complex with the formula $Co(NH_3)_{\mathbf{a}}Cl_3$.

In a ligand exchange reaction, 3.501 g of **D** is dissolved in 500 cm^3 of water. 25.0 cm^3 of this solution requires 18.75 cm^3 of 0.0400 mol dm^{-3} of EDTA(aq) for complete reaction.

In another experiment, when excess $AgNO_3$(aq) is added to 23.340 g of **D**, 14.340 g of solid AgC*l* is formed.

(i) Given that 1 mole of **D** reacts with 1 mole of EDTA, show that the molar mass of **D** is 233.4 g mol^{-1}.

[2]

(ii) Show that 1 mole of **D** will form 1 mole of AgC*l* when reacted with excess $AgNO_3$.

[1]

(iii) Deduce the value of **a**. Hence, state the formula of the cation in **D**.

[2]

(iv) When **D** undergoes reduction, followed by exposure to excess carbon monoxide gas, an octahedral complex **E**, $Co(CO)_4Cl_2$, is formed.

Given that **E** has no net dipole moment, Draw the shape of **E**, showing the arrangement of the ligands.

[2]

[Total: 17]

3 **(a)** Hydration of alkenes can be carried out by reacting alkenes with borane, BH_3, followed by treatment with alkaline hydrogen peroxide, H_2O_2. The product is an alcohol.

An example is shown below in Fig. 3.1.

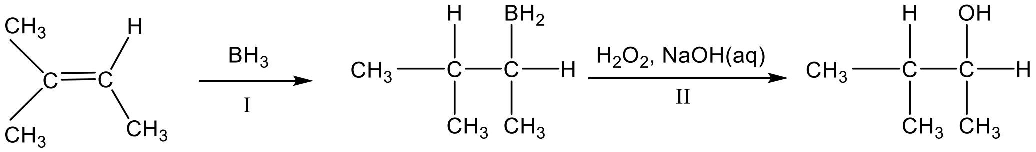

Fig. 3.1

(i) The product of the reaction in Fig. 3.1 exhibits stereoisomerism. State the type of stereoisomerism and draw the structure of each stereoisomer.

……………………………………………………………………………………

[2]

(ii) Step I occurs via a mechanism similar to electrophilic addition and it involves the BH_3 acting as an electrophile.

Explain what is meant by the term *electrophile*.

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…………………………………………………………………………………… [1]

(iii) It is suggested that the mechanism for step I goes through the formation of a transition state as shown in Fig. 3.2.

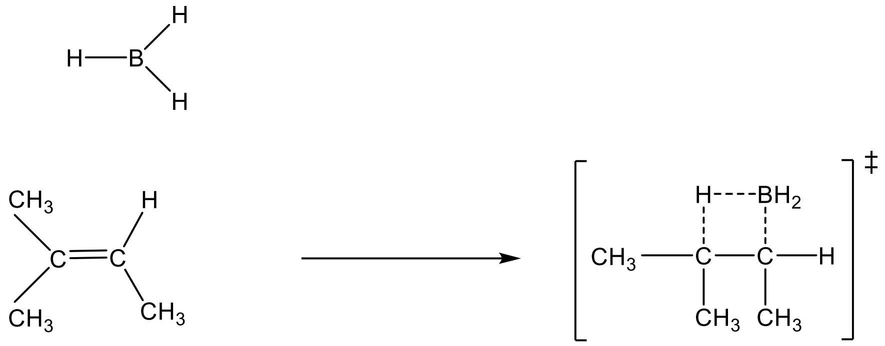
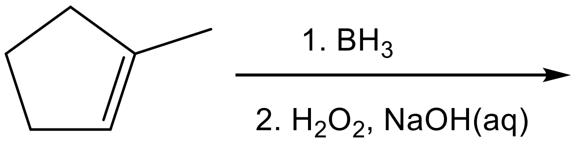


Fig. 3.2

Given that boron is less electronegative than hydrogen, complete Fig. 3.2 to suggest the mechanism for step I. Show relevant dipoles and use curly arrows to indicate the movement of electron pairs.

[2]

(iv) Predict the major product for the following reaction.



