H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME								
CT GROUP	1	3				INDEX NUMBER		

CHEMISTRY 9647/02

Paper 2 Structured **23 September 2014**

2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CT group and index number 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.

Answer **all** 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	/ 12	5	/ 12
2	/ 15		
3	/ 10	Penalty	sf units
4	/ 23	Total	/ 72

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

1 Planning

The label of a bottle of an aqueous acid, represented by H_xA, had been damaged. Only the concentration of the acid, 0.50 mol dm^{-3} was known.

A student was tasked to determine (1) if the acid is monobasic or dibasic, and (2) if the acid is a strong acid or a weak acid.

(a) The student was given a 0.50 mol dm^{-3} sodium hydroxide solution. She proposed to first determine the basicity of the acid in the bottle by mixing different volumes of the acid and sodium hydroxide and measure the maximum temperature change, ΔT, for each of the constant volume mixtures.

The following experiments were performed:

Experiment 1: 50 cm^3 of $H_xA(aq)$ was added to 100 cm^3 of NaOH(aq)
Experiment 2: 100 cm^3 of $H_xA(aq)$ was added to 50 cm^3 of NaOH(aq)

The changes in temperature of the mixture were measured for Experiment 1 and Experiment 2 as ΔT_1 and ΔT_2 respectively.

(i) Write an equation to represent the standard enthalpy change of neutralisation between sodium hydroxide and H_xA.

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(ii) Explain how the basicity of the acid can be determined by comparing the ΔT_1 and ΔT_2 values.

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[5]

(b) It was determined that the acid in the bottle is a monobasic acid, HA.

The student proceeded to determine if HA is a strong or weak acid using the following:

- **FA 1**, a solution of 0.50 mol dm^{-3} sodium hydroxide.
- **FA 2**, a solution of 0.50 mol dm^{-3} HA.
- Thermometers
- Styrofoam cups
- Apparatus normally found in a college laboratory

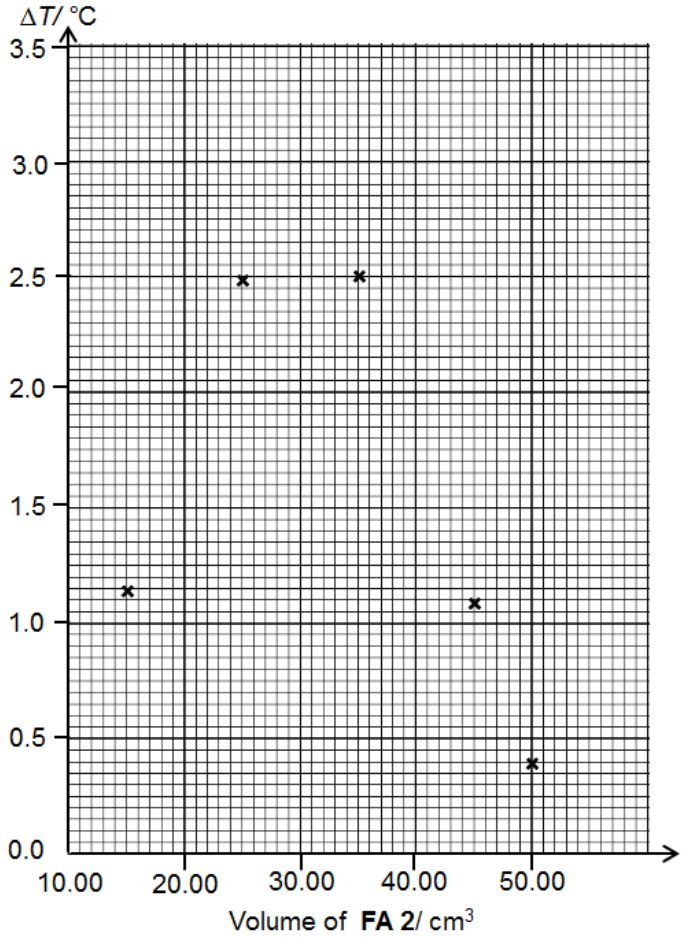
She performed a series of experiments by mixing different volumes of **FA 1** with **FA 2** and measuring the temperature changes of each of these mixtures.

