NAME DATE STARTED TARGET END DATE

GCE A LEVEL — CHEMISTRY UNIT 4 QUESTION PACK

1095-01 (Legacy CH4) · New spec Unit 4 Topic 3 · A2 unit, first sat 2017, 80 marks, 1h 45min paper

REVISE.wales

CHEMISTRY — UNIT 4 · NMR & Chromatography Spectroscopy

Topic 4.8 — Instrumental analysis: ^{1}H and ^{13}C NMR, mass spectrometry fragmentation and chromatography (TLC, GC, HPLC)

Interpreting low and high resolution ^{1}H NMR (chemical shift, integration, splitting, n+1 rule), ^{13}C NMR carbon counts, identifying fragments in mass spectra, TMS reference, deuterated solvents, and using R_f and retention times in TLC, GC and HPLC.

Legacy 2008 specification

Estimated time for entire question pack: ~4 h 8 min

Derived from the legacy CH4 paper's pace of ~1.3 min/mark, padded for long-prose and synthesis answers (155 marks over 8 questions).

*You are advised to **not** attempt to complete all of this in one sitting.*

ABOUT THIS QUESTION PACK

This is a **comprehensive practice question pack**, not a single mock paper. It contains every question from the legacy WJEC CH4 papers (2008 modular spec, Jan 2010 – Jun 2016) that maps onto the new-spec A2 Unit 4 Topic 4.8.

Questions are ordered by source paper date.

INSTRUCTIONS

Use black ink or black ball-point pen. Show all working — quality of written communication will affect marks. A calculator is allowed. You will need the WJEC Periodic Table / Data Booklet.

For Examiner's use only

Q	Source	Max	Mark
1	Jan 10 Q3	15	
2	Jan 11 Q5	20	
3	Jun 11 Q4	20	
4	Jan 12 Q5	20	

Q	Source	Max	Mark
5	Jan 13 Q5	20	
6	Jun 14 Q5	20	
7	Jun 15 Q5	20	
8	Jun 16 Q4	20	
Total		**155**	

NMR & Chromatography Spectroscopy — what the new spec asks

WJEC GCE A Level Chemistry (from 2015) · Unit 4: Organic Chemistry & Analysis · Topic 4.8.

^{1}H NMR — chemical shift

- δ (ppm) relative to TMS (0 ppm).
- Higher δ for protons near electronegative atoms (–OH, halogens, –C=O, aromatic).
- CH_3R: 0.7–1.6 ppm; aromatic H: 6.5–8.0 ppm; RCHO: 9.0–10.5 ppm; RCOOH: 10–13 ppm.
- Use deuterated solvent ($CDCl_3$); D_2O shake removes O–H, N–H signals.

Integration & splitting

- Integration trace height ∝ number of equivalent H giving rise to peak.
- Splitting by n equivalent neighbouring H → (n+1) peaks (multiplicity).
- Singlet, doublet, triplet, quartet, multiplet (sin/d/t/q/m).
- –OH and N–H usually broad singlets (rapid exchange).

^{13}C NMR

- Detects only carbon-bonded environments; 0–220 ppm scale.
- All peaks singlets (proton-decoupled).
- Number of distinct peaks = number of non-equivalent C environments.
- Useful for symmetric molecules to confirm structure.

Mass spectrometry fragments

- Molecular ion $M^{+\cdot}$: gives M_r.
- Common losses: 15 (CH_3), 17 (OH), 29 (CHO or C_2H_5), 28 (CO), 43 (CH_3CO or C_3H_7), 45 (COOH).
- Isotopic pattern: 35Cl/37Cl 3:1; 79Br/81Br 1:1.
- M+1 peak useful for counting carbons (~1.1% × n).

Chromatography basics

- Two phases: stationary (solid/liquid coating) + mobile (liquid or gas).
- Separation by relative affinity for the two phases.
- TLC: R_f = distance moved by spot ÷ distance moved by solvent.
- Identify components by R_f match with known standards.

GC & HPLC

- GC: mobile = inert gas (N_2, He); stationary = liquid film on column.
- Retention time t_R identifies components; peak area ∝ amount.
- HPLC: liquid mobile phase pumped at high pressure through tightly packed column.
- HPLC useful for non-volatile compounds (drugs, proteins); often combined with mass spec (LC-MS).

NMR & Chromatography Spectroscopy in one page

Quick-reference notes — revisit before each question.

Key ^1H shifts

- R_2CH_2: 1.2–1.5
- R-O-CH_3: 3.3–3.9
- $ArCH_3$: 2.3
- Ar-H: 6.5–8.0
- RCHO: 9–10.5
- RCOOH: 10–13

n+1 rule

Number of peaks in a signal = n+1 where n = number of equivalent H on adjacent carbon(s). Doublet (n=1), triplet (n=2), quartet (n=3).

D_2O shake

O–H and N–H exchange with D → their signal disappears or shifts to OD peak at 4.8 ppm. Lets you identify exchangeable Hs.

^{13}C NMR

Each chemically distinct C gives one singlet (proton-decoupled). Equivalent carbons (in symmetric molecules) give one peak. Count peaks → count environments.

MS fragments

M−15: loss of CH_3.
M−17: loss of OH.
M−28: loss of CO (ketone) or C_2H_4.
M−29: loss of CHO (aldehyde).
M−43: loss of CH_3CO (methyl ketone).

R_f values

R_f = (distance spot ↑ from origin) / (distance solvent ↑ from origin). Range 0–1. Identifies a component by comparing to known standards on the same plate.

Questions begin overleaf.

3. *Read the passage below and then answer the question in the spaces provided.*

Carboxylic acids and their esters – versatile materials in industry and in the home

The simplest carboxylic acid, methanoic acid, occurs naturally in stinging nettles and is also used by ants and bees as a form of defence and attack. However, methanoic acid is otherwise limited in its use because of its toxicity, and there is a greater demand for ethanoic acid.

