Name and Form Class	Index Number	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **8872/02**
Higher 1

Paper 2 22 August 2012

2 hours

Candidates answer Section A on the Question Paper.

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluids.

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	
Section A	
B5	
B6	
B7	
Total	

This document consists of **16** printed pages.

Section A

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

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1 **(a)** In an attempt to determine the hydroxide concentration in a titration procedure, a student filled up the burette with sodium chloride instead of hydrochloric acid and starts the titration. He realised something was amiss when the methyl orange indicator did not show any colour change.

If he had correctly filled the burette with hydrochloric acid and carried out the titration, what is the expected colour change at the end point?

..... **[1]**

(b) The student pipetted a 50.0 cm^3 sample containing sodium chloride and sodium hydroxide which he had wrongly prepared in **(a)**, and titrated it with hydrochloric acid. The end point was reached when 13.00 cm^3 of 0.35 mol dm^{-3} of hydrochloric acid was added. Calculate the concentration of sodium hydroxide present in the 50.0 cm^3 sample.

[1]

(c) 22.00 cm^3 of 0.45 mol dm^{-3} of acidified $KMnO_4$ was added in excess to oxidise the chloride ions present in **(b)**. The excess $KMnO_4$ required 14.80 cm^3 of 0.60 mol dm^{-3} of hydrogen peroxide solution for complete reaction.

(i) $KMnO_4$ undergoes a *redox reaction* with H_2O_2. Define the terms in italics.

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.....

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(ii) Write the half equation for the oxidation of hydrogen peroxide to oxygen, and hence the overall balanced equation for the reaction

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between acidified $KMnO_4$ and hydrogen peroxide.

use

(iii) Calculate the amount of $KMnO_4$ used to react with hydrogen peroxide.

(iv) Hence calculate the amount of the sodium chloride in the 50.0 cm^3 sample pipetted in **(b)**.

[8]

[Total: 10]

2 The use of the *Data Booklet* is relevant to this question.

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An experiment was performed to determine the enthalpy change of combustion of cyclohexane, C_6H_{12}. The following results were obtained.

Volume of water used / litre	2.5
Initial temperature of water / ^oC	26.0
Final temperature of water / ^oC	96.0
Mass of spirit lamp and cyclohexane before combustion / g	62.8
Mass of spirit lamp and cyclohexane after combustion / g	47.1

(a) Define standard enthalpy change of combustion, $\Delta H_c^{\ominus}$.

……

……

…… **[1]**

(b) Given the above information, calculate the enthalpy change of combustion of cyclohexane, assuming negligible loss of heat to the surrounding.

[2]

(c) Using your answer in **(b)** and the data given below, calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of cyclohexane.

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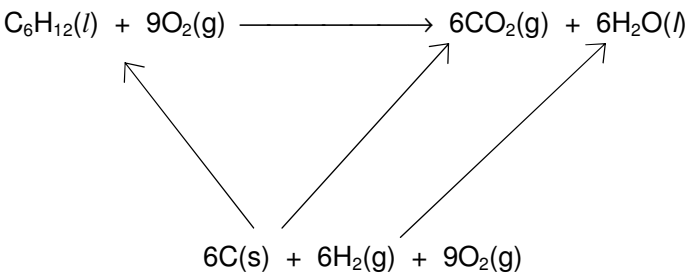
$\Delta H_c^{\ominus}(C) = -393.5 \text{ kJ mol}^{-1}$

$\Delta H_f^{\ominus}(H_2O) = -285.9 \text{ kJ mol}^{-1}$



[2]

(d) In another experiment, cyclohexane undergoes reaction with bromine to give a mixture of dibromocyclohexane.

(i) State the condition required for the reaction to take place and draw the structural formulae of all possible dibromocyclohexane.

(ii) Identify the type of isomerism exhibited by the mixture of dibromocyclohexane

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(iii) State the hybridisation of all the carbon atoms present in dibromocyclohexane and sketch the shape of the hybrid orbitals around each carbon.

