H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured

12 September 2022

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 on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/15
2	/10
3	/6
4	/24
5	/8
6	/12
Total	/75

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

[Turn over

Answer **all** questions in the spaces provided.

1(a) **X** and **Y** are oxides of elements in the third period of the Periodic Table. The oxidation number of the Period 3 element in **X** and **Y** is +3 and +5 respectively.

X reacts with both aqueous sodium hydroxide and aqueous hydrochloric acid.

Y reacts with aqueous sodium hydroxide, but not with aqueous hydrochloric acid.

(i) Identify the formulae of **X** and **Y**.

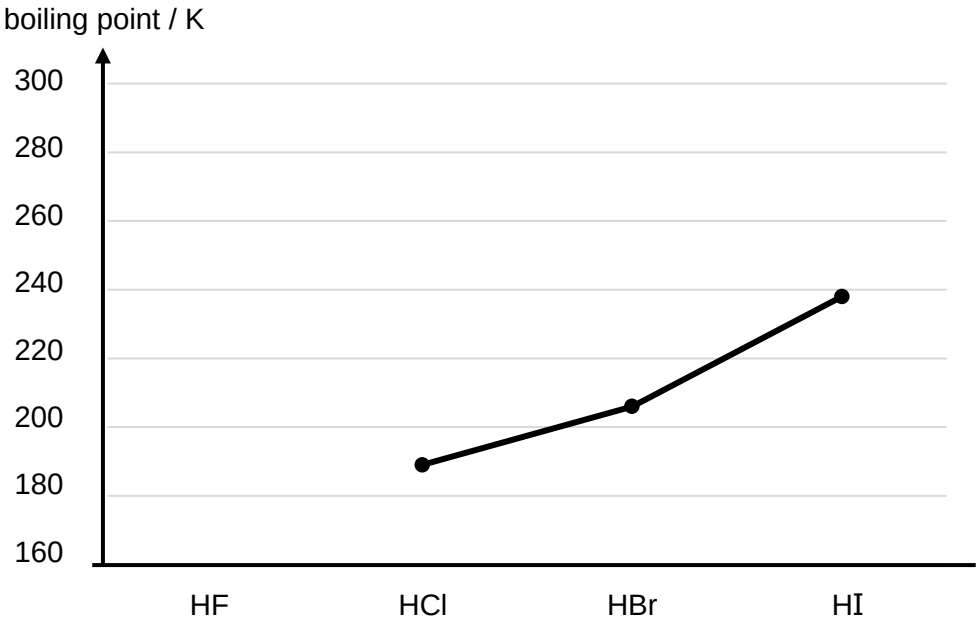
X ..... **Y** ..... [1]

(ii) Write equations for the reactions of **X** and **Y** with aqueous sodium hydroxide.

X: .....

Y: ..... [2]

(b) The graph below shows the boiling points of HCl, HBr and HI.



(i) Explain the trend of the boiling points of HCl, HBr and HI.

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..... [2]

(ii) Complete the sketch on page 2 to predict the boiling point of HF. Explain your answer.

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..... [2]

(c) Zinc nitrate decomposes at 300 °C whereas barium nitrate decomposes at 600 °C.

A 20.0 g sample containing a mixture of zinc nitrate and barium nitrate was heated at 350 °C until no further change occurred. A brown gas and another gas that relights glowing splint were evolved. The remaining white solid weighed 11.3 g.

(i) Draw the dot-and-cross diagram for zinc nitrate.

[2]

(ii) Use data from the *Data Booklet*, explain why zinc nitrate decomposes at a much lower temperature than barium nitrate.

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..... [3]

(iii) Write an equation for the reaction that occurred when the sample is heated at 350 °C.

.....[1]

(iv) Calculate the percentage composition by mass of zinc nitrate in the sample.

[2]

[Total: 15]

2(a) Oxalic acid, HO_2CCO_2H, is a weak diprotic acid.

$$HO_2CCO_2H \text{ Ý } HO_2CCO_2^- + H^+ \qquad pK_{a1} = 1.27$$
$$HO_2CCO_2^- \text{ Ý } {}^-O_2CCO_2^- + H^+ \qquad pK_{a2} = 4.28$$

(i) 10 cm^3 of 0.100 mol dm^{-3} HO_2CCO_2H was mixed with 10 cm^3 of 0.150 mol dm^{-3} HO_2CCO_2Na.

