

Surname	Centre Number	Candidate Number
Other Names		2



GCE A level

1094/01

CHEMISTRY – CH4

P.M. MONDAY, 9 June 2014

1 hour 45 minutes

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A	1.	12
	2.	13
	3.	15
Section B	4.	20
	5.	20
Total		80

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.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

SECTION A

Answer all questions in the spaces provided.

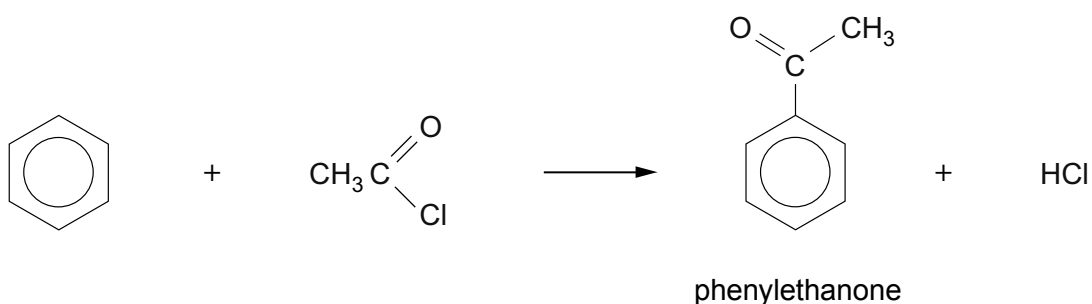
1. (a) 1-Chloropentane can be made by the free radical chlorination of pentane, in a similar way to the reaction of methane with chlorine.

(i) Give the equation for the reaction of pentane with chlorine, showing the displayed formula of 1-chloropentane as part of your answer. [1]

(ii) The free radical reaction of pentane with chlorine gives other chlorinated organic products. Give the structural formula of the carbon-containing free radical that leads to the formation of 2-chloropentane. [1]

- (b) Pentylbenzene can be produced by the reaction of 1-chloropentane and benzene in a Friedel-Crafts reaction. State the name of a catalyst that can be used in this reaction. [1]

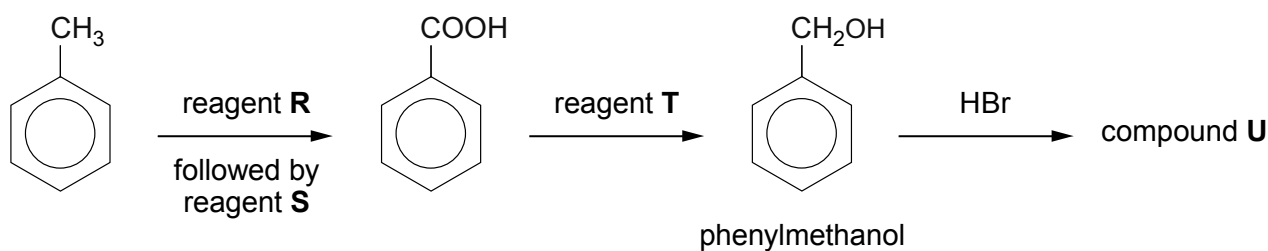
- (c) A Friedel-Crafts reaction can be carried out with ethanoyl chloride in place of 1-chloropentane. This reaction gives phenylethanone as the main organic product.



(i) State what is seen when a few drops of phenylethanone are added to a solution of 2,4-dinitrophenylhydrazine. [1]

- (ii) This preparation of phenylethanone also gives small traces of an impurity. This impurity has a molecular formula $C_{10}H_{10}O_2$ and reacts in a similar way to phenylethanone when it is treated with 2,4-dinitrophenylhydrazine. It does not react with Tollens' reagent. Suggest a displayed formula for this impurity, giving a reason for your choice. [2]
-
-

- (d) Methylbenzene can be oxidised to benzoic acid by heating it strongly with an alkaline solution of reagent **R** followed by treatment with reagent **S**. The benzoic acid can then be used to produce a number of other compounds. A reaction sequence is shown below.



