Please check the examination details below before entering your candidate information

Candidate surname	Other names

Pearson Edexcel International Advanced Level

Centre Number | Candidate Number

Tuesday 29 October 2019

Morning (Time: 1 hour 40 minutes) | Paper Reference **WCH04/01**

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

Candidates must have: Scientific calculator
Data Booklet

Total Marks

Instructions

- Use **black** ink or **black** 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.
- Show all your working in calculations and give units where appropriate.
- Check your answers if you have time at the end.

Turn over ▶

P58273A

1/1/1/1/1/

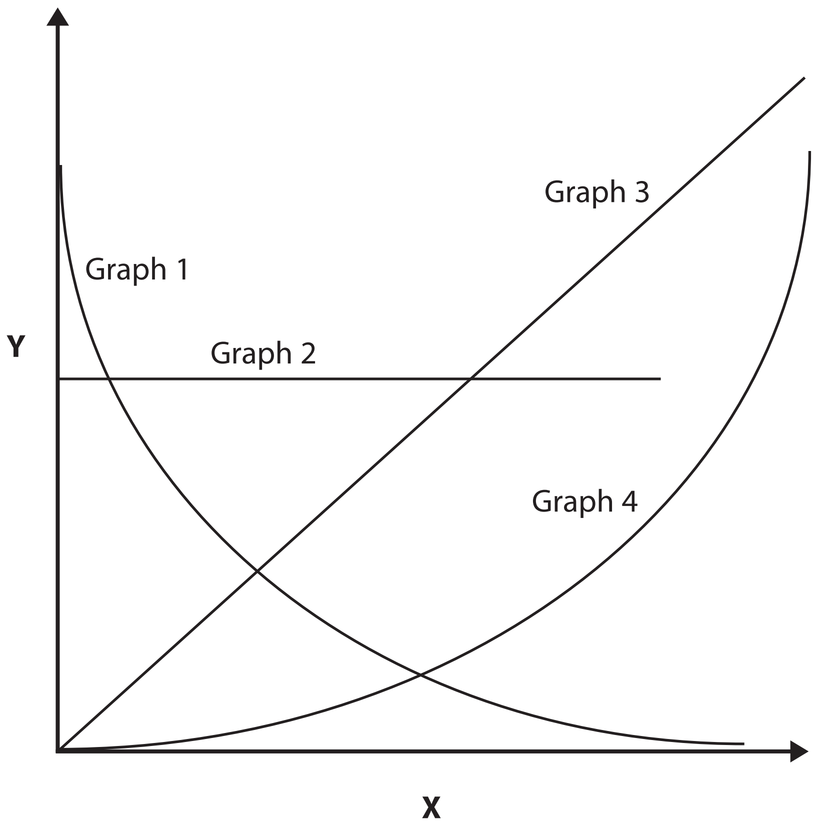
P 5 8 2 7 3 A 0 1 2 8

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 The diagram shows four graphs in which a quantity **Y** has been plotted against a quantity **X**.



(a) Which graph would be obtained when **X** is reactant concentration and **Y** is rate of reaction for a first order reaction?

(1)

☐ **A** Graph 1

☐ **B** Graph 2

☐ **C** Graph 3

☐ **D** Graph 4

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

(b) Which graph would be obtained when **X** is time and **Y** is product concentration for a zero order reaction?

(1)

☒ **A** Graph 1

☒ **B** Graph 2

☒ **C** Graph 3

☒ **D** Graph 4

(c) Which graph would be obtained when **X** is temperature and **Y** is rate of reaction?

(1)

☒ **A** Graph 1

☒ **B** Graph 2

☒ **C** Graph 3

☒ **D** Graph 4

(Total for Question 1 = 3 marks)

2 Hydrogen iodide may be formed from the reaction of hydrogen with iodine.

The transition state is the same in both directions of the equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H_{reaction} = +53\,kJ\,mol^{-1}$$

The activation energy for the forward reaction is 173 kJ mol^{-1}.

The activation energy, in kJ mol^{-1}, for the reverse reaction is

☒ **A** –53

☒ **B** +120

☒ **C** +173

☒ **D** +226

(Total for Question 2 = 1 mark)

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

3 Sodium chloride dissolves in water.

$$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H^\ominus = +3.9\,kJ\,mol^{-1}$$

The best explanation for the fact that sodium chloride dissolves in water spontaneously is that the process has a

☒ **A** low activation energy.