An aqueous solution of ethanoic acid (vinegar) can be made by the atmospheric oxidation of aqueous ethanol using certain bacteria.

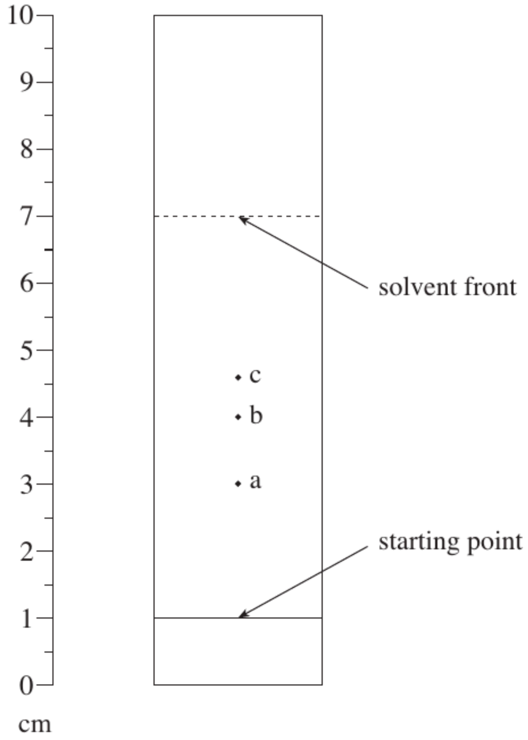
One industrial method for the production of ethanoic acid is to react methanol and carbon monoxide at a temperature of 450 K and a pressure of 30 atmospheres, in the presence of a suitable catalyst. The methanol and carbon monoxide have to be produced from coal, oil or natural gas. The process gives a 99% yield of ethanoic acid.

$$CH_3OH + CO \rightleftharpoons CH_3COOH$$

Another industrial process uses the naphtha fraction from petroleum. This process also requires increased temperatures and pressures. Unfortunately, the yield of ethanoic acid is less than 50% and a number of co-products are produced. These include methanoic, propanoic and butane-1,4-dioic acids, as well as propanone.

Esters of carboxylic acids that have a higher relative molecular mass occur naturally as oils, fats and waxes, and a number of these are used in the perfume industry. Some of these esters are glycerides – esters derived from propane-1,2,3-triol (glycerol). Alkaline hydrolysis of these glycerides produces sodium or potassium salts of large-molecule carboxylic acids that are used as soaps. Many of these oils, fats or waxes contain glycerides of a number of different carboxylic acids and the separation and identification of these is difficult.
One method of identification is to convert the glyceryl esters to simple ethyl esters and then to separate and identify the ethyl esters by thin layer chromatography (TLC).

A typical TLC chromatogram is shown below.



25 Man-made esters have been developed to have specific uses. For example, the polymer PET is used to make bottles and in textiles such as *terylene*, whereas polyvinyl acetate (PVA) is used as an adhesive.

- End of passage -

(a) By law, the concentration of ethanoic acid present in vinegar has to be within certain limits.

50.00 cm^3 of a sample of vinegar was diluted to exactly 500 cm^3 by the addition of distilled water, using a volumetric flask.
25.00 cm^3 of this **diluted** solution was exactly neutralised by 26.25 cm^3 of a solution of sodium hydroxide of concentration 0.100 mol dm^{-3}.

(i) State a procedure that is essential when diluting a solution, so that the results of the titration are accurate. [1]

(ii) Use this information and the equation below to calculate the concentration of ethanoic acid present in the **undiluted** vinegar in mol dm^{-3}. [4]

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

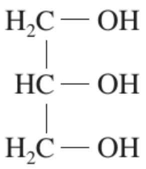
(b) The passage describes two industrial methods for making ethanoic acid *(lines 6 to 14)*. These are summarised in the table below.

Method	Starting materials	Temp / K	Pressure / atmosphere	Yield of ethanoic acid / %
1	methanol, carbon monoxide	450	30	99
2	naphtha from petroleum	450	50	< 50

Use the information in the passage and in the table to discuss the relative advantages and disadvantages of **each** process. [4]

(QWC) [1]

(c) The formulae of glycerol (propane-1,2,3-triol) and lauric acid (dodecanoic acid) are given below.



$$\begin{array}{l} H_2C - OH \\ \quad | \\ \;HC - OH \\ \quad | \\ H_2C - OH \end{array}$$

glycerol

$CH_3(CH_2)_{10}COOH$

lauric acid

Write the structural formula of the tri-ester, glyceryl trilaurate, formed by the reaction of glycerol and lauric acid.

You need not show the bonds between carbon and hydrogen atoms in your answer. [1]

(d) The passage shows a TLC chromatogram of a mixture of three ethyl esters of different carboxylic acids.
The retardation factor (R_f value) of ethyl palmitate (hexadecanoate) is 0.60.
Use the chromatogram to decide which of the three spots, if any, is given by ethyl palmitate, showing how you arrived at your answer. [2]

....

....

....

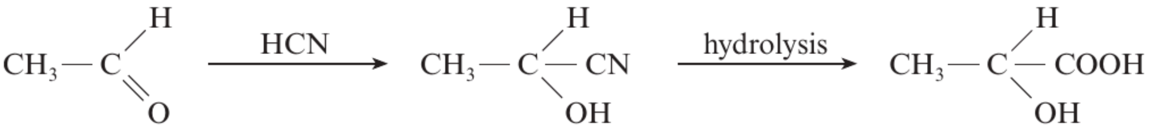
....

