NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME: **Answers**

CLASS:

TUTOR'S NAME:

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# CHEMISTRY

**9746/02**

Paper 2 Structured

**23 September 2009**

**1 hour 30 minutes**

Candidates answer on the Question Paper

Additional Materials: Answer Paper
Data Booklet

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**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.

Answer **all** 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** | |
|---|---|
| **1** | 9 |
| **2** | 16 |
| **3** | 8 |
| **4** | 10 |
| **5** | 13 |
| **6** | 4 |
| **Total** | 60 |

This document consists of **12** printed pages and **0** blank page.

**[Turn over**

Answer **all** questions.

**1** **(a)** *The use of the Data Booklet is relevant to this question.*

Nitrogen dioxide disproportionates in acidic solution to nitrous acid and nitrate ions.

**(i)** Write a balanced equation for the disproportionation reaction. [1]

$2NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+$

**(ii)** Use the data below and any other relevant data in the Data Booklet to determine if this disproportionation reaction would actually occur under standard conditions

$NO_2 + H^+ + e$ □ $HNO_2$ $E^\theta = +1.10\ V$ [2]

$NO_2 + H^+ + e$ □ $HNO_2$ $E^\theta = +1.10\ V$

$NO_3^- + 2H^+ + e$ □ $NO_2 + H_2O$ $E^\theta = +0.81\ V$

$2NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+$

$E^\theta$ cell $= (+1.10) - (+0.81) = +2.9\ V$

Hence disproportionation is favourable

**(b)** A 0.360 g sample of gaseous aluminium chloride takes up a volume of 52 $cm^3$ at a temperature of $200^oC$ and a pressure of $1.02 \times 10^5$ Pa.

**(i)** Under what conditions of temperature and pressure would you expect the behaviour of gaseous aluminium chloride to be most like that of an ideal gas? [1]

High temperature and low pressure.

**(ii)** Calculate the Mr of the vapour at this temperature. [2]

$$Mr = \frac{RT}{PV} \times mass = \frac{0.360 \times 8.31 \times (273+200)}{1.02 \times 10^5 \times 52 \times 10^{-6}} = 267$$

**(c)** Compounds of aluminium have many important uses industrially. For example in the Haber process, $Al_2O_3$ are mixed with iron catalyst to enhance efficiency of the iron catalyst.

Ammonia is manufactured in the Haber process according to the equation:

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \quad \Delta H = -92\ kJmol^{-1}$

**(i)** Write an expression for $K_p$ for this reaction [1]

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3}$$

**(ii)** When a 1:3 mixture of $N_2$ and $H_2$ was allowed to reach equilibrium at 200 atm and 500°C, the partial pressure of $NH_3$ was found to be 40 atm. Using the expression in c) (i) to calculate the value for $K_p$. [2]

$$P_{total} = 200atm, P_{NH_3} = 40atm$$

$$P_{N_2} = \frac{1}{4} \times (200-40) = 40atm$$

$$P_{H_2} = \frac{3}{4} \times (200-40) = 120atm$$

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3} = \frac{40^2}{40 \times 120^3} = 2.31 \times 10^{-5} atm^{-2}$$

[Total:9]

**2** **(a)** $CH_2{=}CHCO_2H\ (l) + H_2(g) \longrightarrow CH_3CH_2CO_2H\ (l) \quad \Delta H = -380\ kJ\ mol^{-1}$

**compound A**

**(i)** Given that the absolute value of ΔS for the above reaction is 68 J $mol^{-1}K^{-1}$. Predict the sign of ΔS, stating your reasons. [2]

ΔS expected to be –ve.

(1 mol of gas + 1 mol of liquid) in reactant give 1 mol of liquid product, system becomes more ordered.

