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**.

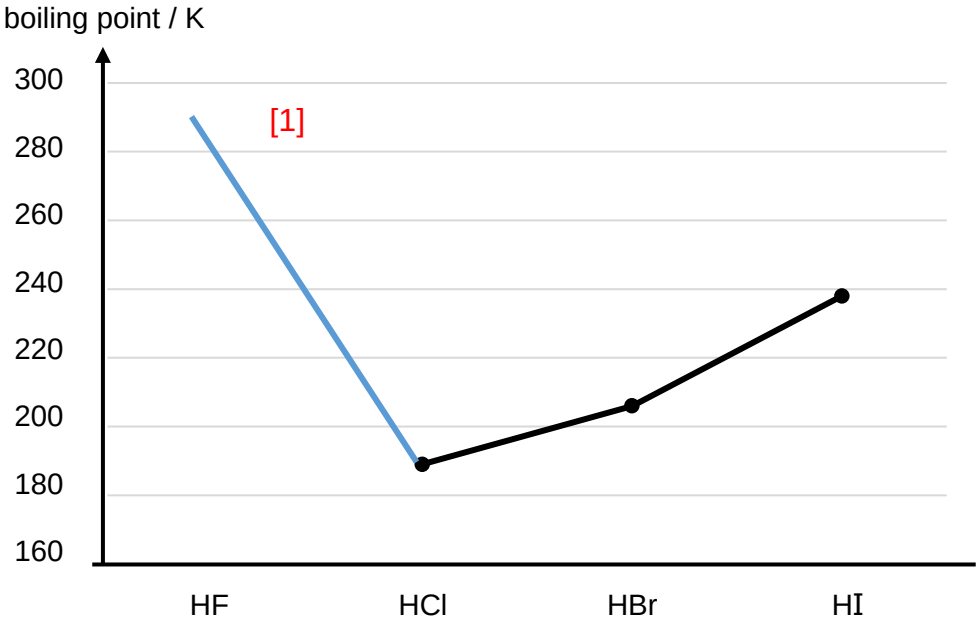
X Al_2O_3 ..... **Y** P_4O_{10} ..... [1]

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

X: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ [1] .....

Y: $P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$ [1] ..... [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.

HCl, HBr and HI have simple molecular structures with weak instantaneous dipoles-induced dipoles (id-id) between molecules. [1] The size of electron cloud increases from HCl to HBr to HI, the electron cloud gets more easily polarised. Hence more energy is required to overcome the stronger id-id, giving rise to increasing boiling points. [1]

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..... [2]

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

HF has hydrogen bonding between molecules. Hydrogen bonding is stronger than id-id hence more energy required to overcome hydrogen bonding. HF has the highest boiling point. [1]

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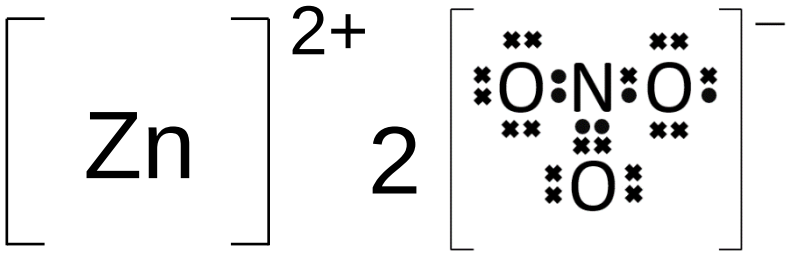
..... [2]

(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.



Balanced charges – 1 mark; correctly drawn nitrate ion – 1 mark

[2]

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

- Ionic radius of Zn^{2+}(0.074 nm) is much smaller than Ba^{2+}(0.135 nm)
- Both have same ionic charge +2 hence charge density (thus polarising power) of Zn^{2+} is higher.
- Electron cloud of NO_3^- is polarised to larger extent in $Zn(NO_3)_2$.
- N–O bond is weakened to larger extent.
- Hence $Zn(NO_3)_2$ has a lower thermal stability/greater ease of thermal decomposition and thermal decomposition temperature is lower.

5●: 3 marks; 4●: 2 marks; 2–3● : 1 mark

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.....[3]

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

$Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + \frac{1}{2} O_2$ [1] .....[1]

Will not accept if it is $Ba(NO_3)_2$ as barium nitrate will not decompose at 350 °C.

