ANDERSON JUNIOR COLLEGE

2014 JC2 PRELIMINARY EXAMINATIONS

NAME:________________________ **PDG:**____ /13 **Register No:** ____

CHEMISTRY **9647/02**

Higher 2 **3 September 2014**

Paper 2 Structured Questions **2 hours**

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 pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** the questions.
The use of an approved scientific calculator is expected where appropriate.
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				
Paper 2	1		Total	/ 72
	2			
	3			
	4			
	5			

This document consists of **24** printed pages and **1** blank page.

1 Planning (P)

At any temperature, equilibrium can be established between a liquid X and the vapour given off by that liquid. The pressure exerted by the vapour in equilibrium with the liquid is known as the vapour pressure.

$$X(l) \rightleftharpoons X(g)$$

As the temperature of the system is raised, the vapour pressure increases. When this vapour pressure becomes equal to the surrounding (ambient) air pressure, the liquid boils.

When the liquid contains a dissolved solid (solute), the vapour pressure above the liquid is reduced.

To investigate how the boiling point of an aqueous solution of potassium chloride changes with concentration, a series of known, but different, concentrations of potassium chloride is prepared. Each solution is heated and its boiling point is determined. A graph of boiling point against concentration is then plotted.

(a) **(i)** By considering how the vapour pressure changes as the concentration of aqueous potassium chloride increases, predict and explain how the boiling point of the solution will be affected by the concentration of the solution.

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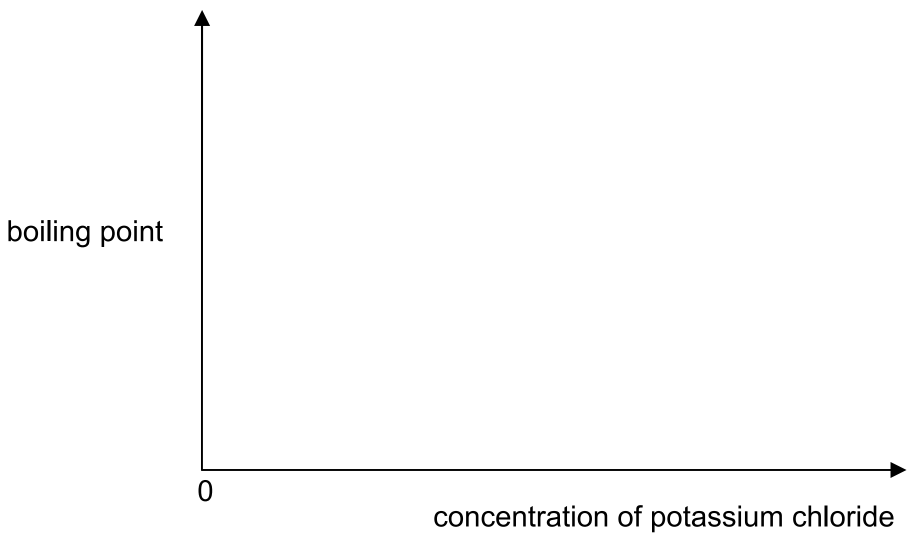
(ii) Display your prediction in the form of a sketch graph, labelling clearly the point representing the boiling point of pure water and its value, stating the units.



[3]

(b) Draw a diagram of the assembled apparatus you would use in the experiment. You should use only the apparatus normally found in a school or college laboratory and show clearly

(i) how the solution will be heated and over–heating of the solution prevented;

(ii) how the thermometer will be positioned.

Label each piece of apparatus used, indicating its size or capacity, where appropriate.

[2]

(c) When investigating how the boiling point of a solution changes with concentration, it is more convenient to represent the concentration of a solution as a ***molality***. The ***molality*** of a solution is defined as the number of moles of a solute dissolved in one kilogram of water.

Using the information given above, you are required to write a plan to investigate how the boiling point of an aqueous solution of potassium chloride changes with concentration of the solution.