[5]

[Total: 10]

3 (a) Describe the reactions and write the equations when samples of sodium is

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(i) added to water,

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(ii) burned in the air.

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[3]

(b) 2-chloropropane, $CH_3CHClCH_3$, can be hydrolysed by NaOH (aq) to form propan-2-ol. Results of an investigation into the kinetics of this reaction are given below.

Experiment number	**[$CH_3CHClCH_3$] / mol dm^{-3}**	**[NaOH] / mol dm^{-3}**	**Relative initial rate**
1	0.10	0.20	1.00
2	0.20	0.10	2.00
3	0.30	0.20	3.00
4	0.60	0.40	6.00

(i) Use the data in the table to deduce the order of reaction with respect to $CH_3CHClCH_3$ and with respect to NaOH.

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(ii) Hence, write a rate equation for the reaction between $CH_3CH_2C\mathit{l}CH_3$ and NaOH.

……..

(iii) Changing the temperature of the reaction mixture will affect the rate of the reaction. With the aid of a suitable diagram, explain how increasing the temperature of the reaction mixture affects the rate of the reaction.

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(iv) Given that the half-life of 2-chloropropane is 50 seconds, how long will it take for a solution of 2-chloropropane in **experiment 4** to reach a concentration of 0.15 mol dm^{-3}?

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[7]

[Total: 10]

4 Ethylbenzene is an important organic compound in the petrochemical industry as an intermediate in the production of styrene, which is used for making polystyrene. A synthetic route involving ethylbenzene is shown below.

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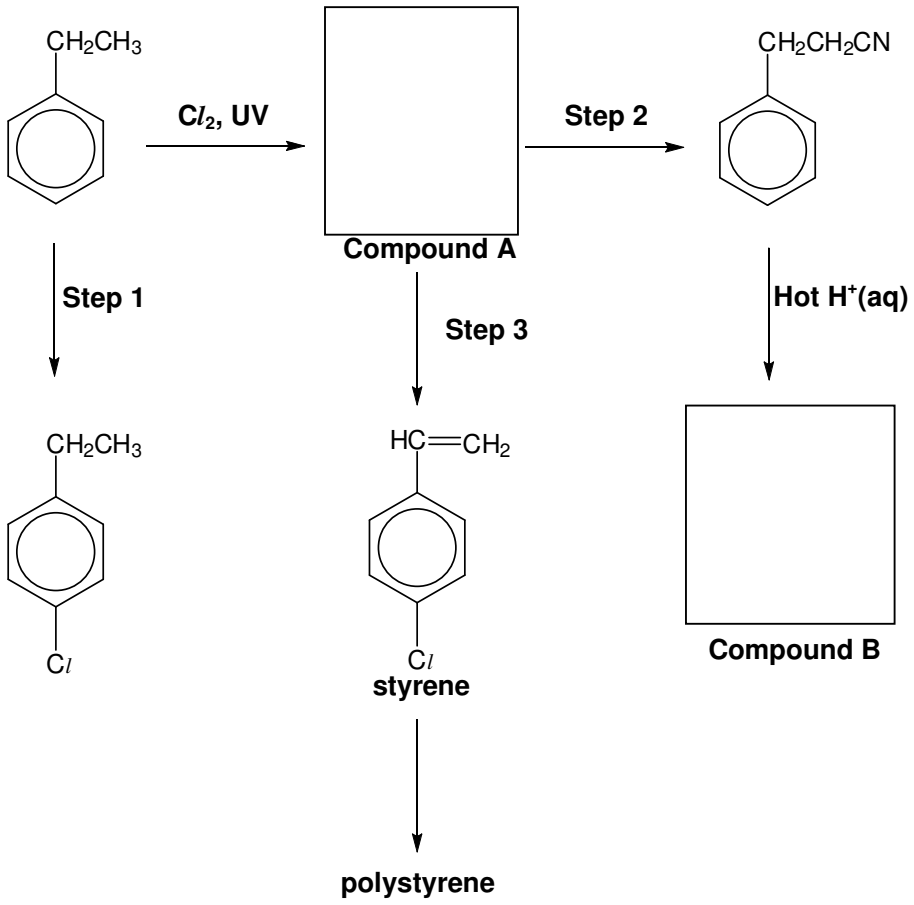

(a) Draw the structures of **Compound A** and **Compound B** in the boxes above, and fill in the table below, stating the reagents and conditions for **Step 1 – 3** in the above synthetic route. Name the type of reaction for each step.

