Class Adm No

Candidate Name: _____

H

millennia institute

2024 Mid-Year Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **5 July 2024**

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so.

Write your name, class and admission number in the spaces at the top of this page.
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** questions.

Section B
Answer **one** question.

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

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.

Question	A				B	**Total**
	1	2	3	4	5 / 6	
Marks	13	15	20	12	20	**80**

Section A

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

1 Manganese is a transition metal.

(a) **(i)** State the full electronic configuration of a manganese atom. [1]

(ii) Draw the shapes of the $3d_{xy}$, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of a manganese atom. Label all your orbitals clearly. [3]

(iii) Compared to main Group metals, transition metals have high melting points and high boiling points.

State two more properties of transition metals that are different from main Group metals. [2]

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(b) Explain, in terms of structure and bonding, why manganese(II) oxide, MnO, and manganese(VII) oxide, Mn_2O_7, have such different melting points.

compound	melting point / °C
MnO	1945
Mn_2O_7	6

[2]

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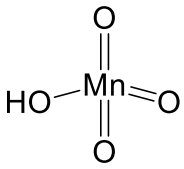
(c) Mn_2O_7 reacts with water to form permanganic acid, $HMnO_4$.



permanganic acid

(i) Write an equation for the reaction. [1]

(ii) Suggest the type of reaction. [1]

(iii) Draw the structure for Mn_2O_7. [1]

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(d) Describe and explain the trend of atomic radii for the period 4 transition metals, starting from titanium and ending with copper. [2]

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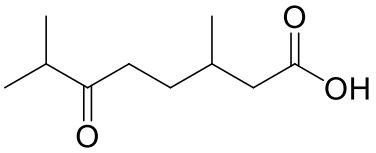
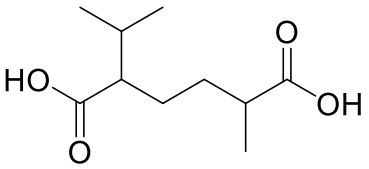
[Total: 13]

2 **(a)** Compound **L**, $C_{10}H_{20}O$, was heated with concentrated sulfuric acid to form **M** and **N**.

When each of **M** and **N** was separately heated with acidified potassium manganate(VII), **M** was converted into **O**, while **N** was converted into **P**.



O
($C_{10}H_{18}O_3$)



P
($C_{10}H_{18}O_4$)

(i) Describe a simple chemical test that can be used to distinguish between samples of **O** and **P**. Give the reagents and describe what you would see. [2]

(ii) Deduce the structures for **L**, **M**, and **N**. Justify your answer. [5]

(iii) Explain whether **M** or **N** was formed to a larger extent when **L** was heated with concentrated sulfuric acid. [1]

(iv) Determine the number of stereoisomers for **L**. [1]

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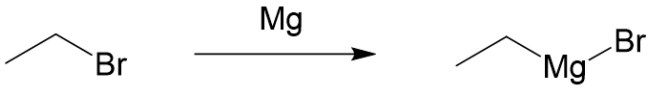
(b) A ketone can react with a bromoalkane to form a tertiary alcohol.

The bromoalkane can be made nucleophilic by mixing with magnesium in a non-polar solvent under an inert gas environment.



The magnesium atom forms one covalent bond to carbon atom, and one covalent bond to bromine atom.

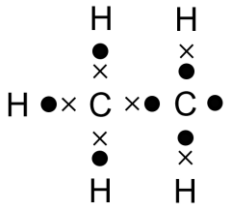


Fig. 2.1

(i) Complete the 'dot-and-cross' diagram on Fig. 2.1 to show the bonding in ethylmagnesium bromide, CH_3CH_2MgBr. [1]

(ii) Pentan-2-one reacts with CH_3CH_2MgBr via a nucleophilic addition reaction.

The mechanism undergoes the following steps:

1. The presence of the magnesium in CH_3CH_2MgBr causes the nucleophile, $CH_3CH_2^-$, to be generated.
2. The nucleophile $CH_3CH_2^-$ attacks pentan-2-one to form an intermediate.
3. The intermediate is protonated with an acid to form a tertiary alcohol.