(i) Write a plan to determine the temperature changes, ΔT, for the following series of reactions between **FA 1** and **FA 2**:

Mixture	Volume of **FA 1** / cm^3	Volume of **FA 2** / cm^3
1	15	45
2	25	35
3	35	25
4	45	15
5	50	10

Your plan should include the apparatus for measurement of volume. Indicate clearly the measurements that will be made during the experiment and show how these measurements can be used to obtain the temperature change, ΔT.

(ii) The student performed the experiment for the series of reactions between **FA 1** and **FA 2** and the temperature changes were plotted as shown below.



By means of two straight lines, determine the ΔT_{max} for the series of experiments.

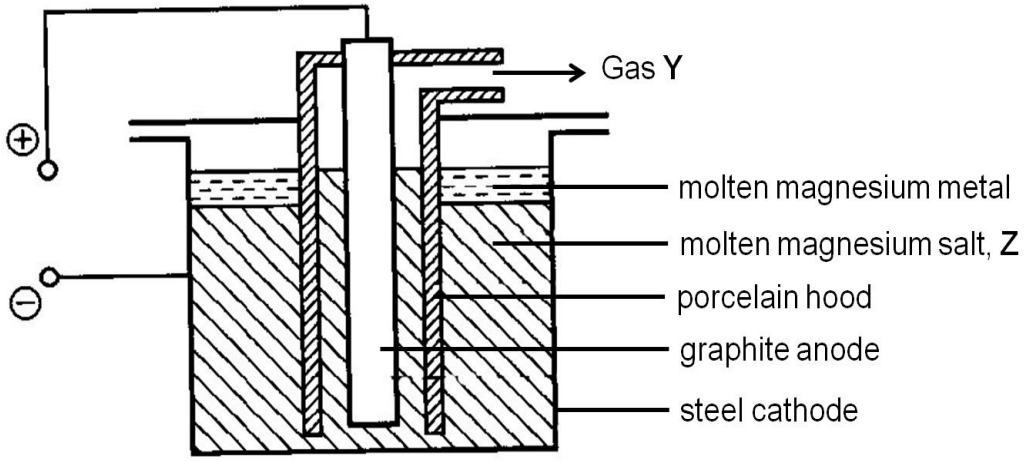
(iii) Using your graph in **(b)(ii)**, calculate the enthalpy change of neutralisation for the reaction between HA and NaOH. [Assume that the heat capacity of the solution = 4.2 J K^{-1} cm^{-3}.]

(iv) Given that the enthalpy change of neutralisation for reaction between HC*l* and NaOH is –57.3 kJ mol^{-1}, deduce whether the unknown acid HA is a strong acid or a weak acid. Explain your answer.

[7]

[Total: 12]

2 Magnesium metal can be manufactured by the electrolysis of molten magnesium salt, **Z** using the setup shown below. During the electrolysis process, 0.912 g of unknown gas **Y** was produced which occupied 500 cm^3 volume at 200 °C and 1 atm.



(a) (i) Determine the M_r of gas **Y** and hence identify it.

(ii) Explain why you would expect the behaviour of gas **Y** to be less ideal at low temperature.

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(iii) Write ion-electron equations for the reaction occurring at the cathode and anode.

Cathode: .....

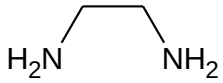
Anode:

(iv) Given that the electrolysis took place for 40 minutes, calculate the current used for the process.

(v) Using relevant $E^{\ominus}$ data from the *Data Booklet*, explain why magnesium metal cannot be obtained by the electrolysis of aqueous magnesium salt.

