Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY CH4

P.M. THURSDAY, 26 January 2012

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1094 010001

ADDITIONAL MATERIALS

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.

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SECTION A

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

1. *(a)* The formulae of some compounds are shown below.

$CH_3CH_2NH_2$	$CH_3CH_2CONH_2$	$CH_3CHCHCHO$
A	**B**	**C**
$CH_3CH(OH)CH_2CH_3$	CH_2CHCH_3	$CH_3CH_2COCH_2CH_3$
D	**E**	**F**

Each letter may be used once, more than once or not at all, to answer the questions below.

Give the letter of the compound which

(i) is most basic, [1]

....

(ii) forms yellow crystals when warmed with iodine in alkaline solution, [1]

....

(iii) forms a silver mirror when warmed with Tollens' reagent, [1]

....

(iv) exhibits E-Z isomerism. [1]

....

(b) (i) Butylamine is one of the compounds responsible for the smell of rotting fish. It can be prepared in the laboratory from 1-chlorobutane.

Classify the reaction mechanism when butylamine is prepared in this way. [1]

....

(ii) Explain why phenylamine, an aromatic amine, cannot be prepared from chlorobenzene using a similar reaction to that in part (i). [2]

....

....

....

....

Examiner only

(iii) Write a **balanced** equation for the reaction of butylamine with ethanoyl chloride, [1]

....

(iv) Phenylamine is normally prepared from nitrobenzene.

I. Give the reagents used in this preparation and a technique to separate the product from the reaction mixture. [3]

....

....

....

....

II. When phenylamine reacts with cold nitric(III) acid (nitrous acid) a colourless solution of benzenediazonium chloride is formed. Write the formula for benzenediazonium chloride. [1]

III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol. [1]

....

Total [13]

1094 010003

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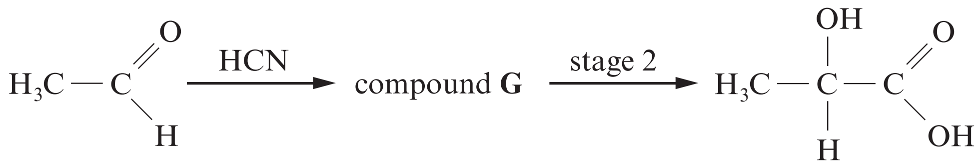
2. *(a)* Lactic acid is a naturally-occurring compound that shows optical activity.
Lactic acid can be prepared from ethanal in the laboratory in a two stage process.



lactic acid

However, a sample prepared in this way was found to be optically inactive.

(i) Explain what is meant by a 'compound that shows optical activity'. [1]

....

....

(ii) Draw diagrams to show the two optical isomers of lactic acid. [1]

(iii) Give the displayed formula for compound **G**. [1]

(iv) State the reagent(s) and condition(s) needed for stage 2. [1]

....

(v) Explain why the sample prepared in the laboratory was optically inactive. [2]

....

....

....

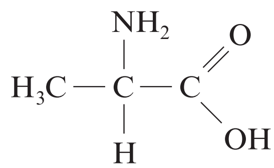
Examiner only

(b) Draw the displayed formula of the organic compound formed when lactic acid reacts with

(i) sodium hydroxide, [1]

(ii) acidified potassium dichromate. [1]

(c) Lactic acid can be formed directly from compound **H**.



compound **H**

(i) Give the **systematic** name for compound **H**. [1]

....

(ii) State the reagent needed to convert **H** into lactic acid. [1]

....

(iii) Explain why compound **H** has a much higher melting temperature than lactic acid. [2]

....

....

....

Total [12]

1094
010005

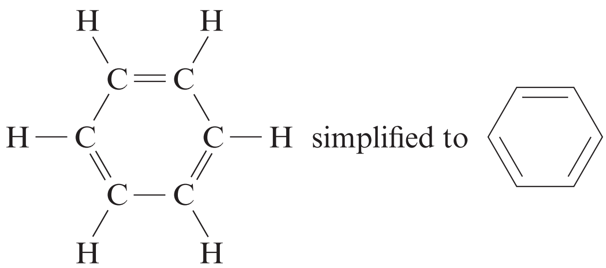
Turn over.

