TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

For Examiner's Use

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2014

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name 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.

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1	/12
2	/ 8
3	/10
4	/16
5	/10
6	/16
Total	

This document consists of **22** printed pages.

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1 Planning (P)

Chromatography is used to separate mixtures of substances into their components. The components move at different speeds when they are carried by a liquid or a gas called the "mobile phase" over an adsorbent material, called the "stationary phase".

(a) A quick and convenient method of chromatographic analysis for organic compounds is thin-layer chromatography (TLC). The stationary phase is silica gel which is coated onto sheets of glass, and the sheets are cut into thin strips.

A solution of a mixture of two organic compounds to be analysed is spotted near the bottom of the plate. The plate is then stood in a closed jar which is saturated with an appropriate solvent as the mobile phase. The reason for covering the jar is to make sure that the atmosphere in the beaker is saturated with solvent vapour. As the solvent travels up the plate by capillary action, the components of the mixture travel upwards at different rates and thus separate. The solvent is allowed to rise until it almost reaches the top of the plate (indicated by the solvent front), giving a maximum separation of the mixture components. The TLC plate is then removed from the jar for further analysis.

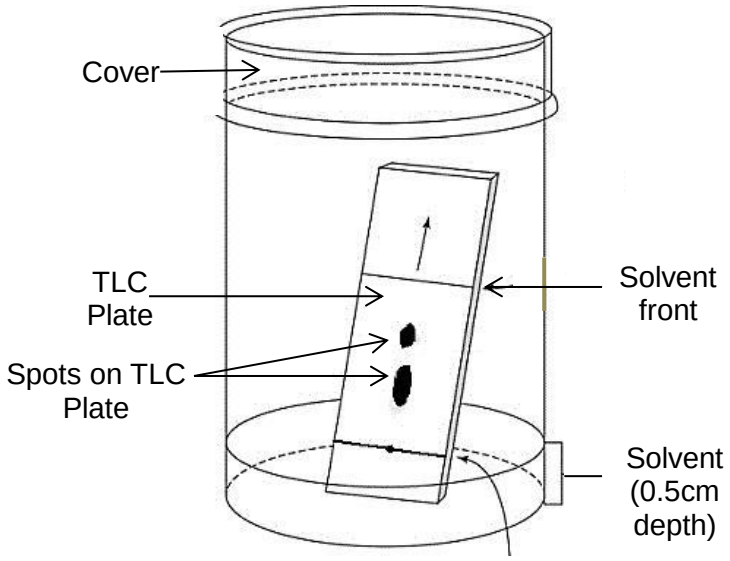

Figure 1: TLC analysing a solution of a mixture of two organic compounds

(i) A pencil line is drawn near the bottom of the TLC plate. Suggest a reason why any labeling on the TLC plate has to be drawn in pencil and not in ink.

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Silica gel is a form of silicon dioxide. At the surface of the silica gel, the silicon atoms are attached to –OH groups. The diagram below shows a small part of the silica surface.

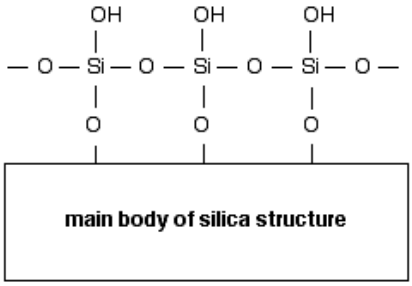

Figure 2: Silica surface

(ii) It is noticed that polar compounds travel a shorter distance on the TLC plate than non-polar compounds. In terms of bonding involved, suggest reasons for the above observation.

Choosing of an appropriate solvent system is very crucial in a thin-layer chromatography (TLC) analysis. The distance at which the compound travel up the plate depends on 2 factors: how soluble the compound is in the mobile phase (solvent) and how strongly the compound is attracted to the stationary phase.