**(ii)** Hence determine the temperature for the reaction to be non-spontaneous. [2]

$\Delta G = \Delta H - T\Delta S$

For reaction to be non-spontaneous $\Delta G > 0$

$-380 - (T)(-0.068) > 0$

$T(0.068) > 380$

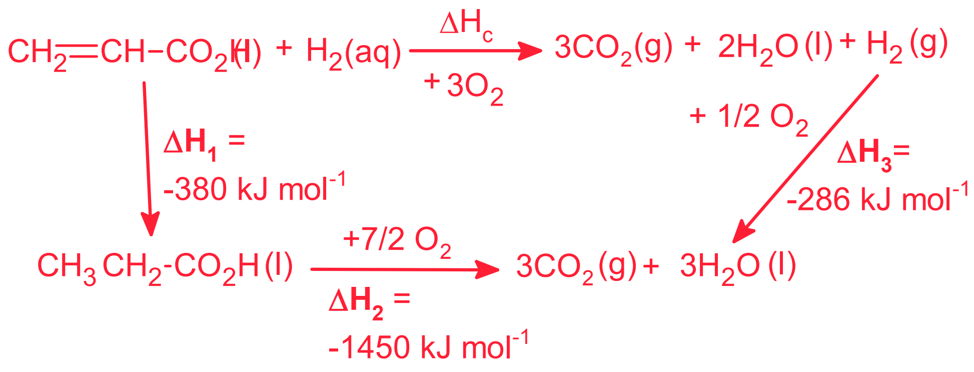
$T > 5588$ K

**(iii)** With the aid of an energy cycle, calculate the enthalpy change of combustion of compound A by using the data provided. [3]

**Data**

$\Delta H_f$ ($H_2O$) = -286 kJ $mol^{-1}$

$\Delta H_c$ ($CH_3CH_2COOH$) = -1450 kJ $mol^{-1}$



–380 = $\Delta H_c$(A) – 286 + 1450

$\Delta H_c$(A) = –1544 kJ $mol^{-1}$

**(b)** Copper is an important metal used extensively in pipes and electrical wires. It can be made extremely pure and corrodes very slowly.

**(i)** Copper corrodes in moist air to first give a thin layer of copper(II) oxide and this process happens much more slowly than the rusting of iron to form the iron(III) oxides. With the use of relevant data from the *Data Booklet*, explain this difference. [2]

- $Cu^{2+} + 2e \rightleftharpoons Cu$ $\quad E^\theta = \underline{+0.34\ V}$
- $Fe^{3+} + 3e \rightleftharpoons Fe$ $\quad E^\theta = \underline{–0.04\ V}$
- $O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$ $\quad E^\theta = \underline{+0.40\ V}$ (**MOIST AIR**)
- **$O_2 + 2H_2O + 2Cu \rightarrow 4OH^- + 2Cu^{2+}$**

  **$E^\theta_{cell}$ = +0.40 – (+0.34) = + 0.06V (close to 0) (feasible)**
- **$3O_2 + 6H_2O + 4Fe \rightarrow 12OH^- + 4Fe^{3+}$**

  **$E^\theta_{cell}$ = +0.40 – (-0.04) = +0.44V > 0 (feasible)**
- $E^\theta_{cell}$ for the oxidation of Fe is much more positive than that for the oxidation of Cu, hence more spontaneous.

**(ii)** Another possible oxidation state that copper can have is +1, such as in copper(I) sulphate, $Cu_2SO_4$. When this sulphate is added to water, blue solution of copper(II) sulphate and pink deposit of copper metal forms. Write a balanced equation for this process and using relevant data from the *Data Booklet*, show that this reaction is feasible. [2]

$2Cu^+ \rightarrow Cu + Cu^{2+}$

$Cu^+ + e$ □ $Cu$ $+ 0.52$ V

$Cu^{2+} + e$ □ $Cu^+$ $+ 0.15$ V

$E^\theta = + 0.52 – (+ 0.15) = + 0.37$ V $> 0$ (feasible)

**(iii)** A copper metal plate was dipped into an aqueous solution of 1.0 mol $dm^{-3}$ copper(II) sulphate solution and this half-cell was connected via a salt bridge, to the following half-cell,

$2CO_2 + 2H^+ + 2e$ □ $H_2C_2O_4$

The **overall cell e.m.f** was found to be +0.83 V and the size of the copper plate *increased* after some time.

Give the cell notation and hence, calculate the reduction potential, $E^\theta$ ($CO_2$ / $H_2C_2O_4$) [2]

The size of Cu increased shows that $Cu^{2+}$ ions is reduced to Cu. Hence oxidation must be occurring at the other $CO_2$ half-cell.