Suggest a mechanism for the reaction.

Include an equation for the generation of the nucleophile, $CH_3CH_2^-$.
Show all relevant dipoles, curly arrows and structure of the intermediate. [3]

(iii) Pentanal can also react with CH_3CH_2MgBr to form a secondary alcohol.
This reaction takes place faster than pentan-2-one reacting with CH_3CH_2MgBr.

Give two reasons why this is so. [2]

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[Total: 15]

3 The reaction of 2-bromobutane with sodium cyanide can proceed via either the S_N2 mechanism (Fig. 3.1) or the S_N1 mechanism.

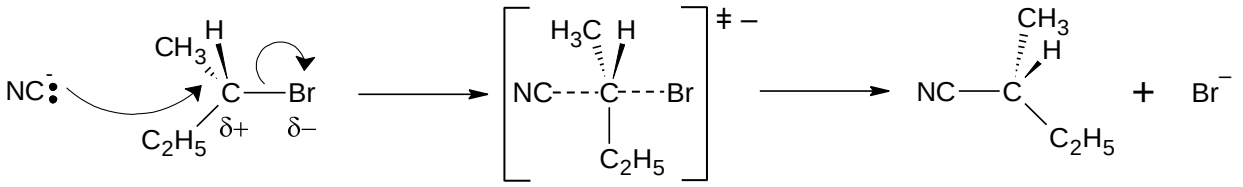

Fig. 3.1

(a) Draw the S_N1 mechanism for the reaction of 2-bromobutane with sodium cyanide.

Show all relevant dipoles, curly arrows and structure of the intermediate. [3]

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(b) The kinetics of the reaction of 2-bromobutane with sodium cyanide would depend on whether the reactants follow the S_N1 or S_N2 mechanism.

The rate equation for the reaction is given as

$$\text{rate} = k\,[\text{2-bromobutane}]^m\,[CN^-]^n$$

where m and n are the orders of reaction with respect to 2-bromobutane and CN^- respectively.

In one experiment, 0.100 mol dm^{-3} of the pure (+) enantiomer of 2-bromobutane, and 2.00 mol dm^{-3} sodium cyanide, were both dissolved in ethanol.

The concentration of 2-bromobutane was followed with time. Fig. 3.2 shows the results.

