H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 1

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

8872/02

Paper 2

14 September 2016

2 hours

Candidates answer Section A on the Question Paper

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 on the question paper.

Section **B**
Answer **two** questions on the writing paper 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	
A1	**/ 8**
A2	**/ 6**
A3	**/ 26**
B1	**/ 20**
B2	**/ 20**
B3	**/ 20**
Total	**/ 80**

Section A

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

For examiner's use only

1(a)(i) A gaseous aromatic hydrocarbon, **X**, was subjected to combustion analysis. **X** on complete combustion gave 0.814 g of carbon dioxide and 0.208 g of water. What is the empirical formula of **X**? [2]

(ii) A 0.245 g sample of **X** has a volume of 51.8 cm^3 at standard temperature and pressure. Determine the molecular formula of **X**. [2]

(iii) Draw all the structural isomers of the aromatic hydrocarbon, **X**. [2]

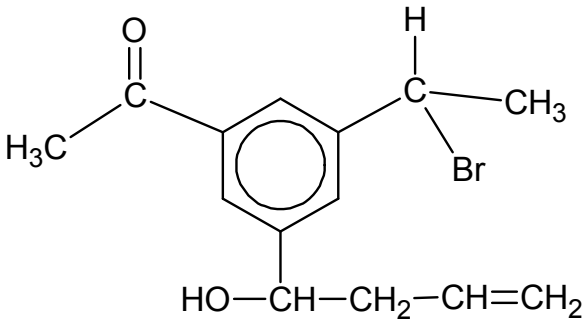
(iv) **X** can undergo two different halogenation reactions with bromine. Write an equation and state the conditions necessary for each of these reactions to occur. [2]

For examiner's use only

[Total: 8]

For examiner's use only

2 Compound **Z** has the following structure.



(a) On the structure above, circle and name four different functional groups present in **Z** that are neither benzene rings nor alkyl groups. [2]

(b) Draw the structural formulae of the organic products formed when **Z** reacts with

(i) warm alkaline aqueous iodine [3]

(ii) hot, acidified manganate(VII) ions [1]

[Total: 6]

For examiner's use only

3 This question is about phosphorus and its chlorides.

(a) Allotropes are two (or more) forms of the same element, in which the atoms or molecules are arranged in different ways.

Elemental phosphorus can exist in several allotropic forms, the most common are white phosphorus and red phosphorus.

When heated to 400 °C in the absence of air, white phosphorus changes into the red form of the element.

(i) White phosphorus exists as molecules made up of four atoms in a tetrahedral structure. Draw the structure of white phosphorus. [1]

(ii) The melting point of white phosphorus and red phosphorus are 44 ^{o}C and 500 ^{o}C respectively. Explain the difference in their melting points.

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.....

.....[2]

(b) Describe how separate samples of phosphorus(III) chloride, PCl_3, and phosphorus(V) chloride, PCl_5 can be made in the laboratory.

.....

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.....

.....

.....[2]

For examiner's use only

(c) Phosphorus(V) chloride is a white solid which sublimes at 160 °C. It dissolves in some polar solvents without reaction and such solutions conduct electricity. This is due to the presence of the two ions, $[PCl_4]^+$ and $[PCl_6]^-$.

Draw the structure and suggest the shape of **each** of these ions. [3]

(d) When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \quad PCl_3(g) + Cl_2(g)$$

Write an expression for K_c for this equilibrium, stating its units.

.....[2]

For examiner's use only

(e) In an experiment, 1.00 mol of PCl_5 vapour was heated in a closed 5.00 dm^3 flask at 500 K until equilibrium has been established.

The gases in the flask were then *rapidly cooled*, causing the formation of crystals of PCl_5 and liquid PCl_3. The chlorine gas present was pumped away and collected.

The amount of chlorine collected was *x* mol.

An excess of water was then *very carefully added* to the two remaining compounds, under suitable conditions, causing the following reactions to occur. The addition of water may cause the mixture to boil.

$$PCl_5 + 4H_2O \rightarrow 5HCl + H_3PO_4$$
$$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$$

You may assume that both H_3PO_4 and H_3PO_3 behave as *dibasic (diprotic) strong acids*.

(i) Explain why the gases in the flask need to be *rapidly cooled*.

.....[1]

(ii) State and explain the reactions of PCl_5 and PCl_3 in water.

.....

.....