In addition to the standard apparatus found in a laboratory, you may assume that you are provided with:

- 100 g of deionised water (you should take particular note of this limited supply of water);
- solid potassium chloride, KCl.
  [solubility of KCl at 25 °C = 35.7 g per 100 g water]

Your plan should include details of:

- the preparation of a series of solutions of potassium chloride that can be used in the apparatus you have shown in **(b)** to obtain sufficient data to plot a graph as in **(a)(ii)**;
- how you would calculate the molality of **one** of these solutions.
  [A_r: K, 39.1; C*l*, 35.5; density of water = 1.00 g cm^{-3}]

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[6]

(d) State a limiting factor that must be taken into account when increasing the concentration of the aqueous potassium chloride.

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[1]

[Total: 12]

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2 Blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows:

BAC = mg of ethanol per 100 cm^3 of blood

At present in Singapore, the legal limit to drive is 80 mg of ethanol per 100 cm^3 of blood. If the blood of the driver is found to exceed this legal limit, he will be charged with drink–driving. Ethanol is sufficiently volatile to pass from the blood into the air in the lungs and the following equilibrium is set up.

$$C_2H_5OH\ (blood) \rightleftharpoons C_2H_5OH\ (g)$$

As the ethanol concentration in the breath is related to that in the blood, a traffic police officer can test the driver's breath using a device called a breathalyzer instead of drawing a driver's blood to test his ethanol level. At the temperature of the human body, the ratio of breath ethanol to blood ethanol is 1 : 2100. This ratio states that 2100 cm^3 of exhaled air (breath) contains the same amount of ethanol as in 1 cm^3 of blood.

In one type of breathalyzer, the exhaled air is passed through a solution of acidified potassium dichromate which oxidises the ethanol to ethanoic acid in an electrochemical cell. The electrical current generated by the oxidation can be used to estimate the ethanol content of blood.

(a) What will be the breath alcohol concentration (in mol cm^{-3}) which corresponds to the legal limit for BAC?

[2]

(b) **(i)** Given that,

$$CH_3CO_2H + 4H^+ + 4e^- \rightleftharpoons C_2H_5OH + H_2O \qquad E^\ominus = +0.058\ V$$

Using the half–equation above and any other relevant data from the *Data Booklet*, calculate the $E^\ominus_{cell}$ and write a balanced equation for the overall reaction that occurs in the breathalyzer.

(ii) During a routine breathalyzer test, a current of 0.1 A is measured for 5 s when a driver breathes into it. Calculate the amount (in moles) of ethanol in his breath.

(iii) If the volume of exhaled air in **(b)(ii)** is 60.0 cm^3, calculate the mass of ethanol per cm^3 of blood.

Hence, or otherwise, deduce whether this driver is drink–driving.

(iv) Describe briefly another way in which the oxidation of ethanol by acidified potassium dichromate can be used to analyse the percentage of ethanol in exhaled air.

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[7]

[Total: 9]

3 *Aerozine 50* is a 50/50 mixture of hydrazine, N_2H_4, and UDMH, $(CH_3)_2N_2H_2$. It is used as a rocket fuel, typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction of the UDMH with dinitrogen tetroxide is given in **Equation 3.1** and relevant thermodynamic data is in **Table 3.1**.

Equation 3.1 $(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \longrightarrow 2CO_2(g) + 4H_2O(g) + 3N_2(g)$

substance	**$\Delta H_f^\ominus$/ kJ mol^{-1}**
$(CH_3)_2N_2H_2(l)$	83.3
$N_2O_4(l)$	9.1
$CO_2(g)$	–393.5
$H_2O(g)$	–241.8

Table 3.1

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

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[1]

(b) **(i)** Calculate the enthalpy change, $\Delta H_r^\ominus$, for the reaction in **Equation 3.1**, giving your answer to one decimal place.

(ii) The entropy change, $\Delta S_r^\ominus$, for the reaction in **Equation 3.1** is +844.1 J K^{-1} mol^{-1}.

Explain, without calculation, why this entropy change has such a large, positive value.

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(iii) Explain the effect of **decreasing** the temperature on the spontaneity of the reaction in **Equation 3.1**.