(e) The polymer PET *(line 24)* is made from ethane-1,2-diol and benzene-1,4-dicarboxylic acid.
Give the formula of a section of this polymer, identifying the repeating unit. [2]

Total [15]

Section A Total [40]

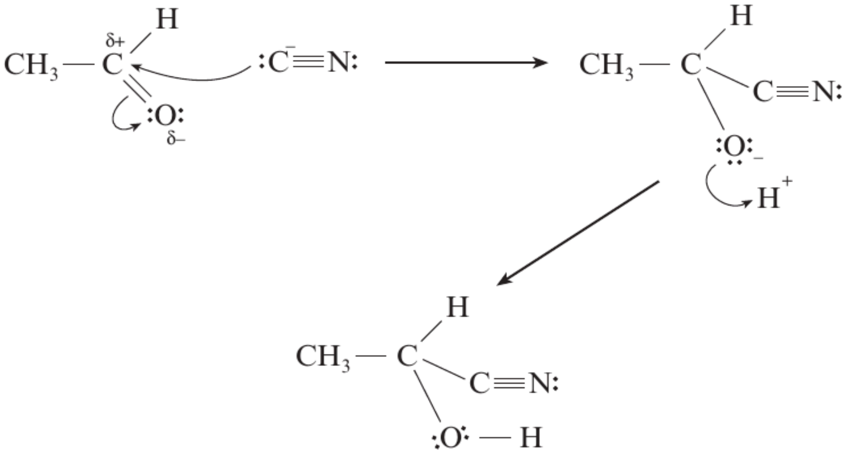
5. *(a)* 2-Hydroxypropanoic acid (lactic acid) can be made from ethanal by reaction with hydrogen cyanide and the subsequent hydrolysis of the 2-hydroxypropanenitrile.



2-hydroxypropanenitrile 2-hydroxypropanoic acid

(i) The mechanism for the reaction between ethanal and hydrogen cyanide is shown below.

$$H-C\equiv N \rightleftharpoons H^{+} + :\bar{C}\equiv N:$$



Describe what is happening at each stage of this reaction mechanism and use your answer to explain why this reaction is described as nucleophilic addition. [4]

(QWC) [1]

(ii) During the second stage of the reaction 2-hydroxypropanenitrile is hydrolysed to 2-hydroxypropanoic acid.
Describe what is meant by the term *hydrolysis* and give the reagent used for this hydrolysis. [2]

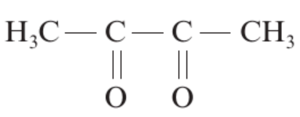
(b) (i) Yoghurt contains lactic acid that has been produced from lactose by certain bacteria.
The percentage of lactic acid in yoghurt can be found by an acid-base titration.
A sample of plain yoghurt of mass 50.0 g was titrated with sodium hydroxide solution of concentration 0.250 mol dm^{-3}. The lactic acid in the yoghurt was exactly neutralised by 20.0 cm^3 of the sodium hydroxide solution.

$$\underset{M_r\,90}{CH_3CH(OH)COOH} \quad + \quad NaOH \quad \rightarrow \quad CH_3CH(OH)COONa \quad + \quad H_2O$$

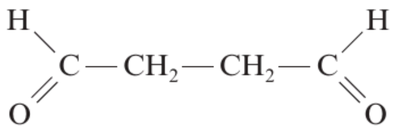
Use the information above and the equation to calculate the percentage of lactic acid present in the yoghurt. [3]

(ii) Some students suggested that it would be less wasteful if just a 10 g sample of yoghurt was used, rather than a 50 g sample, in this titration.
Explain why this would be likely to give a less accurate result. [1]

(c) Butan-2,3-dione (found in yoghurt) and butan-1,4-dial are isomers.



butan-2,3-dione



butan-1,4-dial

Describe the observations made when both compounds are tested with Fehling's reagent. [2]

(d) You are provided with the following information about aliphatic ester **T**.

- the empirical formula is $C_2H_3O_1$
- the relative molecular mass is 172
- all the oxygen atoms are present in ester groupings
- it decolourises aqueous bromine
- methanol is the only alcohol produced on hydrolysis of ester **T**
- the ^1H NMR spectrum consists of two unsplit peaks of equal size

Use **all** this information to deduce the structural formula of ester **T**, showing your reasoning. [6]

(QWC) [1]

Total [20]

Section B Total [40]

GCE A level

1094/01-A

CHEMISTRY CH4
DATA SHEET

A.M. WEDNESDAY, 26 January 2011

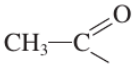
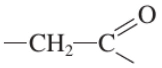
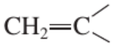
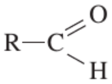
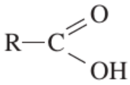
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

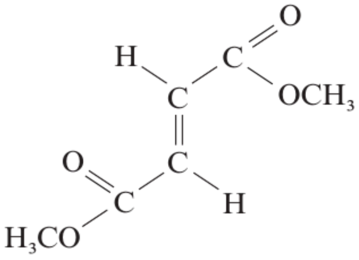
Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, 	3.5 to 4.0
$R-OH$	4.5 *
	4.8
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