[1]

(b) Alkenes undergo electrophilic addition with halogens in an exothermic reaction. Draw the labelled energy profile diagram for the reaction between ethene and liquid bromine.

[2]

(c) Methanol is a colourless and flammable liquid which can be a possible alternative fuel for motor vehicles. The boiling points of methanol and two of its analogues are given in the Table 3.1 below.

Table 3.1

compound	M_r	boiling point/ °C
CH_3OH	32.0	65
CH_3SH	48.1	6
CH_3SeH	95.0	25

Explain the difference in boiling points of the three compounds in terms of structure and bonding.

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(d) One alternative fuel technology involves the conversion of liquid methanol into hydrogen gas, as shown in the equation below.

$$CH_3OH(l) \rightarrow 2H_2(g) + CO(g)$$

Given that the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction is +129 kJ mol^{-1} and the standard entropy change, $\Delta S^{\ominus}$, is +332 J K^{-1} mol^{-1},

(i) Explain the sign of $\Delta S^{\ominus}$.

……………………………………………………………………………………

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…………………………………………………………………………………… [1]

(ii) With the aid of calculations, show whether the reaction is spontaneous at 130 °C.

[2]

[Total: 14]

4 **(a)** The following equilibrium exist in a sample of aluminium chloride vapour.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g) \qquad \Delta H = +63\ \text{kJ mol}^{-1}$$

When 1.50 g of aluminium chloride was introduced into an evacuated steel vessel of 250 cm^3 capacity and heated to 327 °C, the pressure inside the flask rose to 1.60×10^5 Pa.

(i) Assuming the gaseous mixture behaves ideally, calculate the average M_r of the mixture.

[1]

(ii) The M_r of $AlCl_3$ and Al_2Cl_6 are 133.5 and 267 respectively. Using your answer in **(a)(i)** and the above information, calculate the mole fraction of $AlCl_3$ and Al_2Cl_6 respectively, giving your answers to 1 decimal place.

[1]

(iii) Hence, calculate the K_p of the reaction, stating its units.

[3]

(b) Predict the effect of increasing the temperature on the K_p of the above reaction. Explain your answer.

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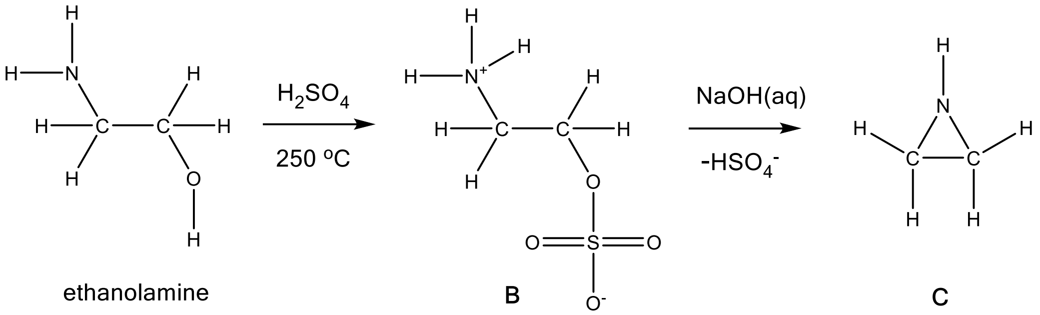
(c) The Wenker synthesis is an organic reaction used to convert a beta amino alcohol, such as ethanolamine, to an aziridine, a three-membered heterocycle which is useful as a starting material in medicinal chemistry.



Ethanolamine will react with sulfuric acid, a strong acid, to form **B**. The monoester is then reacted with sodium hydroxide in the second step to form aziridine **C**.

(i) Write a balanced overall equation for the Wenker synthesis of aziridine **C** from ethanolamine.

…………………………………………………………………………………… [1]

(ii) From your equation, name the type of reaction that occurs in the Wenker synthesis.