[8]

(b) Ethylenediamine (*en*) can act as a bidentate ligand. The structure of *en* is shown below.



ethylenediamine

$[Ni(NH_3)_6]^{2+}(aq)$ and $[Ni(en)_3]^{2+}(aq)$ can be prepared from ligand exchange reaction of 1 mol dm^{-3} $[Ni(H_2O)_6]^{2+}(aq)$ with NH_3 and *en* ligands respectively.

(1): $[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$
(2): $[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$

The standard enthalpy change of reaction, $\Delta H^{\ominus}_r$, and standard entropy change of reaction, $\Delta S^{\ominus}_r$, for the ligand exchange reactions **(1)** and **(2)** are as follows.

Reaction	$\Delta H^{\ominus}_r$ / kJ mol^{-1}	$\Delta S^{\ominus}_r$ / J mol^{-1}
(1)	−27.5	+4.5
(2)	−35.0	+34.0

The $\Delta H^{\ominus}_r$ for both reactions **(1)** and **(2)** are similar as the Ni-O bonds broken and Ni-N bonds formed are similar.

Chelate effect refers to the greater stability of complexes formed by polydentate ligands (e.g. *en*) than those formed by monodentate ligands (e.g. NH_3).

(i) Explain why the $\Delta S^{\ominus}_r$ for reaction **(1)** is so different from that of reaction **(2)**.

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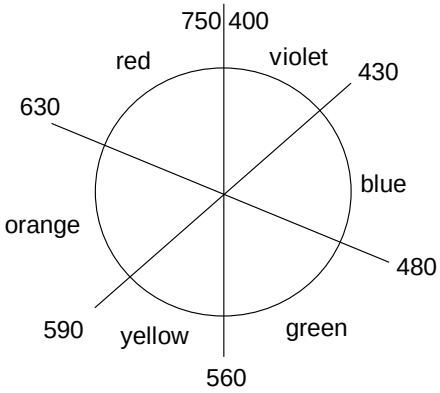
(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}_r$ for reactions **(1)** and **(2)** to show why $[Ni(en)_3]^{2+}$ exhibit the *chelate effect*.

(iii) Using your answers from **(b)(i)** and **(b)(ii)**, comment qualitatively on the statement: "*Chelate effect is an entropy effect.*"

(iv) Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

The figure below shows a colour wheel with approximate wavelength values (in nm) for different colour light. As wavelength decreases, the energy of the light increases.



Various complexes of Ni have different colours. The colours of $[Ni(CN)_6]^{3-}(aq)$ and $[Ni(en)_3]^{2+}(aq)$ are given below.

Complex	Colour
$[Ni(CN)_6]^{3-}(aq)$	red
$[Ni(en)_3]^{2+}(aq)$	violet

State whether CN^- or *en* is a stronger field ligand. Explain your answer.

[7]

[Total: 15]

3 This question is about Group II elements and their compounds.

(a) **(i)** All Group II carbonates and nitrates undergo thermal decomposition.

Write a general equation for the thermal decomposition of Group II nitrates.

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(ii) Magnesium nitrate dissolves in water to give a solution of pH ≈ 6.5.

Write equations to show why the solution formed is slightly acidic.

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(iii) In an experiment, water is added separately to two test tubes containing residues obtained from the thermal decomposition of magnesium carbonate and barium carbonate. This is followed by the addition of dilute sulfuric acid.

Describe and account for what you would see in both test tubes.

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[5]

(b) (i) Given that the solubility product for magnesium hydroxide in water at 25 ºC is 1.10×10^{-11} mol^3 dm^{-9}, calculate the mass of solid magnesium nitrate to be added to 30 cm^3 of sodium hydroxide solution of pH 9.0 to form a saturated solution of magnesium hydroxide.

(ii) Explain, with the aid of equations, how the solubility of magnesium hydroxide in aqueous sodium hydroxide would differ from that in water.