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[4]

(c) **(i)** Hydrazine, N_2H_4, reacts with dinitrogen tetroxide, N_2O_4, to produce nitrogen gas as one of the products.

Write a balanced equation for this reaction.

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(ii) Use the bond energies given in the *Data Booklet* to calculate another value of $\Delta H_r^\ominus$ for the reaction in **(c)(i)**.

[Use a value of 607 kJ mol^{-1} for the bond energy of N=O and 201 kJ mol^{-1} for the bond energy of N–O in N_2O_4].

(iii) Given that the theoretical value of $\Delta H_r^\ominus$ for the reaction in **(c)(i)** is –1140.8 kJ mol^{-1}, suggest a reason for the discrepancy between your value in **(c)(ii)** and the quoted value.

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[3]

(d) Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4, together) used in the thruster rockets in the ascent stage of a lunar module was 244 kg.

(i) Assume that the UDMH and dinitrogen tetroxide were mixed in the molar ratio 1 : 2, calculate the mass of UDMH in the propellant mixture.

(ii) Calculate the total number of moles of gas produced from the complete reaction of this mass of UDMH with dinitrogen tetroxide, as in **Equation 3.1**.

(iii) Calculate the total volume of product gases formed from the reaction of this mass of UDMH with dinitrogen tetroxide, as in **Equation 3.1**, at a temperature of –10.0 °C and a pressure of 600 Pa.

[3]

(e) Dinitrogen tetroxide, N_2O_4, exists in equilibrium with nitrogen dioxide, NO_2, which itself can be decomposed into nitrogen monoxide, NO, and oxygen, as shown in **Equation 3.2**.

Equation 3.2 $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$

The rate equation for this thermal decomposition is as follows.

$$\text{rate} = k\,[NO_2]^2$$

The rate constant, k, for the thermal decomposition of nitrogen dioxide was measured at five different temperatures and the results were used to plot the graph in **Fig. 3.1**.

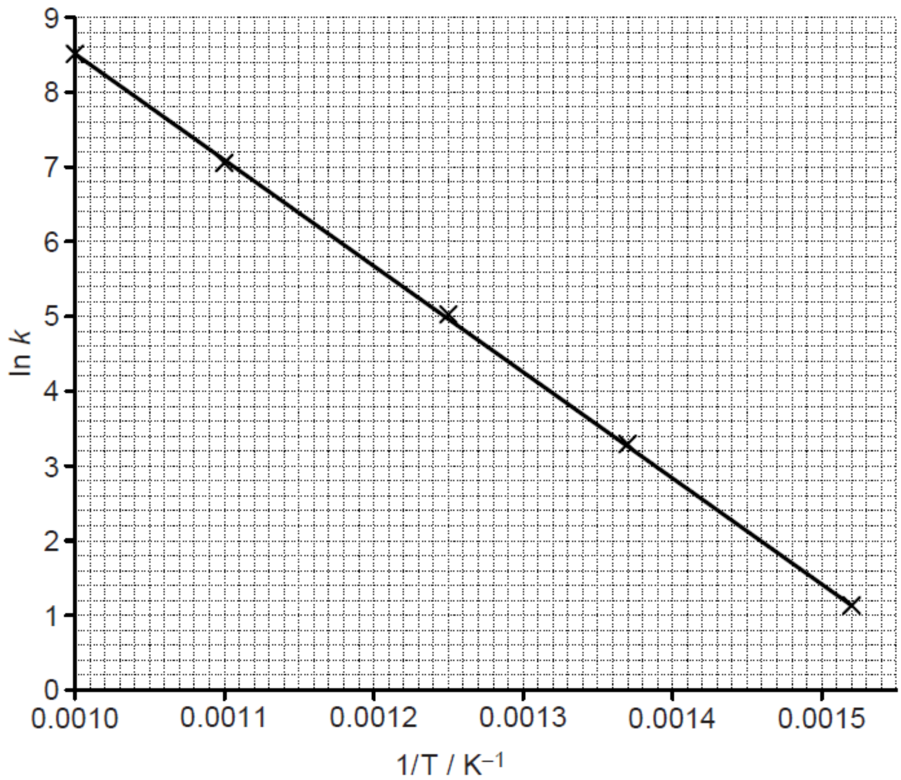

Fig. 3.1

(i) The Arrhenius equation can be used to show the relationship between temperature and reaction rate. It can be rewritten in the form $y = mx + c$, as follows.