SECTION B

Answer **both** *questions in the separate answer book provided.*

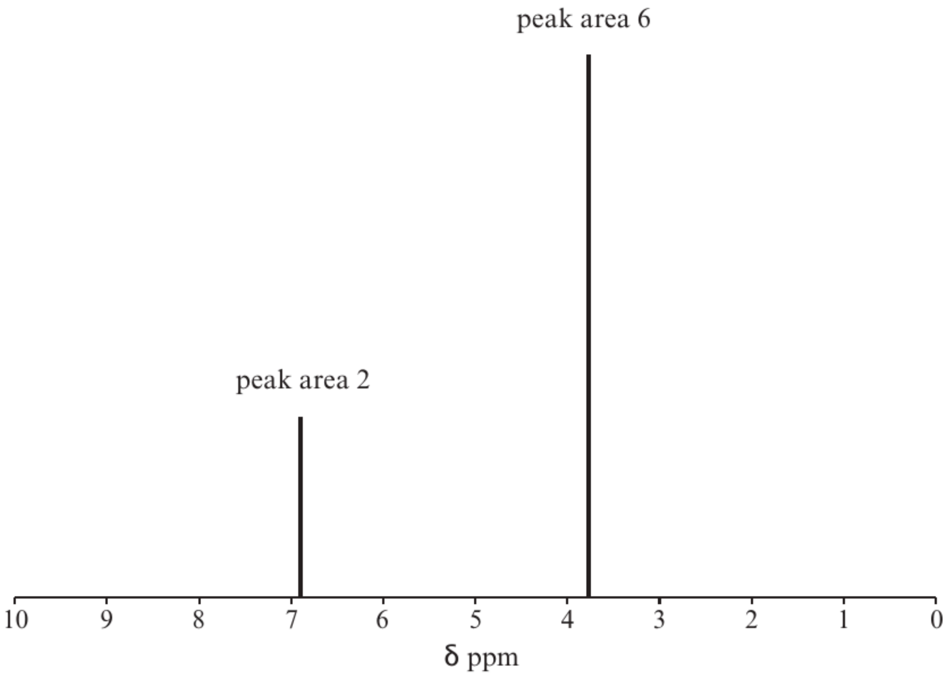
4. *(a)* In 2009 a man received compensation after he received chemical burns from a compound used as an antifungal agent in an imported leather sofa. The compound causing this problem was the ester dimethyl fumarate (DMF).



DMF

(i) DMF is one of a pair of E-Z stereoisomers. State what is meant by *stereoisomerism* and draw the displayed formula of the other stereoisomer of DMF. [2]

(ii) The NMR spectrum of the ester DMF is shown below.



The hydrolysis of dimethyl fumarate produces the dicarboxylic acid, fumaric acid. Describe how the NMR spectrum of fumaric acid would be different from the NMR spectrum of dimethyl fumarate.
Your answer should identify the peaks involved and include reasons for any changes that occur. You should also identify any NMR signal that does not change and the reasons for this. [5]

(QWC) [1]

(iii) The mass spectrum of DMF, $C_6H_8O_4$, shows only a weak signal for its molecular ion at m/z 144. The strongest signal is seen at m/z 113. Suggest a molecular formula for the positive ion at m/z 113, giving your reasoning. [2]

(b) Fumaric acid (*E*-butenedioic acid) is an important starting compound for the manufacture of many other materials. The usual method for producing fumaric acid is from crude oil, but there is increasing interest in a fermentation route, using enzymes, from a sugar such as glucose. A comparison of these two methods is shown in the table.

	Crude oil route	Fermentation route
Raw material	Maleic anhydride	Glucose
Reaction temperature / °C	95	35
Raw material price / £ kg^{-1}	1.00	0.30

(i) Suggest **one** way that the crude oil route could be made more economic to operate. [1]

(ii) At present the crude oil route is the more economic route from which to obtain fumaric acid.
Suggest **one** factor by which the fermentation route could be modified to make it more competitive with the crude oil route, other than by simply increasing the yield. You are reminded that the optimum temperature for enzymes in this reaction is 35 °C. [1]

(iii) Fumaric acid was obtained in a pilot-scale experiment by the fermentation route, using glucose.
A simplified equation for the reaction is shown below.

$$\underset{}{2CO_2} + \underset{M_r\,180}{C_6H_{12}O_6} \longrightarrow \underset{M_r\,116}{2C_4H_4O_4} + 2H_2O$$

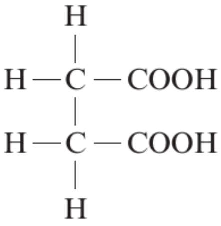
In this experiment 12.6 kg of glucose (70 moles) gave 13.0 kg of fumaric acid. Calculate the percentage yield of fumaric acid. [3]

(iv) Small amounts of other organic acids are produced during the fermentation.

I One of these acids is ethanoic acid.
Outline any **one** other reaction that produces ethanoic acid.
Your answer should include

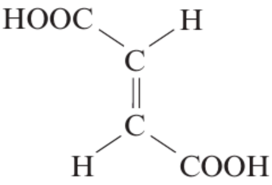
- the name of your starting material,
- any other reagent(s) used,
- the type of reaction occurring. [3]

II A small amount of butanedioic acid is also produced.



butanedioic acid

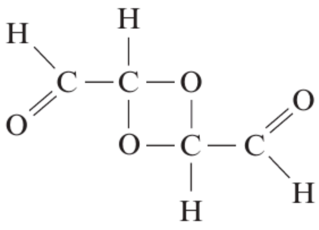
This acid can also be produced by the hydrogenation of the unsaturated acid, fumaric acid.



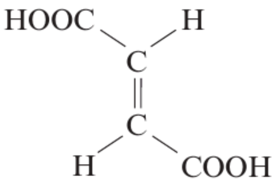
fumaric acid

Suggest a suitable catalyst for this hydrogenation. [1]

(c) A research student claimed to have made compound **U**, which is an isomer of fumaric acid.



compound **U**



fumaric acid

State a reagent that would react with compound **U** and **not** fumaric acid, giving the result of the test. [1]

Total [20]

BLANK PAGE

5. This question concerns isomers with molecular formula $C_5H_{10}O_2$.

(a) Isomers **P**, **Q**, **R** and **S** all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **P** is a straight-chain compound.

Isomer **Q** contains a chiral carbon centre.

Isomer **R** has only two peaks in its NMR spectrum, both of which are singlets.

Draw the displayed formulae for all **four** isomers. [4]

(b) Isomer **T** is a neutral, sweet-smelling compound and is formed by the reaction between compounds **X** and **Y** in the presence of concentrated sulfuric acid.

Compound **X** has an absorption in its infrared spectrum at 1750 cm^{-1} and a broad absorption around 3000 cm^{-1}.

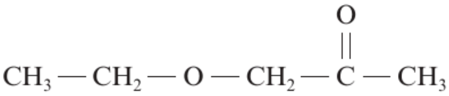
Compound **Y** can be formed directly from ethanal.