Student **A** chose hexane as the solvent while Student **B** chose methanol as the solvent. The results of their thin-layer chromatography (TLC) plates are as follows:

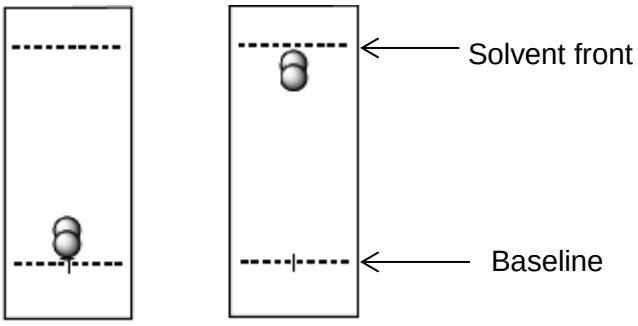

Figure 3: TLC plate of Student **A** Figure 4: TLC plate of Student **B**

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(iii) In terms of bonding involved, suggest reasons why the spots on Student **A**'s TLC plate are close to the baseline while the spots on Student **B**'s TLC plate are close to the solvent front.

(iv) Given the following list of solvent and with reference to both students' TLC plates in **(iii)**, suggest the most appropriate solvent which can better separate the mixture above. Explain your answer.

List of solvent: water, benzene, dichloromethane

[6]

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(b) You are to determine the dye contents of the shell coating of M&M candies through analysis using thin-layer chromatography (TLC). The colours of the shells of M&M candies contain food colouring dye that are FDA approved organic compounds.

Write a plan to identify the possible food colouring dye that are present in the shell coating of a sample of blue M&M candies.

You may assume that you are provided with:

- A sample of a solution containing the shell-coating colouring of M&M candies
- Food colouring dye blue #1
- Food colouring dye blue #2
- TLC plate
- Jar with cover
- Appropriate solvent

Your plan should include details of:

- an outline of how thin-layer chromatography (TLC) is to be carried out
- a sketch of the TLC plate at the start of the experiment which you will use to determine the food dyes present in M&M shell-coating
- how you would determine the food dyes present in the sample of M&M shell-coating.

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[4]

(c) Student **C** is provided with another sample solution containing the shell-coating colouring of M&M candies. The composition of the food dyes present in the sample of M&M shell-coating is determined by comparison of R_f values.

Given that retention factor, R_f, is defined as

$$R_f = \frac{distance\ travelled\ by\ the\ spot}{distance\ travelled\ by\ the\ solvent}$$

where the R_f value is a characteristic property of a given compound in a given solvent on a particular stationary phase.

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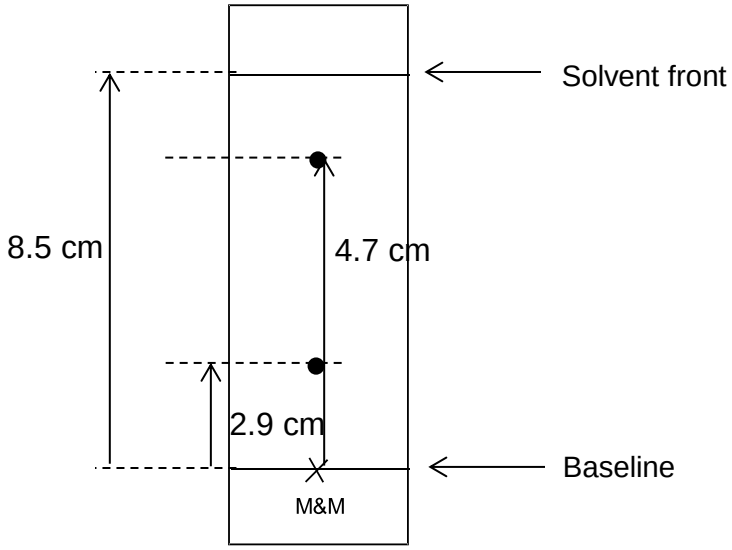
The following TLC plate is developed by Student **C,** using an appropriate solvent **Y**:



Given that the following food dyes have the following characteristics R_f values:

Food colouring dye	**Rf value in solvent Y**
Food colouring dye red #40	0.24
Food colouring dye blue #1	0.34
Food colouring dye blue #2	0.43
Food colouring dye yellow #6	0.55
Food colouring dye yellow #5	0.62

Calculate the R_f values of the 2 components in the shell-coating of M&M candies and determine the composition of the food-dyes present in the shell-coating of M&M candies.