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

where k = rate constant
E_a = activation energy
R = molar gas constant
T = temperature
A = Arrhenius constant

Use the graph to calculate the activation energy, E_a, for the reaction in **Equation 3.2**.

(ii) A mechanism suggested for the thermal decomposition of nitrogen dioxide is shown.

step 1	$NO_2 + NO_2$	$\longrightarrow$ $NO + NO_3$	*slow*
step 2	NO_3	$\longrightarrow$ $NO + O_2$	*fast*

State and explain whether or not this mechanism is consistent with the rate equation given.

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[4]

(f) Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO_2. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures, NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2. In this experiment, *torr* is used as the unit of pressure.

experiment	**initial pressure / torr**		**initial rate of formation of N_2O / torr s^{-1}**
	p_{NO}	p_{H_2}	
1	120.0	60.0	8.66×10^{-2}
2	60.0	60.0	2.17×10^{-2}
3	60.0	180.0	6.62×10^{-2}

(i) Deduce the rate law and calculate the rate constant, giving its units.

(ii) Calculate the initial rate of disappearance of NO, if 200.0 torr NO and 100.0 torr H_2 are mixed at 820 °C.

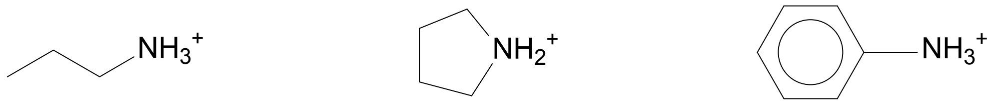
(iii) Calculate the time elapsed to reduce the partial pressure of H_2 to half of its initial value, if 800.0 torr NO and 1.0 torr H_2 are mixed at 820 °C.

[9]

[Total: 24]

4 **(a)** Many drug molecules contain amine groups and are administered to patients in the form of the conjugate acids of the drugs.

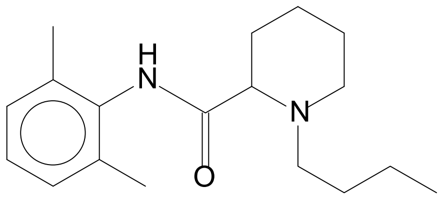
Arrange the following conjugate acids of amines in **increasing order** of their pK_a values.



Order: ………………………………………………………………………………………

[1]

(b) Local anaesthetics are drugs used to provide anaesthesia and relieve pain during a surgery. Bupivacaine is an example of a local anaesthetic used as a spinal and epidural anaesthetic for childbirth and hip replacements.



Bupivacaine

Bupivacaine is usually injected into the patient's bloodstream as a solution of its conjugate acid salt, Bupivacaine hydrochloride, which has a pK_a value of 8.1. When administered, the acid dissociates in the aqueous bloodstream according to the following equation.

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+ \qquad pK_a = 8.1$$

(BH^+ represents the conjugate acid of Bupivacaine, B)