☒ **B** positive enthalpy change.

☒ **C** positive entropy change of the surroundings, $\Delta S^\ominus_{surroundings}$.

☒ **D** positive entropy change of the system, $\Delta S^\ominus_{system}$.

(Total for Question 3 = 1 mark)

---

4 Butane has a higher standard molar entropy than 2-methylpropane at 298 K and 1 atm, when both compounds are gases.

The best explanation for this fact is that butane has

☒ **A** a higher boiling temperature.

☒ **B** a more positive standard molar enthalpy change of formation.

☒ **C** fewer ways of distributing energy quanta.

☒ **D** more ways of distributing energy quanta.

(Total for Question 4 = 1 mark)

---

5 Standard molar entropy is zero for

☒ **A** perfect crystals at absolute zero (0 K).

☒ **B** ideal gases under standard conditions (298 K and 1 atm).

☒ **C** elements in their most stable states under standard conditions.

☒ **D** graphite, containing only the carbon-12 isotope, under standard conditions.

(Total for Question 5 = 1 mark)

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

6 Ethanol is manufactured by the hydration of ethene at 500 K and 60 atm.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \qquad \Delta H^{\ominus} = -53.8\,kJ\,mol^{-1}$$

(a) How does increasing the temperature to 550 K affect the activation energy and equilibrium constant of this reaction?

(1)

	Activation energy	Equilibrium constant
☒ **A**	increases	increases
☒ **B**	decreases	decreases
☒ **C**	unchanged	increases
☒ **D**	unchanged	decreases

(b) How does increasing the pressure to 70 atm affect the rate of the reaction and the equilibrium yield of ethanol?

(1)

	Rate	Equilibrium yield
☒ **A**	increases	increases
☒ **B**	increases	decreases
☒ **C**	decreases	increases
☒ **D**	decreases	decreases

(c) The equilibrium constant for the hydration of ethene is given by the expression

(1)

☒ **A** $K_p = \dfrac{p(C_2H_5OH)}{p(C_2H_4) \times p(H_2O)}$

☒ **B** $K_p = \dfrac{p(C_2H_4) \times p(H_2O)}{p(C_2H_5OH)}$

☒ **C** $K_p = \dfrac{p(C_2H_5OH)}{p(C_2H_4)}$

☒ **D** $K_p = \dfrac{p(C_2H_4)}{p(C_2H_5OH)}$

(Total for Question 6 = 3 marks)

7 The Arrhenius theory defined acids as substances that

☒ **A** have a sour taste.

☒ **B** react with alkalis to form a salt and water only.

☒ **C** produce an excess of hydrogen ions in solution.

☒ **D** accept lone pairs of electrons.

(Total for Question 7 = 1 mark)

8 The dissociation constant of water, K_w , increases with increasing temperature.

Under standard conditions pure water is neutral and has a pH = 7.

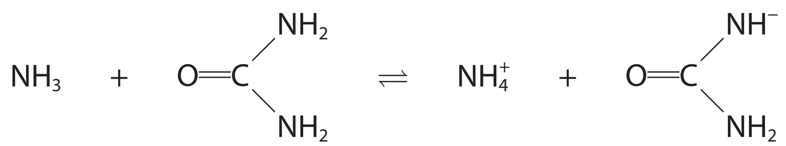
What happens to the acidity and pH of pure water when the temperature is increased?

	Effect of increasing temperature	
	Acidity of water	pH
☒ **A**	increases	increases
☒ **B**	increases	decreases
☒ **C**	remains neutral	increases
☒ **D**	remains neutral	decreases

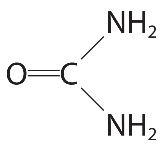
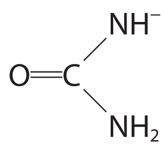
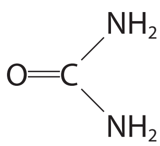
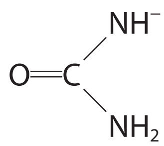
(Total for Question 8 = 1 mark)

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

9 When urea dissolves in liquid ammonia, an acid-base equilibrium is set up.



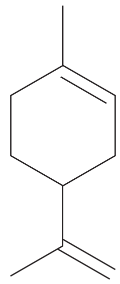
Which species are the Brønsted-Lowry acids in this equilibrium?

