H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAM
Higher 1

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

8872/02

Paper 2

10 Sep 2008

Candidates answer Section A on the Question Paper.

2 hours

Additional Materials: Answer Paper
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.

Section **A**
Answer **all** questions.

Section **B**
Answer **two** questions on separate answer paper.

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	
A1	
A2	
A3	
A4	
B1	
B2	
B3	
Total	

This document consists of **15** printed pages.

Section A

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

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1 The rate of hydrolysis of a chloroalkane, RC*l* with aqueous sodium hydroxide depends on the concentration of the reactants at a fixed temperature $\mathbf{T_1}$. The values for the initial rates of hydrolysis at various initial concentrations have been determined. These are shown in the table below.

Expt	Initial conc. of NaOH / mol dm^{-3}	Initial conc. of RC*l* / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.0200	0.0150	4.0×10^{-4}
2	0.0200	0.0225	6.0×10^{-4}
3	0.0300	0.0225	9.0×10^{-4}
4	0.0600	0.0300	***x***

(a) Deduce the orders of reaction with respect to each of the reactants. Hence, write the rate equation for the hydrolysis of the chloroalkane. **[3]**

(b) Based on your answer above, calculate the magnitude of ***x.*** **[1]**

(c) Describe and explain, with an appropriate diagram, how the rate of this reaction is affected when the experiment is repeated at a higher temperature, T_2. **[3]**

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[Total: 7 marks]

2 Nitrogen and phosphorous are in the same group in the Periodic Table. The information in the following table is provided for compounds of nitrogen and phosphorous.

Compound	M_r	Boiling point / K
NH_3	17.0	240
PH_3	34.0	185

(a) Briefly explain the difference in boiling points of NH_3 and PH_3. **[2]**

……...

……...

……...

(b) Name and sketch the type of hybrid orbital used by nitrogen in forming the N – H bond in NH_3. **[2]**

(c) **(i)** Identify the ion formed by NH_3 when it dissolves in HC*l*(aq). **[1]**

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(ii) The bond angle in NH_3 differs from the ion it formed in part **(c)(i)**. By considering the change in the number and type of electron pairs around the central atom, explain why. **[1]**

[Total: 6 marks]

3 Nitric acid, HNO_3, known to early chemists as aqua fortis (meaning "strong water"), is a major commercial acid. It is available as the concentrated acid which is a 70% aqueous solution. Although colourless when pure, the acid turns yellow when exposed to light as a result of decomposition.

$$4HNO_3(aq) \longrightarrow 4NO_2(g) + 2H_2O(l) + O_2(g)$$ ---------- **(1)**

Pure nitric acid can be prepared by distillation from a mixture of potassium nitrate and concentrated sulphuric acid as shown

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$ ---------- **(2)**

This method was at one time used in the commercial preparation of nitric acid, but it has now been replaced by the Oswald process, discovered in 1902 by the German chemist Wilhelm Ostwald, who received the Nobel Prize in chemistry in 1909 for his work on catalysts. In the Ostwald process, ammonia gas is burned in oxygen over a platinum catalyst. The product is nitric oxide, NO, which reacts with oxygen to give nitrogen dioxide. When dissolved in water, NO_2 produces nitric acid. The equations are

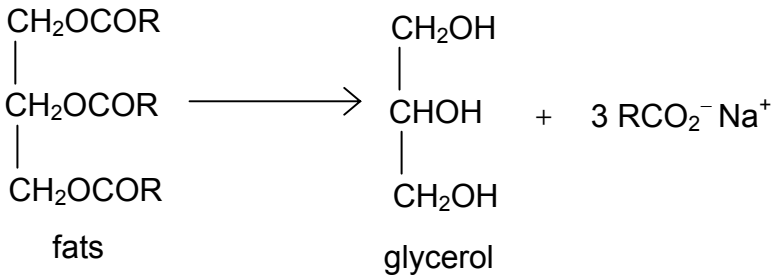
$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \quad ; \quad \Delta H_1 = -906 \text{ kJ mol}^{-1}$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad ; \quad \Delta H_2 = -114 \text{ kJ mol}^{-1}$$

