NAME:_____ **PDG:**_____ **Register No:** ____

ANDERSON JUNIOR COLLEGE

Preliminary Examination 2008

CHEMISTRY **9746/02**

Higher 2 **15 September 2008**

Paper 2 Structured **1 hour 30 minutes**

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
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** the questions.
A Data Booklet is 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	
Q1	
Q2	
Q3	
Q4	
Q5	
Total	

This document consists of **12** printed pages.

1 (a) (i) Define, by means of an equation, what is meant by the first ionisation energy of an element, **M**.

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(ii) Phosphorus and iodine are two elements found in Period 3 and Period 5 of the Periodic Table respectively. Suggest a reason why they have similar first ionisation energies.

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[3]

(b) When iodine is added to a solution of white phosphorus, P_4, in carbon disulphide at room temperature, phosphorus triiodide is formed.

(i) Write an equation for the formation of phosphorus triiodide from white phosphorus.

.....

(ii) Draw a 'dot-and-cross' diagram of the phosphorus triiodide molecule and name its shape.

Shape of molecule .....

(iii) Unlike phosphorus triiodide, phosphorus pentaiodide, PI_5, is highly unstable and cannot be prepared under room temperature. Suggest a reason for this.

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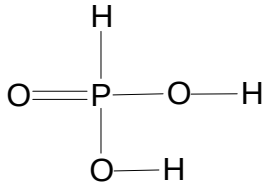
[4]

(c) Phosphorus triiodide is widely used in organic chemistry for converting alcohols to alkyl iodides. Phosphorus acid, H_3PO_3, is formed as a by-product.

$$PI_3 + 3ROH \rightarrow 3RI + H_3PO_3$$

Phosphorus acid has the following structure.



It is a dibasic acid and the two corresponding acid dissociation values are:

$K_{a\,(1)} = 1.0 \times 10^{-2}$ mol dm^{-3}
$K_{a\,(2)} = 2.5 \times 10^{-7}$ mol dm^{-3}

(i) Circle the acidic proton(s) present in the structure of phosphorus acid shown above.

(ii) Write equations to illustrate the dissociation corresponding to each of the K_a values.

$K_{a\,(1)}$ .....

$K_{a\,(2)}$ .....

(iii) Why is the second acid dissociation value smaller than the first?

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(iv) Briefly explain why H_3PO_3 is **not** tribasic.

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[4]

[Total: 11]

2 (a) (i) Hydrogen chloride can be prepared by heating sodium chloride with concentrated sulphuric acid.

Write an equation for the formation of hydrogen chloride in this reaction.

(ii) Hydrogen iodide, however, **cannot** be prepared in a similar manner described in **(a)(i)**. Explain why this is so.

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[2]

(b) Industrially, 1,2-dichloroethane is manufactured through the oxychlorination of ethene. A mixture of dry HC*l* and pure oxygen react with ethene in a reaction chamber maintained at 350 °C to form 1,2-dichloroethane and water.

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} C_2H_4Cl_2 + H_2O$$

To measure the percentage conversion of ethene to 1,2-dichloroethane, the amount of unreacted HC*l* that emerges from the chamber is bubbled through 1 dm^3 of 0.100 mol dm^{-3} NaOH for *one minute*. The resultant mixture is then analysed by a titrimetric method.

In one investigation, the feed gas entering the reaction chamber contains C_2H_4(g), HC*l*(g) and O_2(g) in molar ratio 1 : 2 : $\frac{1}{2}$. The flow rate of HC*l* into the reaction chamber is 3.65 g min^{-1}.

(i) Calculate the flow rate of ethene, in mol min^{-1}, into the reaction chamber?

(ii) In the titrimetric analysis, a 10 cm^3 sample of the resultant mixture requires exactly 2.50 cm^3 of a 0.100 mol dm^{-3} HNO_3 solution for complete neutralization.

Calculate the number of moles of unreacted NaOH present in the 1 dm^3 solution.

(iii) Calculate the number of moles of unreacted HC*l* that emerged from the reaction chamber in one minute.

(iv) Hence, calculate the molar percentage conversion per minute of ethene to 1,2-dichloroethane in the oxychlorination process.

(v) State **one** assumption made in your calculations.