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

Let mass of barium nitrate = x g
mass of zinc nitrate = (20.0 – x) g
mass of zinc oxide = (11.3 – x) g
amount of ZnO = amount of $Zn(NO_3)_2$

- $\frac{11.3 - x}{65.4 + 16.0} = \frac{20.0 - x}{65.4 + 2(14.0) + 6(16.0)}$

$\frac{11.3 - x}{81.4} = \frac{20.0 - x}{189.4}$

$2140.22 - 189.4x = 1628 - 81.4x$

$108x = 512.22$

- $x = 4.742$

- mass of $Zn(NO_3)_2$ = 20.0 – 4.742 = 15.257 g

- % by mass = $\frac{15.257}{20.0} \times 100\% = 76.28\% = 76.3\%$

4●: 2 marks; 2,3● : 1 mark

[2]

[Total: 15]

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

HO_2CCO_2H Ý $HO_2CCO_2^-$ + H^+ $\quad pK_{a1} = 1.27$

$HO_2CCO_2^-$ Ý $^-O_2CCO_2^-$ + H^+ $\quad pK_{a2} = 4.28$

(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.

$OH^- + HO_2CCO_2H \rightarrow HO_2CCO_2^- + H_2O$ [1]..... [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).

	OH^- +	HO_2CCO_2H →	$HO_2CCO_2^-$ +	H_2O
I	**0.0014**	**0.001**	**0.0015**	
C	–0.001	–0.001	+0.001	
F	**0.0004**	0	**0.0025**	

1 mark for the amount of OH^- and $HO_2CCO_2^-$

There is still excess alkali.

	OH^- +	$HO_2CCO_2^-$ →	$^-O_2CCO_2^-$ +	H_2O
I	0.0004	0.0025	0	
C	–0.0004	–0.0004	+0.0004	
F	**0**	**0.0021**	**0.0004**	

1 mark for the **final** amount of the oxalates

Another buffer has been formed.
New total volume = 14.0 + 10 + 10 = 34.0 cm^3
pH = 4.28 + lg [(0.0004 /0.034) / (0.0021/0.034)] = **3.56** **[1]**

[3]

[Turn Over

(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}.

$$K_{sp} \text{ of } CaC_2O_4 = [Ca^{2+}][C_2O_4^{2-}] = \frac{1}{\frac{1}{[Ca^{2+}][C_2O_4^{2-}]}} = \frac{1}{K} = \frac{1}{10^{\lg K}} = \frac{1}{10^{8.63}}$$

$= 2.34 \times 10^{-9}$ [1]

1 mark for establishing the relationship between K_{sp} and lg *K* and calculating the value of the K_{sp} of MgC_2O_4 correctly

(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.

K_{sp} of CaC_2O_4 = $[Ca^{2+}][C_2O_4^{2-}]$ = (0.010) $[C_2O_4^{2-}]$ = 2.34×10^{-9}
minimum concentration of $C_2O_4^{2-}$ needed for the precipitation of Ca^{2+}

$$= \frac{2.34 \times 10^{-9}}{0.010}$$

$= 2.34 \times 10^{-7}$ [1]

K_{sp} of $Ce_2(C_2O_4)_3$ = $[Ce^{3+}]^2[C_2O_4^{2-}]^3$ = **$(0.010)^2[C_2O_4^{2-}]^3$** = 6.60×10^{-31}
minimum concentration of the oxalate ion, $C_2O_4^{2-}$ needed for the precipitation of Ce^{3+}

$$= \sqrt[3]{\frac{6.60 \times 10^{-31}}{(0.010)^2}}$$

$= 1.88 \times 10^{-9}$ [1]

[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+}.

To prevent Ca^{2+} from precipitating as CaC_2O_4, the solution must contain enough H^+ to give a maximum $[C_2O_4^{2-}]$ of 2.34×10^{-7} mol dm^{-3}. [1]

Using the equilibrium constant for the dissociation of oxalic acid from Table 2.1, we can then calculate the required $[H^+]$ in solution A.

$$10^{-5.06} = \frac{[H^+]^2[C_2O_4]^{2-}}{[HO_2CCO_2H]} = \frac{[H^+]^2(2.34 \times 10^{-7})}{1.0}$$

$[H^+] = 6.095$ [1]

pH = –lg(6.095) = – 0.785 [1], ecf allowed

[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 °C.