…………………………………………………………………………………… [1]

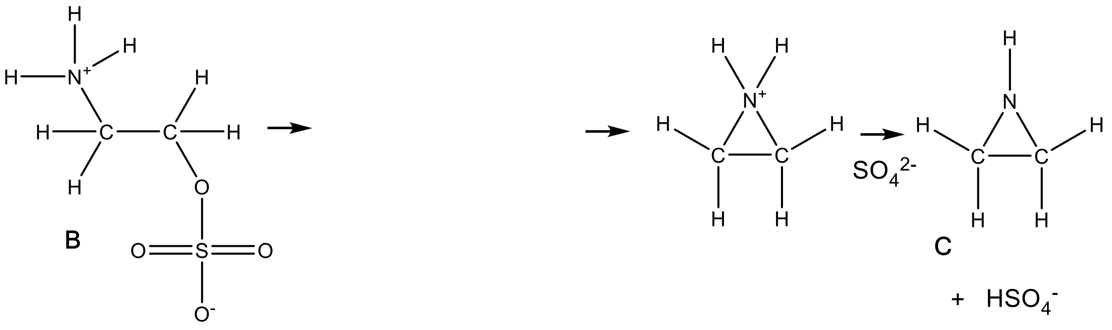
(d) The mechanism of the Wenker synthesis is thought to involve the following steps.

1. Protonation of ethanolamine to form cation **A** with an overall 2+ charge
2. Bond formation on **A** using sulfate anion with simultaneous C–O bond cleavage to give **B**
3. Deprotonation of **B** using OH^-
4. Intramolecular formation of three-membered ring involving the formation of C–N bond and heterolytic bond cleavage of C–O bond
5. Deprotonation to form **C**

(i) Given that sulfuric acid is a strong acid, suggest the structure of cation **A**.

[1]

(ii) Use the information given above in step 3 and 4 to complete the mechanism below for the formation of aziridine from compound **B**. Show all charges, partial charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]

(iii) Name the type of reaction that occurred during the intramolecular cyclisation.

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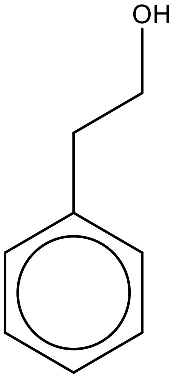
[1]

[Total: 14]

5 Organic chemicals are often used as flavour enhancers. 2-phenylethanol and butanoic acid are commonly used as rose flavour and butter flavour respectively.

(a) 2-phenylethanol, concentrated sulfuric acid and concentrated nitric acid can react together in the laboratory to form 2-(nitrophenyl)ethanol, as described below.



2-phenylethanol

Preparation of 2-(nitrophenyl)ethanol

1. Place 20 g of 2-phenylethanol into a 500 cm^3 conical flask.
2. Add slowly 40 cm^3 of concentrated sulfuric acid to the conical flask. Cool the mixture by immersing the flask in ice water.
3. Mix 15 cm^3 of concentrated nitric acid with 15 cm^3 of concentrated sulfuric acid in an ice bath. This is the nitrating mixture.
4. Using a glass pipette, transfer slowly the nitrating mixture to the contents in the conical flask. After the transfer, stir the reaction mixture in the ice bath for 15 minutes.
5. Carefully pour the reaction into a crushed ice mixture in a 250 cm^3 beaker. Solid crude 2-(nitrophenyl)ethanol will form.

(i) Draw the structural formula of the major organic products that will be formed.

[2]

(ii) The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving 2-phenylethanol.

Write a balanced equation for **each** of these stages.

Stage I ……………..……………………………………………….....

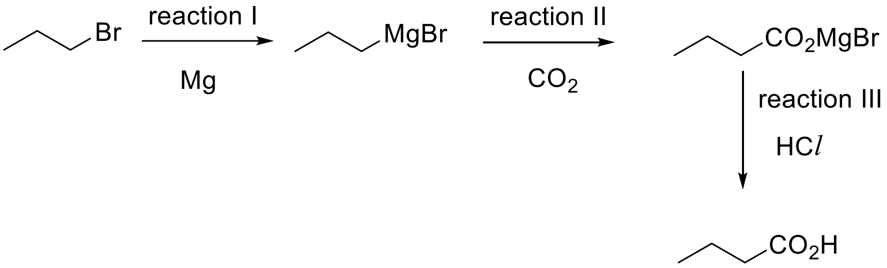
Stage II ……………………..………………………………………… [2]

(iii) When the concentrated sulfuric acid is added to the reaction mixture (step 2), cooling is necessary. An organic by-product may be produced if the temperature is not controlled carefully.