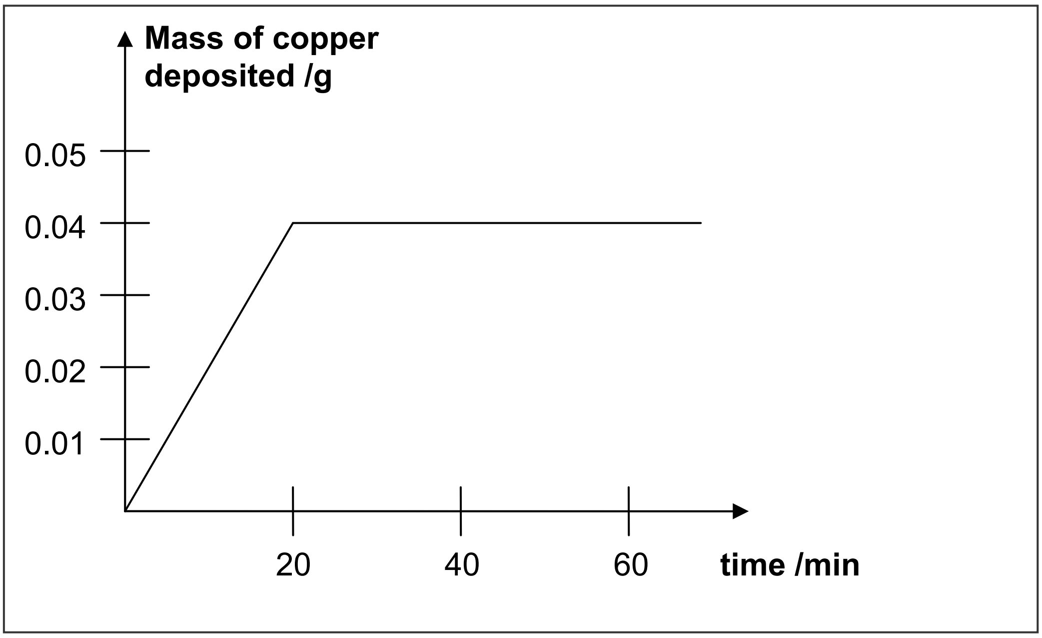
Pt (s) | $H_2C_2O_4$ (aq) , $CO_2$ (g) || $Cu^{2+}$ (aq) | Cu (s)

$E^\theta = E^\theta_R – E^\theta_o$

$+0.83 = +0.34 - E^\theta_o$

$E^\theta_o = - 0.49$ V $= E^\theta$ ($CO_2$ / $H_2C_2O_4$)

**(c)** To obtain a pure metal, electrolysis can be conducted using an aqueous copper(II) sulphate solution and copper electrodes. The results of the experiment are shown below in the graph.



**(i)** Write balanced half-equations, with state symbols, for the reactions at the anode and the cathode. [1]

Cathode: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$

**(ii)** Calculate the current used during electrolysis. [1]

$Q = nzF = (0.04/63.5)(2)(96500) = 121.6$ C

$I = Q / t = 121.6 / (20 \times 60) = 0.101$ A

**(iii)** It is not always possible to accurately predict the electrode reactions that occur during electrolysis. Suggest a reason for this. [1]

Electrolysis may not occur at standard conditions. OR

Rate of reaction may be too slow. OR

The reaction has a high activation energy.

[Total:16]

**3** **(a)** Aluminium(III) oxide and phosphorous(V) chloride differ in their behaviour with water.

**(i)** Write equations (if any) for each of the behaviour. [2]

$Al_2O_3 + H_2O \rightarrow$ No reaction

$PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$

**(ii)** Explain these differences in terms of the different structures and types of chemical bonding in the compounds. [2]

$Al_2O_3$ - very strong ionic bonds, high LE – no reaction with water

$PCl_5$ - simple molecular structure, chloride is acidic – hydrolysis occurs

**(iii)** State the pH of any solution formed in water. [1]

For $PCl_5$ - pH is 2-3

**(b)** In each of the following reactions, describe the way in which the oxide of the named element is reacting and discuss whether its behaviour is what you would expect from the position of the element in the Periodic Table:

(i) Silicon: $MgO + SiO_2 \rightarrow MgSiO_3$

(ii) Beryllium: $2\ NaOH + BeO \rightarrow Na_2BeO_2 + H_2O$ [3]

(i) $SiO_2$ : Gp IV (**non-metallic**) oxide, expected to form **acidic oxide** and to react with **base**. Hence, given reaction is **expected.**

(ii) BeO : Gp II (**metallic**) oxide, expected to form **basic oxide** and to react with **acid**. But given reaction is with an alkali. Hence, given reaction is **not expected.**

[Acceptable answer]: due to high charge density of $Be^{2+}$ion, Beo shows a high degree of covalency, and is amphoteric like $Al_2O_3$). Hence, BeO also shows acidic properties and would react with alkali NaOH to give a salt, $Na_2BeO_2$ and water.]

