Write your name here

Surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number

Candidate Number

Chemistry

Advanced

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

Monday 13 January 2014 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

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.

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6/6/6/6/2/
P 4 4 4 5 1 A 0 1 2 4

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 Select the correct states for the stationary and mobile phases in HPLC.

	Stationary phase	Mobile phase
☒ **A**	liquid	gas
☒ **B**	gas	liquid
☒ **C**	solid	liquid
☒ **D**	solid	gas

(Total for Question 1 = 1 mark)

---

2 This question is about low resolution proton nuclear magnetic resonance spectroscopy, NMR.

(a) NMR involves the interaction of hydrogen nuclei, ^{1}H, in the presence of a powerful magnetic field with

(1)

☒ **A** microwaves.

☒ **B** radio waves.

☒ **C** ultraviolet radiation.

☒ **D** X-rays.

(b) Which of the following has **two** peaks in its low resolution NMR spectrum?

(1)

☒ **A** Dichloromethane, CH_2Cl_2

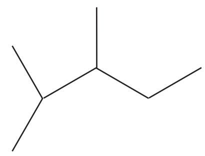
☒ **B** Ethane, CH_3CH_3

☒ **C** Methanal, HCHO

☒ **D** Methanol, CH_3OH

(c) NMR spectra depend on the number of different hydrogen environments in a molecule.

How many different hydrogen environments are there in a molecule of 2,3-dimethylpentane, the skeletal formula of which is shown below?



(1)

☒ **A** Seven

☒ **B** Six

☒ **C** Five

☒ **D** Four

(Total for Question 2 = 3 marks)

3 Energy is given out when one mole of gaseous strontium ions is hydrated.

$$Sr^{2+}(g) + aq \rightarrow Sr^{2+}(aq)$$

This reaction is less exothermic than the corresponding reaction for magnesium ions, $Mg^{2+}(g)$, because

☒ **A** the sum of the first two ionization energies of magnesium is more than that of strontium.

☒ **B** the lattice energies of magnesium compounds are more exothermic than the lattice energies of corresponding strontium compounds.

☒ **C** the solubility of magnesium hydroxide is less than the solubility of strontium hydroxide.

☒ **D** the ionic radius of Mg^{2+} is less than the ionic radius of Sr^{2+}.

(Total for Question 3 = 1 mark)

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

4 Use the data below to calculate the enthalpy change of solution of magnesium chloride.

Lattice energy of magnesium chloride	-2526 kJ mol^{-1}
Enthalpy of hydration of Mg^{2+}(g)	-2003 kJ mol^{-1}
Enthalpy of hydration of Cl^{-}(g)	-340 kJ mol^{-1}

The enthalpy change of solution of magnesium chloride, in kJ mol^{-1}, is

☒ **A** +183

☒ **B** +157

☒ **C** −157

☒ **D** −183

(Total for Question 4 = 1 mark)

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5 In kinetics, the progress of a reaction can be followed by

A colorimetry.

B measurement of optical activity.

C measurement of change in mass.

D quenching with ice-cold water followed by titration with acid.

Which method would be most suitable to investigate the rates of the following reactions?

(a) $CH_3CH_2Br(l) + OH^-(aq) \rightarrow CH_3CH_2OH(l) + Br^-(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $I_2(aq) + CH_3COCH_3(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 5 = 2 marks)

6 A halogenoalkane reacts with hydroxide ions to form an alcohol.
Which of the following statements is true if the reaction is first order?

☒ **A** Increasing the concentration of hydroxide ions increases the rate of the reaction.

☒ **B** The rate equation for the reaction is rate = [halogenoalkane].

☒ **C** The reaction mechanism is S_N1.

☒ **D** The reaction involves the formation of a transition state.

(Total for Question 6 = 1 mark)

---

7 The rate equation for the oxidation of bromide ions by bromate(V) ions in acid solution is shown below.

$$\text{Rate} = k[BrO_3^-(aq)][Br^-(aq)][H^+(aq)]^2$$

If the concentrations of all three reactants double, the rate will increase by a factor of

☒ **A** 2

☒ **B** 4

☒ **C** 8

☒ **D** 16

(Total for Question 7 = 1 mark)

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8 The gaseous first order reaction, A $\rightarrow$ B + C, was found to have a half-life of 20 s when the initial pressure of A was 2 atm.