(i) Use **all** the information given to name compounds **X** and **Y**, giving your reasoning. Draw the displayed formula for isomer **T**. [4]
QWC [2]

(ii) I. State the reagent needed to form compound **Y** from ethanal. [1]

II. State the role of sulfuric acid in the formation of **T**. [1]

(c) Isomer **U** has the structural formula shown below.



$$CH_3-CH_2-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

List the peaks which would be found in the NMR spectrum of isomer **U**. Identify which protons are responsible for each peak, giving the approximate chemical shift (ppm) and the splitting of the peak. [4]

(d) Explain which one of isomers **P**, **T** and **U** would have the highest boiling temperature. [3]
QWC [1]

Total [20]

Section B Total [40]

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET FOR USE WITH CH4

P.M. THURSDAY, 26 January 2012

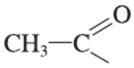
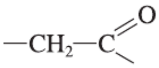
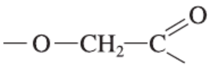
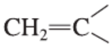
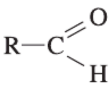
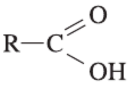
Infrared Spectroscopy characteristic absorption values

Bond	**Wavenumber/cm^{-1}**
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

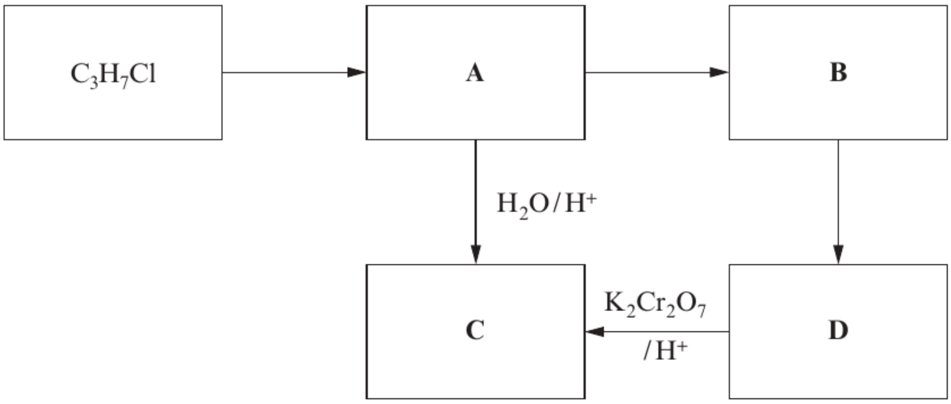
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	**Chemical shift /ppm**
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
 $CH_3-C(=O)-$	2.0 to 2.5
 $-CH_2-C(=O)-$	2.0 to 3.0
 $-O-CH_2-C(=O)-$	2.5 to 3.0
$-O-CH_3$, $-OCH_2-R$,  $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
 $CH_2=C<$	4.8
 $R-C(=O)H$	9.8 *
 $R-C(=O)OH$	11.0 *

*variable figure dependent on concentration and solvent

5. *(a)* Study the reaction scheme shown below and the other information about compounds **A-D** that follows.



Compound **A** contains a straight carbon chain and contains only carbon, hydrogen and nitrogen.

Compound **B** is basic and reacts with hydrochloric acid in a 1:1 molar ratio.

0.395 g of compound **B** in aqueous solution requires 54.00 cm^3 of hydrochloric acid solution of concentration 0.100 mol dm^{-3} for complete neutralisation.

Compound **C** reacts with sodium carbonate giving off carbon dioxide.

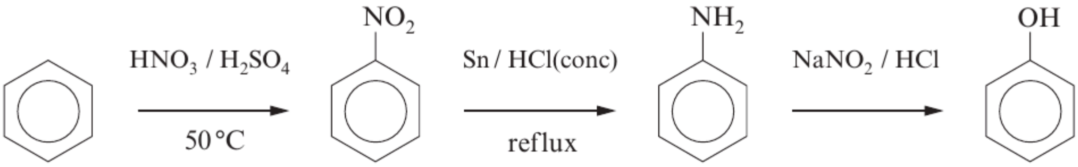
(i) Calculate the relative molecular mass of compound **B**. Show your working. [2]

(ii) Identify the structures of compounds **A-D**, giving your full reasoning. [8]

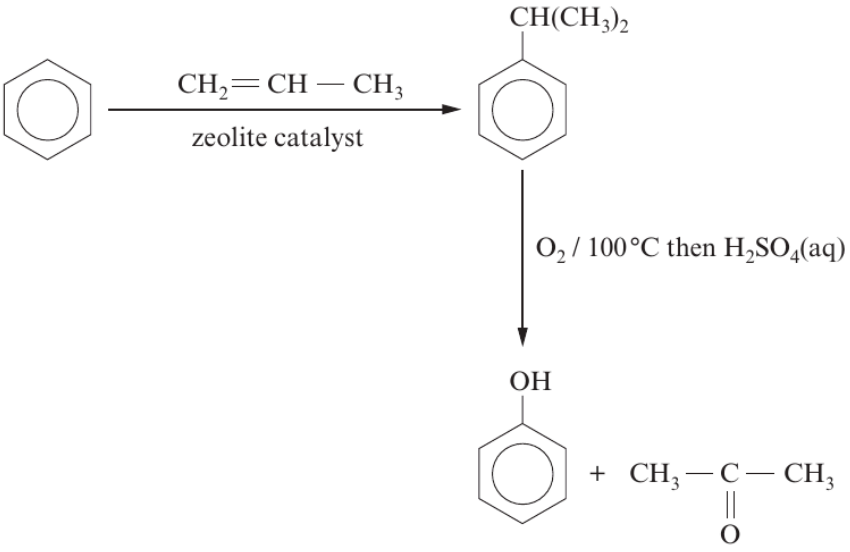
(b) C_3H_7Cl exists as two isomers. Sketch the **low** resolution NMR spectra of both isomers giving the approximate chemical shift (ppm) and the relative area of each peak. [4]

QUESTION 5 CONTINUES ON PAGES 14 AND 15

(c) Phenol can be made by the following three-step synthesis.