[Total: 8]

**4** Chloroethene is the monomer from which the polymer PVC (polyvinylchloride) is produced.

$$CH_2{=}CH_2 \xrightarrow{\text{stage } \mathbf{I}} ClCH_2CH_2Cl \xrightarrow{\text{stage } \mathbf{II}} CH_2{=}CHCl$$

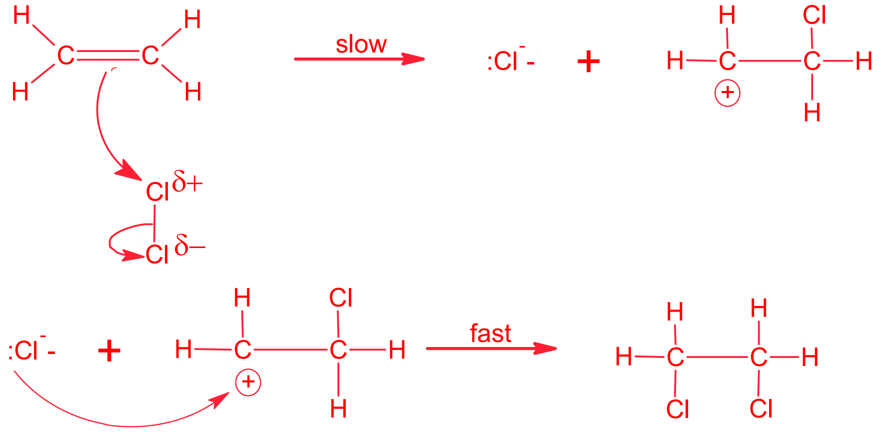
**(a)** Suggest reagents and conditions for stages **I** and **II**. [2]

stage I: $Cl_2$ in $CCl_4$, r.t.

stage II: ethanolic KOH, heat under reflux

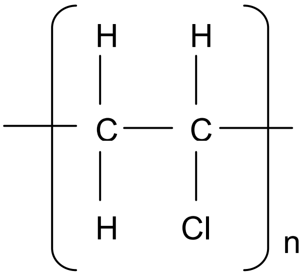
**(b)** Describe the mechanism of stage **I**. [3]

Electrophilic addition [1]



[2m for correct arrow, intermediate ion]

**(c)** A repeat unit of PVC is shown below



Suggest a reason why PVC might break down when exposed to concentrated aqueous sodium hydroxide whereas poly(ethene) does not. [1]

- In conc NaOH, nucleophilic substitution occurs with PVC, C-C*l* bond is broken, the Cl atoms are replaced by the OH groups.
- C-H bond in poly(ethene) is inert to nucleophilic substitution.

**(d)** It was suggested that the intermediate, $ClCH_2CH_2Cl$ used in the production of PVC be formed from ethane instead.

**(i)** Discuss if this will be a good alternative to the method used in stage I in (a). [1]

Poorer method as many other chlorinated products will be formed.

**(ii)** A student proposed that one of the propagation steps in the mechanism when $ClCH_2CH_2Cl$ is formed from ethane to be:

$$CH_3CH_3 + Cl\gamma \longrightarrow CH_3CH_2Cl + H\gamma$$

Using relevant bond energy values from the *Data Booklet*, explain why this is incorrect as compared to the actual step. [3]

Actual mechanism:

$CH_3CH_3 + Cl\gamma \longrightarrow CH_3CH_2\gamma + HCl$ [1m for equation]