When the initial pressure of A is increased to 4 atm, the half-life is

☒ **A** 10 s

☒ **B** 20 s

☒ **C** 40 s

☒ **D** 400 s

(Total for Question 8 = 1 mark)

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

9 The equation for the equilibrium between nitrogen and oxygen may be written in two ways.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ Equilibrium constant K_1

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ Equilibrium constant K_2

The standard enthalpy change, $\Delta H^{\ominus}$, for the reaction as shown in the first equation is $+180\ kJ\ mol^{-1}$.

(a) What is the standard enthalpy change for the reaction as shown in the second equation?

(1)

☒ **A** $+45\ kJ\ mol^{-1}$

☒ **B** $+90\ kJ\ mol^{-1}$

☒ **C** $+180\ kJ\ mol^{-1}$

☒ **D** $+360\ kJ\ mol^{-1}$

(b) The equilibrium mole fraction of NO is increased by

(1)

☒ **A** increasing the temperature.

☒ **B** decreasing the temperature.

☒ **C** increasing the total pressure.

☒ **D** decreasing the total pressure.

(c) Which of the following expressions is correct?

(1)

☒ **A** $K_1 = K_2$

☒ **B** $K_1 = 2K_2$

☒ **C** $K_1 = K_2^2$

☒ **D** $K_1 = K_2^{\frac{1}{2}}$

(Total for Question 9 = 3 marks)

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

10 Which of the following solutions, when mixed, would make a buffer with pH greater than 7?

☒ **A** Ethanoic acid and sodium ethanoate.

☒ **B** Sodium hydroxide and sodium chloride.

☒ **C** Ammonia and sodium chloride.

☒ **D** Ammonia and ammonium chloride.

(Total for Question 10 = 1 mark)

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11 In acid solution, methyl orange is red. When an alkali is added, the solution turns yellow because the indicator

☒ **A** gains OH^- ions to form cations.

☒ **B** loses H^+ ions to form cations.

☒ **C** gains OH^- ions to form anions.

☒ **D** loses H^+ ions to form anions.

(Total for Question 11 = 1 mark)

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12 Which method may be used to make a carboxylic acid in a single reaction?

☒ **A** Hydrolysis of an ester with sodium hydroxide.

☒ **B** Hydrolysis of an ester with hydrochloric acid.

☒ **C** Reaction of acidified potassium manganate(VII) with an alkene.

☒ **D** Reaction of an acyl chloride with ammonia.

(Total for Question 12 = 1 mark)

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13 Which of the following pairs of compounds would react to form a polyester?

☒ **A** Ethanol and benzoic acid.

☒ **B** Ethane-1,2-diol and benzoic acid.

☒ **C** Ethanol and benzene-1,4-dicarboxylic acid.

☒ **D** Ethane-1,2-diol and benzene-1,4-dicarboxylic acid.

(Total for Question 13 = 1 mark)

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14 Which of the following compounds has both optical and *E-Z* isomers?

- ☒ **A** $CH_3CH{=}CHCH_2CH_3$
- ☒ **B** $CH_3CHBrCH{=}C(CH_3)_2$
- ☒ **C** $CHBr{=}CHCHBrCH_3$
- ☒ **D** $CH_2{=}CHCHBrCH_3$

(Total for Question 14 = 1 mark)

15 At which of the following *m/e* values would you **not** expect to find a peak in the mass spectrum of ethanoyl chloride?

- ☒ **A** 35.5
- ☒ **B** 37
- ☒ **C** 43
- ☒ **D** 78

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

16 This question is about the reaction scheme below which may be used to convert propanoic acid to ethyl butanoate in five steps.