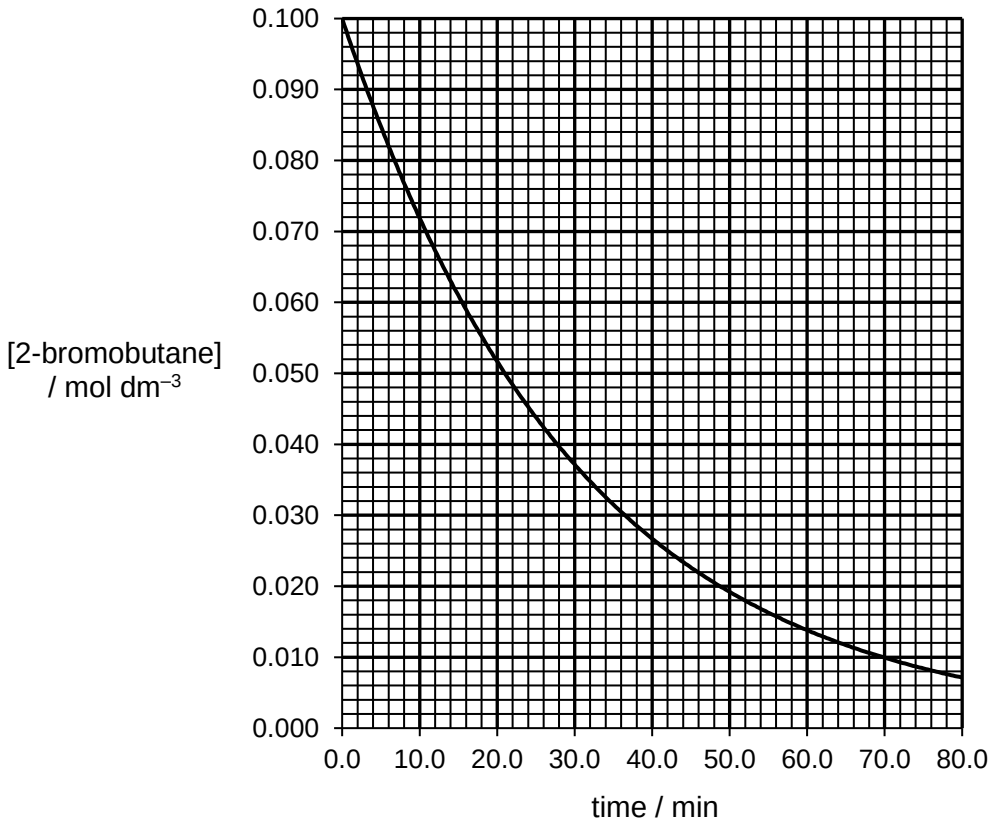

Fig. 3.2

(i) Explain why the concentration of sodium cyanide used must be much higher than 2-bromobutane. [1]

(ii) For both the S_N1 and S_N2 mechanisms, m is always 1. Explain why. [1]

(iii) From a series of experiments using different concentrations of sodium cyanide, the value of n was found to be 0.5.

By obtaining appropriate values from Fig. 3.2, calculate the rate constant, k, of the reaction, and show that it is 0.0233 $mol^{-0.5}\ dm^{1.5}\ min^{-1}$. [2]

(iv) Different concentrations of sodium cyanide were used in the series of experiments.

Table 3.1

$[CN^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1.50	
2.00	0.00330
3.00	
5.00	

Complete Table 3.1 above with the correct values of initial rate of reaction. [1]

(v) Explain why both the S_N1 and S_N2 mechanisms will be favoured by the molecular structure of 2-bromobutane. [2]

(vi) Under certain conditions, the rate of the S_N1 mechanism is equal to the rate of the S_N2 mechanism.

Under these conditions, two different enantiomers of the product molecule, (+) and (–), would be formed from the reaction.

Determine the proportion of (+) enantiomer : (–) enantiomer that would be formed from the reaction of a pure (+) enantiomer of 2-bromobutane. [1]

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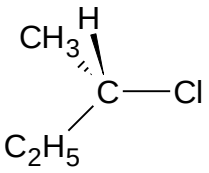
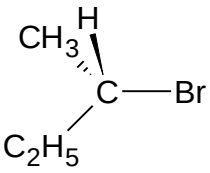
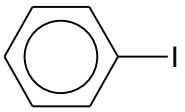
(c) 1.00 mol dm^{-3} of 3 different halogenoalkanes, **P**, **Q** and **R**, were heated under reflux with aqueous sodium hydroxide.



P



Q



R

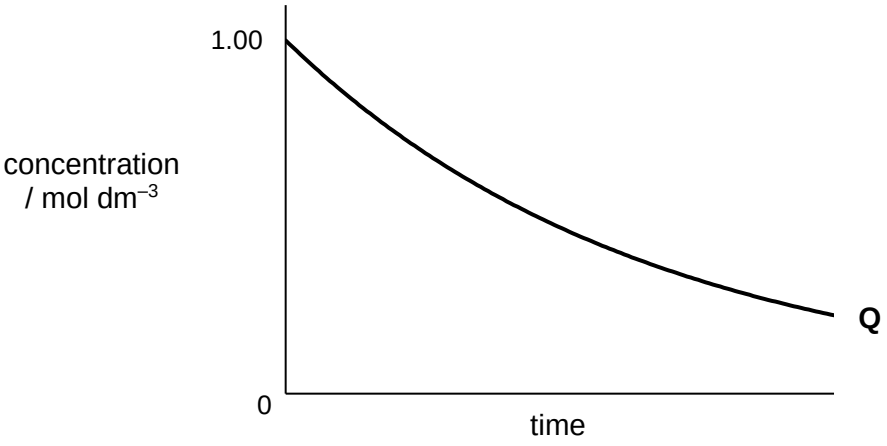


Fig. 3.3

On Fig. 3.3 above, sketch the graphs showing the concentrations of **P** and **R** over time. Label your graphs clearly.