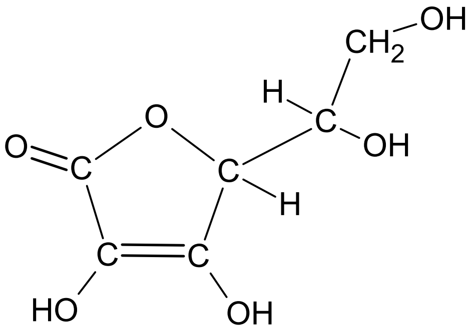
BE (H – Cl) = 431 kJ $mol^{-1}$

BE (C –Cl) = 340 kJ $mol^{-1}$

Formation of H-Cl bond is more favourable (more exothermic) than formation of C-Cl bond

[Total: 10]

**5** Ascorbic acid, also known as vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as food additives.



Ascorbic Acid

**(a)** State the functional group(s) present in the ascorbic acid compound. [2]

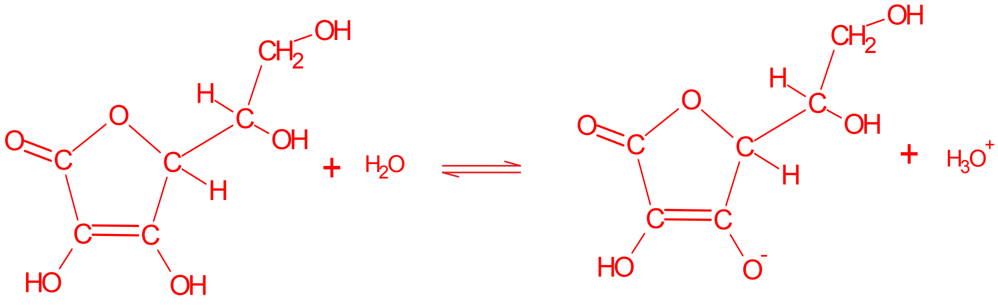
Ester, **secondary** alcohol, **primary** alcohol, alkene

**(b)** Explain in terms of structure and bonding, why Ascorbic Acid is water soluble. [2]

The molecule has **many** OH (or alcohol or hydroxy groups)

that allows it to form (intermolecular) **hydrogen bonds with water** molecules

**(c)** Write an ionic equation to illustrate the acidity of ascorbic acid in water and explain how the stability of the conjugate base gives rise to its acidity. [3]



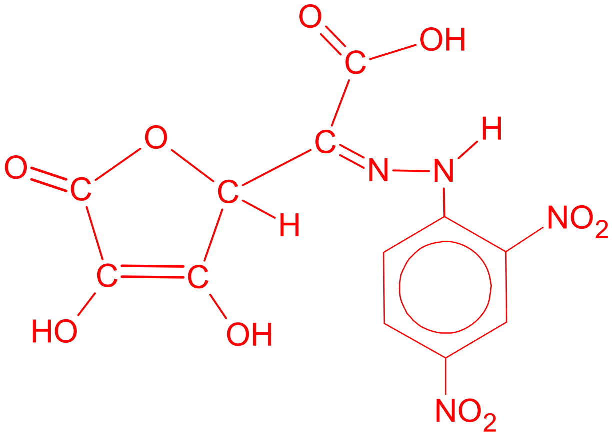
Loss of $H^+$ - must be **from OH group attached to C=C** (either one or two $H^+$ )

The p orbital of oxygen atom overlaps with the ∇ electron cloud of the C-C double bond**.** The negative charge on oxygen is delocalize**d** over the 2 carbon and the oxygen atoms.

The negative charge is **dispersed** and the **conjugate base stabilized**, making ascorbic acid acidic.

**(d)** The ascorbic acid molecule was reacted with acidified potassium dichromate (VI) followed by 2,4-dinitrophenylhydrazine.

Draw the structural formula of the product formed. [2]