[5]

[Total: 10]

4 Alkenes and alkynes are useful starting materials for the synthesis of many organic intermediates.

(a) The "OXO" reaction is industrially important for making alcohols, aldehydes and carboxylic acids from alkenes. For example, ethene can be converted into propanal as follows:

$$CH_2{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CHO(g)$$

(i) Write an expression for K_p for the "OXO" reaction.

(ii) When equimolar mixture of ethene, CO and hydrogen gas at an initial total pressure of 150 atm is allowed to reach equilibrium, the partial pressure of propanal is found to be 49.4 atm.

Calculate the value of K_p and state the units

(iii) Suggest why this reaction is carried out at 150 atm.

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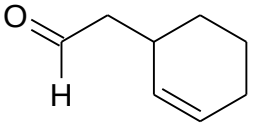
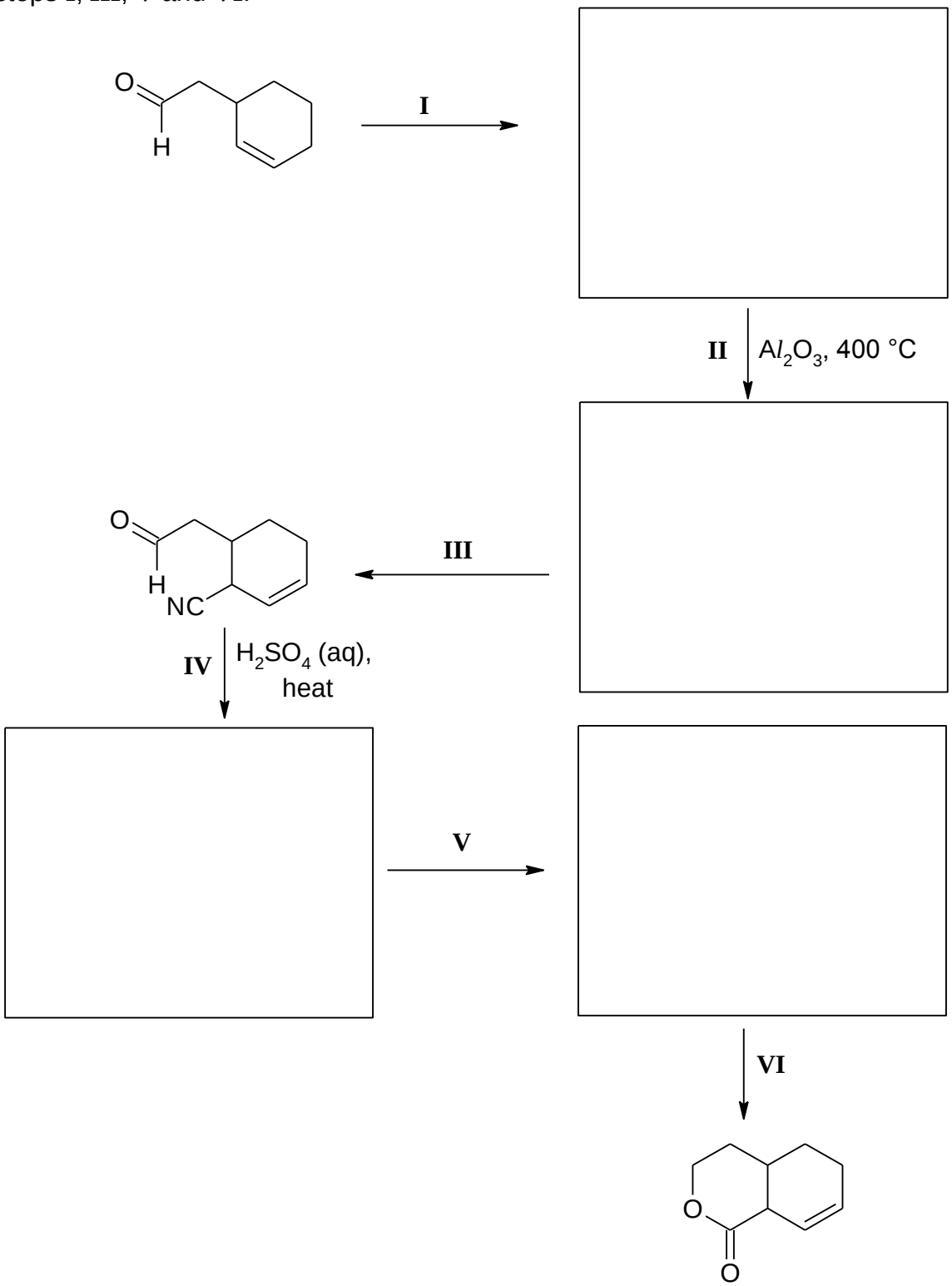
[5]