Write an equation to show how this solution is able to maintain pH upon addition of alkali.

..... [1]

(ii) 14.0 cm^3 of 0.100 mol dm^{-3} KOH was added to the solution in **(a)(i)**.

Calculate the pH of the resultant solution after adding KOH(aq).

[3]

(b) Rare earth ions in the oxidation state of +3, such as cerium(III) ions, Ce^{3+}, are used in the production of luminescent materials.

Solutions containing Ce^{3+} ions may sometimes be contaminated by other cations such as Ca^{2+}. The recovery of Ce^{3+} ions from such solutions can be achieved through selective precipitation using oxalic acid as the precipitating agent. After adding oxalic acid to a solution containing Ce^{3+} ions contaminated with Ca^{2+} ions, the pH of the solution is adjusted through the addition of a strong mineral acid. The purpose is to control the concentration of the oxalate anion, $C_2O_4^{2-}$ in the solution and hence ensure that maximum amount of Ce^{3+} ion is precipitated to achieve an effective separation from the contaminant cation.

Table 2.1 contains the values of the logarithm to the base 10 of the equilibrium constant, *K*, for some of the equilibrium reactions.

Table 2.1

Equilibrium equations	lg *K*
$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \text{ Ý } CaC_2O_4(s)$	8.63
$2Ce^{3+}(aq) + 3C_2O_4^{2-}(aq) \text{ Ý } Ce_2(C_2O_4)_3(s)$	30.18
$HO_2CCO_2H(aq) \text{ Ý } 2H^+(aq) + C_2O_4^{2-}(aq)$	–5.06

The numerical values for the solubility product of CaC_2O_4 and $Ce_2(C_2O_4)_3$ are 2.34×10^{-9} and 6.60×10^{-31} respectively.

(i) Using data from Table 2.1, prove that the numerical value of K_{sp} of CaC_2O_4 is 2.34×10^{-9}.

[1]

[Turn Over

(ii) Solution A contains 0.010 mol dm^{-3} of Ca^{2+}, 0.010 mol dm^{-3} of Ce^{3+} and 1.0 mol dm^{-3} of oxalic acid. Calculate the minimum concentration of $C_2O_4^{2-}$ needed for the precipitation of Ca^{2+} and Ce^{3+} respectively.

[2]

(iii) Using your answers in **(b)(ii)** and data from Table 2.1, calculate the pH of solution A that is required to precipitate the maximum amount of Ce^{3+}.

[3]

[Total: 10]

3 The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. However, many gas molecules do not follow the ideal gas law. Instead of the ideal gas equation, Johannes D. van der Waals suggested a modification to take into account molecular size and molecular interactions. The equation is usually referred to as the van der Waals' equation and it is shown as follows:

$$[p + \mathbf{a}(\frac{n}{V})^2](\frac{V}{n} - \mathbf{b}) = RT$$

Constants **a** and **b** are called van der Waals' constants. They have positive values and are characteristic of the individual gas. If a gas behaves ideally, both **a** and **b** are zero, and the van der Waals' equation approaches the ideal gas equation $pV = nRT$.

Constant **a** provides a correction for the intermolecular forces. Constant **b** adjusts for the volume occupied by the gas particles and is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

The van der Waals' constants of some gases are shown in Table 3.1.

Table 3.1

Gas	**a** (dm^6 atm mol^{-2})	**b** (dm^3 mol^{-1})
N_2	1.37	0.0387
NH_3	4.17	0.0371
N_2H_4	8.46	0.0462

(a) In an experiment, 34 g of NH_3 occupies a 7 dm^3 bottle at 77 ^oC.

(i) Calculate the pressure of NH_3 in this bottle, in atm, using the ideal gas equation.

[1]

(ii) Calculate a value of the ideal gas constant, R, with units dm^3 atm K^{-1} mol^{-1} at s.t.p.

[1]

(iii) Using the van der Waals' equation and the value calculated in **a(ii)**, calculate the pressure of NH_3, in atm, in the same bottle.

