Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY – CH4

	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.

Examiner only

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.

phenylethanone

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

....

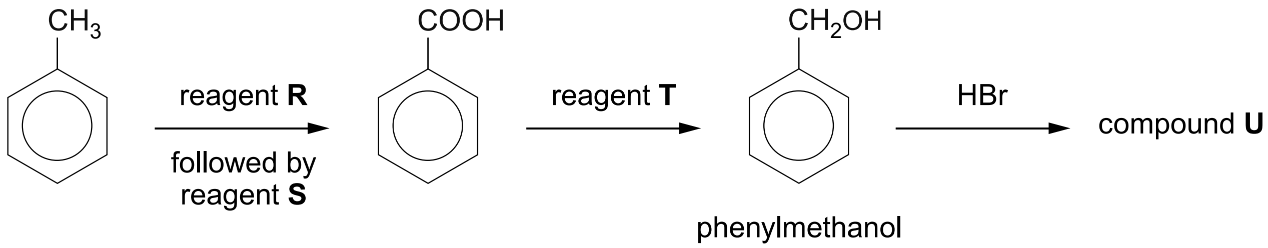
Examiner only

(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.



1094
010003

(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]

....

....

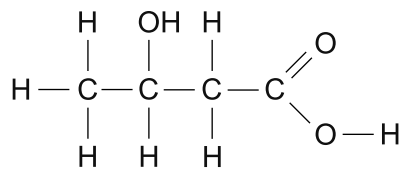
....

Total [12]

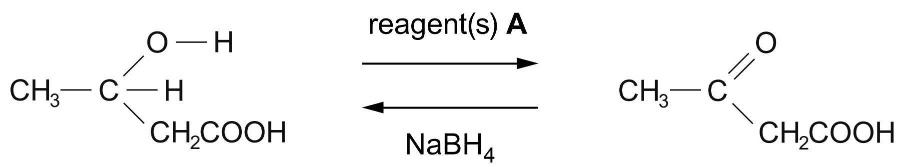
Examiner only

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), $NaBH_4$.



3-oxobutanoic acid

(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]

....

....

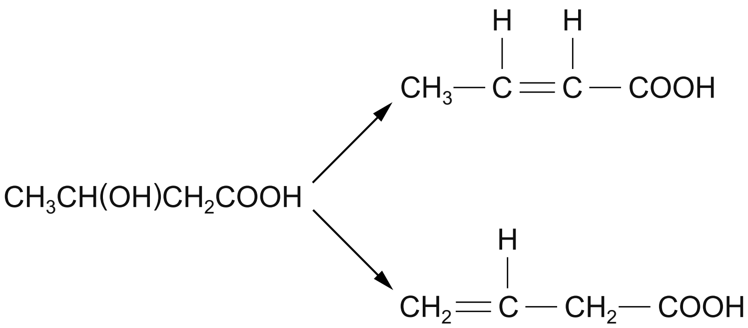
II State the effect (if any) that a racemic mixture has on the plane of polarised light. [1]

....

....

Examiner only

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



but-2-enoic acid

but-3-enoic acid

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

....

....

....

(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]

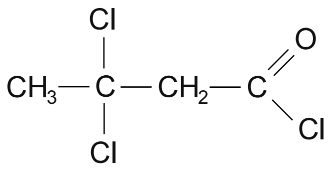
Reagent(s) ....

Observation ....

1094 010005

Examiner only

(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]

....

....

....

....

....

....

....

Total [13]

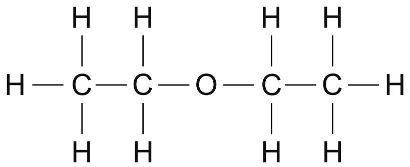
1094
010007

BLANK PAGE

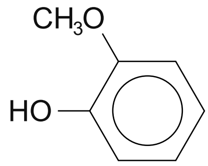
3. *Read the passage below and then answer the questions in the spaces provided.*

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

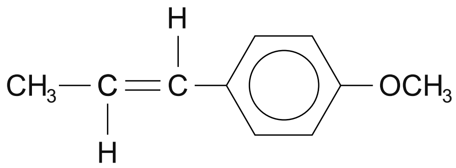
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



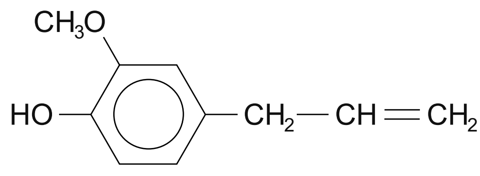
ethoxyethane



guaiacol



anethole



eugenol

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.