Step	Reagents and conditions	Type of reaction
1		
2		
3		

[8]

(b) Suggest one simple chemical method to distinguish the following pair of compounds. State the relevant observations.

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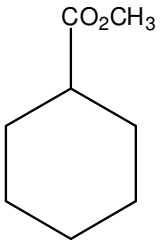

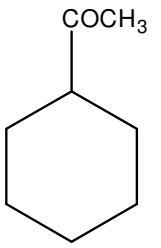

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…….. **[2]**

[Total: 10]

Section B

Answer **two** questions from this section on separate answer paper

5 Methanol is the simplest alcohol that is widely used as fuel and laboratory solvent. It is known as wood spirits or wood alcohol as it was once produced from the distillation of wood. It is produced by reacting carbon monoxide and hydrogen under high pressure in the presence of catalyst.

Like methanol, 2-methylpropan-2-ol is also used as solvent and denaturant for ethanol. It is one of the four isomers of butanol.

(a) Write a balanced equation for the synthesis of methanol from carbon monoxide and hydrogen. **[1]**

(b) Write a balanced equation showing how 2-methylpropan-2-ol can be produced from a suitable alkene. State clearly the relevant reagents and conditions for the reaction. **[2]**

(c) An isomer of butanol can undergo dehydration to produce an alkene which exhibits geometric isomerism.

(i) Give the condensed structural formula of this isomer of butanol.

(ii) Draw the geometric isomers of the alkene produced.

(iii) Explain why the alkene is able to exhibit geometric isomerism. **[4]**

(d) Outline a simple chemical test to distinguish methanol and 2-methylpropan-2-ol and state the observations. **[2]**

(e) Both methanol and butan-1-ol can be oxidized to form their corresponding carboxylic acid. State and explain which carboxylic acid formed has a lower pK_a value. **[2]**

(f) In a synthesis experiment, methanol reacts with 2-methylpropan-2-ol to form an organic compound, methyltert-butylether, $(CH_3)_3COCH_3$ as shown below.

$$CH_3OH\ (l)\ +\ (CH_3)_3COH\ (l) \rightleftharpoons^{H^+} (CH_3)_3COCH_3\ (l)\ +\ H_2O\ (l)$$

(i) Write the K_c expression for the above reaction.

(ii) In order to determine K_c value for the reaction, 8.00 g of methanol and 18.00 g of 2-methylpropan-2-ol were reacted in the presence of concentrated sulfuric acid. At equilibrium, the percentage of 2-methylpropan-2-ol was 72.5%. Calculate the K_c value.

(iii) Explain how the position of equilibrium and K_c value will change when the concentration of methanol decreases.

(iv) When temperature is decreased, the value of K_c is found to be lowered. State and explain if the forward reaction is exothermic or endothermic.

(v) Concentrated sulfuric acid is used in this reaction as a catalyst. Suggest another role for it and briefly explain how it serves its function. **[9]**

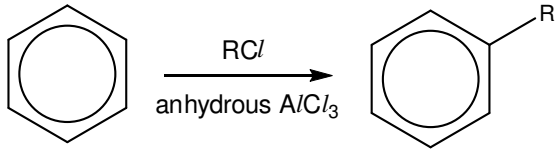
[Total: 20 marks]

6 **(a)** Aluminium is the most abundant metal found on the surface of the earth. Most of the aluminium compounds exhibit low toxicity and they are used at a large scale in many industrial reactions.

(i) Write a complete equation to represent the first ionisation energy of aluminium and state the full electronic configuration of aluminium.