[2]

[Total:12]

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2 (a) The first, second and third ionisation energies of manganese and iron are given in the table below:

	First Ionisation Energy / kJ mol^{-1}	Second Ionisation Energy/ kJ mol^{-1}	Third Ionisation Energy/ kJ mol^{-1}
Manganese	716	1510	3250
Iron	762	1560	2960

(i) Why is there an increasing trend in successive ionisation energies?

(ii) State the electronic configurations of Mn^{2+} and Fe^{2+}.

Mn^{2+}:

Fe^{2+}:

(iii) Account for the difference between the third ionisation energies of manganese and iron.

[3]

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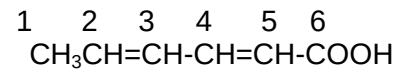
(b) Sorbic acid (hex-2,4-dienoic acid) is a natural organic compound used as a food preservative. It has the following structure:



(i) Although both **C1**–**C2** and **C3**–**C4** bonds are single bonds, they have different bond strengths. Suggest which bond is stronger and explain your answer.

(ii) Draw diagrams to illustrate all the geometrical isomers of sorbic acid.

(iii) On oxidation of sorbic acid with hot acidified $KMnO_4(aq)$, an organic compound **R** is obtained.

Draw the full displayed formula of compound **R.**

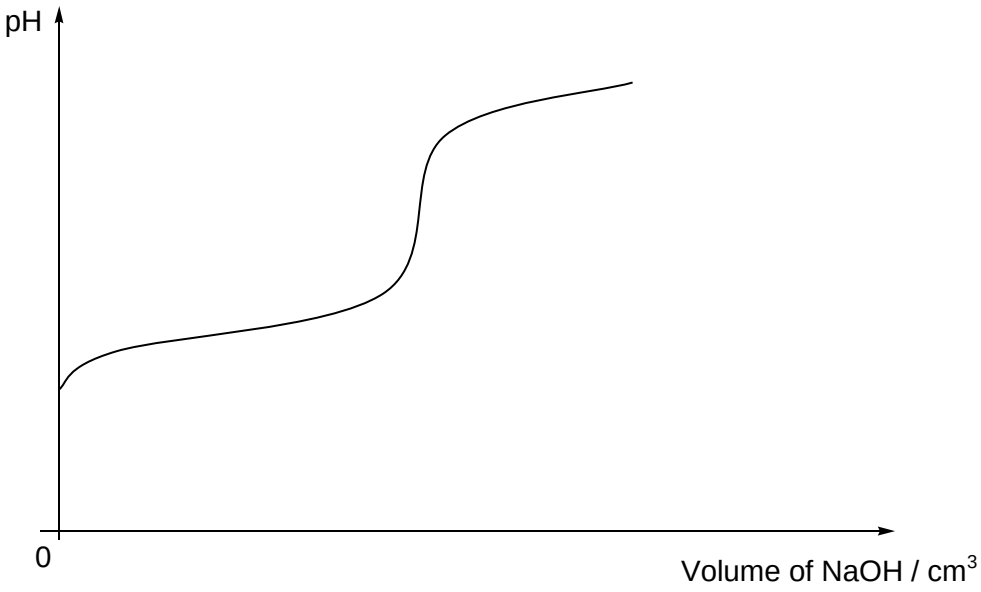
[5]

[Total: 8]

For Examiner's Use

3 Lactic acid, $CH_3CH(OH)CO_2H$ is an α-hydroxy acid (AHA) used as an important flavouring component of many foods such as cheese, yoghurt and pickled cabbage.