(b) The reaction scheme below shows how an ester is synthesised from  .

Complete the reaction scheme below by giving the structural formulae of the organic products in the spaces provided and state the reagents and conditions for steps **I**, **III**, **V** and **VI**.



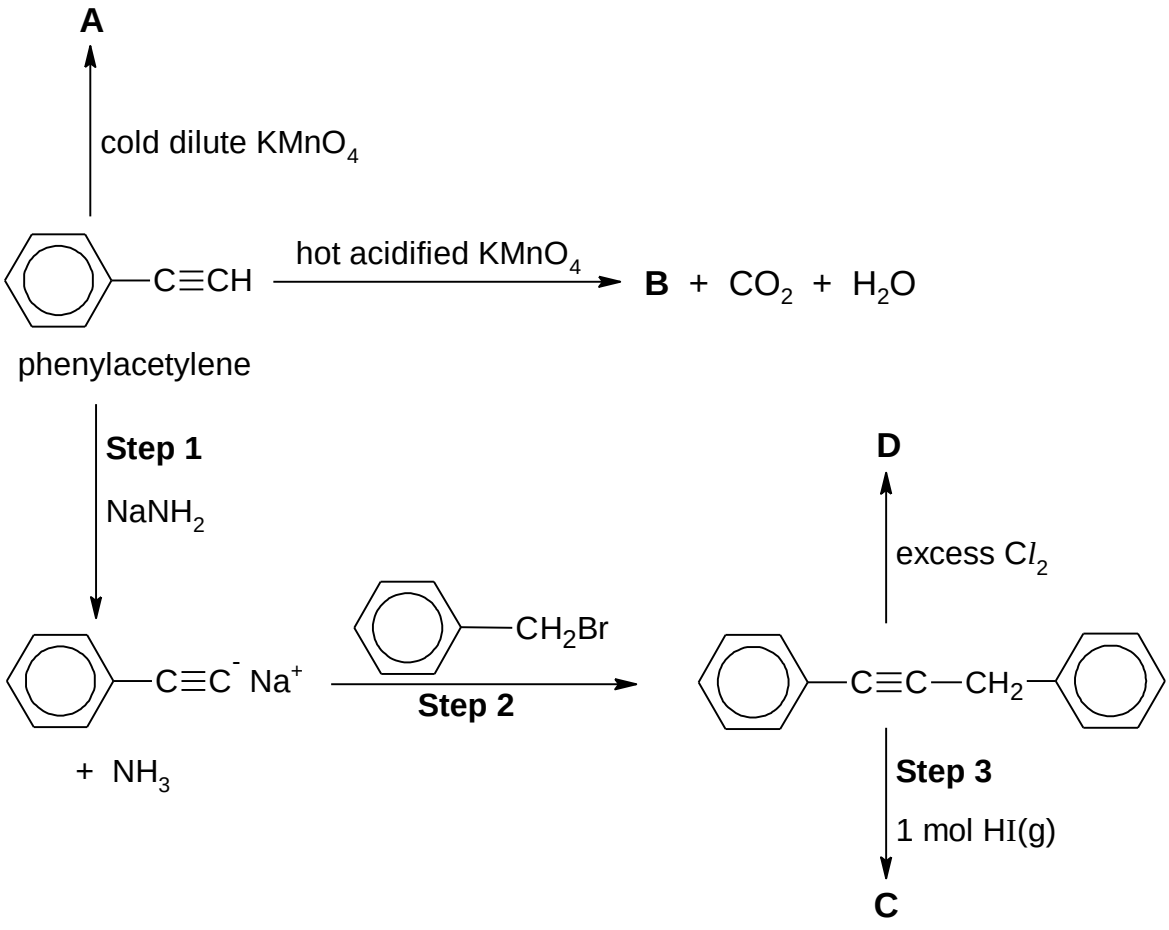
Step	Reagents and conditions
I	
III	
V	
VI	