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

$$p = \frac{34/17.0 \times 8.31 \times (77 + 273)}{7 \times 10^{-3}} = 831 \text{ kPa} = 8.20 \text{ atm}$$ [1]

[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 bar = 0.9869 atm

$$R = \frac{0.9869 \times 22.7}{1 \times 273} = 0.08206 = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$ [1]

[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.

$$[p + 4.17(\frac{2}{7})^2](\frac{7}{2} - 0.0371) = 0.08206(77 + 273)$$

p = 7.953 = 7.95 atm [1]

[1]

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

The assumption using the ideal gas law is that there is no forces of attraction between gas particles. In reality, there is a hydrogen bonds between NH_3 molecules that tends to hold the molecules together which results in the calculated pressure to be smaller than expected. [1]

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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.

The stronger the intermolecular forces of attraction, less energy is required to liquefy (easier to condense from gas to liquid). In the above example, the three gases have simple molecular structure. N_2 has instantaneous dipole-induced dipole forces of attraction between N_2 molecules, while NH_3 and N_2H_4 have hydrogen bonds between NH_3 molecules and between N_2H_4 molecules. [1]

N_2H_4 can form an average of two hydrogen bonds per molecule while NH_3 can form an average of one hydrogen bond per molecule. Hence hydrogen bonds between N_2H_4 molecules is more extensive. [1]

This is in agreement how the a constants increases in order $N_2 < NH_3 < N_2H_4$.

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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.

$Li^+ + e^- \rightleftharpoons Li$ –3.04V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83V
Based on the reduction potential values in the data booklet, since $E^{\ominus}$ (H_2O/ H_2) of water is more positive, water will be preferentially reduced (to H_2 and OH^-) as compared to Li^+ to Li. [1]

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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.

Lattice energy is the energy change/evolved when one mole of Li_3N ionic compound is formed from gaseous Li^+ and N^{3-} ions at standard conditions. [1]

$3Li^+(g) + N^{3-}(g) \rightarrow Li_3N(s)$ [1]

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.....

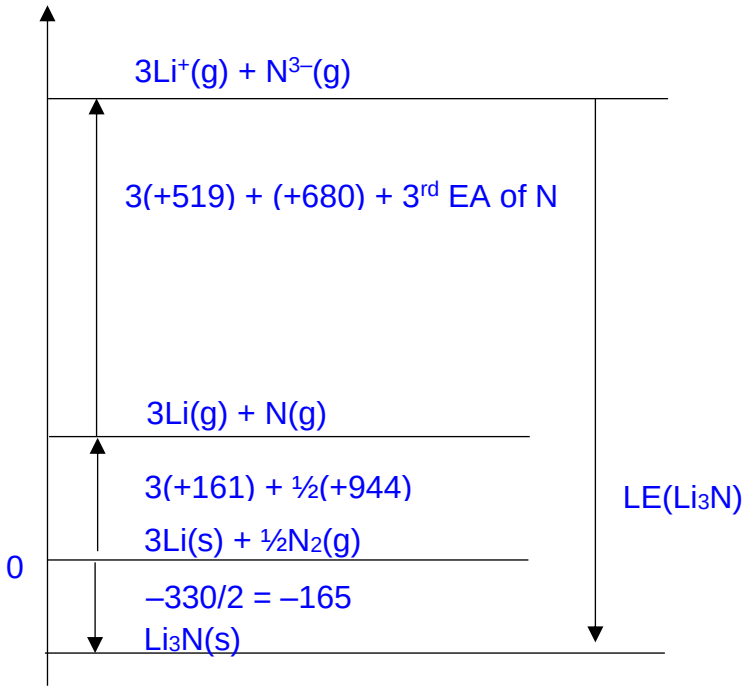
..... [2]

(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

energy / kJ mol^{-1}



All 4 correct levels – [2]; 2,3 correct levels points – [1]

$-165 = 3(+161) + ½(+944) + 3(+519) + (+680) + 3^{rd}$ EA of N + (–4830)

3^{rd} EA of N = +1473 = +1470 kJ mol^{-1} [1]

[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.

(2) x 3: ~~$6LiOH \rightarrow 6Li + \frac{3}{2} O_2 + 3H_2O$~~

(3) ~~$6Li + N_2 \rightarrow 2Li_3N$~~

(4) x 2: ~~$2Li_3N + 6H_2O \rightarrow 6LiOH + 2NH_3$~~

Overall equation: $N_2 + 3H_2O \rightarrow \frac{3}{2} O_2 + 2NH_3$ [1]

[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.