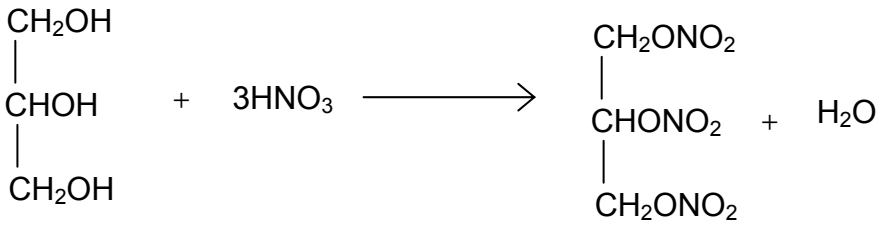
$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \quad ; \quad \Delta H_3 = -137 \text{ kJ mol}^{-1}$$

The largest single use of nitric acid is in the production of ammonium nitrate, NH_4NO_3, which is largely used as an agricultural fertiliser. It is also used to manufacture chemicals for nylon and to make explosives like nitroglycerine, $C_3H_5(NO_3)_3$. In making the explosive nitroglycerine, glycerol, $C_3H_5(OH)_3$, which is obtained from fats is used as the starting material. The manufacturing process is shown in two stages as shown below:

Stage 1



Stage 2



Nitroglycerine is hazardous to handle in the pure state. It is very sensitive to shock, exploding by the following reaction:

$$4C_3H_5(ONO_2)_3(l) \longrightarrow 6N_2(g) + 10H_2O(g) + 12CO_2(g) + O_2(g) \quad ;$$
$$\Delta H_4 = -5.720 \times 10^3 \text{ kJ mol}^{-1}$$

The reaction is highly exothermic and produces large volumes of gas. Alfred Nobel (1833 -1896) discovered that when nitroglycerine was mixed with clay and similar materials, it was much less shock-sensitive. The mixture is called dynamite. One stick of dynamite weighs 500 g and contains 80% of nitroglycerine by mass.

(a) Explain why nitric acid in a bottle often turns yellow after some time. **[1]**

……...

(b) State the type of reaction involved in the making of pure nitric acid as exemplified in reaction **(2)**. Explain your answer. **[2]**

……...

……...

……...

(c) Draw the dot and cross diagram for the NO molecule and hence suggest a reason for the reactivity of NO. **[2]**

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(d) **(i)** Using relevant data from the *Data Booklet* and the given reaction, calculate the average bond energy of the bond found in the NO molecule.

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$; $\Delta H_1 = -906$ kJ mol^{-1}

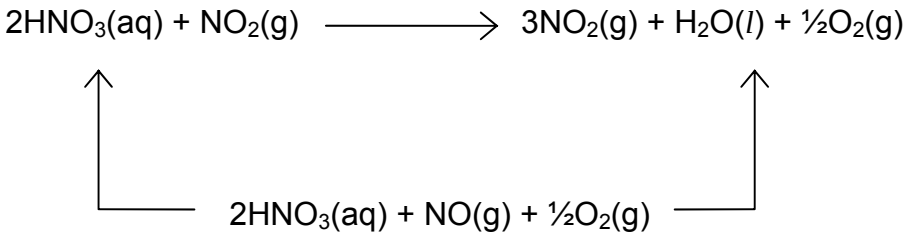
[2]

(ii) Suggest a reason for the discrepancy between your answer in part **(d)(i)** and the experimentally determined value of of 629 kJ mol^{-1}. **[1]**

……...

……...