CH_3CH_2COOH

↓ Step **1**

$CH_3CH_2CH_2OH$

↓ Step **2**

$CH_3CH_2CH_2Cl$

↓ Step **3**

Butanenitrile

↓ Step **4**

$CH_3CH_2CH_2COOH$

↓ Step **5**

$CH_3CH_2CH_2COOCH_2CH_3$

(a) Give the structural formula for butanenitrile, showing any multiple bonds.

(1)

....

(b) Give the formula of the reagent needed for each of the Steps **1**, **2**, **4** and **5**. The reagent for Step **3** has been given.

Conditions and solvents are not required.

(4)

Step **1** ....

Step **2** ....

Step **3** KCN

Step **4** ....

Step **5** ....

(c) Write the equation for the neutralization of sodium carbonate by butanoic acid. State symbols are not required.

(2)

(d) State **two** differences between the **low** resolution proton nuclear magnetic resonance spectra of butan-1-ol and butanoic acid.

(2)

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....

(e) Give **two** differences between the infrared spectra of butan-1-ol and butanoic acid, mentioning any bonds involved with their wavenumber ranges.

(2)

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....

(f) Give the skeletal formula of ethyl butanoate, $CH_3CH_2CH_2COOCH_2CH_3$.

(1)

(g) Suggest the reagents required for a different, two-step method which could be used instead of the single step method you have given for Step **5** in part (b), to obtain ethyl butanoate from butanoic acid.

What is the advantage of using this alternative method?

(3)

Reagent for first step ....

Reagent for second step ....

Advantage ....

....

....

(Total for Question 16 = 15 marks)

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17 The decomposition of dinitrogen pentoxide in a suitable solvent produces nitrogen dioxide, which remains in solution, and oxygen gas which is given off.

The overall equation for the reaction is:

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

(a) Draw a diagram of the apparatus you would use to follow the rate of this reaction and give the measurements you would make.

(3)

....

....

(b) (i) The rate equation for this reaction is:

$$\text{Rate} = k[N_2O_5]$$

What are the units of the rate constant, k?

(1)

....

*(ii) A suggested mechanism for the reaction is:

1st Step	$N_2O_5 \rightarrow NO_2 + NO_3$	....
2nd Step	$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	....
3rd Step	$NO + N_2O_5 \rightarrow 3NO_2$	....

Label these reactions, fast or slow, and explain how your labelling is consistent with the rate equation for the reaction.

(3)

....

....

....

....

(c) The rate constant, *k*, was calculated at different temperatures.

(i) Suggest a practical method for keeping the temperature constant.

(1)

....

....

(ii) The table shows the measurements of the rate constant, *k*, at different temperatures. Some of the corresponding values for reciprocal of temperature and ln *k* are also shown.

Complete the table by calculating the missing values.

(2)

T/K	k	$\frac{1}{T}$ / K^{-1}	ln k
280	3.80×10^{-6}	3.57×10^{-3}	−12.5
290	1.65×10^{-5}	3.45×10^{-3}	−11.0
300	6.87×10^{-5}	3.33×10^{-3}	−9.6
310	2.48×10^{-4}	3.23×10^{-3}	−8.3
320	8.65×10^{-4}		

*(iii) Plot a graph of ln *k* on the vertical axis against 1/T on the horizontal axis.

Calculate the gradient of your graph and use this to calculate the activation energy, E_a. Remember to include units with your answer, which should be given to three significant figures.

The Arrhenius equation can be expressed as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{a constant}$$

[Gas constant , $R = 8.31$ J K^{-1} mol^{-1}]

(7)

(Total for Question 17 = 17 marks)

Turn over

18 (a) Ammonia is a weak alkali. Consider the following equilibrium that exists in an aqueous solution of ammonia.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}\ \text{mol dm}^{-3}$$

The base dissociation constant, K_b, for this reaction is

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

(i) Calculate the concentration of hydroxide ions at equilibrium in a 4.0 mol dm^{-3} aqueous solution of ammonia.

Assume that the concentration of ammonia at equilibrium is 4.0 mol dm^{-3} and that the equilibrium concentration of hydroxide ions is equal to the equilibrium concentration of ammonium ions.

(2)

(ii) Calculate the pH of 4.0 mol dm^{-3} ammonia solution.

