Surname		Centre Number	Candidate Number
Other Names			2

WJEC CBAC

GCE A level

1094/01

CHEMISTRY – CH4

P.M. WEDNESDAY, 12 June 2013

$1\frac{3}{4}$ hours

FOR EXAMINER'S USE ONLY

Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIAL

In addition to this examination paper, you will need:
• a calculator;
• an 8 page answer book;
• a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.
Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

Section B   Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

SM*(S13-1094-01)

2

SECTION A

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

1. *(a)* In 2012 an off-licence in Derby was prosecuted for selling fake vodka.

(i) A report in the local paper stated that this 'vodka' was contaminated by 'tertiary butanol', the formula of which is shown below.

$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-OH \\ | \\ CH_3 \end{array}$$
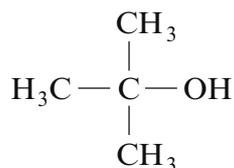
State the **systematic** name of this compound. [1]

....

(ii) Analysis showed that the total alcohol content of a bottle of the fake vodka was 35%.
A gas-liquid chromatogram showed a mixture of alcohols to be present in the following proportions:

tertiary butanol	6 parts
methanol	8 parts
ethanol	86 parts

Calculate the percentage of ethanol by volume in the fake vodka. [1]

.... %

(iii) Tertiary butanol can be dehydrated in an elimination reaction to produce 2-methylpropene. Suggest a suitable dehydrating agent for this reaction. [1]

....

(iv) 2-Methylpropene can be polymerised to give poly(2-methylpropene).
Draw the repeating unit of the polymer. [1]

(v) Write the displayed formula of any isomer of tertiary butanol that contains a chiral centre. Identify the chiral centre by an asterisk (*). [2]

(vi) The main alcoholic compound of the fake vodka is ethanol. This can be oxidised to give ethanal.

I State the reagent(s) used to oxidise ethanol to ethanal in the laboratory. [1]

....

II Ethanal can be polymerised to 'metaldehyde', $(CH_3CHO)_4$, which is used to kill slugs.
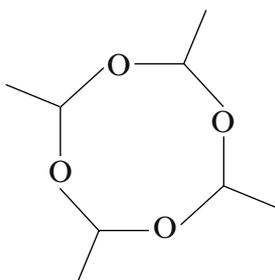
Use the Data Sheet to describe how the infrared spectrum of 'metaldehyde' will differ from the infrared spectrum of its monomer, ethanal, giving the absorption values and the bonds involved. Reference to C—H bonds is not required. [2]

....

....

....

4

(b) The oxidation of tertiary alcohols is different from those of primary and secondary alcohols. 'Tertiary butanol' is oxidised to propanone and methanoic acid.

    (i) State a test that will give a positive result for propanone but not methanoic acid. [2]

        Reagent ....

        Observation ....

        ....

    (ii) State a test, other than the use of an acid-base indicator, that will give a positive result for methanoic acid but not propanone. [2]

        Reagent ....

        Observation ....

        ....

Total [13]

5

2. *(a)* You are given two aqueous solutions in unlabelled bottles. One is methyl propenoate, $CH_2\!=\!CHCOOCH_3$, and the other is phenol, C_6H_5OH.

Give a chemical test, other than the use of an acid-base indicator, which you could use to distinguish between these two compounds, giving the result of the test for **each** compound. [2]

....

....

....

(b) 2,4-Dinitrophenol is a yellow solid that is an inhibitor of ATP production in cells. As a result it has been sold as an aid to slimming, in spite of it being a dangerous and unlicensed product.

(i) State why this compound is seen as yellow in white light. [1]

....

....

(ii) Reduction of 2,4-dinitrophenol, using the same reducing agent that is used for the reduction of nitrobenzene, gives the photographic developer 'amidol'.

OH

NH$_2$

NH$_2$
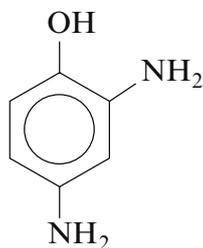
amidol

State the reagent(s) used for this reduction. [1]

....