(a) 0.200 g of lactic acid (M_r = 90.0) was dissolved in 20.0 cm^3 water, and the solution was titrated with 0.100 mol dm^{-3} aqueous NaOH. The following titration curve was obtained.
(K_a of lactic acid = 1.38 x 10^{-4} mol dm^{-3})



(i) Explain the term acid dissociation constant, K_a as applied to lactic acid.

(ii) Calculate the volume of NaOH required to reach the equivalence point in the titration.

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(iii) Calculate the pH of the solution at the equivalence point.

(iv) The table below lists the working ranges of some acid-base indicators.

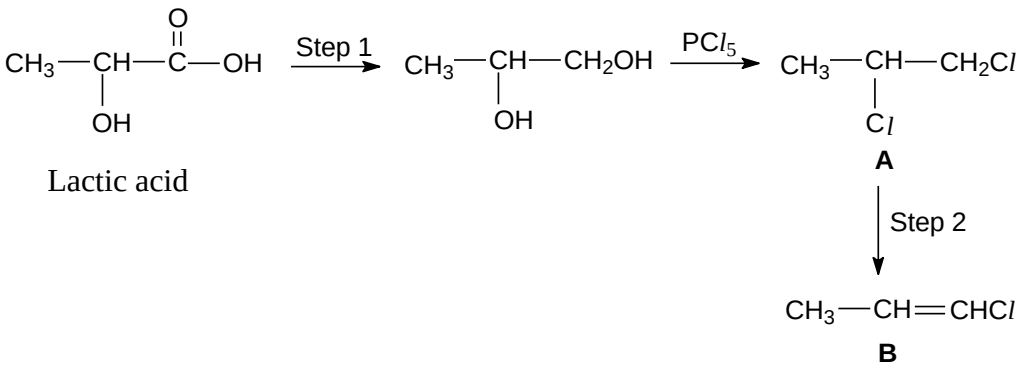
Indicator	Working range	Low pH color	High pH color
Tetrabromophenol blue	3.0 – 4.6	yellow	blue
Methyl red	4.4 – 6.2	red	yellow
Bromothymol blue	6.0 – 7.2	yellow	blue
Cresol red	7.2 – 8.8	yellow	red
Thymolphthalein	9.3–10.5	colorless	blue

Suggest the best indicator that can be used for this titration and give a reason for your choice.

[6]

For Examiner's Use

(b) Lactic acid can undergo a series of reactions as shown below.



Lactic acid

(i) What reagents and conditions are required for the following steps?

Step 1: _____

Step 2: _____

(ii) Arrange the two compounds **A** and **B** in order of increasing ease of hydrolysis, giving your explanations clearly.

_____

_____

_____

_____

_____

[4]
[Total: 10]

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4 The halogens are reactive non-metals which often react by gaining electrons to form halides ions. The halogens are commonly extracted by the electrolysis of their salts. For fluorine, it is obtained by electrolysis of molten potassium hydrogen difluoride, KHF_2, which is an ionic compound containing one cation and one anion.

(a) Suggest a structure for the anion and state what type(s) of bonding occur within it.

[2]

(b) Complete the table to show the colours and physical states of chlorine, bromine and iodine at room temperature and pressure.

Halogen	Colour	Physical state
Chlorine		
Bromine		
Iodine		

[2]

(c) **(i)** How do the bromide and iodide ions differ in their reactions with silver nitrate, followed by ammonia ?

(ii) Explain the differences in their reactions.

For Examiner's Use

[4]

(d) Solid samples of calcium fluoride, calcium chloride, calcium bromide and calcium iodide can be distinguished using concentrated sulfuric acid.

(i) Write equations for the reactions of calcium bromide with concentrated sulfuric acid.

(ii) Name **one** other reduction product which is formed when concentrated sulfuric acid is added to calcium iodide.