[8]

(c) Alkynes are hydrocarbons containing a C≡C triple bond. Reactions involving alkynes resemble that of corresponding alkenes.

For example, alkynes react with bromine in tetrachloromethane to give dibromoalkenes. In the mild oxidation of alkynes, the π bonds are broken and a dicarbonyl compound is formed, while oxidation with powerful oxidising agents such as potassium manganate(VII) cleaves the C≡C triple bond.

The following reaction scheme shows some reactions involving phenylacetylene, an alkyne that is useful in organic synthesis.



(i) State the types of reaction that occur in steps **1** and **2**.

Step **1**: .....

Step **2**: .....

(ii) Draw the structures for the organic products **A** to **D** from the reaction scheme.

A	**B**
C	**D**

(iii) Name and outline the mechanism for step **3**.

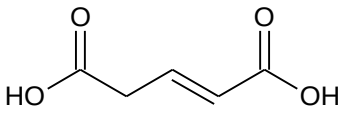
(iv) Phenylacetylene reacts with Br_2 in tetrachloromethane to give a product with molecular formula $C_8H_6Br_2$. Draw the isomers of the product and state the type of isomerism displayed.

Type of isomerism: .....

[10]

[Total: 23]

5 (a) Glutaconic acid is a dicarboxylic acid that has been investigated as a monomer for the production of biodegradable polymers.



glutaconic acid

Draw the organic product formed when glutaconic acid is treated with:

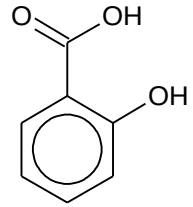
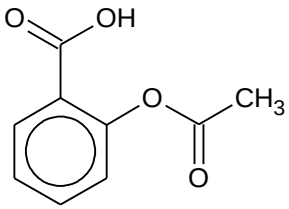
(i) $NH_3(g)$,

(ii) $KMnO_4(aq)$, NaOH(aq) and heated under reflux.

[2]

(b) Salicylic acid is a naturally occurring carboxylic acid found in many plants. It has been used by many native American tribes as a pain reliever. Salicylic acid is also used to produce acetylsalicylic acid.

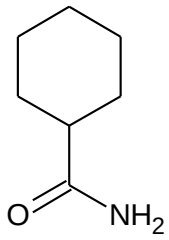
The following table compares the pK_a values of the two acids.

acid	pK_1	pK_2
 Salicylic acid	2.97	13.8
 Acetylsalicylic acid	3.40	-

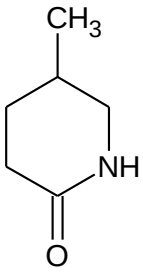
With the aid of a diagram, explain why the pK_1 of the salicylic acid is lower than that of acetylsalicylic acid. [4]

(c) For each of the following pairs of compounds, describe one simple chemical test which would enable you to distinguish between them. State clearly how each compound behaves in the test and write equations for the reactions occurred.

(i)

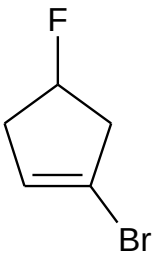


A

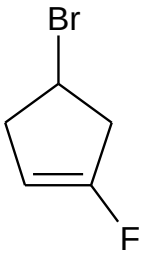


B

(ii)



C



D

[6]

[Total: 12]

End of Paper