6

(c) (i) 2,4-Dinitrophenol reacts with ethanoyl chloride to produce 2,4-dinitrophenyl ethanoate.
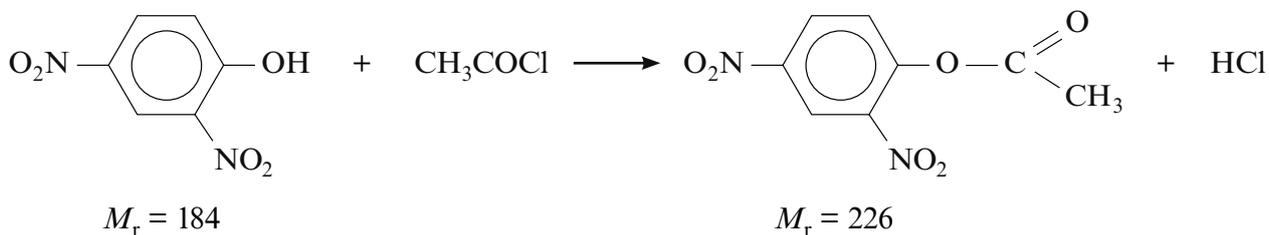
O_2N—⬡—OH + CH_3COCl ⟶ O_2N—⬡—O—$C$$\overset{O}{\underset{CH_3}{\diagdown}}$ + HCl

NO_2 NO_2

$M_r = 184$ $M_r = 226$

In an experiment 7.36 g of 2,4-dinitrophenol produced 7.91 g of 2,4-dinitrophenyl ethanoate. Calculate the percentage yield of 2,4-dinitrophenyl ethanoate.   [3]

Percentage yield = ... %

(ii) The 2,4-dinitrophenyl ethanoate obtained in *(c)*(i) was impure and contained some unreacted 2,4-dinitrophenol. The presence of this phenol was detected using thin layer chromatography.

Calculate the R_f value of 2,4-dinitrophenol from this chromatogram.   [2]

....

....

....

(d) 'Urushiol' is a yellow liquid that is found in the plant poison ivy. It causes an allergic skin rash. Urushiol is not a single compound but a mixture of phenolic compounds that have long saturated or unsaturated alkyl groups bonded to the benzene ring.
It contains, for example, the following compound.

$$OH$$
$$OH$$
$$(CH_2)_7CH = CH(CH_2)_5CH_3$$

(i) Suggest a catalyst that could be used in the hydrogenation of the unsaturated alkyl side chain. [1]

....

(ii) By analogy with carboxylic acids, explain why 1,2-dihydroxybenzene is soluble in water but urushiol is not. [2]

....

....

....

Total [12]

8

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

Citric acid – its production and chemistry

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is a weak organic acid that occurs naturally in many fruits.

$M_r = 192$

citric acid

5   This acid has been known since the 8th century and from about 1890 it began to be isolated from citrus fruits. The concentration of citric acid in the juices of these fruits varies from about 0.005 mol dm^{-3} for oranges to 0.300 mol dm^{-3} for lemons. However, most citric acid is now made from sugars by the use of a fungus. After treatment with this material the mixture is filtered and then reacted with calcium hydroxide, to precipitate insoluble calcium citrate. This is then treated with sulfuric acid to produce citric acid and calcium sulfate.

10
$$(C_6H_5O_7)_2Ca_3 \ + \ 3H_2SO_4 \ \longrightarrow \ 2C_6H_8O_7 \ + \ 3CaSO_4$$
calcium citrate

$M_r = 498$ $M_r = 98$ $M_r = 192$

On heating, citric acid gives two unsaturated acids by the loss of water and subsequent decarboxylation.

citric acid

acid **A**

acid **B**

When citric acid is treated with concentrated sulfuric acid, acid **C** is formed.