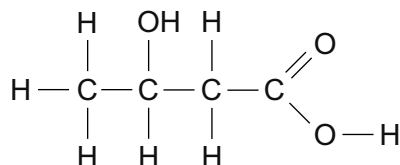
- (i) State the name of reagent **R**. [1]
- (ii) State the name of reagent **S**. [1]
- (iii) State the name of reagent **T**. [1]
- (iv) Give the displayed formula of the organic compound **U**. [1]

- (e) State and explain how the infrared spectrum of benzoic acid would differ from that of phenylmethanol. [2]
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-
-

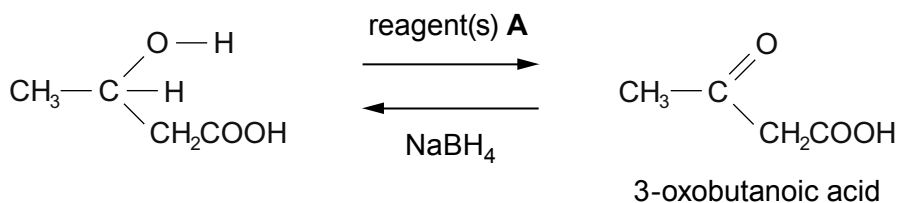
Total [12]

2. 3-Hydroxybutanoic acid is a white solid that can react as a carboxylic acid and an alcohol.

- (a) Indicate the position of any chiral centre in the formula of 3-hydroxybutanoic acid by use of an asterisk (*). [1]



- (b) The acid can be oxidised to an oxoacid by using reagent(s) **A**. This oxoacid can then be reduced back to the hydroxyacid by sodium tetrahydridoborate(III), NaBH_4 .



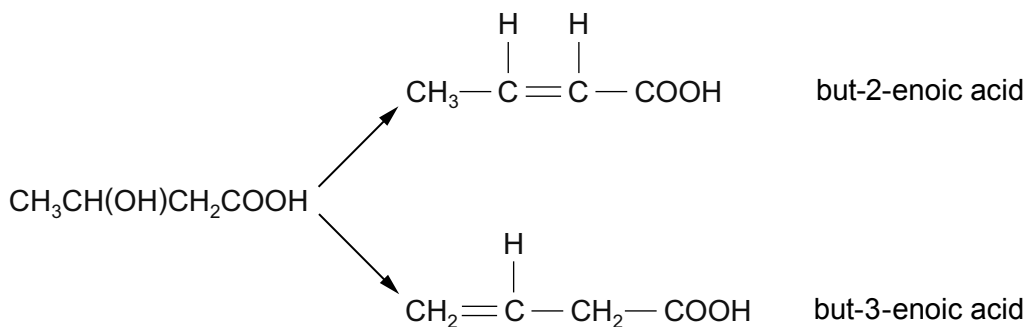
- (i) State the name(s) of reagent(s) **A**. [1]

- (ii) The reduction of the oxoacid gives 3-hydroxybutanoic acid, which is present as a racemic mixture.

- I State what is meant by the term *racemic mixture*. [1]

- II State the effect (if any) that a racemic mixture has on the plane of polarised light. [1]

- (c) 3-Hydroxybutanoic acid readily undergoes an elimination reaction to form a mixture of unsaturated acids.



- (i) State which of these unsaturated acids exists as *E-Z* isomers, giving a reason for your answer. [1]

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- (ii) A scientist reported that the yield of the products was
- | | |
|--|-----|
| but-2-enoic acid | 89% |
| but-3-enoic acid | 4% |
| together with unreacted 3-hydroxybutanoic acid | 7% |

State any additional information that another scientist would have to know so that the experiment could be repeated to confirm these yields. [2]

1

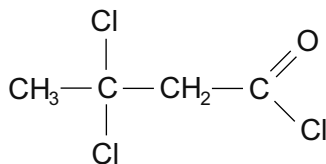
2

- (d) Both 3-hydroxybutanoic acid and 3-oxobutanoic acid will undergo the triiodomethane (iodoform) reaction. State the reagent(s) used for this reaction and the observation made. [2]

Reagent(s)

Observation

- (e) 3-Oxobutanoic acid reacts with phosphorus(V) chloride to give 3,3-dichlorobutanoyl chloride.



Describe the NMR spectrum of this chloro-compound.
In your answer you should include the following points, **giving an explanation for each.**

- the number of peaks (and their approximate position in ppm)
- the relative peak areas
- any splitting pattern

[3]
QWC [1]

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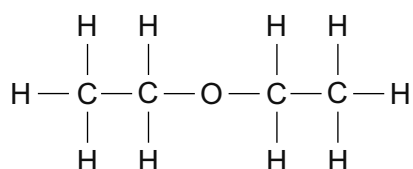
Total [13]

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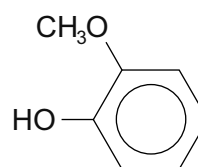
3. Read the passage below and then answer the questions in the spaces provided.