$\Delta G^{\ominus} = \Delta G_f^{\ominus}$(products) – $\Delta G_f^{\ominus}$(reactants)
$\Delta G_f^{\ominus}$ for elements = 0
$\Delta G^{\ominus}$ for the production of 2 mol NH_3 = –17(2) – (–237)(3) = +677 kJ mol^{-1} [1]

[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)**.

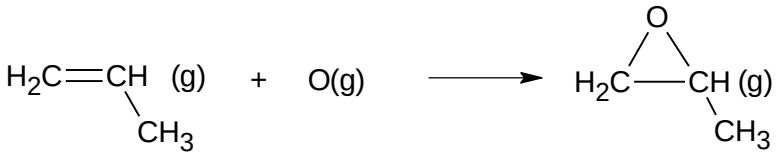
$\Delta G^{\ominus}$ for equation 1 = –17(2) = –34 kJ mol^{-1} [1]

Based on the $\Delta G_f^{\ominus}$ data given, H_2O is thermodynamically much more stable than NH_3 as compared to their respective reactants. The overall equation derived in **(a)(iv)** involved the formation of NH_3 from H_2O and it is thus highly unfavourable ($\Delta G^{\ominus} > 0$). For equation 1, it simply involves the formation of NH_3 from its elements ($\Delta G^{\ominus} < 0$). [1]

[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.

From the *Data Booklet*,
BE(C−C) + 2×BE(C−O) = 350 + 2×360 = +1070 kJ mol^{-1} **[1]**

[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.

$\Delta H_r^{\ominus}$ = ∑BE(bonds broken) − ∑BE(bonds formed)
−363 = BE(C=C) – [BE(C−C) + 2×BE(C−O)]
−363 = (+610) – [BE(C−C) + 2×BE(C−O)]
−363 = 610 – [BE(C−C) + 2×BE(C−O)]
BE(C−C) + 2×BE(C−O) = +973 kJ mol^{-1} **[1]**

The actual value is less endothermic as the C–O and C–C bonds in the 3-membered ring are weaker due to ring strain/ angle strain (bond angles of 105^o and 109^o respectively are now 60^o in a 3 membered ring). **[1]**

..... [2]

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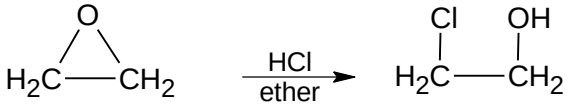
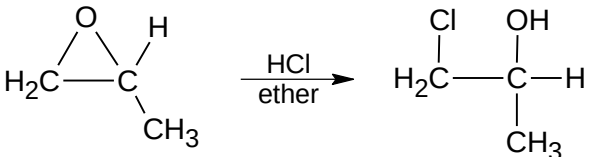
(c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



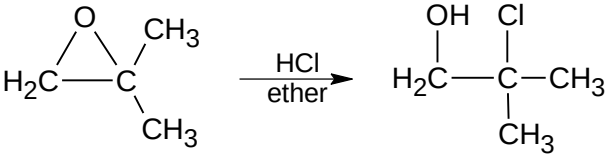
The ring–opening reaction of epoxides can proceed by either S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane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

● S_N2 mechanism is favoured since there is little steric hindrance as the electron deficient (δ+) carbon (–O–CH_2–) in 1,2-epoxypropane is attached to only 1 bulky alkyl group. Hence the Cl^- nucleophile can attack the electron deficient (δ+) carbon readily.
● S_N1 mechanism is not favoured as it will result in the formation of a primary carbocation that is unstable as it has no electron donating groups to disperse the positive charge.