When calcium fluoride reacts with concentrated sulfuric acid, gaseous hydrogen fluoride is produced. Hydrogen fluoride is unique in attacking glass, and is used in etching apparatus and making decorative glass. The most common constituent of sand is silicon dioxide, SiO_2. When HF reacts with silicon dioxide, gaseous silicon tetrafluoride and steam are formed. The enthalpy change for this reaction is -1032 kJ mol^{-1}.

(iii) Write an equation, with state symbols, for the reaction between hydrogen fluoride and silicon dioxide.

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(iv) Using relevant data from the *Data Booklet*, calculate the bond energy of the Si-F bond.

(v) Sodium fluoride is added to toothpaste to strengthen tooth enamel. The data on a 50 g tube of toothpaste states that it contains "1450 ppm fluoride" and the density of the toothpaste is 1.6 g cm^{-3}. Calculate the concentration of sodium fluoride in the toothpaste.

[8]

[Total:16]

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5 Corrosion is a common problem for structures made from metals. For example, iron can undergo electrochemical oxidation, i.e. rusting.

(a) A ship's hull made from steel contains iron that, when exposed to moisture in air or aerated seawater, rusts easily. Rusting is a multi-step process, involving first the formation of iron(II) ions, which then precipitates as iron(II) hydroxide. Iron(II) hydroxide readily becomes further oxidised, and in the final step, forms rust, iron(III) oxide.

(i) Seawater has a typical pH range of 7.5 to 8.4.

With reference to the *Data Booklet*, explain why the oxidation of iron to iron(II) ions is spontaneous when both moisture and air are present.

(ii) Explain how the formation of iron(II) hydroxide causes the actual cell potential to be more positive than the calculated value at standard conditions.

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(iii) With reference to the *Data Booklet*, explain why iron(II) hydroxide readily becomes further oxidised.

(iv) Write a balanced equation for the oxidation of iron(II) hydroxide to iron(III) hydroxide.

(v) Write a balanced equation for the conversion of iron(III) hydroxide to iron(III) oxide.

[7]

(b) In ship construction, in order to protect the iron in the hull, another metal is placed on the hull within the ship, in physical and electrical contact with the iron. Even when the iron is the metal exposed to moisture and air, this metal eventually corrodes in place of iron through establishing a galvanic reaction with iron.

Suggest a suitable metal that can be used, and explain how it protects the iron in the ship's hull.

[3]

[Total:10]

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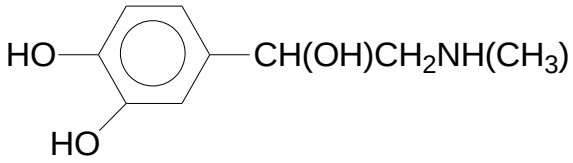
6 This question is about adrenaline and a specialty compound **C** whose structure is to be determined.

(a) Adrenaline is an important hormone concerned with 'fight' and 'flight' situations.



In the boxes below, give the structural formulae of the organic products formed when adrenaline reacts with each of the following reagents.

Reagents	Product
(i) $SOCl_2$	
(ii) Dilute hydrochloric acid	
(iii) Excess NaOH(aq)	

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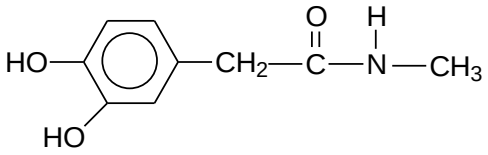
(iv) Suggest a simple chemical test that can be used to distinguish between adrenaline and the following compound **Z**:



Z

[5]