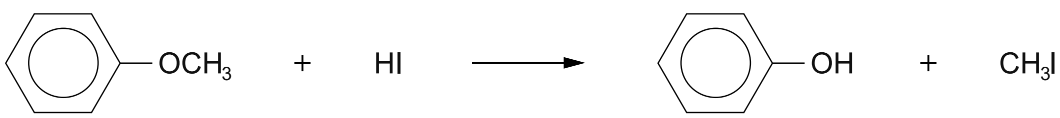
$$2CH_3CH_2OH \xrightarrow{-H_2O} CH_3CH_2OCH_2CH_3$$

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

$$CH_3CH_2Br \quad + \underset{\text{ethoxide ion}}{{}^{-}OCH_2CH_3} \longrightarrow CH_3CH_2OCH_2CH_3 \quad + \quad Br^{-}$$

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).



methoxybenzene

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 -

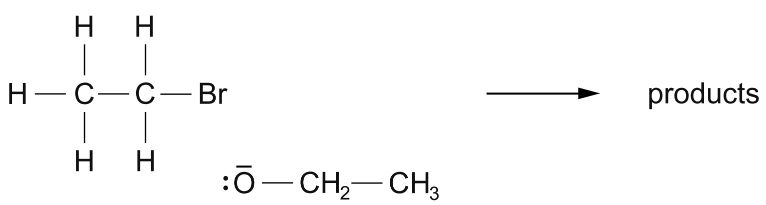
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol (M_r = 46) and obtained a 45 % yield of ethoxyethane (M_r = 74). Calculate the mass of ethoxyethane obtained. [3]

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 (δ+, δ-). [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]

....

....

Examiner only

(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]

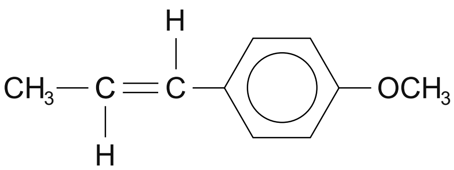
Reagent ....

Observation ....

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

....

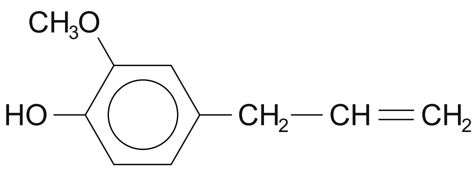
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



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]

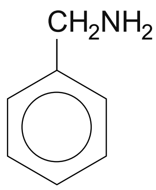
Total Section A [40]

BLANK PAGE

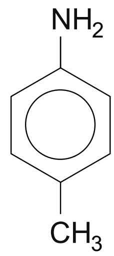
SECTION B

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

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



phenylmethylamine



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]

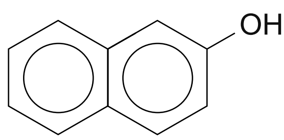
(ii) State and explain how the mass spectra of these two compounds would differ. [1]

(iii) Phenylmethylamine 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.

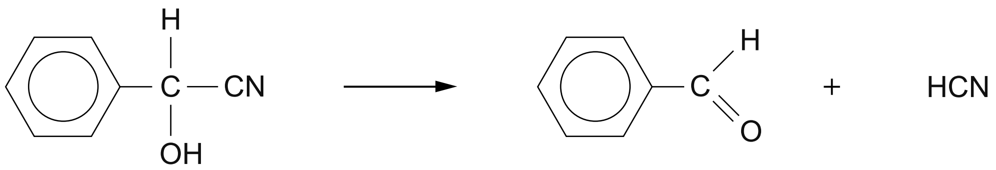


naphthalene-2-ol

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]

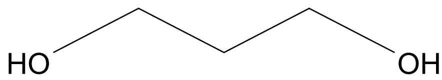
TURN OVER FOR QUESTION 5

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.



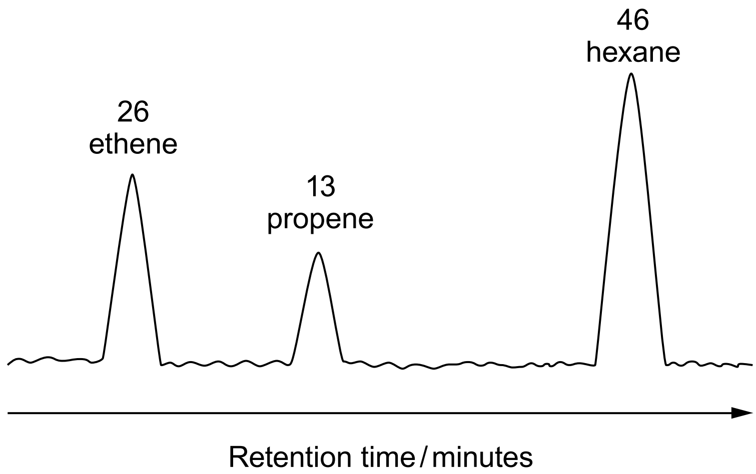
One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.

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

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

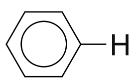
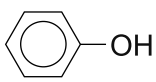
Infrared Spectroscopy characteristic absorption values

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
$CH_3-C(=O)-$	2.0 to 2.5
CH_3-CCl_2-	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$R-CCl_2-CH_2-C(=O)Cl$	2.5 to 3.0
$R-CH_2-Cl$	3.3 to 4.3
$R-OH$	4.5 *
$CH_2{=}C{<}$	4.8
	6.5 to 7.5
	7.0 *
$R-C(=O)H$	9.8 *
$R-C(=O)OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

Group

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

s Block, d Block, p Block

Period	1	2											3	4	5	6	7	0
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