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Type of mechanism for reaction 2: S_N1

● 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,

4 points – **[3]** 3 points – **[2]** 2 points – **[1]**

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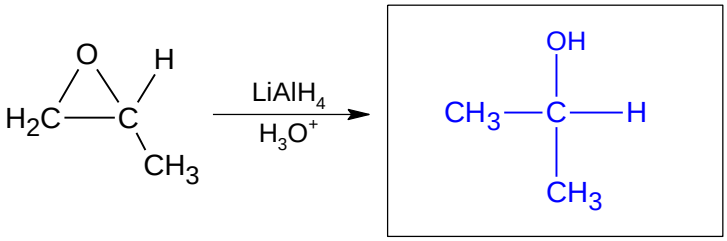
..... [3]

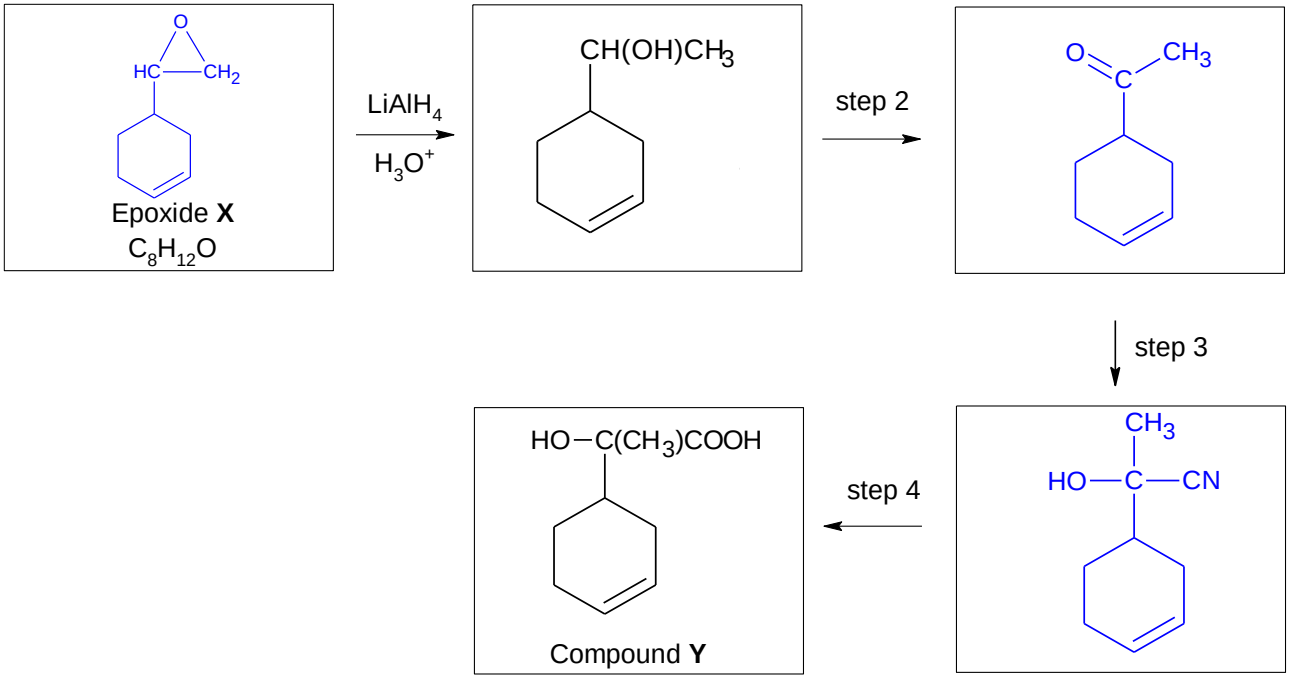
Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides. S_N2 mechanism usually predominates with these reagents.

(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.

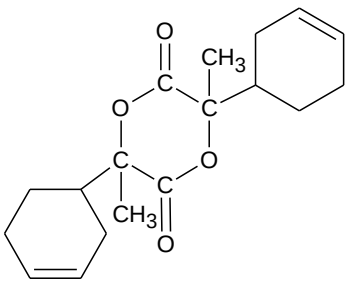


step 2: $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat under reflux [1]

step 3: HCN, traces amount of NaCN, 10 – 20 ^oC [1]

step 4: dilute H_2SO_4, heat under reflux [1]

(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]

