GradeMax

Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

1516755053

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **May/June 2016**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
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.

This document consists of **17** printed pages and **3** blank pages.

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

1 **(a)** Limewater is a saturated solution of $Ca(OH)_2$ in water. It is used to test for the presence of CO_2 in a gaseous mixture.

(i) Write an equation for the reaction between limewater and CO_2.

..... [1]

A saturated solution of $Ba(OH)_2$ can be used instead of $Ca(OH)_2$ to test for CO_2. A saturated solution of $Mg(OH)_2$ cannot be used for this test.

(ii) Explain why a saturated solution of $Ba(OH)_2$ **can** be used to test for CO_2.

.....

..... [1]

(iii) Explain why a saturated solution of $Mg(OH)_2$ **cannot** be used to test for CO_2.

.....

.....

..... [2]

(b) Describe and explain the trend in the thermal stabilities of the carbonates down Group 2.

.....

.....

.....

.....

..... [3]

(c) Nickel carbonate, $NiCO_3$, decomposes on heating.

Use the *Data Booklet* to explain whether $NiCO_3$ will decompose more or less readily than $CaCO_3$.

.....

.....

.....

..... [2]

[Total: 9]

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2 (a) (i) Complete the following electronic configurations.

- the cobalt atom, Co $1s^2 2s^2 2p^6$ .....
- the cobalt(II) ion, Co^{2+} $1s^2 2s^2 2p^6$ .....

[1]

(ii) State the colours you would observe when concentrated HC*l*(aq) is added to an aqueous solution of cobalt(II) nitrate, $Co(NO_3)_2$.
Give the formulae and geometry of the complexes formed.

.....

.....

.....

.....

..... [5]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.

$Ni(R_3P)_2I_2$

$Ni(R_3P)_2I_2$

$Co(R_3P)_2I_2$

[3]

[Total: 9]

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3 One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

(a) Write the expression for K_p for this reaction, and state its units.

K_p =

units .....
[2]

(b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

$H_2S(g)$ 200 atm $CH_4(g)$ 100 atm

The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $CS_2(g)$ is 2 atm and that of the remaining $CH_4(g)$ is 98 atm.

(i) Calculate the equilibrium partial pressures of $H_2S(g)$ and $H_2(g)$.

$p(H_2S)$ = ... atm

$p(H_2)$ = ... atm
[2]

(ii) Calculate the value of K_p at this temperature.

K_p = ... [1]

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(c) (i) Predict the sign of $\Delta S^{\ominus}$ for this reaction. Explain your answer.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^{\ominus} = +241\,kJ\,mol^{-1}$$

.....

..... [1]

The free energy change, $\Delta G^{\ominus}$, for this reaction at 1000 K is +51 kJ mol^{-1}.

(ii) Calculate the value of $\Delta S^{\ominus}$ for this reaction, stating its units.

$\Delta S^{\ominus}$ = ... units ..... [2]

(d) How would the value of $\Delta G^{\ominus}$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

.....

.....

..... [2]

[Total: 10]

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[Turn over

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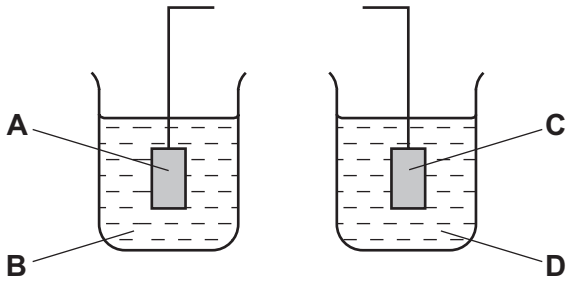
4 **(a)** **(i)** Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

.....

.....

..... [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E^{\ominus}_{cell}$ for a cell composed of the Fe^{3+}/Fe^{2+} and Ag^{+}/Ag half-cells.



(ii) Complete the diagram, labelling the components you add. [1]

(iii) Identify the components **A**-**D**.

A .....

B .....

C .....

D .....

[3]

(b) **(i)** Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in **(a)** are connected by a wire and the circuit is completed.

.....

..... [1]

(ii) Another electrochemical cell was set up using $0.31\,mol\,dm^{-3}$ $Ag^{+}(aq)$ instead of the standard Ag solution.

Use the Nernst equation, $E = E^{\ominus} + 0.059\log[Ag^{+}(aq)]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

[Total: 8]

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5 Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\rightleftharpoons} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\rightleftharpoons} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

(a) The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a of ethanoic acid, CH_3CO_2H, is 4.76.

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

..... [1]

(ii) With reference to the table above, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,

.....