The chemistry of some compounds containing the ether (R–O–R) linkage

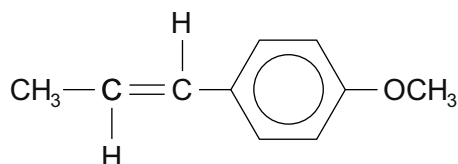
- 1 Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



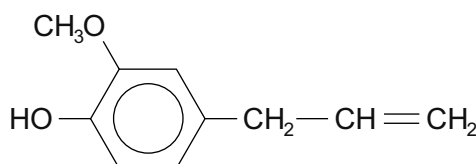
ethoxyethane



guaiacol



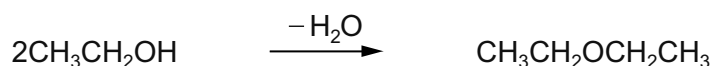
anethole



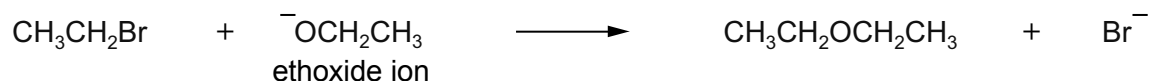
eugenol

5

Ethoxyethane (diethyl ether) is one of the most familiar compounds containing the ether linkage. It can be made by heating ethanol with an excess of concentrated sulfuric acid, which acts as a dehydrating agent.

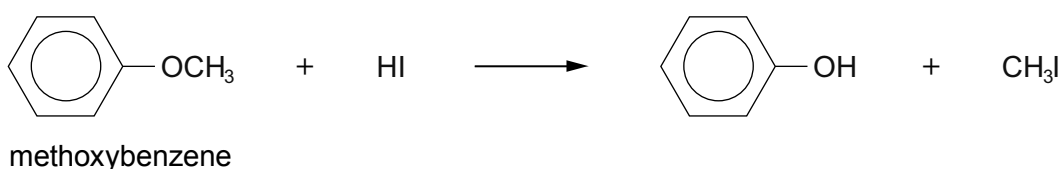


- 10 Another method is by reacting bromoethane with sodium ethoxide (a source of the ethoxide ion).



- 15 Ethoxyethane has a boiling temperature of 35 °C whereas ethanol, a smaller molecule, boils at 78 °C. The solubility of these two compounds in water also varies. Ethanol is completely miscible with water but ethoxyethane has a much reduced solubility.

The strong C—O bond means that compounds such as ethoxyethane and methoxybenzene have relatively few reactions. However, carbon–oxygen bond fission occurs when they are heated with concentrated hydrobromic (HBr) or hydriodic acid (HI).



- 20 Naturally occurring compounds that contain the ether linkage often owe their reactions to other functional groups present in the molecule. Both eugenol (found in cloves) and guaiacol (from wood) have medicinal uses. Anethole (occurring in aniseed) has a promising use as an insecticide and is also effective against some bacteria and fungi.

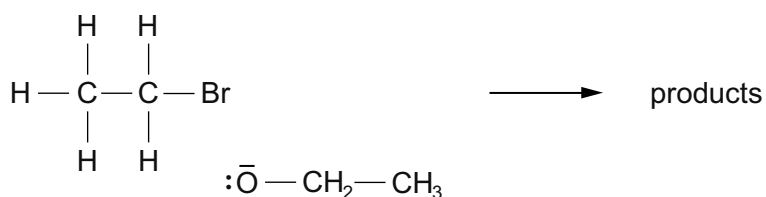
- End of passage -

- (a) (i) Bethan prepared some ethoxyethane (*line 6*) by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol ($M_r=46$) and obtained a 45% yield of ethoxyethane ($M_r=74$). Calculate the mass of ethoxyethane obtained. [3]

Mass = g

- (ii) One of the reasons for only obtaining a 45% yield of ethoxyethane was that sulfuric acid reacted with ethanol in a different reaction. State the organic product of this side reaction. [1]

- (iii) Bethan would have obtained a higher percentage yield of ethoxyethane if she had reacted bromoethane with sodium ethoxide (*line 10*). This reaction is an example of nucleophilic substitution. Complete the mechanism below by inserting curly arrows and appropriate partial charges ($\delta+$, $\delta-$). [2]



- (iv) Ethoxyethane has a much lower boiling temperature than ethanol because its molecules are unable to hydrogen bond with each other. State the feature of a molecule that needs to be present for hydrogen bonding to occur. [1]

(b) Guaiacol (*line 4*) reacts with (aqueous) bromine.