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

Benzene

Benzene, C_6H_6, is a colourless, highly flammable liquid with a sweet smell, but it is carcinogenic. The word “benzene” derives historically from “gum benzoin”, an aromatic resin known to European pharmacists and perfumers since the 15th century.

Discovering the structure of benzene proved to be quite difficult. Benzene was first isolated and identified by Michael Faraday in 1825 from the oily residue derived from the production of illuminating gas. However, it was not until 1865 that Kekulé proposed this structure for benzene.

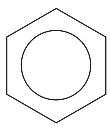


However this structure fails to explain why benzene does not react like an alkene. Ethene reacts readily with bromine as follows:

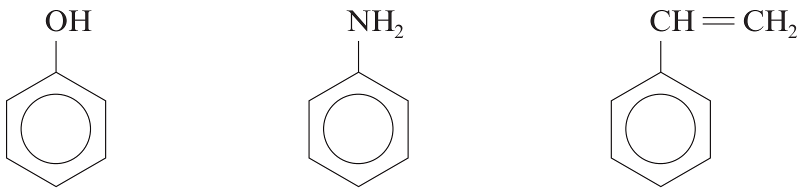
$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br\,CH_2Br$$

In contrast, benzene needs far more stringent conditions to react with bromine.

It was around 1930 that the structure of the benzene ring was finally confirmed using X-ray diffraction. It was shown that all the carbon-carbon bonds were of the same length. To account for this, it was proposed that three pairs of electrons were not localised in particular double bonds, but were shared equally amongst all six carbons. These electrons were said to be delocalised giving benzene great stability (delocalisation energy of benzene). The structure of benzene is therefore usually represented as:



An understanding of the structure of benzene was crucial to early chemists since benzene is the parent molecule of all arene or ‘aromatic’ compounds and a huge variety of compounds are derived from benzene. Simple benzene derivatives include:

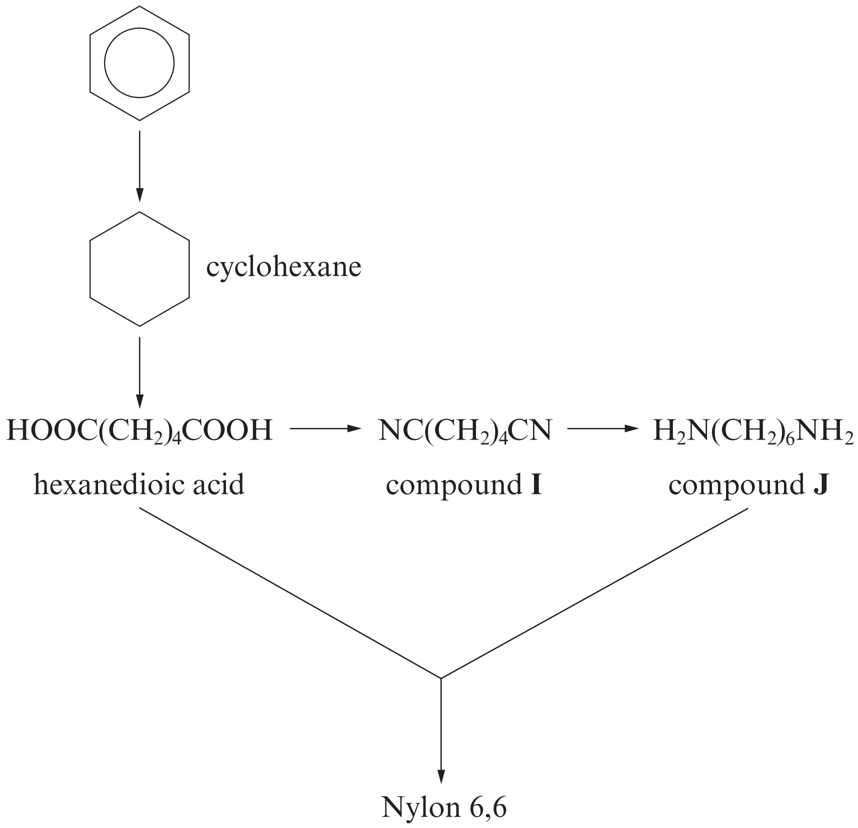


phenol phenylamine phenylethene

In the 19th and early 20th centuries, benzene was used as an after-shave lotion because of its pleasant smell, but today benzene is used to make other chemicals.

Examiner only

One of its most widely-produced derivatives is cyclohexane, which is used in the manufacture of Nylon 6,6 as shown in the scheme below:



28

– End of passage –

(a) Benzene reacts with bromine *(line 12)* in the presence of an iron(III) bromide catalyst to form bromobenzene.

(i) Classify the reaction mechanism. [1]

....

(ii) Draw the mechanism for this reaction. [3]
(The mechanism is similar to that for the chlorination of benzene.)

Turn over.

Examiner only

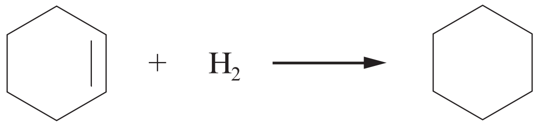
(b) (i) Explain what is meant by the *delocalisation energy* of benzene *(line 17)*. [1]

....

....

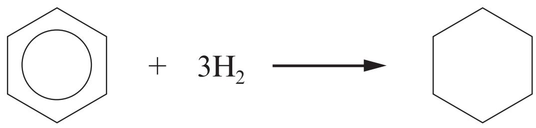
....

(ii) Given that the enthalpy change of hydrogenation of cyclohexene is –120 kJ mol^{-1} and that the enthalpy change of hydrogenation of benzene is –208 kJ mol^{-1}, calculate the delocalisation energy of benzene. [2]



$\Delta H^{\ominus} = –120\ kJ\ mol^{-1}$

cyclohexane



$\Delta H^{\ominus} = –208\ kJ\ mol^{-1}$

benzene

....

....

....

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

(c) Use the information in the passage to give a reason why benzene is no longer used in after-shave lotion. [1]

....

(d) In the production of Nylon 6,6 *(line 28)* each of the repeating units requires **two** molecules of benzene; one for the formation of hexanedioic acid and one for the formation of compound **J**.

(i) Draw the **skeletal** formula of hexanedioic acid. [1]

(ii) Name the type of reaction occurring when compound **I** is converted to compound **J**. [1]

....

(iii) State the name of compound **J**. [1]

....

Examiner only

(iv) Draw the repeating unit in Nylon 6,6. [1]

(v) What type of condensation polymer is Nylon 6,6? [1]

....

(vi) A typical plant makes 800 tonnes of nylon per day. Given that the relative molecular mass of each repeating unit is 226 and assuming yields of 100% at each step, calculate the mass of benzene needed per day to produce this quantity of nylon. [2]

....

....

....