(ii) Using the *Data Booklet*, explain the difference in the first ionisation energy of magnesium and aluminium. **[3]**

(b) Aluminium chlorides are very commonly used in chemical industry as a catalyst for Friedel-Crafts reactions. An example of a Friedel-Crafts reaction is shown below.



In this reaction, $AlCl_3$ act as a *halogen carrier* to form $AlCl_4^-$, which catalyses the reaction.

(i) Suggest the shape and angle found in a molecule of aluminium chloride.

(ii) The melting point of anhydrous aluminium chloride was found to be 192 ^oC while the melting point of aluminium fluoride was found to be 1291 ^oC.

Explain the difference in the melting point of the two aluminium compounds in terms of their structure and bonding.

(iii) Explain why aluminium chloride has the ability to act as a *halogen carrier*. **[4]**

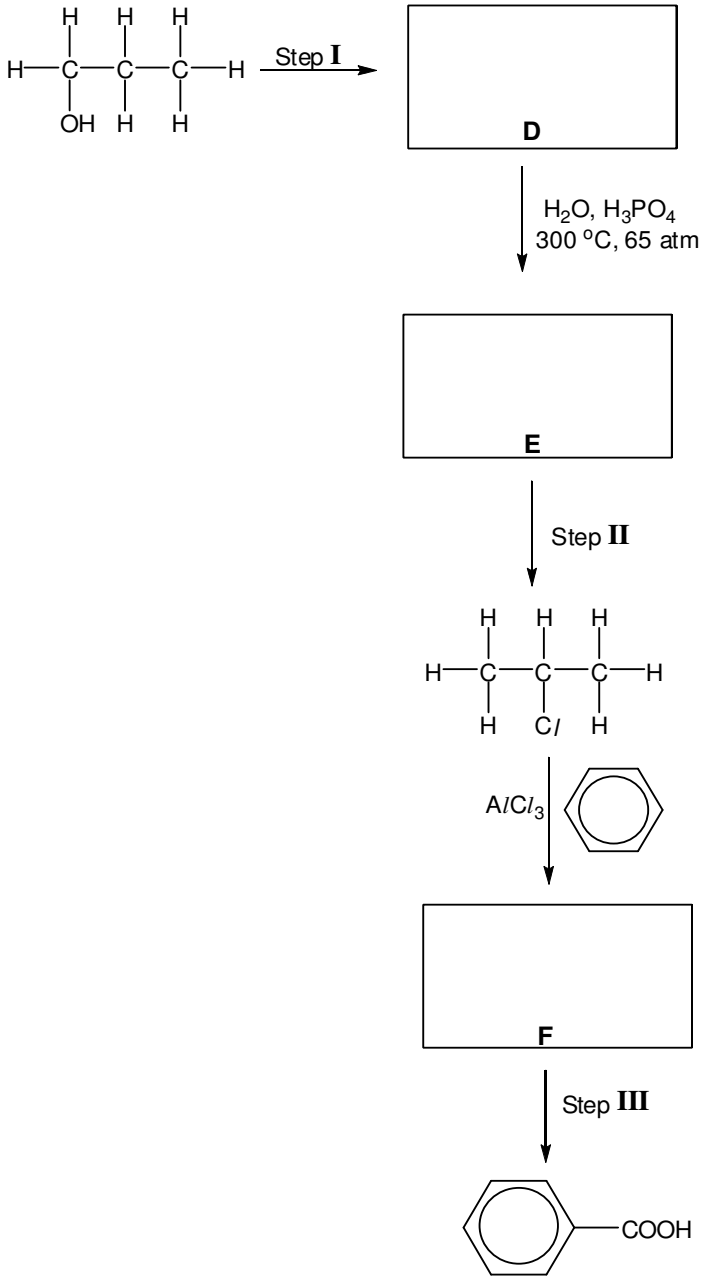
(c) The use of *Data Booklet* is relevant in this question.

Chlorides of elements in period 3 dissolve in or react with water to form solutions with different pH.

(i) Sketch a graph with clearly labeled axis, to show the difference in pH of the solutions formed when the chlorides of sodium to phosphorous react with water.