	Acid 1	Acid 2
☒ **A**	NH_3	NH_4^+
☒ **B**		NH_4^+
☒ **C**	NH_3	
☒ **D**		

(Total for Question 9 = 1 mark)

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

10 Limonene is a major component of the oil found in citrus fruits.



Limonene

Limonene will show

☒ **A** geometric and optical isomerism.

☒ **B** geometric isomerism only.

☒ **C** optical isomerism only.

☒ **D** neither geometric nor optical isomerism.

(Total for Question 10 = 1 mark)

11 Ethanal has a much higher boiling temperature and is much more soluble in water than propane.

These differences in properties are best explained by the fact that, in addition to London forces, ethanal forms

☒ **A** hydrogen bonds in the liquid state and in aqueous solution.

☒ **B** permanent dipole-dipole forces in the liquid state and hydrogen bonds in aqueous solution.

☒ **C** hydrogen bonds in the liquid state and permanent dipole-dipole forces in aqueous solution.

☒ **D** permanent dipole-dipole forces in the liquid state and in aqueous solution.

(Total for Question 11 = 1 mark)

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

12 Butanone may be converted into propanoic acid by

☒ **A** refluxing with acidified potassium dichromate(VI).

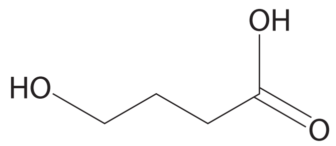
☒ **B** warming with iodine and sodium hydroxide followed by acidifying with sulfuric acid.

☒ **C** heating with hydrogen gas in the presence of a nickel catalyst.

☒ **D** heating with hydrogen cyanide and potassium cyanide followed by refluxing with sulfuric acid.

(Total for Question 12 = 1 mark)

13 The structure of 4-hydroxybutanoic acid is



(a) The presence of the alcohol functional group and the carboxylic acid functional group may be confirmed by reacting under suitable conditions

(1)

☒ **A** a sample of the compound with phosphorus(V) chloride.

☒ **B** a sample of the compound with sodium hydrogencarbonate solution.

☒ **C** separate samples of the compound with ethanol and with ethanoic acid.

☒ **D** separate samples of the compound with acidified potassium dichromate(VI) and with 2,4-dinitrophenylhydrazine.

(b) The high resolution proton nmr spectrum of 4-hydroxybutanoic acid will have

(1)

☒ **A** two singlets, two triplets and one quintet.

☒ **B** two singlets and three triplets.

☒ **C** one singlet, two triplets, one quartet and one quintet.

☒ **D** two singlets, two triplets, one quartet and one quintet.

(Total for Question 13 = 2 marks)

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

14 Transesterification involves reactions in which

☒ **A** alkyl groups of alcohols replace alkyl groups of esters.

☒ **B** alkyl groups of carboxylic acids replace alkyl groups of esters.

☒ **C** trans isomers of long-chain esters are formed.

☒ **D** diacyl chlorides and diols combine to form polyesters.

(Total for Question 14 = 1 mark)

---

15 The main characteristic of HPLC is the use of

☒ **A** polymeric liquids.

☒ **B** high pressures.

☒ **C** helium-cadmium lasers.

☒ **D** long columns.

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

BLANK PAGE

SECTION B

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

16 Ammonium nitrate, NH_4NO_3, is used as a fertiliser.

(a) When heated gently at 160 °C, ammonium nitrate decomposes.

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g) \qquad \Delta H^{\ominus} = -36.0\,kJ\,mol^{-1}$$

(i) Predict the sign of the entropy change in the system, $\Delta S^{\ominus}_{system}$.
Justify your answer.

(1)

....

....

....

(ii) Calculate the entropy change in the system, $\Delta S^{\ominus}_{system}$, for the decomposition of ammonium nitrate, using data from your Data Booklet.
Include a sign and units with your answer.

(3)

(iii) Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, for the decomposition of ammonium nitrate at 160 °C.
Include a sign and units with your answer.

(3)

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

(iv) Use your answers to (a)(ii) and (a)(iii) to calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for the decomposition of ammonium nitrate.
Give your answer to an appropriate number of significant figures and include a sign and units with your answer.