Explain your answer. [4]

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(d) **(i)** The value of the K_{sp} of silver carbonate, Ag_2CO_3, is 8.46×10^{-12}.

Calculate the solubility of silver carbonate. [1]

(ii) Explain how the solubility of silver carbonate would be different, if it was dissolved into the following solutions instead of water:

- $Na_2CO_3(aq)$
- $NH_3(aq)$
- $HNO_3(aq)$. [4]

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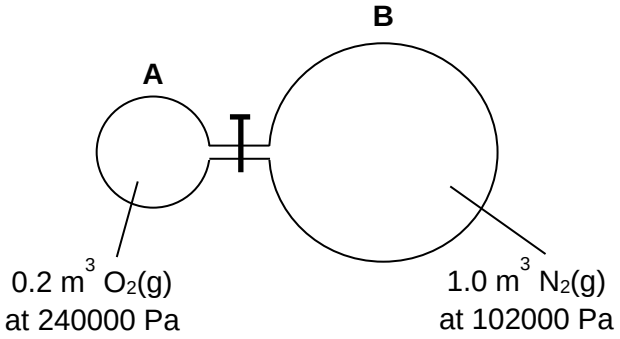
[Total: 20]

4 **(a)** Nitrox is a gas mixture containing 32% oxygen and 68% nitrogen.

The apparatus shown below was held under constant temperature, and was used to mix oxygen gas and nitrogen gas in predetermined proportions to form nitrox.



(i) Calculate the overall pressure of the gas mixture, after mixing the $O_2(g)$ in **A** with the $N_2(g)$ in **B** in the apparatus shown above. [2]

(ii) A 1.5 m^3 sample of nitrox gas at 1 bar has to be compressed to 230 bar before it can be pumped into an underwater diving tank.

Calculate the volume of nitrox that would be formed after it was compressed. [1]

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(b) An underwater diver may experience an accumulation of carbon dioxide in their bloodstream if oxygen supply from the tank is insufficient.

This can result in blood becoming more acidic.

This process is governed by two reactions:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad (1)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad (2)$$

(i) Explain how an accumulation of carbon dioxide in the blood makes it more acidic. [2]

(ii) Identify a conjugate acid-base pair from the equations above, explaining their relationship clearly. [1]

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(c) Chlorine gas is produced when concentrated sodium chloride is electrolysed.

(i) Use values from the *Data Booklet* to explain why different products are formed when dilute sodium chloride is electrolysed, compared to when concentrated sodium chloride is electrolysed. [2]

(ii) Write the half-equations for the reactions occurring at each of the two electrodes, assuming they are both inert, when concentrated sodium chloride is electrolysed. [1]

(iii) Cl_2 undergoes disproportionation in cold aqueous sodium hydroxide to form sodium hypochlorite, NaC*l*O, and sodium chloride, NaC*l*.

Write an equation for the reaction. [1]

(iv) The electrolysis of concentrated sodium chloride is often used to produce bleach, which is a solution of sodium hypochlorite, NaC*l*O.

A current of 2.5 A was passed through concentrated sodium chloride for 2 hours.

The chlorine gas produced was then mixed with the electrolyte solution at low temperature to form NaC*l*O.

Using your answers from **(c)(ii)** and **(c)(iii)**, calculate the maximum mass of NaC*l*O that could be produced with this procedure. [2]

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[Total: 12]

Section B

Answer **one** question from this section.

5 (a) The reaction of bromine with alkenes can be carried out in an inert solvent or in water as shown in Fig. 5.1.

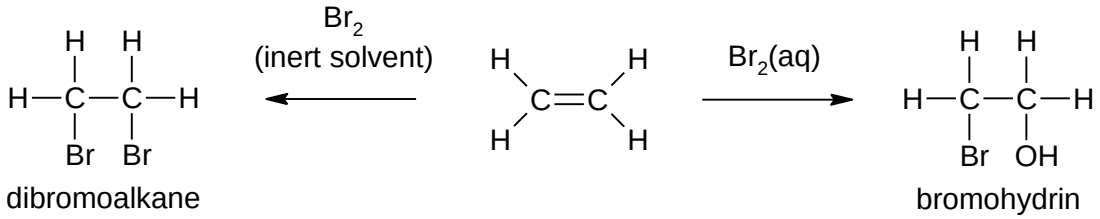

Fig. 5.1

A proposed mechanism for the formation of a bromohydrin occurs in two steps as shown in Fig. 5.2.