(e) Using appropriate enthalpy change values given for the Ostwald Process and the following energy cycle, calculate the enthalpy change for reaction **(1)**. **[2]**



(f) State the reagents and conditions used for the formation of glycerol from fats. **[1]**

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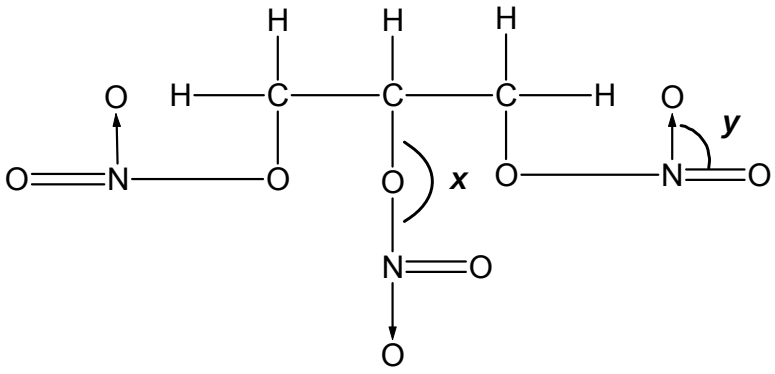
(g) The molecule of glycerine has the following structure:



(i) State the C–O–N angle (***x***) and the O–N–O bond angle (***y***) as indicated in the diagram above. **[2]**

(ii) Dynamite is still widely used in many countries for clearing of obstacles and for mining resources. Its potential danger however cannot be underestimated. Calculate the average change in temperature of the surrounding 20 m^3 of air around **one** stick of exploding dynamite.
[Volumetric heat capacity of air = 1.297 kJ m^{-3} K^{-1}] **[2]**

[Total: 15 marks]

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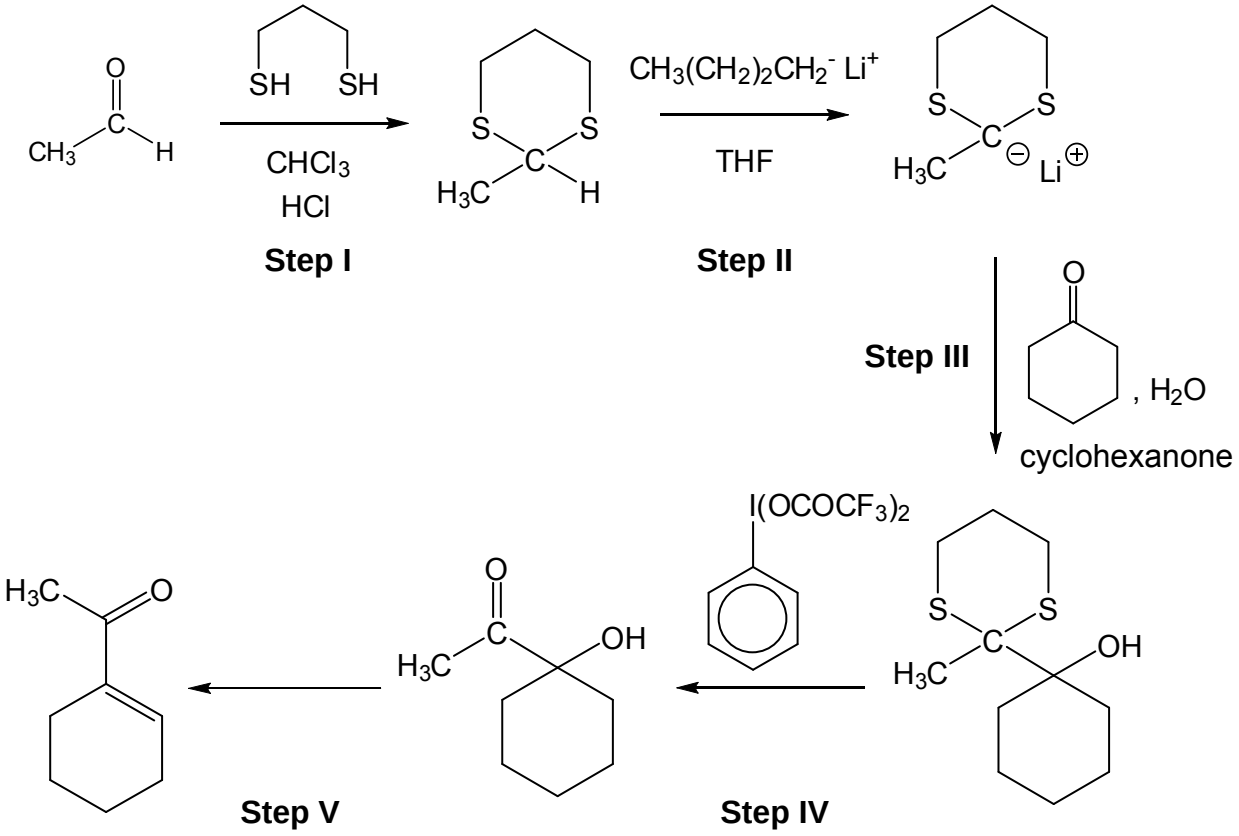
4 *Umpolung* in organic chemistry is the chemical modification of a functional group with the aim of the reversal of polarity of that group. This allows the functional group to undergo reactions that will otherwise not be possible.

