Write your name here

Surname	Other names

Pearson Edexcel GCE

Centre Number

Candidate Number

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Monday 9 June 2014 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01R

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
  – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
  – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

P42988A
P 4 2 9 8 8 A 0 1 2 4

6/6/6/6/3/

PEARSON

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Four organic compounds are:

A CH_3OH

B HCHO

C HCOOH

D $HCOOCH_3$

(a) Which of these compounds has a fruity smell?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) 0.01 mol of each compound is added separately to identical volumes of water. Which solution would have the lowest pH?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) 0.01 mol of each compound is heated separately with excess acidified sodium dichromate(VI) solution. Which compound reduces the largest amount of sodium dichromate(VI)?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) Which compound has the highest boiling temperature?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(e) Which of these compounds can be oxidized by ammoniacal silver nitrate?

(1)

☒ **A**

☒ **B**

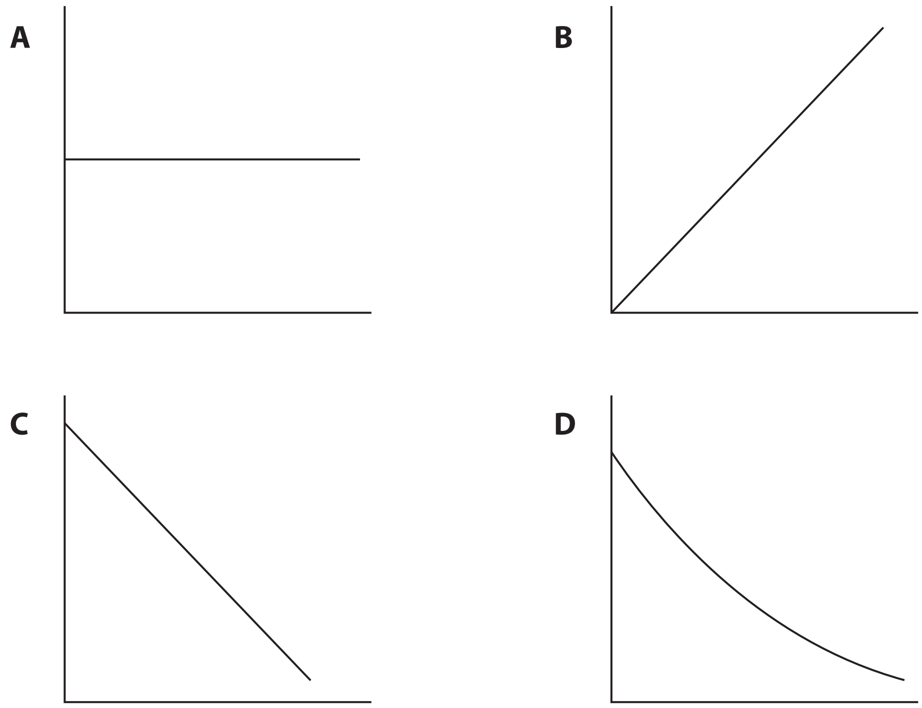
☒ **C**

☒ **D**

(Total for Question 1 = 5 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

2 Four sketch graphs are shown below.



(a) Which could be a graph of rate of reaction, on the vertical axis, against the concentration of a reactant for a zero order reaction?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which could be a graph of rate of reaction, on the vertical axis, against the square of the concentration of a reactant for a second order reaction?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a first order reaction?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) Which could be a graph of ln(rate), on the vertical axis, against reciprocal of temperature, 1/T, for a reaction?

You may use the equation $\ln(\text{rate}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 2 = 4 marks)

3 Which of the following mixtures would form the best buffer solution with pH 5 for use in a school laboratory?

☒ **A** Ethanoic acid and sodium ethanoate

☒ **B** Hydrochloric acid and sodium chloride

☒ **C** Sodium hydroxide and sodium methanoate

☒ **D** Ammonium chloride and ammonia

(Total for Question 3 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

4 Suggest the most likely pH for each of the following solutions.

(a) 5.0 mol dm^{-3} hydrochloric acid.