(2)

(b) When ammonium nitrate is heated rapidly, it decomposes as shown.

$$NH_4NO_3(s) \rightarrow N_2(g) + 2H_2O(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = -118.0\,kJ\,mol^{-1}$$

(i) The total entropy change, ΔS_{total}, for this decomposition of ammonium nitrate is $+555\,J\,K^{-1}\,mol^{-1}$.

Calculate the equilibrium constant for this decomposition.
Units are not required.

(2)

*(ii) Explain, in terms of entropy, how this equilibrium constant for the complete decomposition of ammonium nitrate would be affected if the temperature was increased. No calculation is required.

(2)

....

....

....

....

....

....

(Total for Question 16 = 13 marks)

P 5 8 2 7 3 A 0 1 3 2 8

17 The reaction of 2-bromobutane with aqueous alkali is a nucleophilic substitution.

$$C_4H_9Br + NaOH \rightarrow C_4H_9OH + NaBr$$

Depending on the conditions, the mechanism of this reaction may be S_N1 or S_N2.

(a) Experiments were carried out to determine the rate equation for a reaction of 2-bromobutane with aqueous sodium hydroxide.

In each experiment, the reactants were mixed and the concentration of 2-bromobutane was measured at various times as the reaction proceeded.

The initial rate of the reaction was determined using these data.

(i) Describe how the **initial** rate would be determined from the results of one experiment.

(3)

....

....

....

....

....

....

....

....

....

(ii) Give a reason why the concentration of sodium hydroxide used was very much greater than the concentration of 2-bromobutane.

(1)

....

....

....

....

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(b) The results of a set of experiments are shown.

Experiment	Initial $[C_4H_9Br]$ / mol dm^{-3}	Initial [NaOH] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.020	1.0	1.5×10^{-5}
2	0.030	1.0	2.3×10^{-5}
3	0.040	2.0	5.9×10^{-5}

(i) By referring to the data in the table, show that the reaction was first order with respect to both C_4H_9Br and NaOH.

(2)

(ii) Calculate the rate constant for the reaction.
Use the data from experiment 1 and include units with your answer.

(2)

(c) (i) State why the reaction of 2-bromobutane with aqueous sodium hydroxide being second order indicates an S_N2 mechanism.

(1)

....

....

....

(ii) Draw the first step of the mechanism, showing the transition state in the S_N2 mechanism for the reaction of 2-bromobutane with aqueous sodium hydroxide. Include curly arrows, and any relevant dipoles and lone pairs of electrons.

(3)

(d) 2-bromobutane and butan-2-ol are chiral molecules.

(i) State the meaning of the term chiral molecule.

(1)

....

....

....

....

*(ii) When a single enantiomer (optical isomer) of 2-bromobutane reacts with aqueous alkali, the stereochemistry of the butan-2-ol formed depends on whether the mechanism is S_N1 or S_N2.

Explain how the stereochemistry of the butan-2-ol differs with the different mechanisms.

(4)

....

....

....

....

....

....

....

....

....

....

....

....

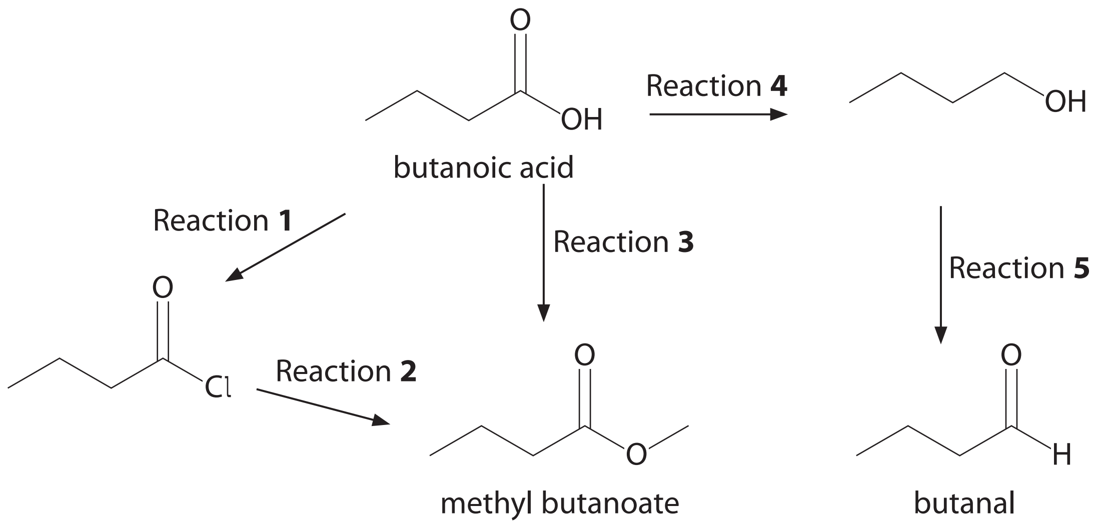
....