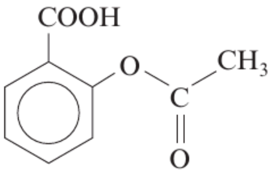
However, the industrial method of making phenol uses a different route as shown below.



(i) Give **two** possible advantages of the industrial route. [2]

(ii) Until 1995 solid phosphoric acid was used as the catalyst for the first stage of the industrial route. Suggest a reason, apart from an increased reaction rate, why this was changed to a zeolite catalyst. [1]

(d) Phenol can be converted into aspirin.



aspirin

When 58.75 g of phenol was reacted with the appropriate chemicals, the yield of aspirin was 65%. Calculate the mass of aspirin produced in this process. [3]

Total [20]

Section B Total [40]

END OF PAPER

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET FOR USE WITH CH4

P.M. MONDAY, 14 January 2013

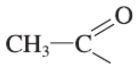
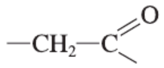
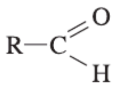
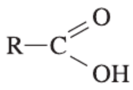
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
$—CH_3$	0.1 to 2.0
$R—CH_3$	0.9
$R—CH_2—R$	1.3
$CH_3—C≡N$	2.0
	2.0 to 2.5
	2.0 to 3.0
$R—CH_2Cl$, $R—CHCl—R$	3.0 to 4.3
R—OH	4.5 *
	9.8 *
	11.0 *

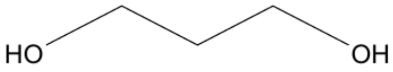
*variable figure dependent on concentration and solvent

5. *(a)* An Australian cockroach protects itself from attack by spraying predators with an unpleasant unsaturated compound **E**. Analysis of this unsaturated compound, which is not cyclic, gave the following information.

- It contains C, 71.3 % and H, 9.6 % by mass. The remainder is oxygen.
- Only one oxygen atom is present in each molecule.
- It gives a silver mirror with Tollens' reagent (ammoniacal silver nitrate solution).
- The mass spectrum shows a fragmentation ion, containing only carbon and hydrogen, at m/z 29.

Use **each** piece of information to help you deduce a possible displayed formula for compound **E**. [6]

(b) Propane-1,3-diol is a starting compound for the manufacture of some economically important materials.



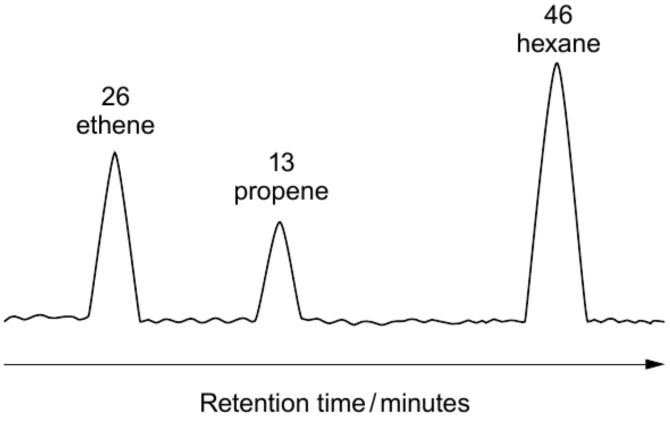
One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.

$$\text{propene} \xrightarrow{O_2\text{ (from air)}} \text{propenal} \xrightarrow{\text{hydration}} \text{propane-1,3-diol}$$

A newer method uses a strain of the bacterium *E. coli* to obtain propane-1,3-diol directly from maize.

(i) Give the equation for the cracking of undecane, $C_{11}H_{24}$, into hexane, ethene and propene. [1]

(ii) A simplified gas chromatogram for the cracking of undecane is shown below.



The peak areas indicate the relative volumes of each compound.
Use the chromatogram to calculate the percentage by volume of propene present. [1]

(iii) You are a research chemist investigating the production of propane-1,3-diol from a cereal. Suggest **three** features of the process that could encourage your company to adopt this biochemical process, rather than the older process starting with propene. A simple reference to reduced costs is insufficient. [3]

(iv) Compound **W** is formed when propane-1,3-diol is heated with ethanoic acid in the presence of a suitable catalyst. It has the molecular formula $C_7H_{12}O_4$.
Give the displayed formula of compound **W**. [1]

(c) The polyester PET is made from ethane-1,2-diol and benzene-1,4-dioic acid. In a similar way PTT is made from propane-1,3-diol and benzene-1,4-dioic acid.

(i) Give the formula of the repeating unit of PTT. [1]

(ii) State how this type of polymerisation differs from the type of polymerisation occurring when poly(propene) is made from propene.
In your answer you should

- state the type of polymerisation occurring in each case,
- state the type of functional groups present in the starting materials for each process,
- compare the atom economy of each process. [6]

QWC [1]

Total [20]

Total Section B [40]

END OF PAPER

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. MONDAY, 9 June 2014

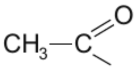
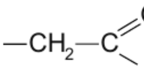
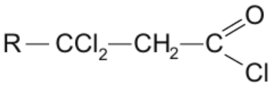
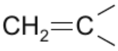
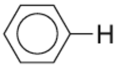
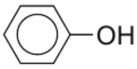
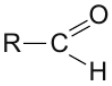
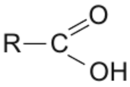
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	**Chemical shift/ppm**
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
CH_3-CCl_2-	2.0 to 2.5
	2.0 to 3.0
	2.5 to 3.0
$R-CH_2-Cl$	3.3 to 4.3
$R-OH$	4.5 *
	4.8
	6.5 to 7.5
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

5. *(a)* Primary aliphatic amines react with nitric(III) (nitrous) acid to give a quantitative yield of nitrogen gas, and an alcohol as the major organic product.