.....[2]

(iii) Explain why an excess of water must be *very carefully added* to PCl_5 and PCl_3.

.....[1]

(iv) It is assumed that H_3PO_4 and H_3PO_3 behave as *dibasic (diprotic) strong acids*. Define the terms in italics, using H_3PO_4 as an example.

.....

.....

.....[2]

For examiner's use only

(v) Determine, in terms of x, the number of moles of H^+ that will be formed after the addition of water to the mixture of PCl_5 and PCl_3. [4]

(f) The resulting solution was made up to 1.00 dm^3 in a standard flask. 25.0 cm^3 of this solution was titrated with 4.00 mol dm^{-3} NaOH and required 37.4 cm^3 for neutralisation.

(i) Calculate the total amount, in moles, of H^+ ions present in the 1.00 dm^3 standard flask. [2]

(ii) Using your answers to **(e)(v)** and **(f)(i)** to calculate the amounts, in moles of PCl_5, PCl_3 and Cl_2 in the original equilibrium at 500 K. [2]

(iii) Use your answer to **(d)** and **(f)(ii)** to calculate a value for K_c for the equilibrium. [2]

[Total: 26]

Section B

Answer **two** questions in this section on the writing paper provided.

1(a) Benzoic acid is a colourless crystalline solid. Salts of benzoic acid are used as food preservatives. The salts can be prepared by reacting benzoic acid with either sodium metal or sodium hydroxide.

(i) Benzoic acid can be prepared from methylbenzene.

Write a balanced equation for this reaction, state the reagents and conditions necessary and name the type of reaction occurring. (In this equation the symbol [O] is acceptable.) [3]

(ii) State the type of reaction when benzoic acid reacts with sodium metal. [1]

(b) When sodium hydroxide is added to benzoic acid, a buffer solution may be formed.

(i) With an aid of an equation, explain how this buffer solution behaves when a small amount of acid is added to it. [2]

(ii) Calculate the pH of 25.0 cm^3 benzoic acid solution where the hydrogen ion concentration, $[H^+(aq)]$, is 0.025 mol dm^{-3}. [1]

(iii) Calculate the end-point volume of 0.05 mol dm^{-3} sodium hydroxide when added to the solution in **(b)(ii)**. [1]

(iv) The table below shows the pH range of colour change for two acid-base indicators.

indicator	pH range of colour change
bromocresol-green	3.8 – 5.5
phenol-red	6.8 – 8.5

Suggest which indicator in the table above is a suitable indicator when benzoic acid is titrated against sodium hydroxide, explaining your answer. [2]

(v) Draw a labelled reaction pathway diagram for the reaction between sodium hydroxide and benzoic acid. [2]

(vi) Suggest and explain the effect on the rate of the reaction of

(I) an increase in concentration of benzoic acid,

(II) a decrease in temperature of the solutions. [3]

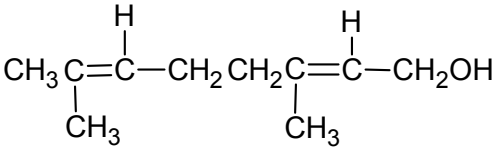
(c) **(i)** Define the first *ionisation energy* of sodium. [1]

(ii) Sketch a graph to show the variation of the first ionisation energies of elements across the third period from Na to Ar. [2]

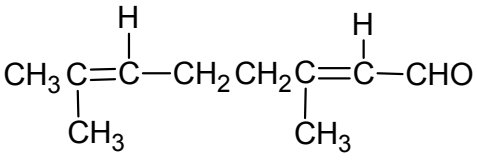
(iii) Explain the variation to the first ionisation energies you have illustrated in your sketch in part **(ii)**. [2]

[Total: 20]

2 Many of the natural compounds which are responsible for aromas in perfumes were first extracted from plants. Geraniol and citral, with the structures shown below, are found in roses and lemon grass and are attractants for honey bees.

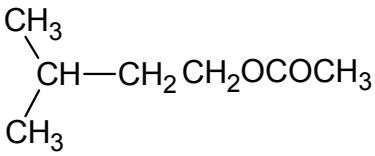


Geraniol



Citral

Banana oil is a bee alarm pheromone which is released during bee stings to attract other bees and provoke them to sting. Banana oil also have an odour similar to the smell of bananas.



Banana oil

(a) Identify the type of isomerism present in geraniol, and draw the structural formulae to illustrate the isomerism. [3]

(b) Geraniol can be easily converted into citral.