(i) By analogy with the reaction of phenol with (aqueous) bromine, suggest a displayed formula for the organic product of the reaction between guaiacol and (aqueous) bromine. [1]

(ii) Describe what is seen during this reaction. [1]

.....

(c) The article shows the formulae of anethole and eugenol (*line 5*). State a reagent that will react with eugenol but not with anethole, giving the observation. [2]

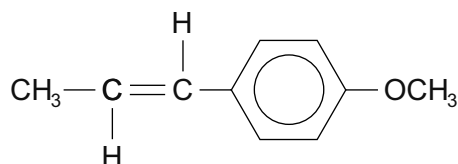
Reagent

Observation

(d) (i) State the molecular formula of anethole (*line 5*). [1]

.....

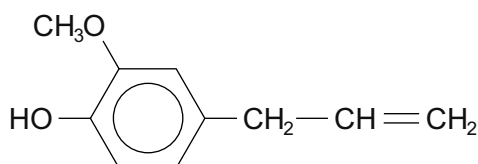
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid (*lines 17-18*). Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



anethole

displayed formula of product

(e) An isomer of eugenol (*line 5*), compound **Y**, reacts with sodium carbonate giving carbon dioxide. Suggest a displayed formula for compound **Y** and state the name of the functional group present in the organic compound that produces carbon dioxide in this reaction. [2]



eugenol

displayed formula for compound **Y**

Functional group

Total [15]

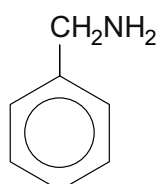
Total Section A [40]

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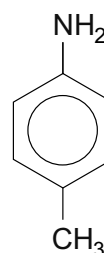
SECTION B

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

4. (a) The formulae of the isomers phenylmethanamine and 4-methylphenylamine are shown below.



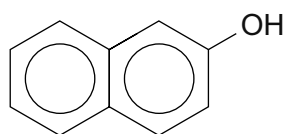
phenylmethanamine



4-methylphenylamine

These compounds are colourless liquids with different boiling temperatures.

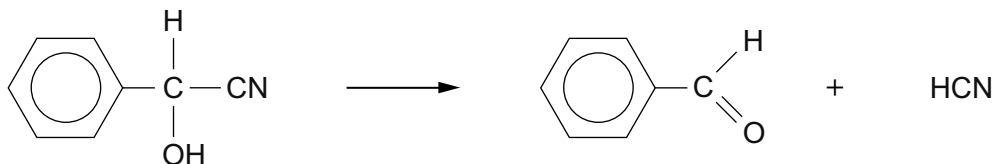
- (i) Give the name of a technique that can be used to separate these two liquids. [1]
- (ii) State and explain how the mass spectra of these two compounds would differ. [1]
- (iii) Phenylmethanamine reacts with ethanoyl chloride to give a white solid, compound **G**.
 - I Give the equation for this reaction. [1]
 - II Compound **G** was purified by recrystallisation from ethanol. It has a melting temperature of 60 °C. Describe how you would recrystallise compound **G** from ethanol to obtain a pure dry product. You should assume that you are starting with cold ethanol and impure solid compound **G**. Washing of the purified solid product is unnecessary. [5]
QWC [1]
- (iv) 4-Methylphenylamine can be used to make an azo dye by reaction of its diazonium compound with an alkaline solution of naphthalene-2-ol.



naphthalene-2-ol

- I State how the diazonium compound can be made from 4-methylphenylamine, giving the reagents used and any essential conditions. [2]
- II Give the structural formula of the azo dye produced. [1]

- (b) A species of millipede can protect itself by producing hydrogen cyanide. This poisonous gas is produced from mandelonitrile by enzyme action.



2-phenyl-2-hydroxyethanenitrile
(mandelonitrile)

benzaldehyde

The reaction can be carried out in the reverse direction in the laboratory.

- (i) Draw the mechanism for the reaction between benzaldehyde and the cyanide ion. State the type of mechanism occurring. [4]
- (ii) Mandelonitrile is a yellow material. State the general name for groups that cause colour in organic compounds and give the appearance of mandelonitrile when viewed under blue light, giving a reason for your answer. [3]
- (iii) Give the structural formula of the organic compound obtained when mandelonitrile is warmed with dilute hydrochloric or sulfuric acid. [1]

Total [20]

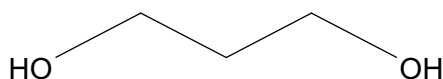
TURN OVER FOR QUESTION 5

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.