15

$$H_2C-COOH$$
$$|$$
$$C=O$$
$$|$$
$$H_2C-COOH$$
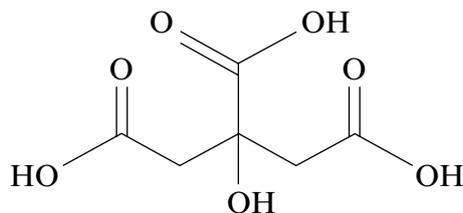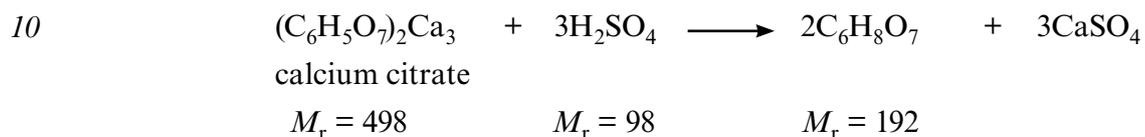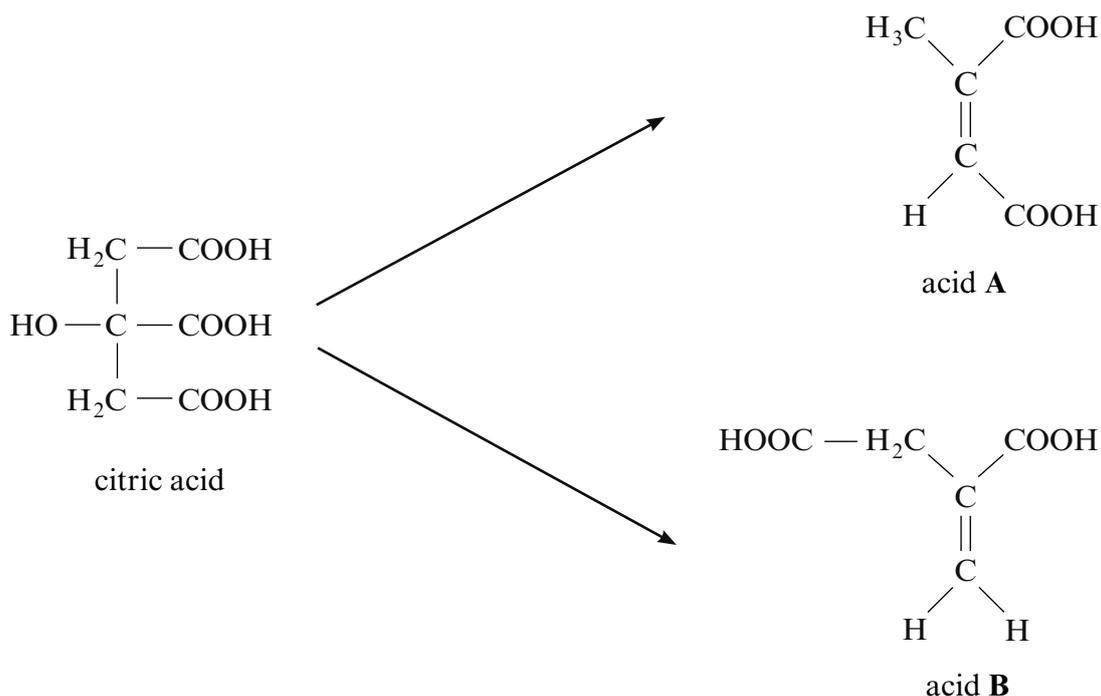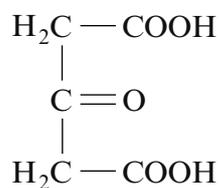
acid **C**