The reactions below show a classic example of *umpolung* involving dithiane chemistry.



(a) **(i)** Identify the type of reactions taking place for the following steps. **[2]**

Step I	
Step II	
Step III	
Step V	

(ii) State reagents and conditions to carry out **Step V**. **[1]**

……

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(b) Aldehydes such as ethanal usually undergo attack by negatively charged species. One example is the reaction of ethanal with HCN, carried out at low temperatures in the presence of trace amounts of NaOH.

(i) Draw a displayed diagram to show the product of the reaction. **[1]**

(ii) Suggest the identity of the chemical species attacking ethanal. **[1]**

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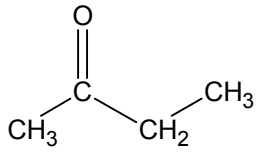
(c) In another dithiane reaction, butan-2-one was used instead of cyclohexanone in **Step III**.



butan-2-one

(i) When butan-2-one was used, three different products were obtained after **Step V**. Draw their structural formulae in the space below. **[3]**

(ii) Explain why only one product was obtained when cyclohexanone was used. **[2]**

……...

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(iii) Suggest a simple chemical test that could be carried out to distinguish between *two* of the products. Give the observation for each of the product. **[2]**

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[Total: 12 marks]

Section B

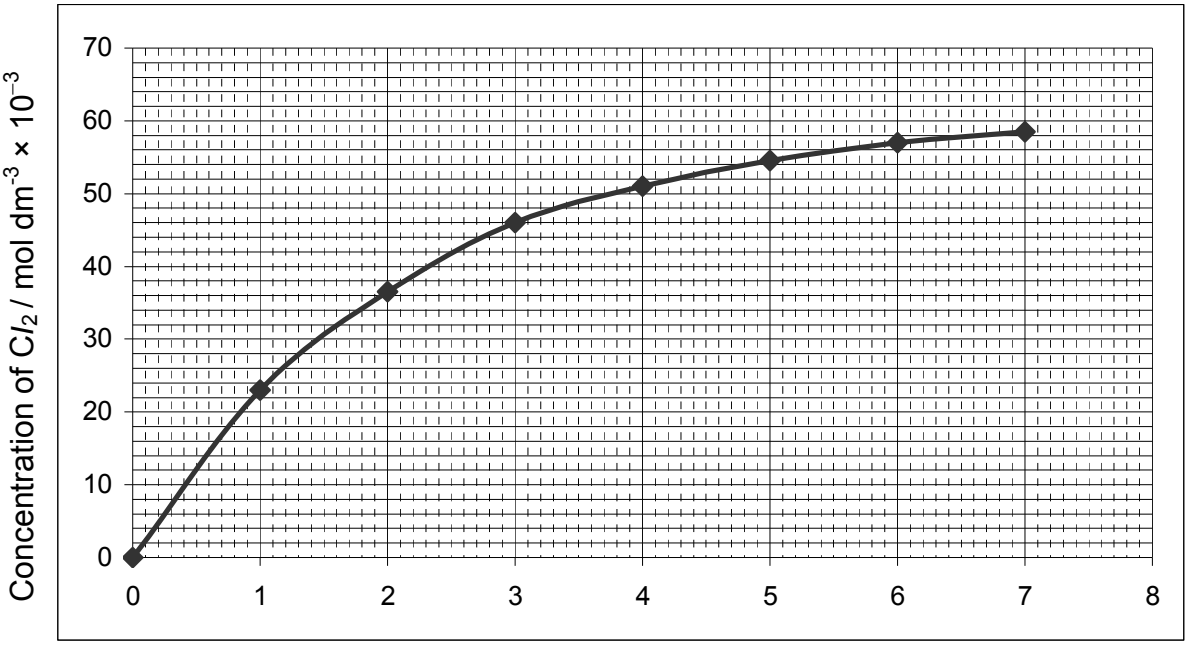
Answer **two** of the following three questions.
Answer these questions on separate answer paper.