Step 1 is the generation of the electrophile HOBr and step 2 is the electrophilic addition reaction.

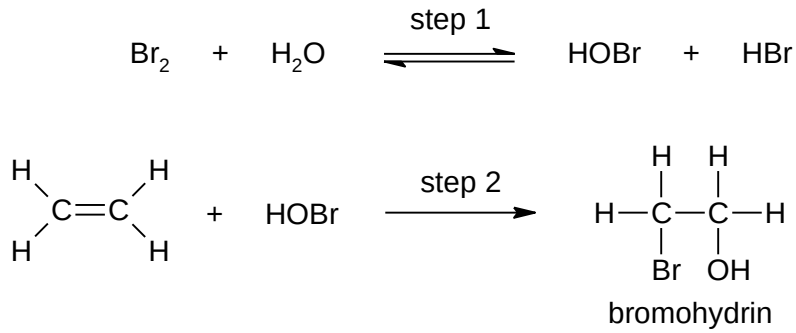

Fig. 5.2

(i) But-1-ene reacts with $Br_2(aq)$ to form a mixture of two constitutional isomers by a similar reaction to that shown in Fig. 5.2.

Suggest a mechanism for step 2 for the reaction of but-1-ene with the electrophile HOBr(aq) to form one of the isomers.

Show all relevant dipoles, curly arrows and structure of the intermediate. [3]

(ii) Give the structure of the other isomer for the mechanism that you have drawn in **(a)(i)**, and explain which of the isomers would be formed in a larger amount. [2]

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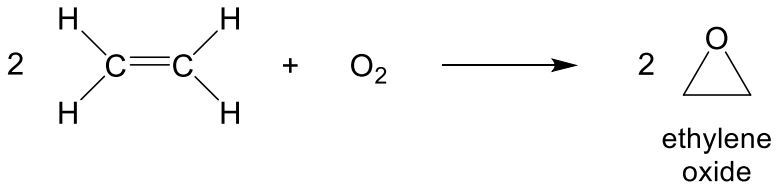
(b) Alkenes are used to produce epoxides. Epoxides contain a three-membered ring, which is made up of an oxygen atom with two carbon atoms.

In the reaction, ethene undergoes oxidation to form ethylene oxide, an epoxide.

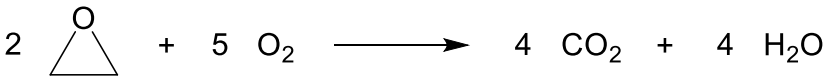


ethylene oxide

The reaction makes use of the following conditions:

- a temperature of 280 °C
- a pressure of 3 MPa
- oxygen with a purity of 95%
- silver used as catalyst.

Due to the conditions used, some ethylene oxide will undergo further oxidation to form carbon dioxide, which is a by-product of the reaction.



(i) Give the oxidation numbers of the carbon atoms found in ethylene oxide and in carbon dioxide. [2]

(ii) A temperature higher than 280 °C will decrease the yield of ethylene oxide. Suggest how this can occur. [1]

(iii) Suggest two benefits of using 95% oxygen instead of air. [2]

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(c) Silver is a heterogeneous catalyst.

(i) Define *heterogeneous catalyst*. [1]

(ii) Outline the mode of action of silver as a heterogeneous catalyst for the reaction between ethene and oxygen to form ethylene oxide. [2]

(iii) One of the species formed during the reaction is AgO_2.

The superoxide ion, O_2^-, is very reactive as it has one unpaired electron.

Draw the 'dot-and-cross' diagram for O_2^-. [1]

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(d) (i) Epoxides undergo ring-opening reactions.

One example is the reaction of ethylene oxide with cyanide ion, CN^-, followed by protonation by an acid.