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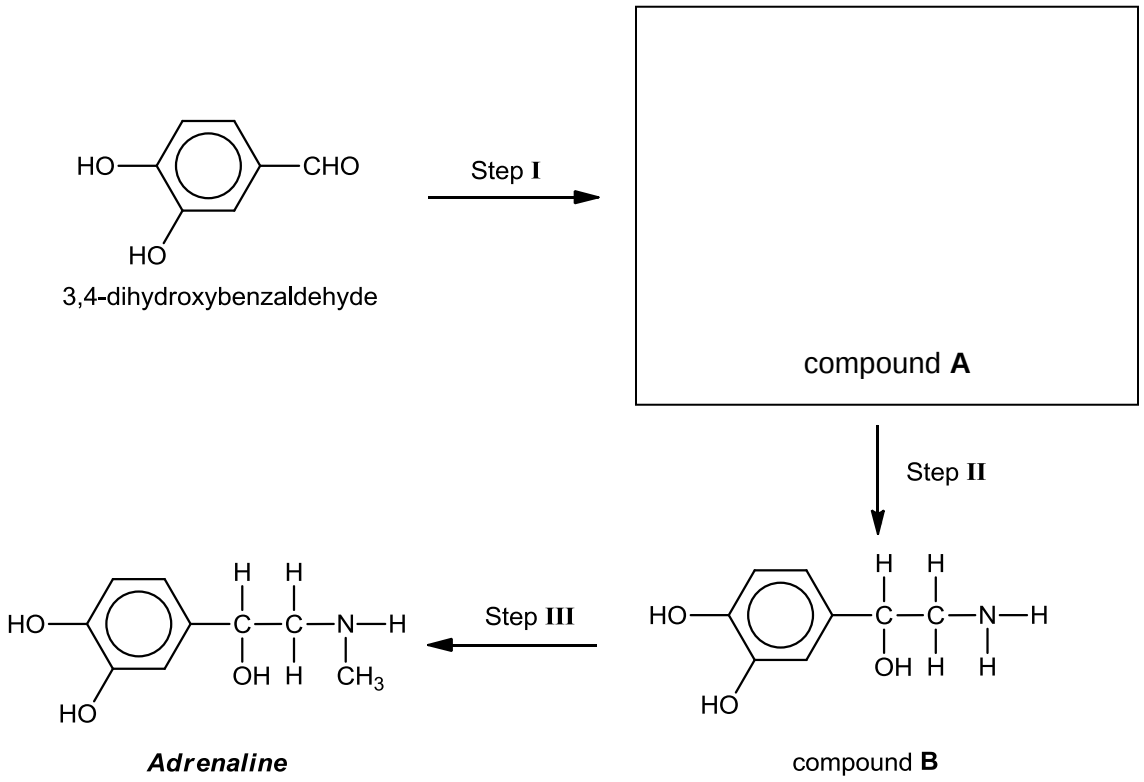
(b) Adrenaline can be synthesised from 3,4-dihydroxybenzaldehyde via the following reaction pathway with a hydroxynitrile being the intermediate.



(i) Draw the structural formula of compound **A** in the box provided above.

(ii) State the reagents and conditions required for Steps **I** – **III** by completing the table below.

Steps	Reagents and conditions
I	
II	
III	

[4]

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(c) Compound **C** is a specialty product for proteomics research. Refluxing **C** in dilute sulfuric acid produces **D** and ethanoic acid.

Elemental analysis of compound **D** gives the following results:

Elemental Analysis (% by mass)		
C	**H**	**O**
60.8	4.4	34.8

Some reactions of **D** are given below:

Reaction 1 : **D** + $Br_2(aq)$ $\longrightarrow$ White solid, **E** (M_r = 374.7)

Reaction 2 : **D** + $Na_2CO_3(aq)$ $\longrightarrow$ Effervescence of gas.

(i) When vaporised in a suitable vessel, 1g of **D** occupies a volume of 282 cm^3 at 200 ^oC and a pressure of 101 kPa. Calculate the M_r of **D**.

(ii) Using the elemental analysis results and your answer in **(c)(i)** , deduce the molecular formula of **D**.

Molecular formula of **D:**

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(iii) Name the functional groups present in **D**.

(iv) State the molecular formula of **E** in reaction **1**.

Molecular formula of **E** :

(v) Draw the structure of **D** below.

(vi) Hence deduce the structure of compound **C**.

[7]

[Total 16]

End of Paper