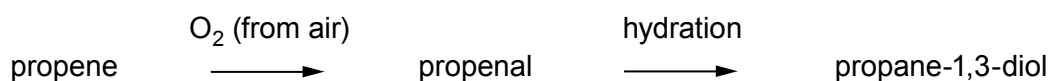
- It contains C, 71.3% and H, 9.6% by mass. The remainder is oxygen.
- Only one oxygen atom is present in each molecule.
- It gives a silver mirror with Tollens' reagent (ammoniacal silver nitrate solution).
- The mass spectrum shows a fragmentation ion, containing only carbon and hydrogen, at m/z 29.

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.

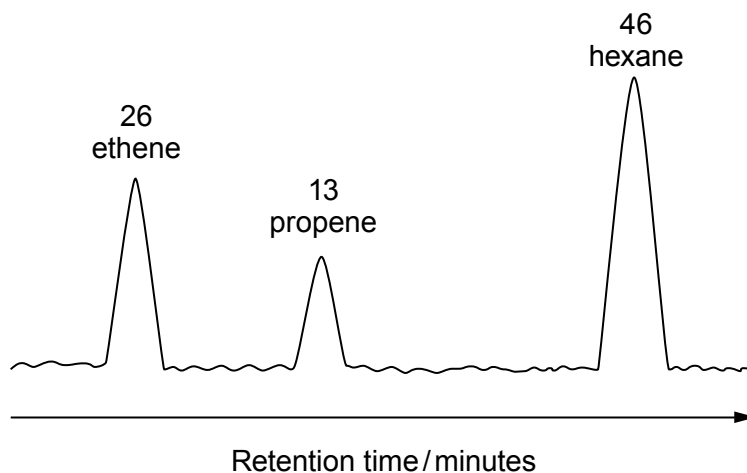


One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.



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, $\text{C}_{11}\text{H}_{24}$, 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

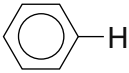
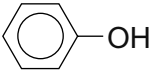
Infrared Spectroscopy characteristic absorption values

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
$-\text{CH}_3$	0.1 to 2.0
$\text{R}-\text{CH}_3$	0.9
$\text{R}-\text{CH}_2-\text{R}$	1.3
$\text{CH}_3-\text{C}\equiv\text{N}$	2.0
$\text{CH}_3-\text{C}(=\text{O})$	2.0 to 2.5
$\text{CH}_3-\text{CCl}_2-$	2.0 to 2.5
$-\text{CH}_2-\text{C}(=\text{O})$	2.0 to 3.0
$\text{R}-\text{CCl}_2-\text{CH}_2-\text{C}(=\text{O})\text{Cl}$	2.5 to 3.0
$\text{R}-\text{CH}_2-\text{Cl}$	3.3 to 4.3
$\text{R}-\text{OH}$	4.5 *
$\text{CH}_2=\text{C}$	4.8
	6.5 to 7.5
	7.0 *
$\text{R}-\text{C}(=\text{O})\text{H}$	9.8 *
$\text{R}-\text{C}(=\text{O})\text{OH}$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

Group 1 2 3 4 5 6 7 0

Period 1 2 3 4 5 6 7

s Block

1.01	H	Hydrogen	1
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6.94	Li	Lithium	3
9.01	Be	Beryllium	4

23.0	Na	Sodium	11
24.3	Mg	Magnesium	12

39.1	K	Potassium	19
40.1	Ca	Calcium	20

85.5	Rb	Rubidium	37
87.6	Sr	Strontium	38

133	Cs	Caesium	55
137	Ba	Barium	56

(223)	Fr	Francium	87
(226)	Ra	Radium	88
(227)	Ac	Actinium	89

Key

Ar	Symbol
Name	Name
Z	atomic number
relative atomic mass	relative atomic mass

d Block

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

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

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

f Block

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

▶ Lanthanoid 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

▶▶ Actinoid elements

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

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

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

115	In	Indium	49
119	Sn	Tin	50
122	Sb	Antimony	51
128	Te	Tellurium	52
127	I	Iodine	53
131	Xe	Xenon	54

204	Tl	Thallium	81
207	Pb	Lead	82
209	Bi	Bismuth	83
(210)	Po	Polonium	84
(210)	At	Astatine	85
(222)	Rn	Radon	86