Lemons, from which citric acid was formerly extracted, contain a number of other compounds. Lemon oil is obtained by crushing the peel of lemons. This oil contains about 90% limonene and 5% citral.
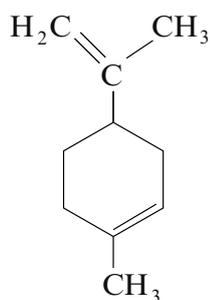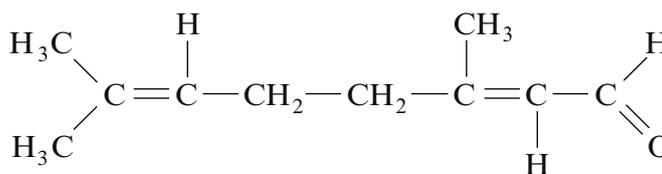
limonene   citral

20 Citric acid remains a very important material today with extensive uses for soft drinks and other important uses in the food and detergent industries.

– End of passage –

(a) (i) Calculate the atom economy when citric acid is made by the acidification of calcium citrate *(line 10)*. [1]

Atom economy = ... %

(ii) Suggest a way in which this stage of the process could be made more cost effective. [1]

....

....

(b) Citric acid occurs in two forms – an anhydrous form and a hydrate.
Some students were given samples of the **hydrated** form of this tribasic acid and were asked to find its relative molecular mass by a titration with aqueous sodium hydroxide, using a suitable indicator to monitor complete neutralisation of the acid.

2.31 g of the hydrated acid was dissolved and made up to 250 cm^3 with distilled water. A 25.00 cm^3 sample of this solution needed 26.40 cm^3 of a sodium hydroxide solution for complete neutralisation.

Calculate the total volume of sodium hydroxide solution needed to neutralise all of the acid and then use the graph opposite to help you calculate the relative molecular mass of the hydrated citric acid. Use your answer to calculate the value of *n* in hydrated citric acid, $C_6H_8O_7.nH_2O$. You are required to show your working in this calculation. [5]

n = ...

Total volume of
aqueous sodium
hydroxide / cm³

Amount of hydrated citric acid × 10⁻³ / mol
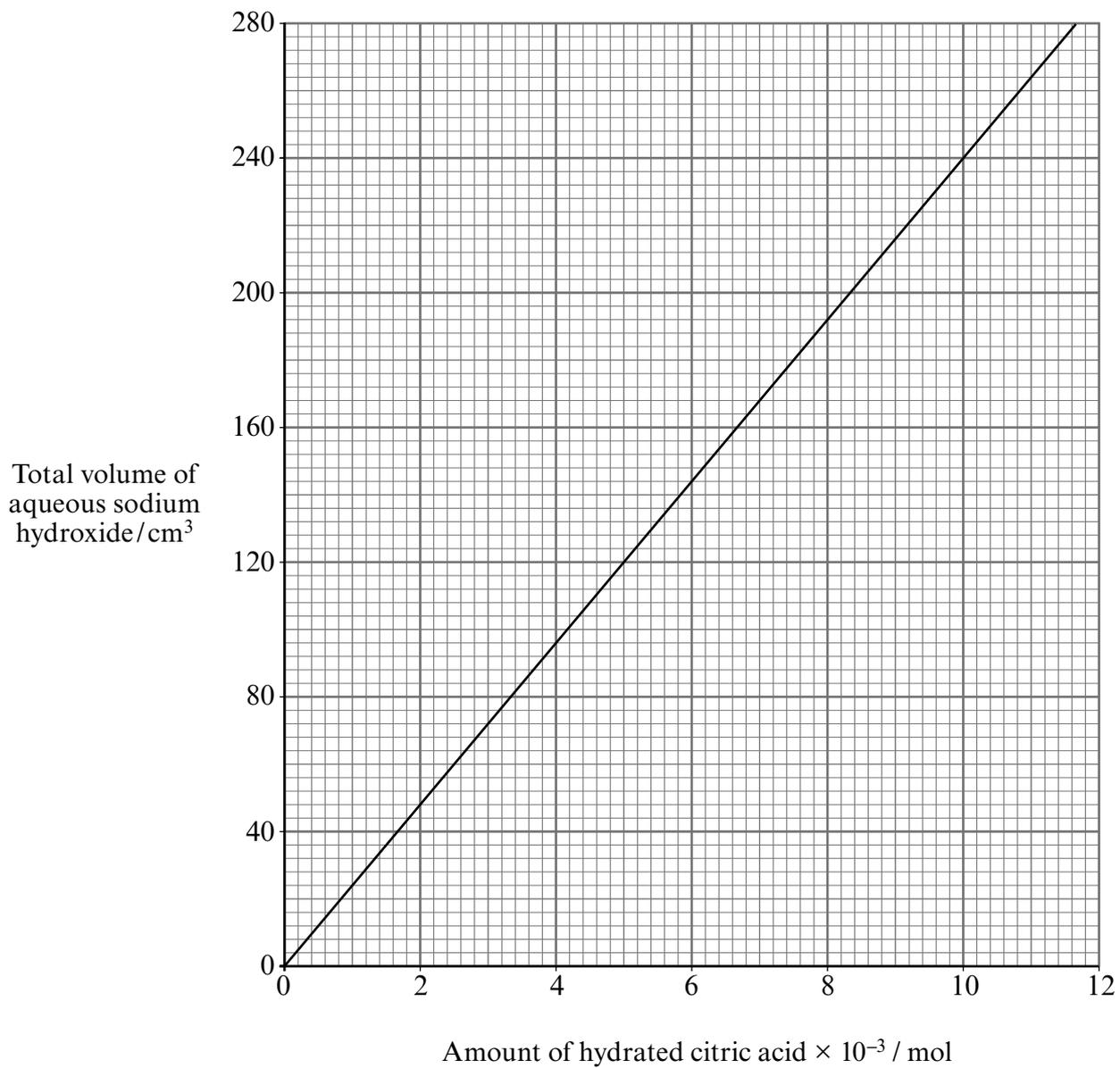
(c) Explain why acids **A** and **B** *(line 13)* are **not** *E*- and *Z*- isomers of each other. [1]