[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K]

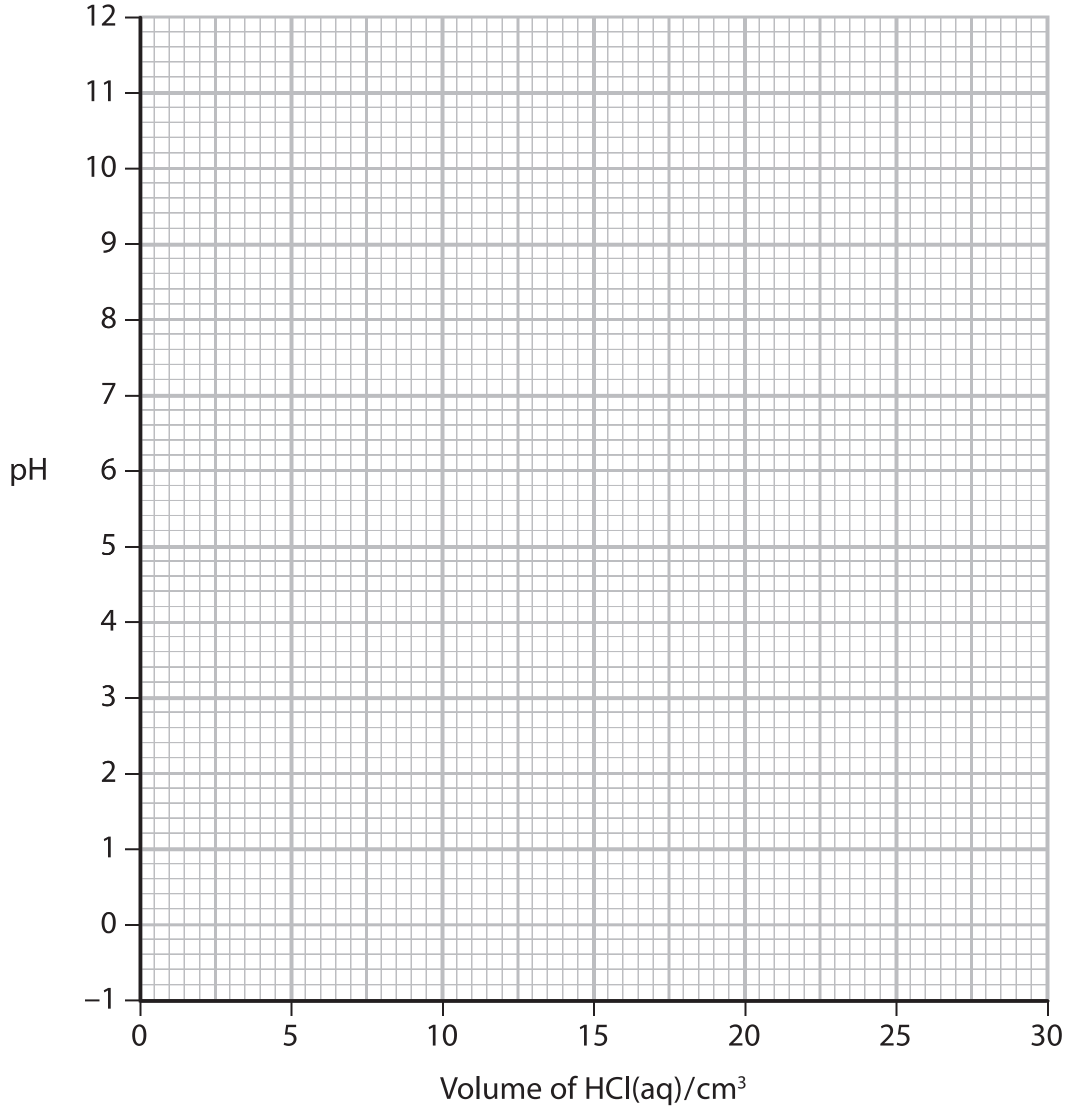
(2)

(b) (i) Calculate the pH of 4.0 mol dm^{-3} hydrochloric acid, assuming it is fully ionized.