(1)

- ☒ **A** +5
- ☒ **B** +0.7
- ☒ **C** –0.7
- ☒ **D** –5

(b) 0.20 mol dm^{-3} strontium hydroxide, $Sr(OH)_2$

$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

(1)

- ☒ **A** 13.3
- ☒ **B** 13.6
- ☒ **C** 14.0
- ☒ **D** 14.3

(c) A mixture of 20 cm^3 of 1.0 mol dm^{-3} nitric acid and 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide.

(1)

- ☒ **A** 0
- ☒ **B** 0.30
- ☒ **C** 0.48
- ☒ **D** 7

(Total for Question 4 = 3 marks)

5 In liquid ammonia the following equilibrium is present.

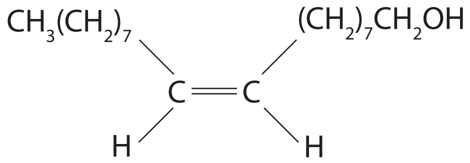
$$NH_2^- + NH_4^+ \rightleftharpoons 2NH_3$$

Identify the Brønsted-Lowry base(s).

- ☒ **A** NH_2^- only
- ☒ **B** NH_4^+ only
- ☒ **C** NH_2^- and NH_3
- ☒ **D** NH_4^+ and NH_3

(Total for Question 5 = 1 mark)

6 The formula for oleyl alcohol, which is present in sperm whale oil and was used as a lubricant, is shown below.



(a) The systematic name for oleyl alcohol is

(1)

☒ **A** *E*-octadec-9-en-1-ol.

☒ **B** *Z*-octadec-9-en-1-ol.

☒ **C** *E*-octadec-8-en-1-ol.

☒ **D** *Z*-octadec-8-en-1-ol.

(b) Which intermolecular forces are present between oleyl alcohol molecules?

(1)

☒ **A** London forces only

☒ **B** Hydrogen bonds and London forces only

☒ **C** Hydrogen bonds and permanent dipole–dipole forces only

☒ **D** Hydrogen bonds, permanent dipole–dipole and London forces

(c) Which of the following is the most likely structure of the species to cause a peak at *m/e* 31 in the mass spectrum of oleyl alcohol?

(1)

☒ **A** CH_3O

☒ **B** CH_2OH

☒ **C** CH_3O^+

☒ **D** CH_2OH^+

(d) What would you expect to see if oleyl alcohol is tested separately with bromine water and heated with acidified sodium dichromate(VI) solution?

(1)

	Bromine water	Acidified sodium dichromate(VI) solution
☒ **A**	Decolorises	Turns green
☒ **B**	No colour change	No colour change
☒ **C**	Decolorises	No colour change
☒ **D**	No colour change	Turns green

(Total for Question 6 = 4 marks)

7 Methane hydrate is found on continental shelves deep in oceans. It forms methane in an endothermic equilibrium reaction, which may be represented as

$$CH_4.6H_2O(s) \rightleftharpoons CH_4(g) + 6H_2O(l)$$

(a) Which of the following changes would **decrease** the equilibrium yield of methane?

(1)

☒ **A** Decreasing the temperature and decreasing the pressure.

☒ **B** Increasing the temperature and decreasing the pressure.

☒ **C** Decreasing the temperature and increasing the pressure.

☒ **D** Increasing the temperature and increasing the pressure.

(b) Which of the following would **increase** the value of the equilibrium constant, K_p, for the above equilibrium?

(1)

☒ **A** Decreasing the pressure

☒ **B** Increasing the pressure

☒ **C** Decreasing the temperature

☒ **D** Increasing the temperature

(Total for Question 7 = 2 marks)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

8 This question is about calcium chloride, $CaCl_2$.

It can be formed by burning calcium in chlorine.

$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) \qquad \Delta S^{\ominus}_{surroundings} = +2670\ J\ mol^{-1}\ K^{-1}$$

You must include a sign and units in your answers to the calculations in this question.

(a) (i) The standard molar entropy at 298 K for 1 mole of chlorine molecules, Cl_2, is $+165\ J\ mol^{-1}\ K^{-1}$. Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change, $\Delta S^{\ominus}_{system}$, for this reaction.

(2)

*(ii) Explain fully why the sign for the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, is as you would expect.

(2)

....

....

....

....

(b) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, in $J\ mol^{-1}\ K^{-1}$, for this reaction, giving your answer to three significant figures.