....

....

12

(d) Acids **A** and **B** are formed by dehydration and by decarboxylation (where the compound is heated with sodalime). Give any other decarboxylation reaction of your choice, stating the organic starting material and the organic product of your chosen reaction. [2]

....

....

(e) On heating to 130 °C, acid **C** *(line 15)* decomposes to give only propanone and carbon dioxide. Give the equation for this reaction. [1]

....

(f) Give the **displayed** formula of the product formed when acid **C** is reduced by lithium tetrahydridoaluminate(III) (lithium aluminium hydride). [1]

(g) The boiling temperatures of limonene and citral, both present in lemon oil, are 177 °C and 228 °C respectively. State a method by which these two liquids can be separated. [1]

....

(h) Limonene occurs in some substances as a single enantiomer and in others as a racemic mixture.

  (i) State what is meant by the term *enantiomer*. [1]

....

....

  (ii) State what is meant by the term *racemic mixture*. [1]

....

....

Total [15]

Total Section A [40]

15

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14

SECTION B

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

4. *(a)* Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions. [6]

QWC [2]

(b) Methylbenzene can be made by the Friedel-Crafts alkylation of benzene.
Give the equation for this reaction and name a catalyst that can be used. [2]

(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.
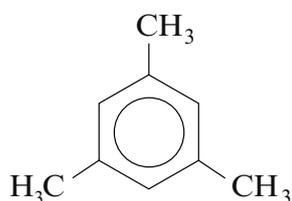
(i) The NMR spectrum of mesitylene is shown opposite.
Use the chemical formula to help you explain the peaks in this spectrum, including the relative peak areas and the absence of splitting. [3]