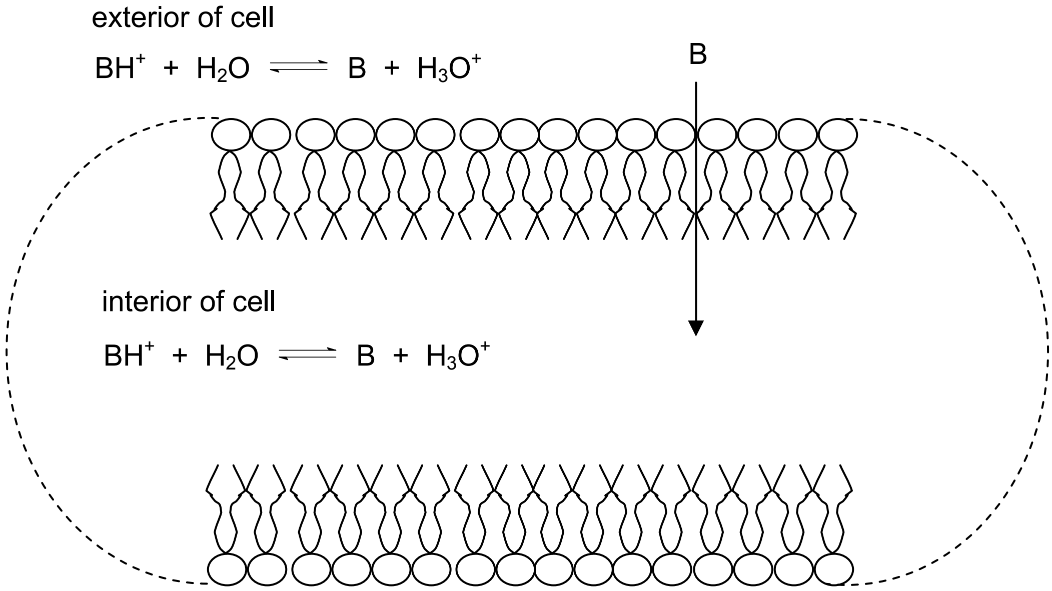
Normal tissue fluids are buffered at a pH of 7.4.

Calculate the ratio $\frac{[B]}{[BH^+]}$ at pH 7.4 and hence calculate the percentage of unionised Bupivacaine in the tissue fluids of a patient after the drug is being administered.

[2]

In order to exert its anaesthetic effects, it is essential that the unionised Bupivacaine, B, can enter a nerve cell where its ionised conjugate acid form, BH^+, can interact with its target site within the cell.

The cell membrane is essentially a bilayer of phospholipids containing long hydrocarbon chains of lipid molecules (fatty acid molecules which are soluble in organic solvents) forming the interior of the membrane. For a drug molecule to pass through the membrane, it is essential that the molecule is lipid–soluble.



represents a phospholipid molecule

where the 'head' (◯) is a negatively charged phosphate group and the 'tail' ( ) is a long chain hydrocarbon.

(c) **(i)** Identify structural features of the Bupivacaine molecule which renders it lipid–soluble.

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(ii) Briefly explain, in terms of bonding, why the conjugate acid of Bupivacaine is more soluble in an aqueous environment than Bupivacaine itself.

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[2]

(d) With reference to the diagram on page 17, and by applying *Le Chatelier's principle* to the acid–base equilibrium (1) below, suggest how Bupivacaine, injected as its conjugate acid, can pass through the cell membrane as Bupivacaine and then converts back to its conjugate acid form within the cell where it can exert its effect.

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+ \quad \text{———— (1)}$$

[You may use B and BH^+ to represent Bupivacaine and its conjugate acid respectively in your answer.]

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[3]

(e) The anaesthetic effect of Bupivacaine is known to be delayed, thus rendering it less effective, when administered on infected tissues where the pH of infected tissue fluids is lower than 7.4.

Suggest a reason for the delayed effect of the drug under this condition.

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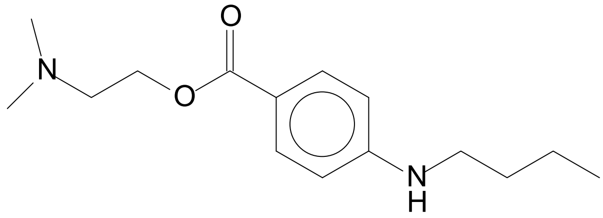
[1]

(f) Amethocaine is used as a local anaesthetic for eye surgery.



Amethocaine

Amethocaine is known to be more easily hydrolysed than Bupivacaine.

Suggest a reason why Bupivacaine is not as readily hydrolysed as Amethocaine.