[1]

(iv) Give a possible reason why the pressure calculated in **(iii)** is more accurate.

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..... [1]

Liquefaction of gases is the condensation of gases into a liquid form. In general, gases with large van der Waals' **a** constants are relatively easier to liquefy.

(b) Explain, in terms of structure and bonding, why this is so by making reference to the gases found in Table 3.1.

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..... [2]

[Total: 6]

4(a) The Haber–Bosch process remains the primary industrial route to synthesise ammonia. It involves the breaking of the triple bond in molecular nitrogen at high pressures and temperatures and the hydrogen gas it requires to turn nitrogen to ammonia comes mainly from natural gas.

equation 1 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

This process however is responsible for up to 3% of global CO_2 emissions.

The electrochemical lithium cycling process to make ammonia is a more sustainable approach. It is reported to have achieved an efficiency of 88.5% in lab-scale tests. The process uses electricity, which can have a renewable source, such as wind or solar energy.

In the first stage, the electrolysis of molten lithium hydroxide produces molten lithium metal at the cathode. Oxygen and steam are formed at the anode.

equation 2 $2LiOH(l) \rightarrow 2Li(s) + \frac{1}{2}O_2(g) + H_2O(g)$

(i) Using data from the *Data Booklet*, explain why an aqueous solution of LiOH cannot be used to produce lithium metal by electrolysis.

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..... [1]

The next stage in the process involves gently heating the lithium metal in a stream of nitrogen to produce lithium nitride.

equation 3 $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$

(ii) Define, with the aid of an equation, lattice energy of lithium nitride.

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..... [2]

(iii) Using the data in Table 4.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the third electron affinity of nitrogen. Show your working clearly.

Table 4.1

	value / kJ mol^{-1}
sum of 1st and 2nd electron affinity of N	+680
lattice energy of Li_3N	–4830
enthalpy change of sublimation of Li: $Li(s) \rightarrow Li(g)$	+161
enthalpy change of reaction for the following reaction: $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$	–330

[3]

The last stage in the process involves reacting lithium nitride with water. A solution containing ammonia and lithium hydroxide is produced.

equation 4 $Li_3N(s) + 3H_2O(l) \rightarrow 3LiOH(aq) + NH_3(g)$

The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(iv) The following equation represents the overall equation for electrochemical lithium cycling process.

$$\_\_\_N_2 + \_\_\_H_2O \rightarrow \_\_\_O_2 + \_\_\_NH_3$$

Complete the balancing of the above equation. Show your working clearly.

[1]

The standard Gibbs free energy changes of formation, $\Delta G_f^{\ominus}$, of several compounds are listed in Table 4.2.

Table 4.2

compound	$\Delta G_f^{\ominus}$ / kJ mol^{-1}
LiOH(s)	–439
$Li_3N(s)$	–137
$H_2O(l)$	–237
$NH_3(g)$	–17

(v) Using your equation in **a(iv)**, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, when 2 mol of ammonia are produced.

[1]

(vi) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the Haber-Bosch process shown in equation 1. By considering the stability of the reactants and products, explain why this value is different from that calculated in **a(v)**.

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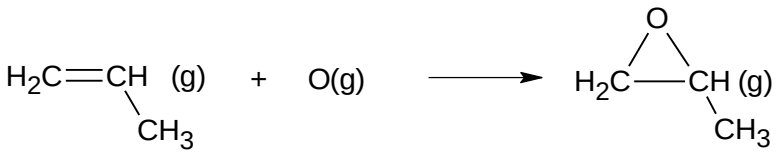
..... [2]

(b) An epoxide is a cyclic ether (C–O–C) that is highly reactive. Like all compounds containing a 3-membered ring, the bonds in 1,2-epoxypropane are weaker. This can be illustrated by the following calculation, in which you can assume that the C–H bond energy is the same in propane and 1,2-epoxypropane.

The $\Delta H^{\ominus}$ for the reaction between propene molecules and oxygen atoms has been calculated to be -363 kJ mol^{-1}.



(i) Use the data from the *Data Booklet* to calculate a theoretical value for the sum of the C–C and 2 × C–O bond energies in 1,2-epoxypropane.