relative peak area 3

relative peak area 1

δ / ppm
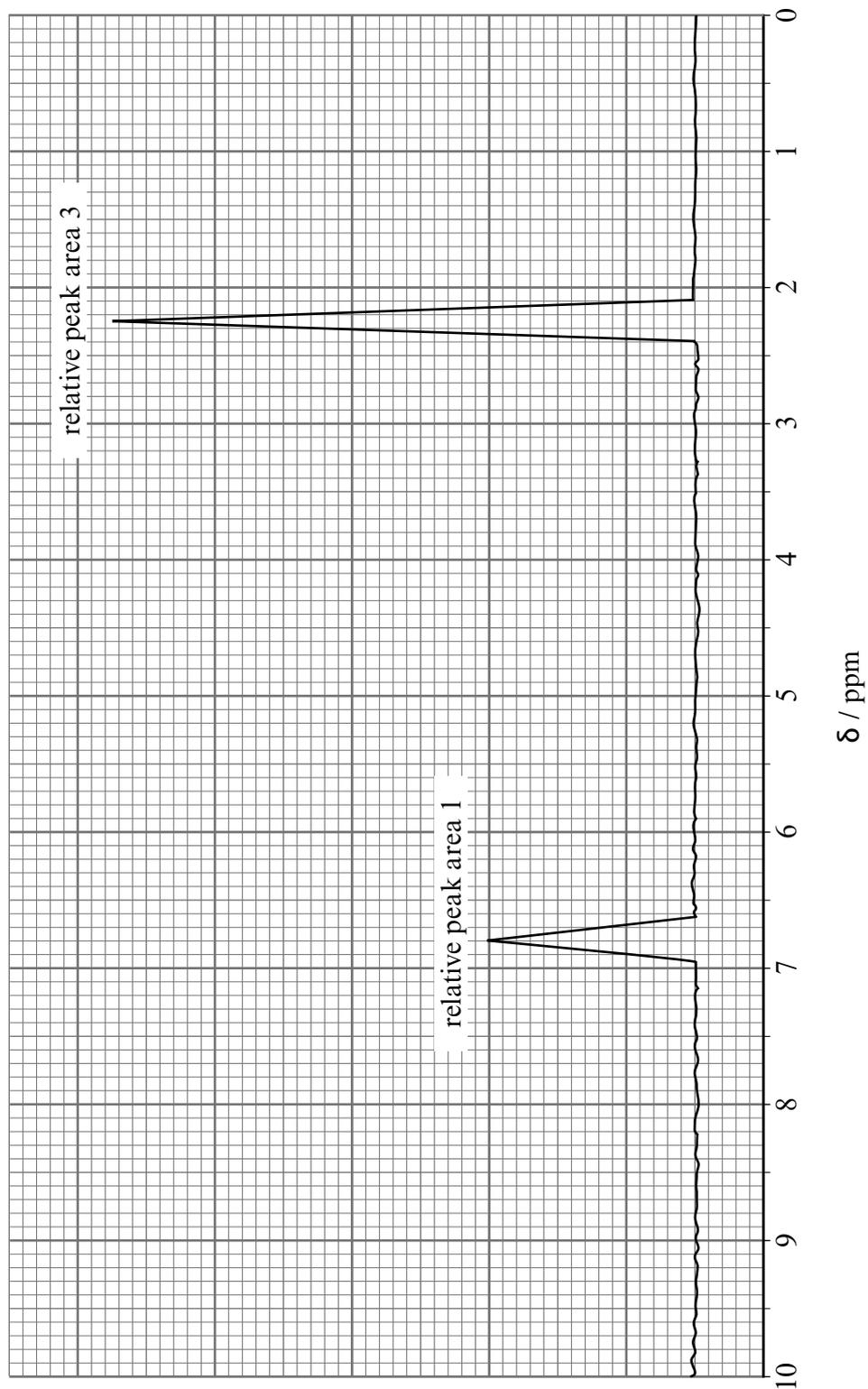
(ii)   The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.
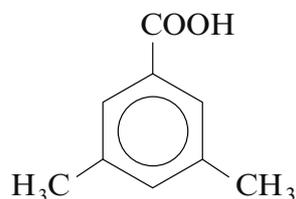
melting temperature 172 °C

Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water.   [4]