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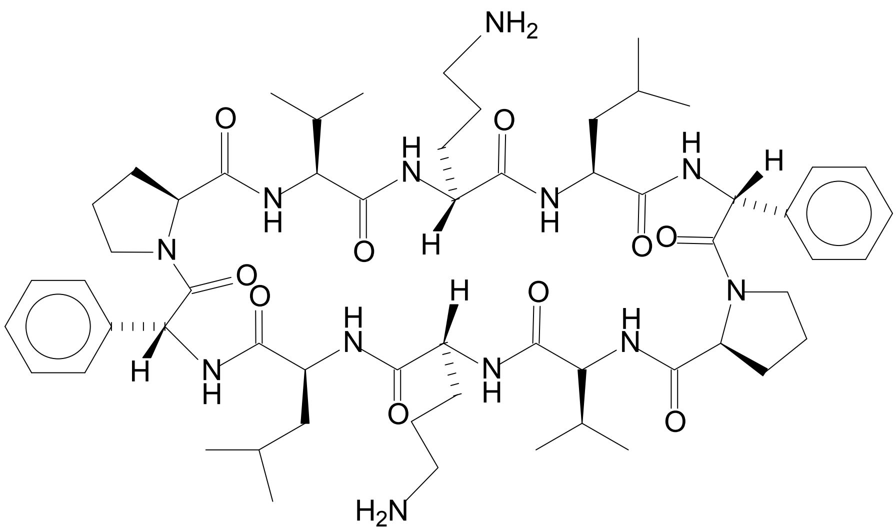
[2]

(g) Gramicidin S is a cyclic peptide which can be used as an anti–fungal drug.



Gramicidin S

(i) How many **different** amino acids are present in the molecule of Gramicidin S?

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(ii) Suggest reagents and conditions for the complete hydrolysis of Gramicidin S.

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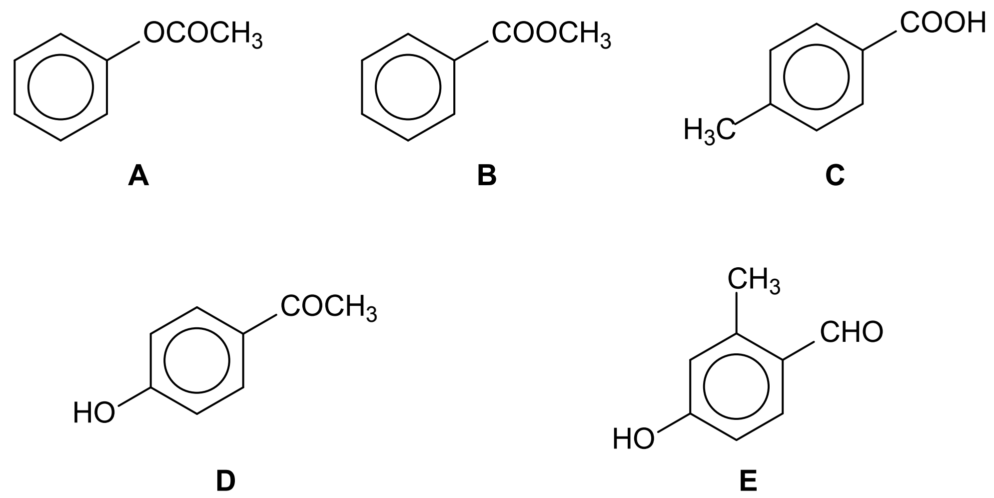
(iii) Draw the structural formulae of **two** products from the hydrolysis above.

You may use skeletal representations in your answer.

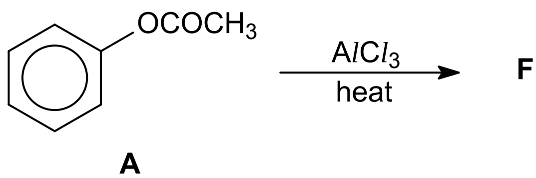
[4]

[Total: 15]

5 Five possible compounds with molecular formula $C_8H_8O_2$ are given below.



(a) When compound **A** is heated with $AlCl_3$, it is converted to compound **F** with the same molecular formula $C_8H_8O_2$. This reaction is known as the *Fries rearrangement*.