(2)

(c) Use the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, to calculate the standard enthalpy change, $\Delta H^{\ominus}$, in kJ mol^{-1}, for the reaction at 298 K.

(2)

(d) 0.0500 mol of calcium chloride, prepared by burning calcium in chlorine, is added to 51.8 cm^3 of water.

50.0 cm^3 of a 1.00 mol dm^{-3} solution is formed, and the temperature rise, ΔT, is 15.0°C.

(i) Calculate the energy transferred, in joules, for this process using:

Energy transferred in joules = volume of **solution formed** × 4.2 × ΔT

(1)

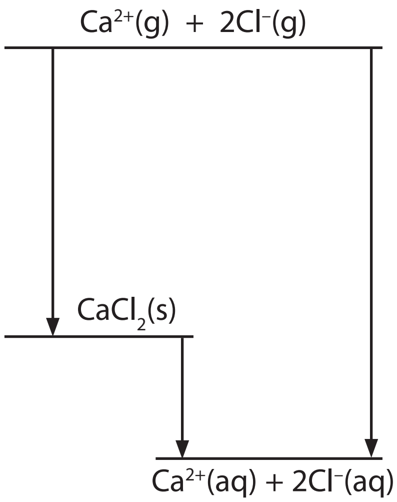
(ii) Calculate the enthalpy change of solution, $\Delta H_{solution}$, of calcium chloride in kJ mol^{-1}.

(2)

*(iii) The enthalpy change of hydration of $Ca^{2+}(g)$ is –1560 kJ mol^{-1}.

Use this, your value from (d)(ii) and the experimental lattice energy from your Data Booklet, to calculate the standard enthalpy change of hydration of $Cl^{-}(g)$.

(3)



Answer .... kJ mol^{-1}

(iv) Draw diagrams to represent hydrated calcium ions and hydrated chloride ions.

(2)

(v) Suggest why the addition of anhydrous calcium chloride to water results in an increase in temperature and a decrease in volume.

(2)

Temperature increases ....

....

....

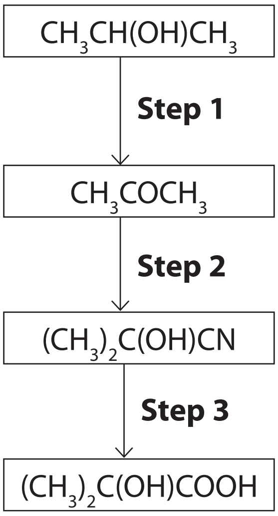
Volume decreases ....

....

....

(Total for Question 8 = 18 marks)

9 A flow chart for making 2-hydroxy-2-methylpropanoic acid from propan-2-ol is shown below.



(a) (i) Give the reagents and conditions for **Step 1**.

(2)

(ii) Propanone is formed in **Step 1**.
Give a chemical test to identify the carbonyl group and a further test to show the presence of the $H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$ group.

For both tests, give the observations that you would make.

(4)

Carbonyl group

$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$ group

(b) (i) In **Step 2**, propanone undergoes an addition reaction with HCN in the presence of CN^- ions.
Give the mechanism for this reaction.

(3)

(ii) Explain why this reaction would not take place at either a very low or very high pH.

(2)

Low pH ....

....

High pH ....

....

(c) (i) The reaction in **Step 3** forms 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)COOH$.
Suggest the type of reaction occurring in **Step 3**.

(1)

....

(ii) Explain why the presence of the alcoholic hydroxyl group cannot be confirmed in the infrared spectrum of 2-hydroxy-2-methylpropanoic acid.

(1)

....

....

(iii) The hydrogen of the alcohol group in 2-hydroxy-2-methylpropanoic acid can be identified by a single peak in the nmr spectrum.

Give the chemical shift you would expect for this peak.

(1)

....

(iv) How many peaks would you expect in a high resolution nmr spectrum for 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)COOH$?

(1)

....

(v) Explain why, in high resolution nmr, the peak due to the hydrogens of the 2-methyl group in 2-hydroxy-2-methylpropanoic acid is a singlet.

(1)

....

....

(vi) Would you expect 2-hydroxy-2-methylpropanoic acid to have optical isomers? Justify your answer.

(1)

....

....

....

....

(d) (i) Molecules of 2-hydroxy-2-methylpropanoic acid react together to form a condensation polymer.