(ii) Write relevant equations, including state symbols, to show how aluminium chloride reacts with water to form the resulting solution with the pH you have sketched in **(c)(i)**. **[3]**

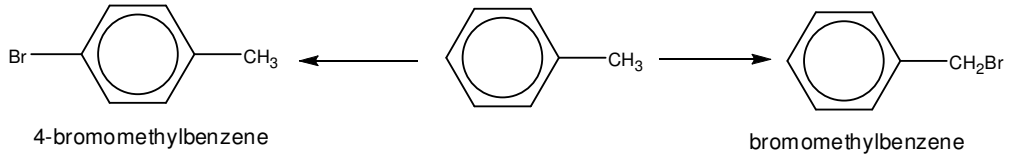
(d) The following reaction pathway shows how $AlCl_3$ can be used as a halogen carrier in an electrophilic substitution reaction.



(i) Give the reagents and conditions for Step **I**, **II** and **III** and deduce the correct structures for **D**, **E** and **F**.

(ii) State 2 observations that would be seen in Step **III** when benzoic acid is formed. **[8]**

(e) Methylbenzene reacts with bromine under different conditions to form bromomethylbenzene and 4-bromomethylbenzene. **[2]**



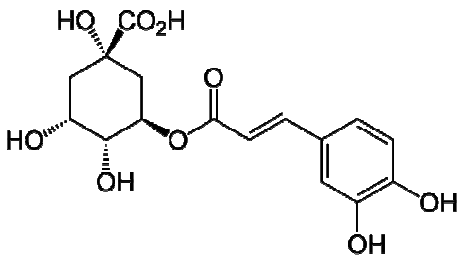
4-bromomethylbenzene

bromomethylbenzene

Describe a simple chemical test to distinguish bromomethylbenzene from 4-bromomethylbenzene and state the observations that would be seen.

[Total: 20 marks]

7 **(a)** Chlorogenic acid, a monobasic acid commonly found in coffee brew, has been shown in clinical studies to reduce the absorption of carbohydrates. It has the structure as shown:



Molar mass = 354 g mol^{-1}

(i) What do you understand by the Bronsted-Lowry theory of acids and bases? Support your answers with the aid of equations.

(ii) A solution is made by dissolving 1.53 g of chlorogenic acid in 500 cm^3 of water. Calculate the pH of this solution.

[K_a of chlorogenic acid = 3.21 x 10^{-4} mol dm^{-3}]

(iii) Explain what is meant by a buffer solution.

(iv) In the above solution, 2.65 g of the sodium salt of chlorogenic acid is added to make a buffer solution. Using the formula given,

$$\text{pH of a buffer solution} = pK_a + \lg \frac{[\text{conjugate base}]}{[\text{acid}]}$$

calculate the pH of the buffer solution.

(iii) Write equations to illustrate, how the above solution acts as a buffer when a small amount of base is added. You may use HA and A^- to represent the acid and conjugate base respectively. **[10]**

(b) Bromoalkanes are often used in the synthesis of other organic compounds as they can undergo a wide variety of reactions.

A bromoalkane **P**, $C_5H_{11}Br$, was heated with aqueous sodium hydroxide. The product **Q**, $C_5H_{12}O$, when distilled with acidified potassium dichromate gives **R**, $C_5H_{10}O$. A brick-red precipitate is formed when **R** is treated with Fehling's solution.

Both **Q** and **R**, on heating with acidified potassium manganate(VII), produce **S**, $C_5H_{10}O_2$. Reaction between **S** and ethanol in the presence of concentrated sulfuric acid gives a sweet smelling liquid **T**. **P** when heated with ethanolic sodium hydroxide produces **U**, C_5H_{10}. Heating **U** with acidified potassium manganate(VII) gives 2-methylpropanoic acid and a colourless gas.

(i) Draw the **displayed** formula of 2-methylpropanoic acid.

(ii) Deduce the identities of compounds **P** to **U**, explaining the chemistry of the reactions wherever possible. **[10]**

[Total: 20 marks]