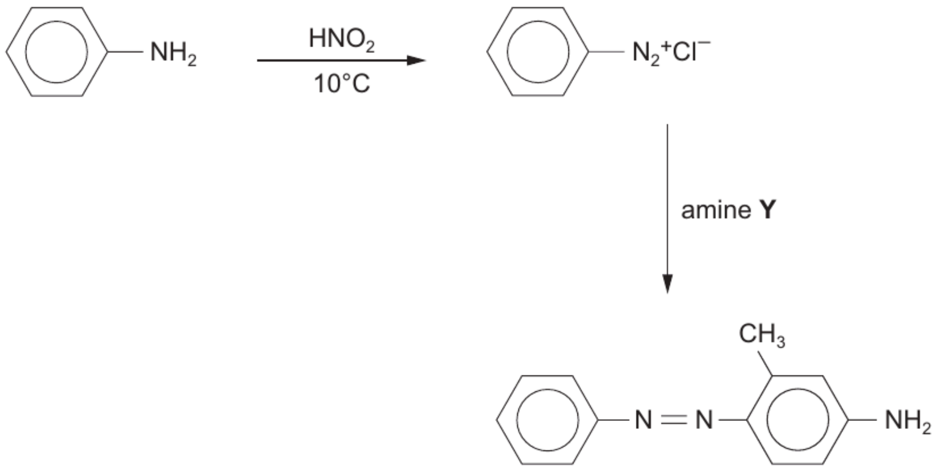
$$R{-}NH_2 + HNO_2 \longrightarrow R{-}OH + N_2 + H_2O$$

In an experiment 2.54 g of an amine gave 1.00 dm^3 of nitrogen, measured at 10 °C.

Calculate the relative molecular mass of the amine and hence its structural formula.

[At 10 °C, 1 mol of nitrogen gas has a volume of 23.2 dm^3] [3]

(b) At 10 °C and below a primary aromatic amine reacts with nitric(III) acid, HNO_2, to give a diazonium compound, which can then be coupled with a phenol or an amine.
An example of this reaction is shown below.



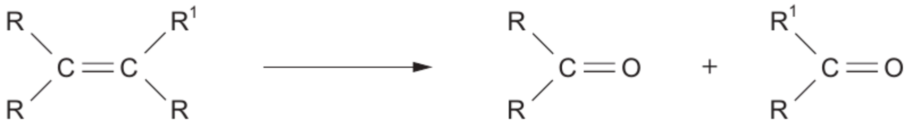
(i) The benzenediazonium ion acts as an electrophile in this reaction.
State the meaning of the term electrophile. [1]

(ii) State the **name** of amine **Y**. [1]

(iii) The product of this reaction contains an —N═N— group bonded to aromatic systems. State the general name for this type of grouping, which can give coloured compounds, and state why this type of reaction has industrial importance. [2]

Turn over.

(c) Alkenes react with ozone to give an intermediate product that can then be reduced to give aldehydes or ketones.



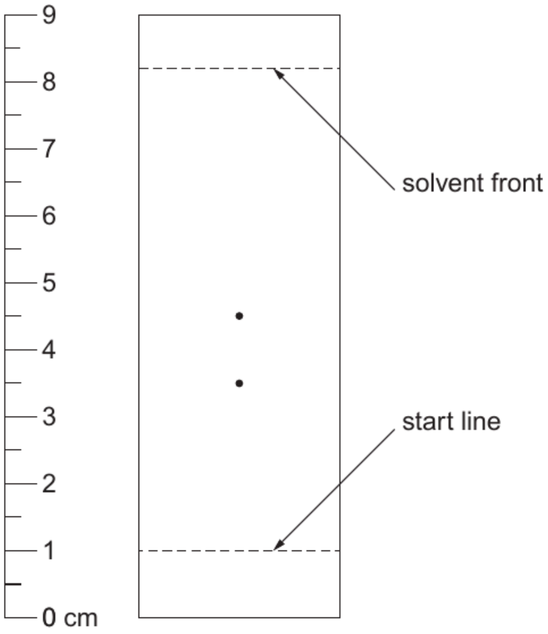
alkene **W**

An alkene **W** was reacted in this way to give two different ketones. R and R^1 represent **two different** alkyl groups.

These ketones were then separated by thin layer chromatography to give two spots. The ketone spots were colourless and their presence was found by spraying the chromatogram with a solution of 2,4-dinitrophenylhydrazine.

(i) State the type of reaction that occurs when a ketone reacts with 2,4-dinitrophenylhydrazine and how this reaction is able to show the presence of these ketones in the chromatogram. [2]

(ii) The chromatogram that was obtained is shown below.
Use the table of R_f values to identify the two ketones present and hence the displayed formula and the name of alkene **W**. [4]
QWC [1]



Ketone	R_f value
propanone	0.35
butanone	0.40
pentan-2-one	0.49
pentan-3-one	0.60
hexan-2-one	0.68

(iii) State how the **equation** for the reaction of alkene **W** with ozone shows that **W cannot be** 2-methyl-3-ethylpent-2-ene, $(CH_3)_2C{=}C(CH_2CH_3)_2$. [1]

(d) This is a brief method written by a student to enable others to prepare ethyl ethanoate by esterification.