....

(Total for Question 17 = 17 marks)

18 Butanoic acid is found in milk, butter and cheese and its name comes from the Latin word for butter. It has an unpleasant smell, which can be detected at very low concentrations, whereas the esters of butanoic acid, such as methyl butanoate, have pleasant smells and tastes, and are added to food and perfumes.

(a) Some reactions of butanoic acid are shown.



(i) Identify, by name or formula, the reagents and any essential conditions for Reactions **1** to **4**.

(5)

Reaction **1** ....

Reaction **2** ....

Reaction **3** ....

....

Reaction **4** ....

....

(ii) The reagents used in Reaction **5** are potassium dichromate(VI) and sulfuric acid.

State how this reaction must be carried out to ensure that the main product is butanal.

(1)

....

....

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

P 5 8 2 7 3 A 0 1 8 2 8

(iii) Give **one** advantage and **one** disadvantage of preparing methyl butanoate using Reactions **1** and **2** rather than Reaction **3**.

(2)

(iv) Suggest why butanal is **not** made from butanoic acid in a single step.

(1)

(b) Give **two** ways in which the infrared spectra of butanoic acid and methyl butanoate differ, other than in their fingerprint region.
Quote values from your Data Booklet for the wavenumber ranges of specific bonds.

(2)

(c) Butanoic acid can be detected by animals with a good sense of smell at concentrations of 10 parts of butanoic acid vapour per billion (1×10^9) of air at room temperature and pressure (r.t.p.).

Calculate the minimum concentration, in mol dm^{-3}, of butanoic acid that can be detected by these animals.

(2)

[Molar volume of gases at r.t.p. = 24.0 $dm^3 mol^{-1}$]

(Total for Question 18 = 13 marks)

19 Heating fructose with hydrochloric acid produced an aliphatic compound, **G**, which has five carbon atoms in an **unbranched** chain.

G gave an orange precipitate with 2,4-dinitrophenylhydrazine but **no reaction** when warmed with ammoniacal silver nitrate. Addition of **G** to sodium hydrogencarbonate solution resulted in vigorous effervescence.

In the mass spectrum of **G**, the molecular ion peak was at $m/e = 116$.

Draw the **three** possible structures of **G**. Explain your reasoning.

(7)

(Total for Question 19 = 7 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

20 Methanoic acid, HCOOH, is a weak acid that is present in the stings of ants and nettles. It is used as a preservative and antibacterial agent in livestock feed.

(a) An aqueous solution of methanoic acid has a concentration of $30\,g\,dm^{-3}$.

(i) Write the equation for the dissociation of methanoic acid in water. State symbols are not required.

(1)

(ii) Write the expression for K_a for methanoic acid.

(1)

(iii) Calculate the pH of a solution of methanoic acid with a concentration of $30\,g\,dm^{-3}$.

[K_a of methanoic acid $= 1.70 \times 10^{-4}\,mol\,dm^{-3}$]

(4)

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(iv) State **two** approximations used in the calculation of the pH in (a)(iii).

(2)

(b) A solution which contains both methanoic acid and sodium methanoate acts as a buffer.

(i) State the meaning of the term buffer.

(2)

*(ii) Explain how a solution which contains both methanoic acid and sodium methanoate acts as a buffer.

(4)

(c) A buffer solution **Q** is prepared by dissolving 1.25 mol of methanoic acid and 1.50 mol of sodium methanoate in distilled water and making up the solution to 1.00 dm^3.

(i) Calculate the pH of **Q**.

[K_a of methanoic acid = 1.70×10^{-4} mol dm^{-3}]

(3)

(ii) Calculate the pH of **Q** after the addition of 2.0 g of sodium hydroxide. Assume that the volume of **Q** is unchanged at 1.00 dm^3.

(3)

(Total for Question 20 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS

BLANK PAGE

BLANK PAGE

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

BLANK PAGE

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