.....

.....

- become larger as n increases.

.....
[3]

(iii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid.

.....

..... [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

.....

..... [2]

(ii) Write two equations to show how monosodium butanedioate, $HO_2CCH_2CH_2CO_2Na$, acts as a buffer.

.....

..... [2]

[Total: 9]

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6 Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, in acid solution in a two step process.

(a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$$C_6H_5NO_2 + ...e^- + ...H^+ \rightarrow C_6H_5NH_2 + ...H_2O \quad [1]$$

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

$$.....C_6H_5NO_2 + ...HCl + ...Sn \rightarrow .....C_6H_5NH_3Cl + ...SnCl_4 + ...H_2O \quad [2]$$

(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $C_6H_5NH_3Cl$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

(c) Following the reaction in **(b)**, an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

(i) Calculate the mass of phenylamine, $C_6H_5NH_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of NaOH(aq).

mass of phenylamine = ... g [1]

The final volume of the alkaline solution of phenylamine in **(i)** was 25.0 cm^3. The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

(ii) Use the data to calculate the partition coefficient, $K_{partition}$, of phenylamine between dichloromethane and water.

$K_{partition}$ = ... [2]

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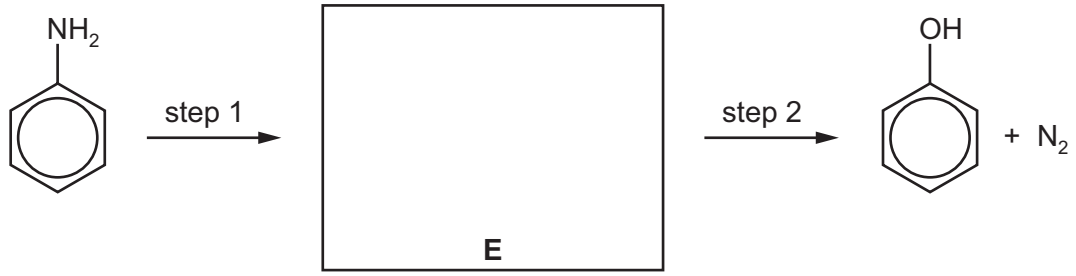
(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

.....

.....

..... [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1 .....

step 2 .....
[2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

[Total: 13]

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7 **(a)** **(i)** Use the *Data Booklet* to draw the structure of the tripeptide Ala-Ser-Gly showing its peptide bonds in full.

Ala-Ser-Gly

[2]

(ii) Calculate the relative molecular mass, M_r, of Ala-Ser-Gly.

M_r = ... [1]

(b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

(i) Draw the structure of serine at pH 11.

[1]

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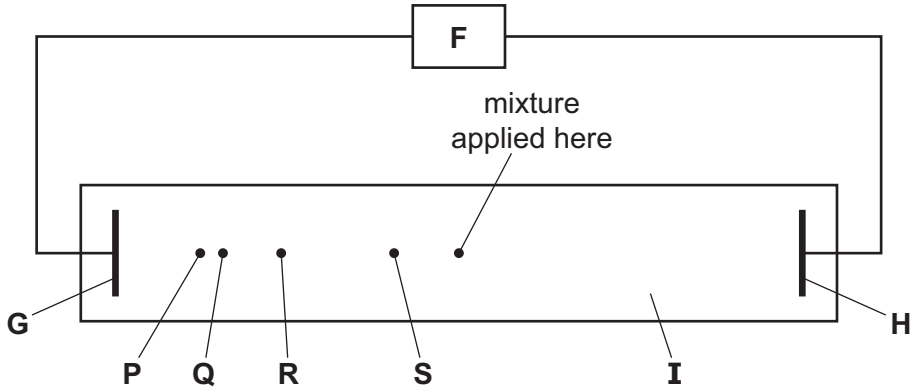
At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F**-**I** in the above diagram.

F .....

G .....

H .....

I .....

[4]

(iii) Suggest the identities of the species responsible for

spot **P**, ...

spot **S**. .....

Explain your answers.

.....

..... [3]

(c) (i) State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

..... [1]

(ii) Name the *type of reaction* in **(i)**.