Draw a **displayed** formula for this polymer, showing two repeating units.

(2)

(ii) Give the name of the functional group that links the two molecules in the polymer.

(1)

....

(Total for Question 9 = 20 marks)

10 Persulfate ions, $S_2O_8^{2-}$, oxidize iodide ions in aqueous solution to form iodine and sulfate ions, SO_4^{2-}.

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) The effect of iodide ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to a known volume of potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium iodide, but the same volumes and concentrations of sodium thiosulfate solution and potassium persulfate solution.

The rates of the reaction were compared using the reciprocal of the time (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

(1)

....

(ii) What would be observed if the reaction was carried out without the addition of sodium thiosulfate?

(1)

....

....

....

(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)

....

....

....

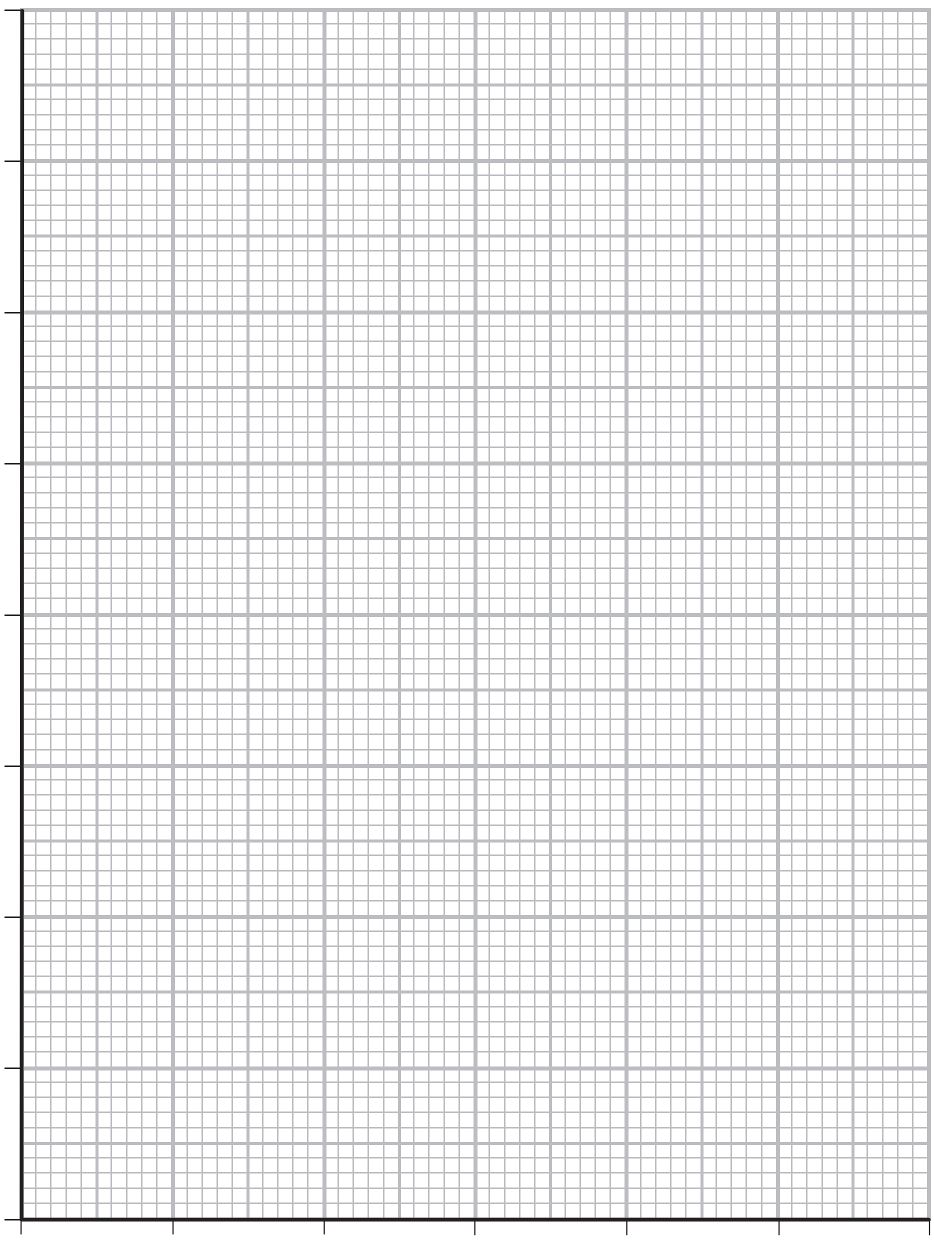
....