The identity of **F** could either be compound **B**, **C**, **D** or **E**. The following chemical tests have been performed to determine the identity of **F**.

Answer questions **(i)** to **(iii)** by using **only** the letters **B**, **C**, **D** or **E**. The letters could be used more than once.

(i) When **F** is treated with aqueous Br_2, a white precipitate $C_8H_6O_2Br_2$ is formed.
State the compounds that give this observation.

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(ii) **F** gives an orange precipitate with 2,4–dinitrophenylhydrazine.
State the compounds that give this observation.

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(iii) **F** does **not** give a silver mirror with Tollens' reagent.
State the compounds that give this observation.

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(iv) Identify **F** using your answers from **(a)(i)** to **(a)(iii)**.

Suggest **another** simple chemical test that will distinguish **F** from the other three compounds. State the expected observation and give the structural formula of the organic product(s) formed from this test.

identity of **F**: …………………………

chemical test:

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expected observation:

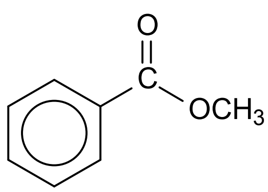
……………………………………………………………………………………………………

structural formula of organic product(s):

(v) **Use the table of characteristic values for infra–red absorption in the *Data Booklet* (Page 8) to answer this question.**

Other than chemical tests, infra–red absorptions can be used to identify functional groups in organic compounds which can aid in distinguishing between organic compounds.

For example, **B** shows absorptions at 1000−1300 cm^{-1} and 1680−1750 cm^{-1}.



B

Use the table to identify an infra–red absorption range that will be shown by **D** but not by **A**.

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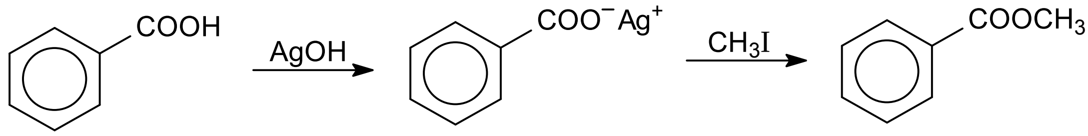
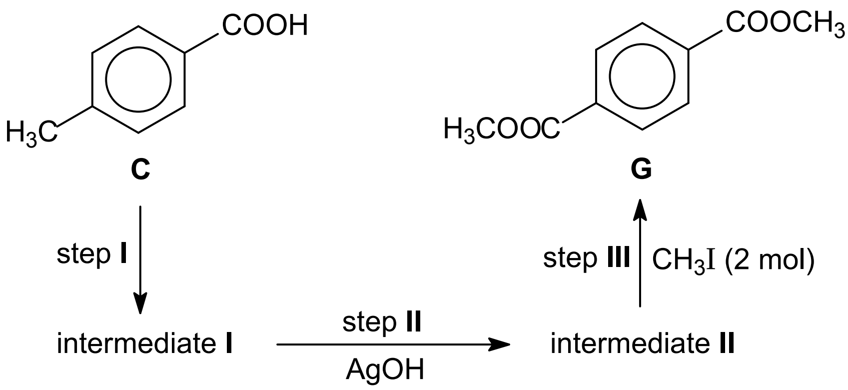
[7]

(b) Compound **B** can be formed in the following reaction involving benzoic acid and an alkyl halide.



B

This reaction is used in the reaction scheme below involving compound **C** as the starting material.



(i) State the type of reaction for step **III**.

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(ii) Deduce the structure for intermediate **I**.

(iii) Describe a simple chemical test by which **C** can be distinguished from **G**. State clearly how **each** compound behaves in the test.

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(iv) Silver iodide, AgI, is produced as a by–product in step **III** of the reaction involving **C** to form **G**. AgI is insoluble in aqueous ammonia but is soluble in aqueous sodium thiosulfate, $Na_2S_2O_3$, to form a complex in which the coordination number of silver is 2.

Write an ionic equation for the formation of the complex.

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[5]

[Total: 12]