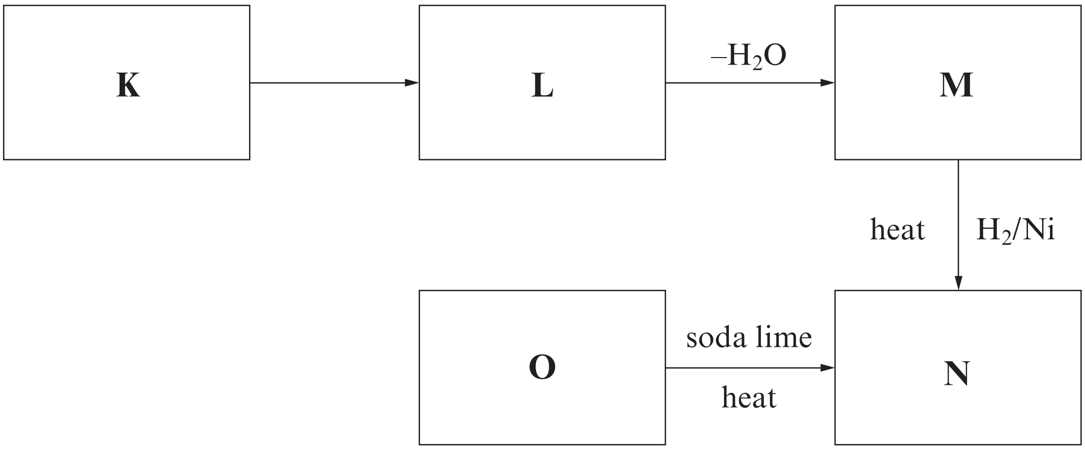
Total [15]

Total Section A [40]

SECTION B

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

4. *(a)* Study the reaction scheme shown below and the other information about compounds **K–O** that follows:



Compound **K** has a relative molecular mass of 58.06. It gives an orange-yellow solid with 2, 4-dinitrophenylhydrazine and gives a positive triiodomethane (iodoform) test.

0.500 g of compound **O** in aqueous solution requires 56.75 cm^3 of sodium hydroxide solution of concentration 0.100 $mol\,dm^{-3}$ for complete neutralisation.
Compound **O** reacts with sodium hydroxide in a 1:1 molar ratio.

Compound **L** cannot be oxidised to compound **O**.

(i) Calculate the relative molecular mass of compound **O**. [2]

(ii) Identify compounds **K** and **O**, giving your full reasoning. [5]

(iii) Identify compounds **L**, **M** and **N**. [3]

(iv) State the reagent(s) needed for the conversion of **L** to **M**. [1]

(b) Rhodri prepared benzenecarboxylic acid, C_6H_5COOH, by hydrolysing ethyl benzenecarboxylate, $C_6H_5COOC_2H_5$.

The overall equation for this hydrolysis is:

$$C_6H_5COOC_2H_5 + H_2O \longrightarrow C_6H_5COOH + C_2H_5OH$$

He used the following method.

- Dissolve 3.20 g of sodium hydroxide in water and make up to 40.0 cm^3.
- Add the aqueous sodium hydroxide to 2.90 cm^3 of ethyl benzenecarboxylate in a round bottomed flask and reflux for 30 minutes.
- Transfer the mixture into a beaker and add dilute sulfuric acid until the solution is acidic.
- Filter the crystals obtained and recrystallise the benzenecarboxylic acid by dissolving in the minimum amount of hot water.

At the end of the experiment Rhodri's yield of benzenecarboxylic acid was 1.45 g.

(i) Suggest why Rhodri had to add sulfuric acid before recrystallising. [1]

(ii) State why water is a suitable solvent for the recrystallisation. [1]

(iii) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide used. [2]

(iv) The density of ethyl benzenecarboxylate is 1.06 g cm^{-3}. Calculate how many moles of ethyl benzenecarboxylate were used. [2]

(v) Calculate the percentage yield obtained by Rhodri. [2]

(vi) Give a reason why the percentage yield was substantially lower than 100%. [1]

Total [20]

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
$CH_3—C≡N$	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

THE PERIODIC TABLE

Key: A_r (relative atomic mass) / Symbol / Name / Z (atomic number)

Period	Group 1	Group 2											Group 3	Group 4	Group 5	Group 6	Group 7	Group 0
	s Block		d Block										p Block					
1	1.01 H Hydrogen 1																	4.00 He Helium 2
2	6.94 Li Lithium 3	9.01 Be Beryllium 4											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											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
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