(iii) Further oxidation of mesitylene gives 5-methylbenzene-1,3-dicarboxylic acid.
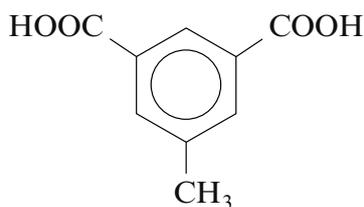
By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol.   [1]

(iv)   The oxidation of methylbenzene to benzenecarboxylic acid needs stronger oxidising conditions than are required for the oxidation of mesitylene. State the reagents **S** and **T** necessary for this reaction.   [2]
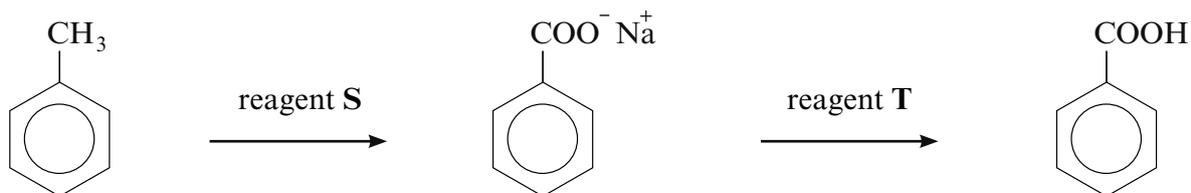
Total [20]

5. *(a)* Cathinone, $C_9H_{11}NO$, is a naturally-occurring psycho-active drug.
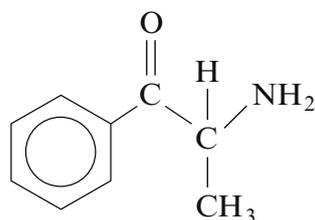
(i) Explain why this molecule can act as a base. [1]

(ii) You are provided with some information about an **isomer** of cathinone, compound **L**.
- It contains a peptide linkage.
- It can be hydrolysed by aqueous sodium hydroxide giving primary aromatic amine **M** as one of the products.
- Primary aromatic amine **M** reacts with nitric(III) acid (nitrous acid) to give a phenol with the molecular formula C_7H_8O.

Use **all** this information to suggest a **structural** formula for compound **L**, giving your reasons throughout. [6]
QWC [1]

QUESTION 5 CONTINUES ON PAGES 18 AND 19

(b) Proline is a cyclic α-amino acid. In an aqueous solution of pH 6.3, proline exists largely as its zwitterion form.
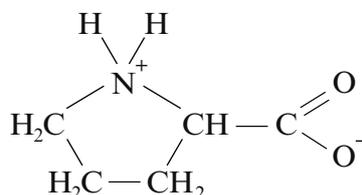
  (i)   Write the structural formula of proline in its non-zwitterion form.   [1]

  (ii)   Proline forms two different dipeptides when it reacts with aminoethanoic acid. Give the structural formula of **one** of these dipeptides.   [1]

(c) (i)   (Chloromethyl)benzene, $C_6H_5CH_2Cl$, reacts with chlorine in the presence of a catalyst to produce a mixture of isomers, **one** of which is 1-(chloromethyl)-4-chlorobenzene.
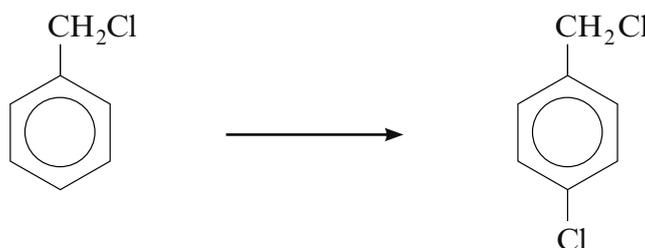
The mechanism of this electrophilic substitution reaction is similar to the reaction of benzene with chlorine. Give the mechanism for the reaction to produce the 4-isomer.