[1]

(ii) Use the $\Delta H^{\ominus}$ value for the reaction between propene and oxygen atoms given above to calculate the actual value for the sum of the C–C and 2 × C–O bond energies in 1,2-epoxypropane. Suggest an explanation for the difference between the theoretical and actual values.

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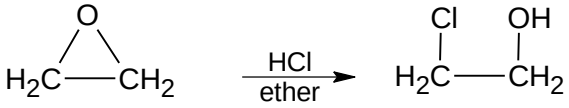
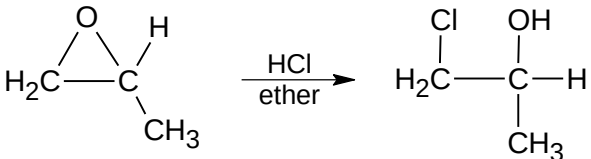
(c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



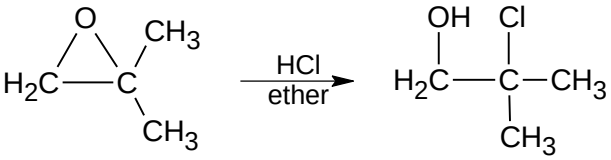
The ring–opening reaction of epoxides can proceed by either S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane reacts with HCl via different mechanisms to give the following major products.

Reaction 1



1,2-epoxypropane

Reaction 2



2-methyl-1,2-epoxypropane

(i) Explain why the reaction proceeds via the given predominant mechanism and not the other.

Type of mechanism for reaction 1: S_N2

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Type of mechanism for reaction 2: S_N1

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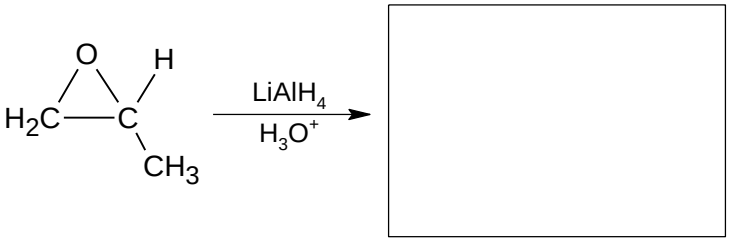
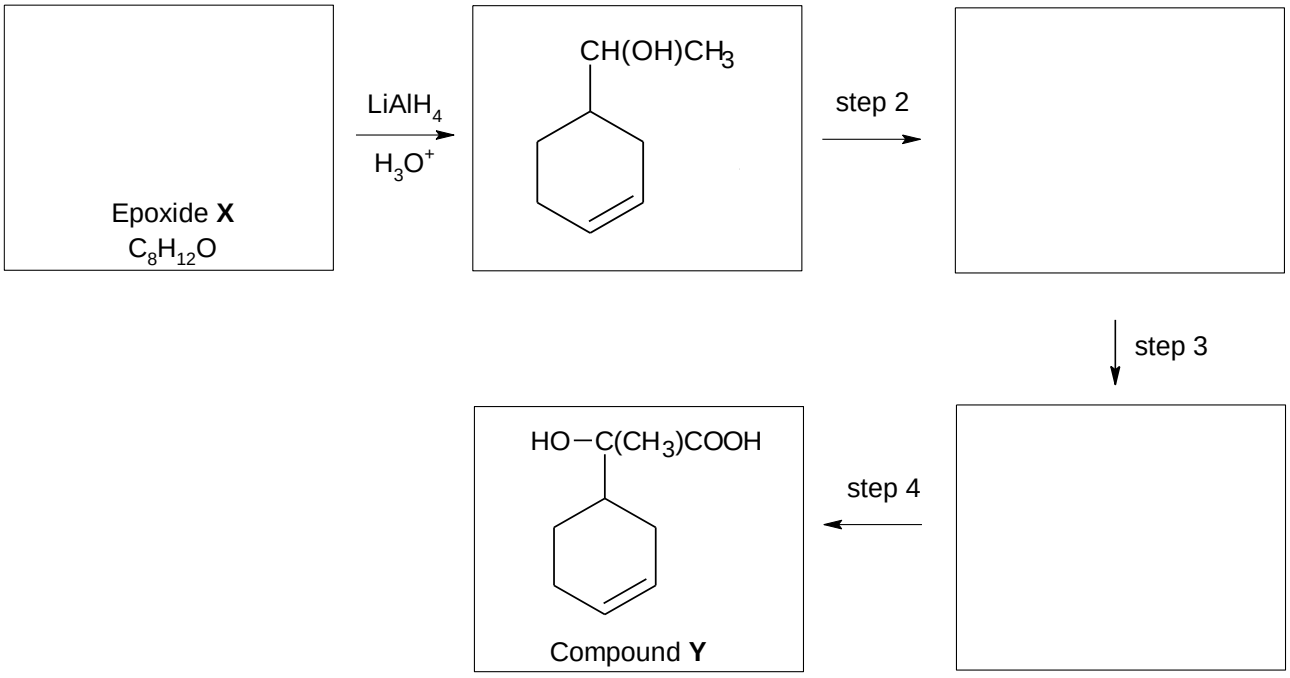
Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides. S_N2 mechanism usually predominates with these reagents.