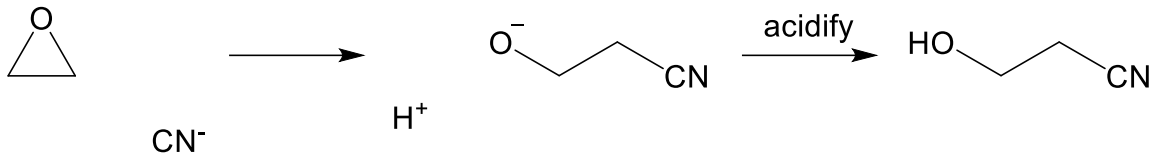
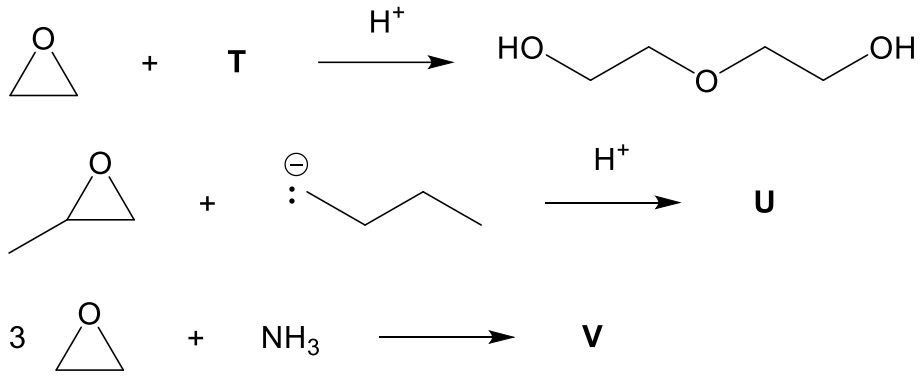


Fig. 5.3

Complete the mechanism on Fig. 5.3 by adding lone pairs, curly arrows and a dipole. [2]

(ii) Suggest the type of reaction occurring in **(d)(i)**. [1]

(iii) Draw the structures of the molecules or ions **T**, **U** and **V** for the reactions involving epoxide rings shown below.



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[Total: 20]

6 (a) (i) State and explain the trend of atomic radii of the elements down Group 2. [2]

(ii) State and explain the trend of thermal stability for the nitrates of Group 2 elements. [2]

(iii) A Group 2 metal nitrate, $\mathbf{X}(NO_3)_2$, undergoes thermal decomposition.

$$2\mathbf{X}(NO_3)_2(s) \longrightarrow 2\mathbf{X}O(s) + 4NO_2(g) + O_2(g)$$

When 5.00 g of $\mathbf{X}(NO_3)_2$ was heated strongly until no further change, the solid lost 2.55 g in mass.

Calculate the relative atomic mass of **X**, and identify the element **X**. [3]

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(b) Describe the reactions of aluminium chloride, $AlCl_3$, with water. Write equations for the reactions and explain how an acidic solution is formed. [3]

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(c) Aluminium chloride exists in equilibrium with its dimer, Al_2Cl_6.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

(i) Draw the structure of Al_2Cl_6. Label the co-ordinate bonds on your structure. [1]

(ii) Al_2Cl_6, being a dimer of $AlCl_3$, has two times the relative molecular mass, M_r, of $AlCl_3$.

Explain the effect of an increased temperature on the average M_r of the mixture. [2]

(iii) The forward reaction describes the dissociation of Al_2Cl_6 dimers.

Explain whether the forward reaction is spontaneous at high temperatures, and at low temperatures. [3]

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(d) 0.840 g of $Al_2Cl_6(g)$ was heated to 400 °C at atmospheric pressure.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

The gas mixture reached equilibrium and occupied a volume of 268 cm^3.

(i) Calculate the total number of moles of gases in the mixture after it has reached equilibrium, and calculate the average M_r of the gas mixture. [2]

(ii) Calculate the number of moles of 0.840 g of $Al_2Cl_6(g)$, and the number of moles of 0.840 g of $AlCl_3(g)$. [1]

(iii) Hence, calculate the percentage of $Al_2Cl_6(g)$ dimers that have undergone dissociation into $AlCl_3(g)$ at equilibrium. [1]

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Additional answer space

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