Your mechanism should show any necessary polarisation, curly arrows, the structure of the intermediate and how the catalyst is regenerated so that it can be used again.   [4]

  (ii)   A student made (4-chlorophenyl)methanol by refluxing 1-(chloromethyl)-4-chlorobenzene (shown in (i)) with aqueous sodium hydroxide.
He obtained a 72% yield.
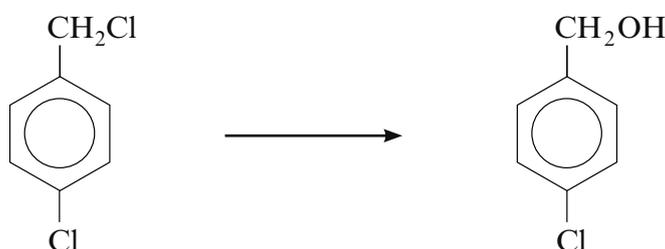
He wrote an outline of his method as follows.
- Place 0.1 mol of the chloro-compound in a flask and add some sodium hydroxide solution of concentration 2 mol dm⁻³.
- Reflux this mixture using an electrical heater.

Suggest **two** other details that you would need to know before you could test the reliability and validity of his method.   [2]

(iii) Explain why the product of the reaction in (ii) is (4-chlorophenyl)methanol and not (4-hydroxyphenyl)methanol. [2]
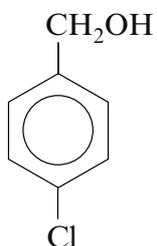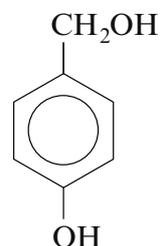
(4-chlorophenyl)methanol   (4-hydroxyphenyl)methanol

(iv) (4-Chlorophenyl)methanol was oxidised to give (4-chlorophenyl)methanal.
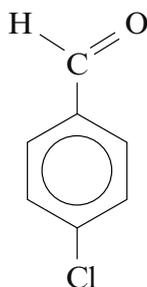
The mass spectrum of the product of this reaction showed traces of another compound with molecular ions, m/z, of 156 and 158 in a ratio of 3:1.
Suggest a structural formula for this compound and state why it has these two molecular ions. [2]

Total [20]

Total Section B [40]

END OF PAPER

WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 12 June 2013

2

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
$CH_3-C{\overset{\displaystyle O}{<}}$	2.0 to 2.5
$-CH_2-C{\overset{\displaystyle O}{<}}$	2.0 to 3.0
⟨○⟩$-CH_3$	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
⟨○⟩$-H$	6.5 to 7.5
⟨○⟩$-OH$	7.0 *
$R-C{\overset{\displaystyle O}{\underset{\displaystyle H}{}}}$	9.8 *
$R-C{\overset{\displaystyle O}{\underset{\displaystyle OH}{}}}$	11.0 *
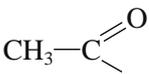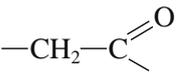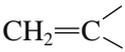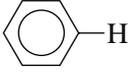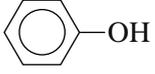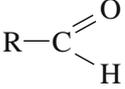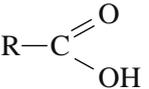
*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

Group

Period	1	2		3	4	5	6	7	0
	s Block								4.00 He Helium 2
1	1.01 H Hydrogen 1								
2	6.94 Li Lithium 3	9.01 Be Beryllium 4	p Block	10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12	d Block	27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	40.0 Ar Argon 18

Key

A_r	Symbol	— relative atomic mass
Name	Z	— atomic number

d Block

Period	1	2	3	4	5	6	7	8	9	10	11	12	3	4	5	6	7	0
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98.9 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
6	133 Cs Caesium 55	137 Ba Barium 56	139 La ▲ Lanthanum 57	179 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86
7	(223) Fr Francium 87	(226) Ra Radium 88	(227) ▲▲ Ac Actinium 89															

f Block

▲ Lanthanoid elements

140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	(153) Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71

▲▲ Actinoid elements

232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103