.....

[6]

(c) 1,2-dichloroethane can be prepared from ethene in the laboratory via a different reaction.

(i) State the reagent(s) and condition(s) for the laboratory preparation.

reagent(s) .....

condition(s) .....

(ii) Name and outline the reaction mechanism for the laboratory preparation of 1,2-dichloroethane from ethene.

Type of reaction mechanism .....

(iii) Sketch and label a reaction pathway diagram for the proposed mechanism in **(c)(ii)**, assuming that the reaction is exothermic.

(iv) Both the industrial and laboratory preparations of 1,2-dichloroethane are carried out in an anhydrous environment to reduce the formation of by-products.

Suggest a possible by-product that can be produced in a non-anhydrous environment and explain why it is formed.

[8]

[Total: 16]

3 (a) Magnesium and barium are two alkaline earth metals which react differently with water. However, their nitrates decompose similarly on heating.

(i) How and under what conditions do magnesium and barium react with water? State what you would observe in **each** reaction.

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(ii) Write an equation for the decomposition of **either** of the metal nitrate.

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(iii) There is a noticeable difference in the decomposition temperatures of these two nitrates. State and explain which of these nitrates decomposes at a lower temperature?

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.....

[6]

(b) The numerical value for K_{sp} of magnesium fluoride is 3.70×10^{-8}.

(i) Write an expression for the *solubility product of magnesium fluoride*.

(ii) Calculate the solubility, in mol dm^{-3}, of magnesium fluoride.

(iii) In the treatment of drinking water, fluoride ions are added to natural water as a means to fight tooth decay. Fluorinated drinking water contains about 1 ppm fluoride ions.

With reference to your answers in **(b)(ii)**, deduce whether magnesium fluoride is a good source of fluoride ions for water treatment.

(Given: Density of solution = 1 g cm^{-3},
1 ppm fluoride ions = 1 g of fluoride per 10^6 g of solution)

(iv) Equal volumes of 0.02 mol dm^{-3} aqueous sodium fluoride and an unknown concentration of aqueous magnesium nitrate were mixed in a beaker.

Calculate the maximum concentration of magnesium nitrate such that no precipitate of magnesium fluoride is formed upon mixing the two solutions.

[6]

[Total: 12]

4 Photochemical smog consists of a mixture of pollutants which includes oxides of nitrogen, namely nitric oxide (NO) and nitrogen dioxide (NO_2). The smog often has a brown haze due to the presence of NO_2. In most major cities, such as Mexico and Los Angeles, the exhaust fumes from cars are the main sources of these oxides of nitrogen.

In car engines, nitric oxide is formed when atmospheric nitrogen reacts with oxygen:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \text{ -------- } (\mathbf{I})$$

When oxygen is present in excess, nitric oxide will be further converted to nitrogen dioxide:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \text{ ------- } (\mathbf{II})$$

The variation in equilibrium constant, K_p, with temperature for the two equilibria is given by the data:

temperature / K	300	900	2800
K_p for equilibrium (**I**)	7.6×10^{-31}	4.0×10^{-10}	9.0×10^{-3}
K_p for equilibrium (**II**) / atm^{-1}	2.0×10^{12}	5.0×10^{-2}	3.4×10^{-15}

(a) With reference to **equilibrium (II)**,

(i) Write an expression for K_p for the production of NO_2 from NO and O_2.

(ii) At which of the above temperatures will there be maximum conversion of NO and O_2 to NO_2? Explain your answer.

(iii) Calculate the mole ratio of NO_2 to NO in the atmosphere at 900K given that air consists of 20% O_2 and pressure is 1 atm.

[5]

(b) Using the values of K_p for both equilibria, explain why the formation of NO occurs mainly in car engines while that of NO_2 occurs mainly outside the engines.