(i) Suggest reagents and conditions for this reaction and state the type of reaction. [2]

(ii) Suggest a simple chemical test to distinguish between geraniol and citral. [2]

(iii) Draw the structure of the organic product when geraniol is heated under reflux with HBr. [2]

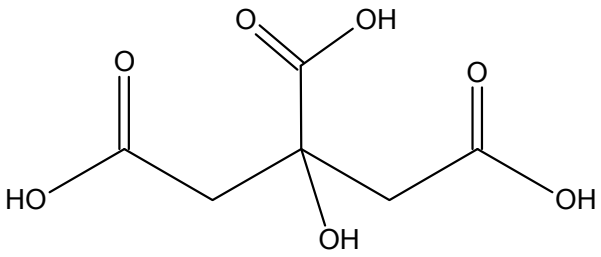
(c) When banana oil is refluxed with aqueous NaOH, a slow reaction takes place to give compounds **A** and **B**. When compound **A** and **B** react with PCl_5 separately, compound **A** gives steamy white fumes but not compound **B.** Compound **A** forms compound **C** with the molecular formula, $C_5H_{10}O_2$ when heated with acidified $KMnO_4$.

(i) Identify the structural formula of compounds **A**, **B** and **C**. State the type of reaction that have undergone and write balanced equations for all reactions that occurs. [9]

(ii) Compound **C** has a boiling point of 176 ^oC whereas banana oil has a boiling point of 142 ^oC. With reference to the structures and type of bonding present in both compounds, explain why compound **C** has a higher boiling point than banana oil. [2]

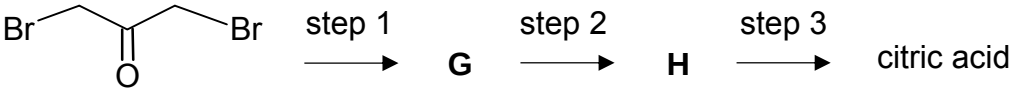
[Total: 20]

3 Citric acid, $C_3H_5O(COOH)_3$ occurs in lemons and limes. It is often used as a flavouring and preservative in food and beverages.



citric acid

(a) Suggest the reagents and conditions you would use in a three-step synthesis of citric acid from 1,3-dibromopropan-2-one, identifying the intermediates **G** and **H**.



[5]

(b) Citric acid can be converted into many other compounds when treated with different reagents.

(i) Draw the structural formulae of the compounds formed when citric acid is treated with

- $LiAlH_4$ in dry ether,
- CH_3CO_2H, conc. H_2SO_4, heat under reflux,
- Al_2O_3, 350 ^oC. [3]

(ii) State the number of mole(s) of $H_2(g)$ produced when 1 mole of citric acid is treated with Na. [1]

(c) The enthalpy change of neutralisation of citric acid by sodium hydrogencarbonate, $NaHCO_3$, was determined experimentally by mixing known volumes of 0.20 mol dm^{-3} $C_3H_5O(COOH)_3(aq)$ and 1.00 mol dm^{-3} $NaHCO_3(aq)$.

$$C_3H_5O(COOH)_3(aq) + 3NaHCO_3(aq) \rightarrow C_3H_5O(COONa)_3(aq) + 3CO_2(g) + 3H_2O(l)$$

The following results were obtained.

volume of $C_3H_5O(COOH)_3(aq)$ used	= 50 cm^3
volume of $NaHCO_3(aq)$ used	= 50 cm^3
change in temperature	= −0.5 ^oC

(i) Define the term *standard enthalpy change of neutralisation*. [1]

(ii) Use the data above to determine, by calculation, which reactant, $C_3H_5O(COOH)_3$ or $NaHCO_3$ is in excess. [2]

(iii) Hence, calculate the standard enthalpy change of neutralisation of citric acid by $NaHCO_3$. [3]

(d) 1,3-dibromopropan-2-one undergoes hydrolysis with the water present in silver nitrate solution.

(i) Describe how this reaction could be used to distinguish between 1,3-dibromopropan-2-one and 1,3-dichloropropan-2-one, including all observations that would be made. Write relevant equations using 1,3-dibromopropan-2-one as your example. [3]

(ii) Explain the difference in the relative ease of hydrolysis between 1,3-dibromopropan-2-one and 1,3-dichloropropan-2-one. [2]

[Total: 20]