(1)

(ii) Draw the titration curve, showing the change in pH when 4.0 mol dm^{-3} hydrochloric acid is added to 25 cm^3 of 4.0 mol dm^{-3} ammonia solution, until 30 cm^3 of the acid have been added.

(4)



*(iii) Select a suitable indicator for this titration, giving the colour change you would expect to see.

Justify your selection.

(3)

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(c) The titration above can be used to determine the concentration of ammonia solution when ammonia is distributed between the two immiscible solvents, trichloromethane and water.

An experiment is carried out to find the equilibrium constant for the reaction:

$$NH_3(CHCl_3) \rightleftharpoons NH_3(aq)$$

75 cm^3 of 4.0 mol dm^{-3} aqueous ammonia solution and 75 cm^3 of the trichloromethane are shaken together. The two liquids are allowed to separate and 25.0 cm^3 of the aqueous layer is taken and titrated with 4.0 mol dm^{-3} hydrochloric acid. The whole procedure is repeated.

The average titre is 24.0 cm^3.

(i) Calculate the number of moles of ammonia, and hence the concentration of ammonia, in mol dm^{-3}, in the aqueous layer.

(3)

(ii) The initial volumes of the two solvents are the same.

Hence deduce the concentration of ammonia in the trichloromethane layer in mol dm^{-3}.

(1)

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(iii) Write the expression for the equilibrium constant, K_c, for this reaction and calculate its value.

(1)

(iv) Suggest why ammonia is much more soluble in water than in trichloromethane.

(1)

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(Total for Question 18 = 18 marks)

TOTAL FOR SECTION B = 50 MARKS

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SECTION C

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

19 This question is about sucrose, the chemical commonly known as sugar. Some thermochemical data for sucrose and oxygen are given in the table below.

Standard entropy of sucrose, $S^{\ominus}$ [$C_{12}H_{22}O_{11}(s)$]	+392.4 J mol^{-1} K^{-1}
Standard enthalpy change of combustion of sucrose, $\Delta H_c^{\ominus}$	–5639.7 kJ mol^{-1}
Standard entropy of oxygen, $S^{\ominus}$ [$\frac{1}{2}O_2(g)$]	+102.5 J mol^{-1} K^{-1}

The equation for the complete combustion of sucrose, $C_{12}H_{22}O_{11}$, is

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$$

(a) (i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this combustion, using the data given in the table and your Data Booklet. Include a sign and units in your answer.

(3)

(ii) Calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this combustion at 298 K. Include a sign and units in your answer.

(2)

(iii) Calculate the total standard entropy change for the combustion, $\Delta S^{\ominus}_{total}$, at 298 K.

State the significance of your answer.

(2)

....

....

(iv) State and explain the effect, if any, of increasing the temperature on $\Delta S^{\ominus}_{surroundings}$, $\Delta S^{\ominus}_{total}$ and the extent of the reaction.

(3)

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(v) Icing sugar can be hazardous when it is being finely powdered in a factory.

Explain why sucrose is stable at room temperature, in spite of your answer to part (iii), but its manufacture is hazardous.

(2)

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....

....

....

(vi) Suggest **two** risks associated with high levels of sucrose in the diet.

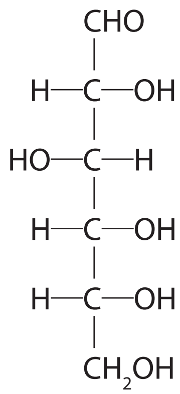
(2)

....

....

(b) Sucrose can be hydrolysed by warming with dilute hydrochloric acid to form glucose and fructose.

In aqueous solution, a structure of glucose is



(i) Circle or mark with an asterisk (*) all the chiral centres on the structure of glucose.

(2)

(ii) State the physical property associated with molecules which have chiral centres.

(1)

(iii) State what change you would expect to see when glucose is boiled with Benedict's or Fehling's solutions.

Explain the chemistry involved in this reaction.

(3)

(Total for Question 19 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (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

Series														
* 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