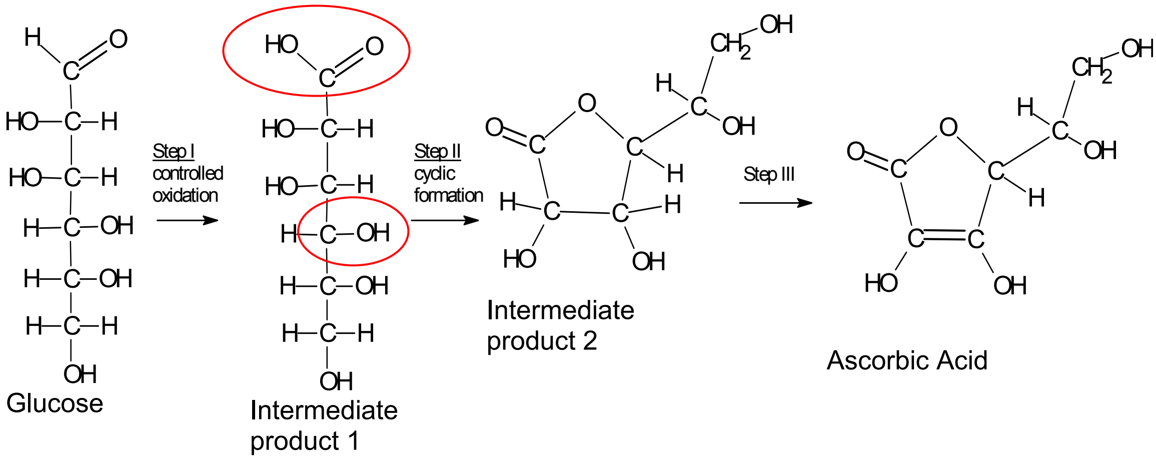


For changing primary alcohol to carboxylic acid. [1]

For reacting resultant ketone with 2,4-DNPH [1]

(minus [1] for any other mistakes until 0)

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway was proposed:



**(i)** State the type of reaction found in **step II** and hence **circle** the functional group(s) present in the intermediate product 1 that is/are involved in the reaction. [3]

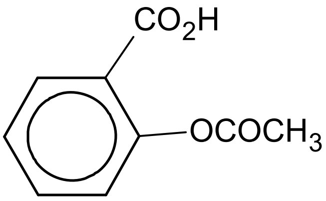
Condensation (or esterification)

**(ii)** State the type of reaction present in **Step III** [1]

Elimination

[Total: 13]

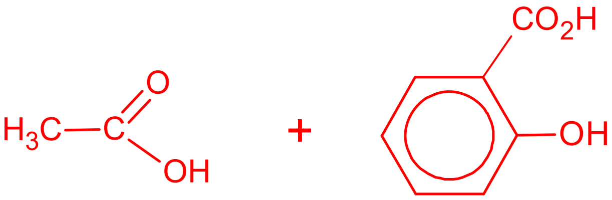
**6** Aspirin, also known as acetylsalicylic acid is often used as an analgesic (pain-remover) to relieve minor aches and pains. It is readily absorbed from the intestines since it diffuses rapidly into the tissues.



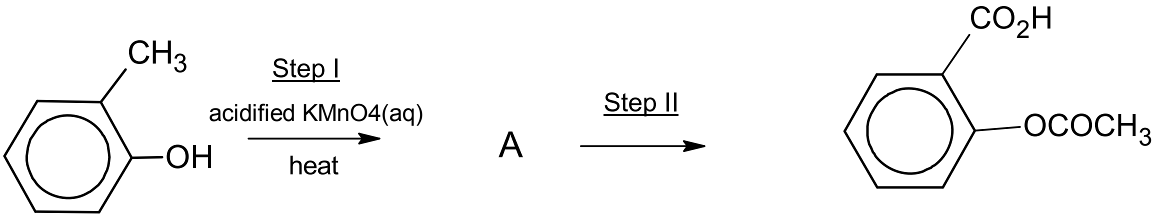
Aspirin

The molecule is hydrolysed by acids in the stomach.

**(a)** Draw the structural formulae of the hydrolysis products. [2]



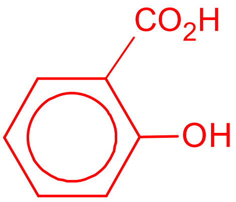
Aspirin can be synthesised from 2-methylphenol via the following steps:



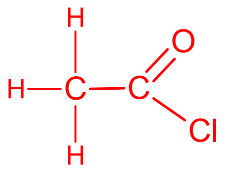
2-methylphenol

Aspirin

**(b)** Draw the structural formula of the intermediate **A** [1]



**(c)** For step II, draw the displayed formula of the reactant and give the necessary reagents/conditions that will allow intermediate A to react **completely**. [1]

| Reactant | Reagents/Conditions |
|---|---|
|  | Room Temperature |

[Total:4]

**[End of Paper]**