Identify the organic by-product.

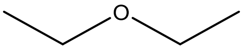
[1]

(b) Butanoic acid can be synthesised in the laboratory using the Grignard reaction, as described below.



Data on these four compounds are given in Table 1.1.

Table 1.1

compound	boiling point/ °C	density/ g cm^{-3}	molar mass/ g mol^{-1}	solubility in diethyl ether	solubility in water
butanoic acid	164	1.14	88	soluble	moderate
1-bromopropane	71	1.35	123	soluble	insoluble
magnesium	1091	1.74	24.3	-	-
diethyl ether 	35	0.71	74	-	insoluble
water	100	1.00	18	insoluble	-

Preparation of butanoic acid

1. Place 1.5 g of magnesium, 60 cm^3 of diethyl ether in a 100 cm^3 round bottom flask attached to a reflux condenser. Add 5 cm^3 of 1-bromopropane to start the reaction. Keep the contents well mixed.
2. After 10 minutes, bubble carbon dioxide gas through the reaction mixture for 15 minutes.
3. Transfer the reaction mixture to a 250 cm^3 conical flask and add 60 cm^3 of 3.0 mol dm^{-3} HC*l* to the reaction mixture.

Purification of butanoic acid

4. Transfer the mixture into a separatory funnel. Shake well. The mixture will separate into two distinct layers. Reject the aqueous layer.
5. Return the organic diethyl ether layer to the funnel. Add 20 cm^3 of 3.0 mol dm^{-3} NaOH, and shake. Separate and keep the aqueous layer containing the alkali. Reject the organic layer.

6. Return the aqueous layer to the funnel. Add 20 cm^3 of 3.0 mol dm^{-3} HC*l*, and shake. Separate and keep the organic diethyl ether layer. Reject the aqueous layer.
7. Transfer the organic diethyl ether layer into a 100 cm^3 conical flask. Add some granular anhydrous calcium chloride. Swirl the mixture until the liquid is clear.
8. Filter the pure butanoic acid into a clean round bottom flask and distil it. Collect the fraction by boiling over a suitable range.

(i) Suggest the type of reaction which occurs in reaction III.

……………………..………………………………………………….….. [1]

(ii) One of the reagents, magnesium or 1-bromopropane, will be present in an excess in this preparation.

Use the data above to determine, by calculation, which reagent is in excess.

[2]

(iii) In step 3, effervescence was observed when HC*l* was added. Write an equation to show the formation of the gas.

……………………..………………………………………………….….. [1]

(iv) In step 4, the reaction mixture will separate to give two layers.

Will butanoic acid mostly be in the upper or lower layer?

…………………….....

Explain your answer.

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………………………..…………………………………………………….. [2]

(v) After separating butanoic acid from the aqueous layer, there will still be a very small amount of unwanted organic impurity present. To remove this, the reaction mixture is shaken with NaOH (step 5).

Suggest the identity of the organic impurity.

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Suggest why the aqueous layer is retained and how the impurity will be removed.

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(vi) Suggest what is removed when the impure butanoic acid is then treated with calcium chloride (step 7).

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(vii) The final step in the process of purification is distillation of the pure product (step 8). Suggest a suitable range of temperature for the collection of the required fraction.

from ……………°C to ……………°C [1]

(c) Butanoic acid is a weak acid in water, with a pK_a value of 4.82.

(i) Calculate the pH of a 0.20 mol dm^{-3} solution of butanoic acid.

[2]

(d) Deuterated water is a form of water that contains deuterium (^{2}H or D) instead of hydrogen. At 25 °C, the pK_w of deuterated water is 14.95.

(i) Calculate the pH of neutral deuterated water at 25 °C.

…………………………………………………………………………….. [1]

(ii) Considering the ionic products (K_W) of water and deuterated water, deduce whether the O–H bond or O–D bond is likely to be a stronger bond.

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[Total: 21]

Additional answer space

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