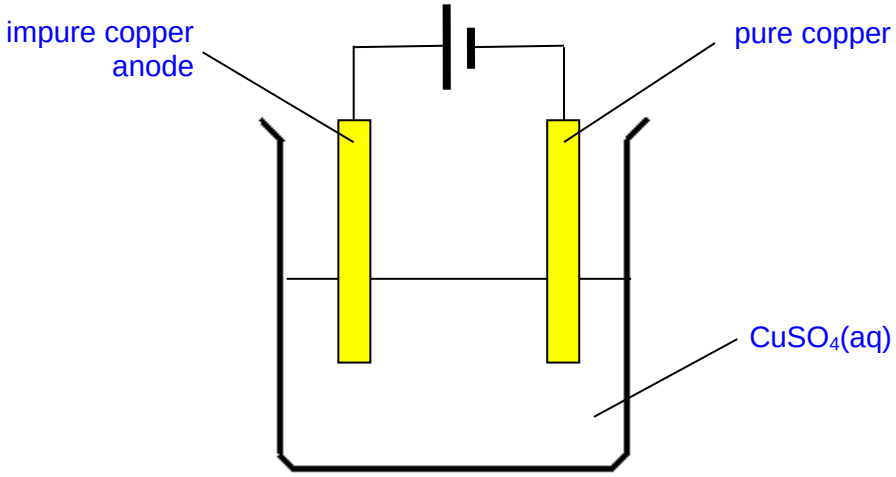
[Total: 24]

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

Cu $1s^2$ $2s^2$$2p^6$$3s^2$$3p^6$$3d^{10}$$4s^1$ .....

Cu^{2+} $1s^2$$2s^2$$2p^6$$3s^2$$3p^6$$3d^9$..... [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.



Reaction at anode: $Cu \rightarrow Cu^{2+} + 2e$ and $Zn \rightarrow Zn^{2+} + 2e$
Reaction at cathode: $Cu^{2+} + 2e \rightarrow Cu$
[1] – equations

- Since $E(Zn^{2+}/Zn)$ is *more negative* than $E(Cu^{2+}/Cu)$, Zn will also be oxidised at anode to form Zn^{2+} and migrate to the cathode.
- Zn^{2+} will not be reduced at the cathode since $E(Zn^{2+}/Zn)$ is *more negative* than $E(Cu^{2+}/Cu)$ (or $E(Cu^{2+}/Cu)$ is more positive than $E(Zn^{2+}/Zn)$)
- Since $E(Ag^+/Ag)$ is *more positive* than $E(Zn^{2+}/Zn)$, Ag (and any other less reactive metals e.g. Au) will not be oxidised.
- Ag drops off the electrode as the copper around dissolves, and fall to the bottom of the electrolytic tank to form anode sludge.

4 points: 2 marks; 2 – 3 points: 1 mark

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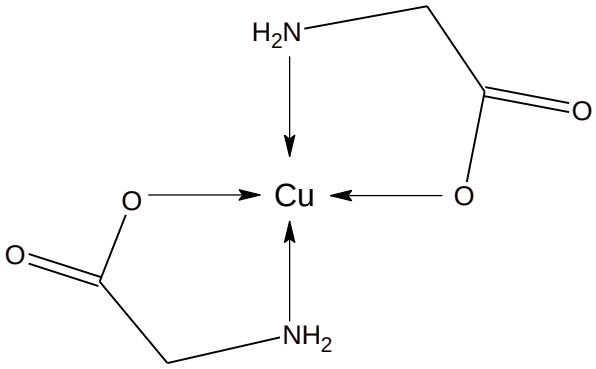
..... [3]

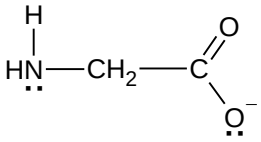
(b) Copper(II) ions will form a complex with the basic form of the amino acid glycine as the ligand. The formula of this complex may be written as $Cu(CH_2(NH_2)CO_2)_2$.

Complete the diagram to suggest the structure for this complex.



or

Legend:



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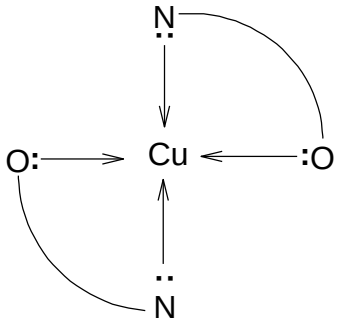

[1]

[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.

- A blue ppt of $Cu(OH)_2$ is formed which dissolves in excess NH_3 to form a deep blue solution.
- Ammonia which is a weak base which dissociates partially in water to produce OH^-.
  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ – Eqn (1)
- OH^- precipitates $Cu(OH)_2$
  $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$ – Eqn (2)
- When ammonia is added in excess, ligand exchange takes place. Stronger NH_3 ligands replace weaker H_2O ligands. It forms a stable soluble complex of $[Cu(NH_3)_4]^{2+}$.
  $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$ – Eqn (3)
- This causes concentration of $[Cu(H_2O)_6^{2+}]$ to decrease. By Le Chatelier's Principle, position of equilibrium for Eqn (2) shifts to the left and blue ppt $Cu(OH)_2$ dissolves.
- Ionic product of $Cu(OH)_2$ falls lower than its K_{sp}, hence $Cu(OH)_2$ ppt dissolves.