(c) The results obtained were tabulated as follows.

$[I^-]$ /mol dm^{-3}	Time /s	1/time /s^{-1}
0.0100	40.0	0.0250
0.0075	53.3	0.0188
0.0050	80.0	0.0125
0.0040	100.0	0.0100

(i) Plot a graph of 1/time on the vertical axis against concentration of iodide ions.

(2)



(ii) 1/time is a measure of the initial rate of the reaction.

Deduce the order of reaction with respect to iodide ions.

Justify your answer.

(2)

....

....

....

....

(iii) The reaction is first order with respect to persulfate ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

(2)

Rate =

Units for the rate constant..

(d) The reaction in part (b) is repeated at two different temperatures, keeping the initial volumes and concentrations of the solutions constant.

T (Temperature) /K	1/time /s^{-1}	1/T /K^{-1}	ln(1/time)
293	0.0215	3.31×10^{-3}	–3.84
303	0.0430	3.20×10^{-3}	–3.15

(i) Calculate, without drawing a graph, the activation energy of the reaction. Remember to give a sign and units with your answer.

$$\ln(1/\text{time}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad [R = 8.31\ \text{J mol}^{-1}\text{K}^{-1}]$$

(3)

(ii) Suggest how the reliability of the activation energy determination could be improved, without changing the apparatus, solutions or method.

(1)

....

....

....

....

(Total for Question 10 = 14 marks)

TOTAL FOR SECTION B = 52 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

11 The decomposition of hydrogen iodide to form iodine and hydrogen is an equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(g) + H_2(g)$$

The equilibrium was investigated by taking sealed tubes containing the same mass of hydrogen iodide and heating them at 700 K for some time. At this temperature, the equilibrium takes about two days to be established.

The tubes were rapidly cooled to room temperature, which maintained the equilibrium concentrations, because at this temperature the reaction is extremely slow.

Each tube was opened under an aqueous solution of potassium iodide, which dissolved the hydrogen iodide and the iodine. The amount of iodine was found by titration and the composition of the equilibrium mixture calculated. From the number of moles of each substance at equilibrium, and the volume of the tubes, the equilibrium concentrations were calculated.

(a) (i) How would the appearance of the contents of a tube change as it was cooled to room temperature?

(2)

....

....

....

(ii) How could you show that equilibrium had been established?

(2)

....

....

....

....

(b) The equilibrium concentrations of one experiment are shown in the table below.

$[HI]$ /mol dm^{-3}	$[H_2]$ /mol dm^{-3}	$[I_2]$ /mol dm^{-3}
0.00353	0.00048	0.00048

*(i) The volume of the tube in this experiment was 30 cm^3. Calculate the initial mass of hydrogen iodide. Show your working.

(5)

(ii) Write an expression for the equilibrium constant, K_c, at 700 K.

(1)

(iii) Calculate the value for this equilibrium constant.

(1)

(iv) Does this equilibrium constant have units? Explain your answer.

(1)

....

....

....

....

(c) The equation for the reaction at 700 K can also be written

$$HI(g) \rightleftharpoons \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g)$$

(i) Write the equilibrium constant, K_c', for this reaction.

(1)

(ii) Using the same equilibrium concentrations as below, calculate the equilibrium constant, K_c'.

Deduce the relationship between this value and the value calculated in part (b)(iii).

(2)

[HI] /mol dm^{-3}	[H_2] /mol dm^{-3}	[I_2] /mol dm^{-3}
0.00353	0.00048	0.00048

(d) Consider the following equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(s) + H_2(g)$$

For this reaction $K_p = \dfrac{P_{H_2}}{P_{HI}^2}$

Use the expression for K_p to explain the effect of an increase in total pressure on the position of the equilibrium.

(3)

....

....

....

....

....

....

(Total for Question 11 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass **atomic symbol** name atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	*(18)*
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **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
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	39.9 **Ar** argon 18
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
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] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **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
* Actinide series	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