..... [1]

[Total: 13]

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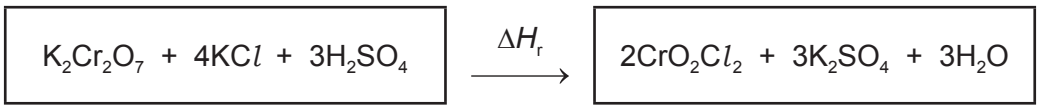
8 **(a)** Chromyl chloride, CrO_2Cl_2, can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

Use the following data to complete the Hess' Law cycle and calculate the enthalpy change of the reaction, ΔH_r.

compound	enthalpy change of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}
$K_2Cr_2O_7$	–2061
KCl	–437
H_2SO_4	–814
CrO_2Cl_2	–580
K_2SO_4	–1438
H_2O	–286





ΔH_r = ... kJ mol^{-1} [2]

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(b) There are two isomeric complex ions with the formula $[Cr(NH_3)_4Cl_2]^+$. One is green and the other is violet.

(i) Suggest the *type of isomerism* shown by these complex ions.

..... [1]

(ii) Explain why these two complex ions

- are coloured, ...

.....

.....

.....

- have **different** colours. .....

.....

.....

.....

[4]

[Total: 7]

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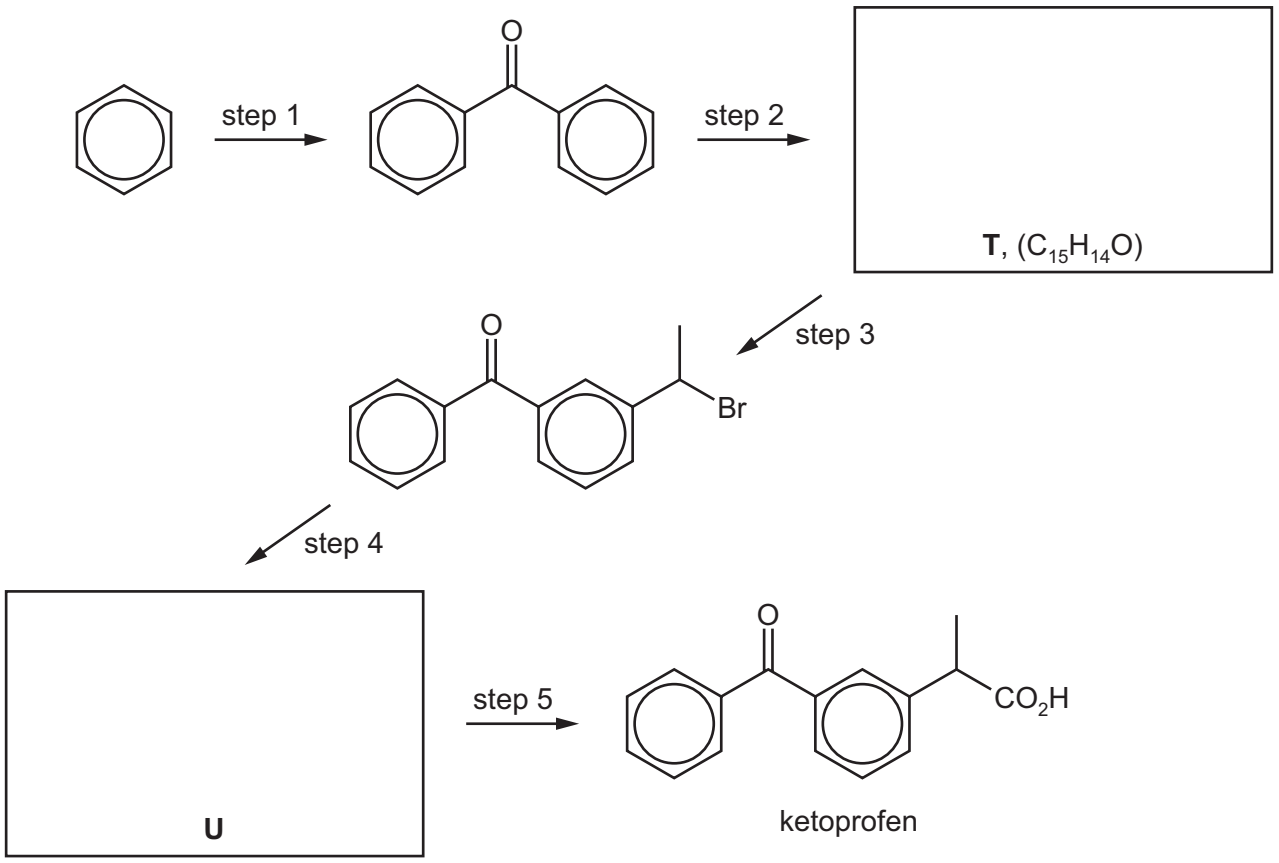
[Turn over

9 The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



(a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

[2]

(b) Suggest reagents and conditions for steps 1-5.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

[5]

(c) What *types of reaction* are steps 1 and 5?

step 1 .....

step 5 .....