- Heat under reflux together 0.45 mol of ethanoic acid with an equimolar quantity of ethanol
- Add 5 cm^3 of sulfuric acid
- Distil off everything boiling up to 82 °C
- Add the distillate to aqueous sodium hydrogencarbonate in a separating funnel
- Run off the ethyl ethanoate layer and dry it over anhydrous calcium chloride
- Distil off the dried ethyl ethanoate and collect the fraction boiling at 75-78 °C

(i) Give the equation for this reaction. [1]

(ii) Calculate the mass of ethanoic acid needed for this experiment. [1]

(iii) State an important detail that is missing from the first bullet point. [1]

(iv) State why the sulfuric acid should have been added at the refluxing stage. [1]

(v) State why sodium hydrogencarbonate needed to be added to the distillate. [1]

Total [20]

Total Section B [40]

END OF PAPER

GCE A level

1094/01-A

S15-1094-01A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 10 June 2015

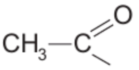
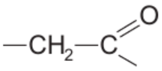
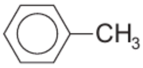
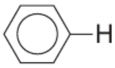
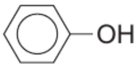
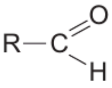
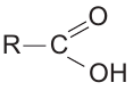
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift/ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
$R-CH_2-$Halogen	3.3 to 4.3
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
	6.5 to 7.5
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

SECTION B

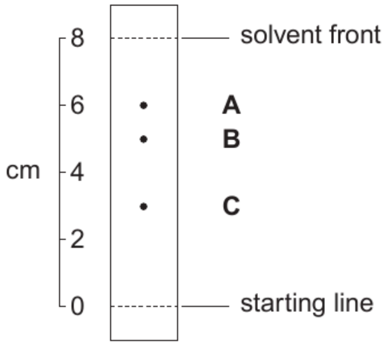
Answer **both** *questions in the separate answer book provided.*

4. There are many different types of chromatography and spectroscopy that can be used to investigate the identity and structure of unknown substances. In this question you will consider some of these techniques.

(a) Explain briefly how the peaks in NMR spectra and the absorptions in IR spectra are formed. [3]

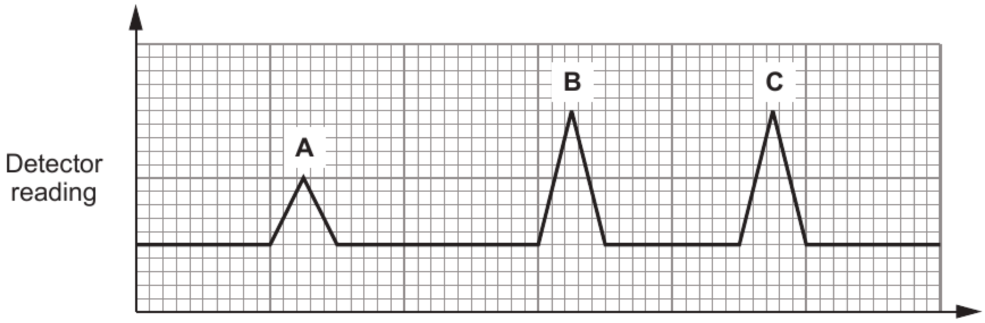
(b) A sample of unknown substances was investigated using different chromatographic techniques.

(i) Thin layer chromatography gave the chromatogram shown below.



Calculate the R_f value for the substance that gives the spot labelled **B**. [1]

(ii) Gas chromatography gave the chromatogram shown below.

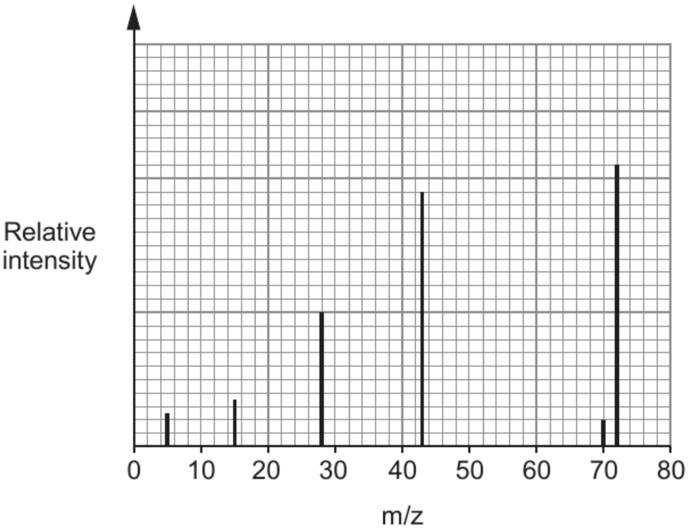


I. What label should be used for the x-axis? [1]

II. Use the chromatogram to estimate the percentage of compound **A** in the sample. Explain how you reached this conclusion. [2]

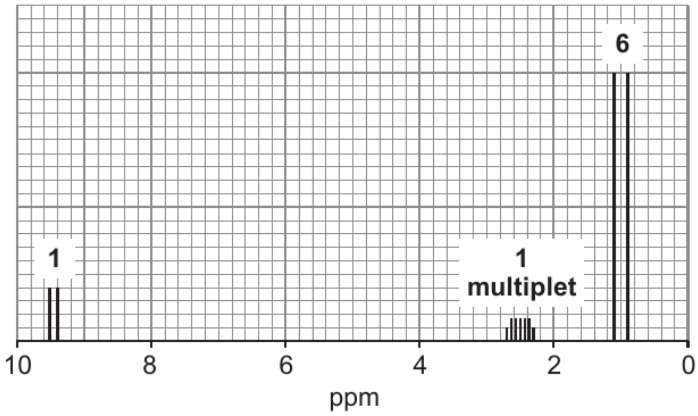
(iii) Thin layer chromatography and gas chromatography give different information about unknown substances. Describe what information can be obtained from each type of chromatography. [2]

(c) (i) A compound **Y** contains carbon, hydrogen and oxygen. It has 66.7% by mass of carbon. The mass spectrum of compound **Y** is below.



Use these data to determine the molecular formula of compound **Y**. Explain your reasoning. [4]

(ii) The NMR spectrum of compound **Y** is below.



Use this spectrum to determine as much information as possible about the structure of compound **Y**. [4]

QWC [2]

(iii) Use your answers to parts (i) and (ii) to give the structural formula of compound **Y**. [1]

Total [20]

END OF QUESTION PACK

8 questions · 155 marks · ~4 h 8 min
Source: WJEC CH4 (2008 modular spec, Jan 2010 – Jun 2016)
Curated for WJEC Chemistry 2015 spec A2 Unit 4 — Topic 3 (4.8)