(ii) Draw the structural formula of the major product formed when 1,2-epoxypropane reacts with $LiAlH_4$.



[1]

(iii) Compound **Y** can be formed via a four-step synthesis with epoxide **X** as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step.



step 2: .....

step 3: .....

step 4: ..... [6]

(iv) A small amount of a sweet-smelling side product, $C_{18}H_{24}O_4$, is formed in step 4. Draw the structure of this side product.

[1]

[Total: 24]

5(a) **(i)** Complete the electronic configurations for copper atom and its copper(II) ion.

Cu $1s^2$ .....

Cu^{2+} $1s^2$ ..... [1]

(ii) The copper used for electrical wiring must be very pure. An impure copper bar containing silver and zinc impurities is purified by electrolysis. Describe the electrode reactions that take place and explain in detail how each of the two impurity metals is removed.

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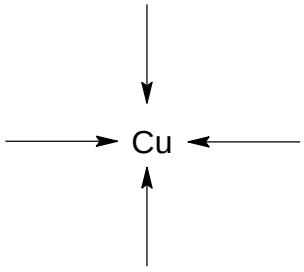
(b) Copper(II) ions will form a complex with the basic form of the amino acid glycine as the ligand. The formula of this complex may be written as $Cu(CH_2(NH_2)CO_2)_2$.

Complete the diagram to suggest the structure for this complex.



[1]

(c) Describe and explain what you would see when $NH_3(aq)$ is added slowly to a solution of copper(II) nitrate, until the $NH_3(aq)$ is in an excess. Write equations for any reactions that occur.

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[Total: 8]

6 Compound **W** has the molecular formula C_7H_7OCl. It is an aromatic compound which contains two functional groups.

Data about the reactions of **W** are given in the table.

reaction	reagent	result
1	$AgNO_3$(aq), warm	white solid formed which is soluble in an excess of NH_3(aq)
2	Br_2(aq) in an excess	white solid formed which has M_r = 379.2
3	MnO_4^-/ OH^- heat under reflux then acidify	MnO_4^- is decolourised; one organic product formed with M_r = 138
4	Na	colourless gas evolved; white solid formed which is soluble in H_2O
5	NaOH(aq) at room temperature	colourless solution formed

In this question, when identifying functional groups, your answers should be unambiguous.

(a) **(i)** Name the functional group that reaction **1** shows to be present in **W**.

.....[1]

(ii) Based only on reaction **4**, give the names of two different functional groups that could be present in **W**.

..... and .....[1]

(iii) Which of the functional groups you have named in **(ii)** is confirmed by reaction **5**? Explain your answer.

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.....[2]

(b) **(i)** Deduce the molecular formula of the white solid formed in reaction **2**.

[1]

(ii) Explain clearly how the formation of this compound shows that compound **W** is an aromatic compound rather than an aliphatic compound.

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..... [2]

(iii) Which other reaction confirms that **W** is aromatic? Explain your answer.

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..... [1]

(c) You now have enough information to determine the structural formula of **W**.

(i) Draw the fully displayed structure of **W**.

[2]

(ii) Explain clearly why you have placed **each** of the two functional groups in their particular positions.

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..... [2]

[Total:12]

[End of Paper]