[2]

[Total: 9]

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10 (a) Ethanedioic acid, $C_2O_4H_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with 0.0200 mol dm^{-3} $KMnO_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.

$$2MnO_4^- + 6H^+ + 5C_2O_4H_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the titration, 15.20 cm^3 of $KMnO_4$ was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

percentage of ethanedioic acid = ... % [3]

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[Turn over

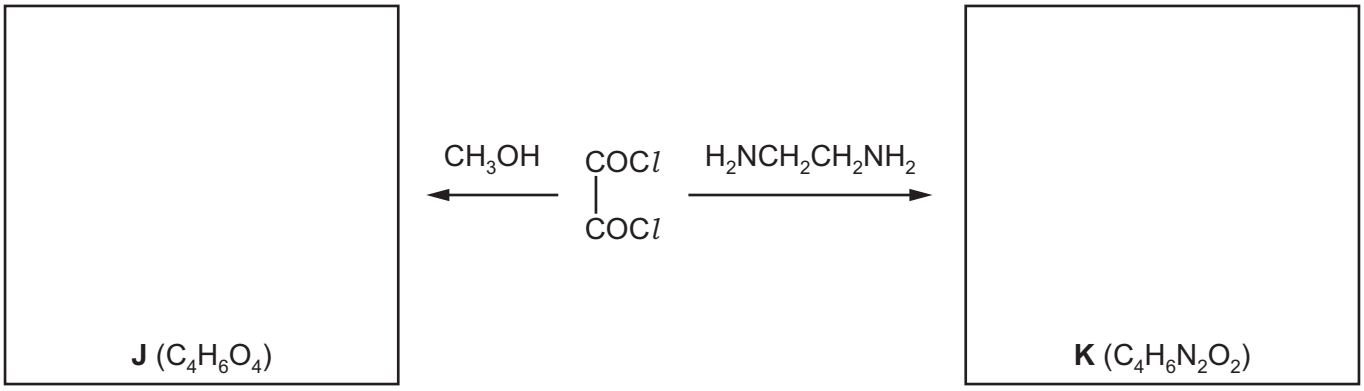
(b) Ethanedioic acid can be converted into ethanedioyl chloride:

$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(i) State a suitable reagent for this reaction.

..... [1]

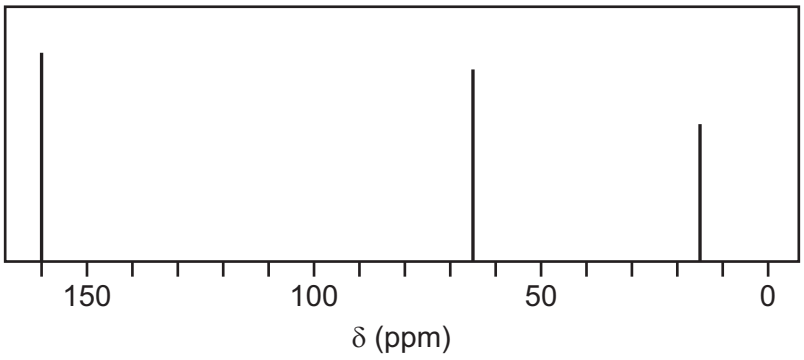
(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.



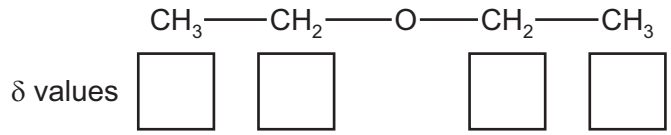
[2]

(c) When ethanedioyl chloride is reacted with silver ethanedioate, AgO_2CCO_2Ag, in ethoxyethane at –30 °C, an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6.

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $CH_3CH_2OCH_2CH_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.



[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

..... [1]

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(d) When pure **L** is reacted with an excess of CH_3OH, a mixture of three compounds is formed.

$$\underset{(C_4O_6)}{\mathbf{L}} \text{ and } CH_3OH \rightarrow \underset{(C_2H_2O_4)}{\mathbf{M}} \text{ and } \underset{(C_3H_4O_4)}{\mathbf{N}} \text{ and } \underset{(C_4H_6O_4)}{\mathbf{O}}$$

M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.

M, $(C_2H_2O_4)$

N, $(C_3H_4O_4)$

O, $(C_4H_6O_4)$

[3]

(ii) Suggest a structure for **L** that fits all the data given in **(c)** and **(d)**.

L, (C_4O_6)

[1]

[Total: 13]

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