Total 6 points. Any 2 points [1]

..... [3]

[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**.

Alkyl halide / Alkyl chloride / Halogenoalkane / Chloroalkane [1]..... [1]

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

Alcohol..... and Phenol [1]..... [1]

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

Phenol.
Phenol is a stronger acid than alcohol and hence will be able to undergo neutralisation with NaOH(aq) at room temperature. [1]

[1] to explain why phenols are more acidic (accept also why alcohols are less acidic)
The phenoxide ion is more stable than the alkoxide ion as the p orbital of O overlaps with the π orbital of the benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into the benzene ring. The negative charge on O atom is dispersed over the benzene ring and one oxygen atom, hence stabilising the phenoxide ion.
Therefore, phenol is the more acidic and POE of dissociation lies more to the right compared to that of alcohols.

The alkoxide ion is less stable as the negative charge on O atom is intensified by electron donating alkyl group, hence destabilising the alkoxide ion. Therefore, alcohol is the less acidic, and POE of dissociation lies more to the left compared to that of phenols.

FYI (If qn has more marks):

A phenoxide ion is formed which is soluble in aqueous solution as it is able to form extensive ion-dipole interaction with water molecules (energy released in forming ion-dipole interaction between phenoxide ion and water molecules is sufficient to overcome the ionic bonds between Na^+ and phenoxide ion) hence a colourless solution is formed after reaction. If an alcohol was present, no reaction occurred and the expected observation is two immiscible layers as the alcohol is bonded to a non-polar bulky benzene ring (present as C:H ≈ 1:1) and forms predominantly id-id interactions.

[2]

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

Reaction 2 involves the ES bromination of phenol to form either a di- or tri-substituted product.

Assuming di-substitution, Mr = 7(12.0) + 5.0 + 16.0 + 35.5 + 2(79.9)
= 300.3
Assuming tri-substitution, Mr = 7(12.0) + 4.0 + 16.0 + 35.5 + 3(79.9)
= 379.2

Molecular formula of the organic product: $C_7H_4OClBr_3$. [1]

[1]

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

Consider the change in molecular formulae of W (C_7H_7OCl) → $C_7H_4OClBr_3$.
There is a loss of 3 H atoms and they are replaced by 3 Br atoms. This shows that substitution must have occurred. Aliphatic alkenes will undergo addition reaction and there is no alkyl sidechain in W for the substitution of 3 H atoms, since the side chain is a -CH_2Cl group. **[1]**

W must be an aromatic compound to undergo **electrophilic substitution** reactions
- To prevent the ring of delocalised electrons from breaking OR
- To prevent the loss of aromatic stability. (either pt 1mk)

.....

..... [2]

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

reaction 3;
side-chain oxidation occurs when the carbon containing side-chain is attached to an aromatic ring. [1]

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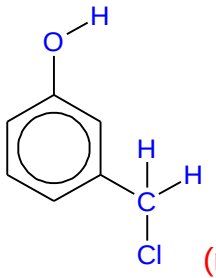
..... [1]

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

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



(no other structures possible)

Correct side-chain, displayed structure [1]

[2]

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

Based on the answer in (c)(i), tri-substitution of benzene occurs because −OH is a strong electron-donating group. It increases electron-density in the benzene ring. It activates the ring towards electrophilic substitution. Hence Br will be substituted onto the benzene ring at the 2,4 and 6 position. As such the substituent group $-CH_2Cl$ must be in the 3rd position from the –OH group. **[1]**

The chlorine atom must be in the aliphatic side-chain and not attached to the benzene ring because W undergoes nucleophilic substitution (reaction 1).
If chlorine atom is attached directly to the benzene ring, the p orbital of Cl will overlap with the π orbital of benzene ring causing the lone pair of electron on Cl atom to be delocalized into the benzene ring, strengthening the C–Cl bond, and W will not be able to undergo reaction 1. **[1]**

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..... [2]

[Total:12]