1(a) Chloride ions react with peroxodisulphate ions, $S_2O_8^{2-}$, in a redox reaction. Lead (II) ions are used as catalyst to increase the rate of reaction.

$$S_2O_8^{2-}(aq) + 2Cl^-(aq) \rightarrow 2SO_4^{2-}(aq) + Cl_2(aq)$$

(i) Explain in terms of oxidation numbers whether sulphur is oxidised or reduced in the reaction.
(ii) Suggest a reason why the uncatalysed reaction is slow.

The following graph shows the production of chlorine as the reaction proceeded to completion.



(iii) The reaction follows *first order* kinetics. Explain the term in *italics*.
(iv) Explain why the experimental results indicate that the overall kinetics are first order.
(v) Suggest why a large excess of chloride solution was used. **[6]**

(b) The following table compares the atomic and ionic radii of sodium and chlorine.

	Atomic radius / nm	Ionic radius / nm
Sodium	0.186	0.095
Chlorine	0.099	0.181

The ionic radius of sodium is smaller than its atomic radius. However, the ionic radius of chlorine is larger than its atomic radius.
Explain the above observations. **[3]**

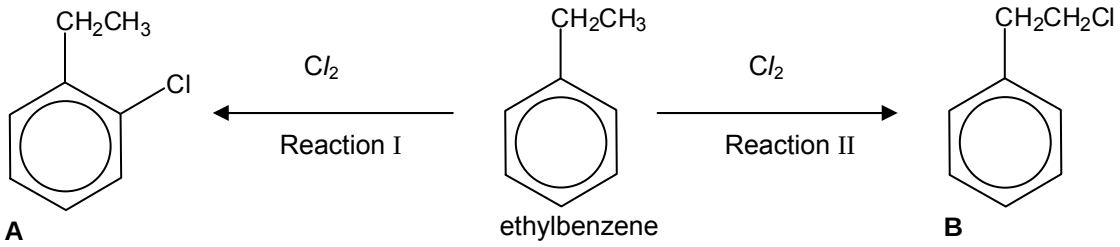
(c) Beryllium is in Group II of the Periodic Table. It shows a diagonal relationship with aluminium hence they exhibit similar physical and chemical properties.

(i) Beryllium chloride forms an acidic solution when added to water. Explain the observation, writing equations where relevant.

(ii) Beryllium chloride forms a product with ammonia.

- State the molar ratio in which beryllium chloride reacts with ammonia.
- Draw the structural formula of the product formed, showing clearly the type of bonding formed. **[5]**

(d) Ethylbenzene can undergo substitution reaction with chlorine in two ways.



(i) State the conditions needed for reaction I and reaction II.

(ii) Describe a simple test that could be used to distinguish between ethylbenzene and **B**. Include your observations for each compound.