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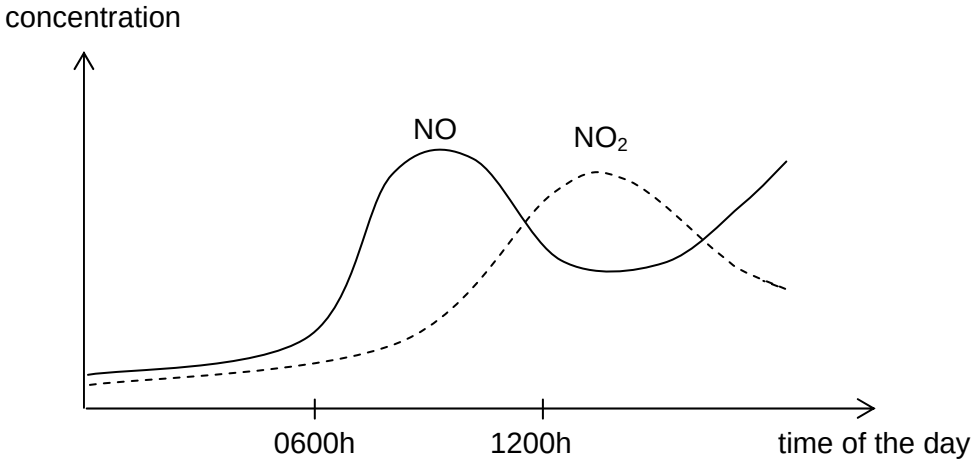
..... [2]

(c) The peak in the atmospheric level of NO is closely related to the peak in traffic density.

The following graph shows the concentration of atmospheric NO and NO_2 in a city measured on a particular day.



Explain why the peak of atmospheric NO_2 is observed only a few hours after the peak of atmospheric NO.

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..... [1]

(d) State and explain how lowering of pressure in the engine cylinders will affect the amount of NO produced.

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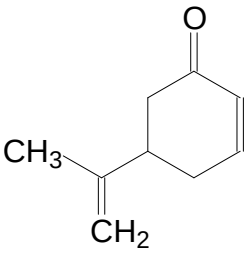
..... [2]

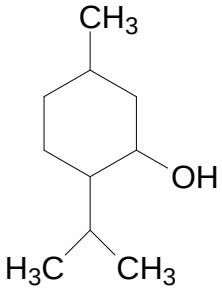
[Total: 10]

5 Terpenoids is a family of chemicals that are the primary constituents of the essential oils of many plants and flowers. Such essential oils are widely used as natural flavour additives for food, as fragrances in perfumery, and in aromatherapy.

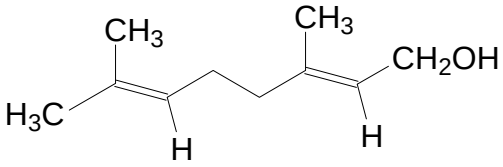
Carvone, menthol and geraniol are three examples of such terpenoids.



Carvone



Menthol



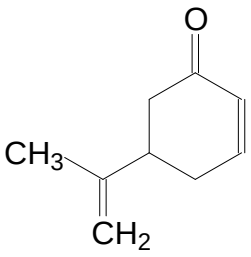
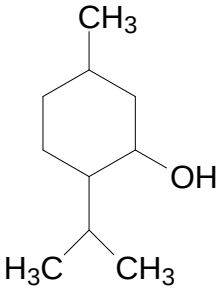
Geraniol

(a) Both carvone and menthol exhibit optical isomerism.

In the following table,

(i) circle the chiral carbon(s) present in each molecule, and

(ii) deduce the number of stereoisomers each of these compounds possesses.

	structural formula	no. of stereoisomers
Carvone		
Menthol		

[3]

(b) Draw the structural formulae of the organic products formed when the three terpenoids separately react with the given reagents.

terpenoid	reagent and condition	structural formula of the product
Carvone	2,4-dinitrophenylhydrazine, room temperature	
Menthol	CH_3CH_2COCl, room temperature	
Geraniol	excess HBr, heat	

[3]

(c) When geraniol is heated under reflux with acidified $KMnO_4$(aq), three organic compounds, **A**, **B** and **C** are formed. Further heating with $KMnO_4$(aq) causes **A** to produce a gas.

(i) Write an equation to explain the formation of the gas from **A**.

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(ii) Draw the structural formulae of compounds **B** and **C**.

compound **B**

compound **C**

(iii) Suggest a simple chemical test, using reagent(s) other than those used in **(b)**, to distinguish compound **B** from **C**.

test .....

observations .....

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[5]
[Total: 11]