(iii) If the C*l* substituent in **B** is replaced by Br, explain the difference in the rate of reaction with aqueous sodium hydroxide. **[6]**

2 Ethanol can be prepared industrially using ethene as the starting material as shown in Reaction **I**.

Reaction **I**: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$

(a) State the conditions required for the industrial preparation of ethanol. **[1]**

(b) The standard enthalpy change of formation of ethanol, $C_2H_5OH(l)$ can be determined by using the values of the standard enthalpy changes given:

Reaction **II**: $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$ $\Delta H_r^{\ominus} = -44.0$ kJ mol^{-1}

	$\Delta H_f^{\ominus}$/ kJ mol^{-1}
$C_2H_4(g)$	+ 52.0
$H_2O(l)$	– 285.8

(i) Define the term *standard enthalpy change of formation* of a compound.

(ii) Calculate the standard enthalpy change of formation of ethanol, $C_2H_5OH(l)$.

(iii) Explain why the state symbols for water and ethanol given in reaction **II** are different from those quoted in the industrial process as seen in reaction **I**. **[4]**

(c) Ethene can also be used as the starting material for the 3 steps synthesis of propanoic acid.

$$C_2H_4 \rightarrow \mathbf{P} \rightarrow \mathbf{Q} \rightarrow CH_3CH_2COOH$$

Suggest structures for **P** and **Q** and the reagents and conditions required to carry out the above transformations. **[5]**

(d) Propanoic acid is a weak acid whereas phosphoric acid, H_3PO_4 can act as a strong monoprotic acid.

Using propanoic acid and phosphoric acid as examples, illustrate, with the help of equations, what is meant by a *strong* acid and a *weak* acid. **[2]**

(e) **(i)** Explain what is meant by a *buffer solution*.

(ii) Suggest a suitable compound that can be added to a solution of propanoic acid to make the resulting mixture a *buffer solution*.

(iii) With the aid of **two** equations, explain how the *buffer solution* which you suggested in **part (e)(ii)** can control pH. **[4]**

(f) Information about a commercial cola drink containing phosphoric acid is given in the table below.

	Added acid	Acid concentration in drink / g dm^{-3}	Volume, at s.t.p., of CO_2 dissolved in 1 volume of drink
cola	Phosphoric acid	0.49	1.12

(i) Calculate the concentration, in mol dm^{-3}, of phosphoric acid, H_3PO_4, in the cola drink. **[1]**

(ii) Hence, calculate the pH of the cola drink. **[1]**

(iii) Calculate the amount of carbon dioxide dissolved in 1 dm^3 of cola drink at s.t.p. **[2]**

3(a) Ethanoic acid, also known as vinegar, is made by the traditional method of oxidative fermentation of aqueous solutions of ethanol.

(i) Construct a balanced equation for the formation of ethanoic acid from ethanol.

(ii) Explain, with the help of a suitable diagram, why the M_r of ethanoic acid in a non polar solvent is approximately 120.

(iii) Explain why ethanoic acid is a stronger acid than ethanol. **[5]**

(b) A mixture of 0.80 mol of ethanoic acid and 1.30 mol of ethanol was shaken for a long time to reach equilibrium. The mixture was titrated quickly with 2.00 mol dm^{-3} of NaOH and 80 cm^3 of alkali was required.

(i) Write an equation for the reaction between ethanoic acid and ethanol.

(ii) Calculate a value for the equilibrium constant K_c for this reaction.

(iii) Deduce what will happen to the value of the equilibrium constant if concentrated sulphuric acid is added to the reaction chamber. **[5]**

(c) Sodium is in Period three of the Periodic Table.

(i) Write a balanced equation, including state symbols, to show the reaction between sodium and ethanoic acid.

(ii) The elements in third period show a change from metallic to non-metallic nature, which is reflected in the chemical properties of their compounds. Describe the reactions of the oxides of elements sodium to phosphorous with water. Write balanced equations to illustrate your answer. **[6]**

(d) For the following compounds PCl_3 and $POCl_3$,

(i) Draw diagrams to show the shape of each molecule.

(ii) Deduce the polarity of each molecule. **[4]**

End of Paper