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 **6CH04/01**

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.

Turn over ▶

6/6/6/6/3/e2/

P 4 2 9 7 2 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 This question is about four organic compounds, each containing two carbon atoms.

A CH_3CH_2OH

B CH_3CHO

C CH_3COOH

D CH_3COCl

(a) Which is oxidized by ammoniacal silver nitrate?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which has the highest boiling temperature?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) 0.01 mol of each compound is heated separately with excess acidified sodium dichromate(VI).

Which compound reduces the largest amount of sodium dichromate(VI)?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

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

(1)

☒ **A**

☒ **B**

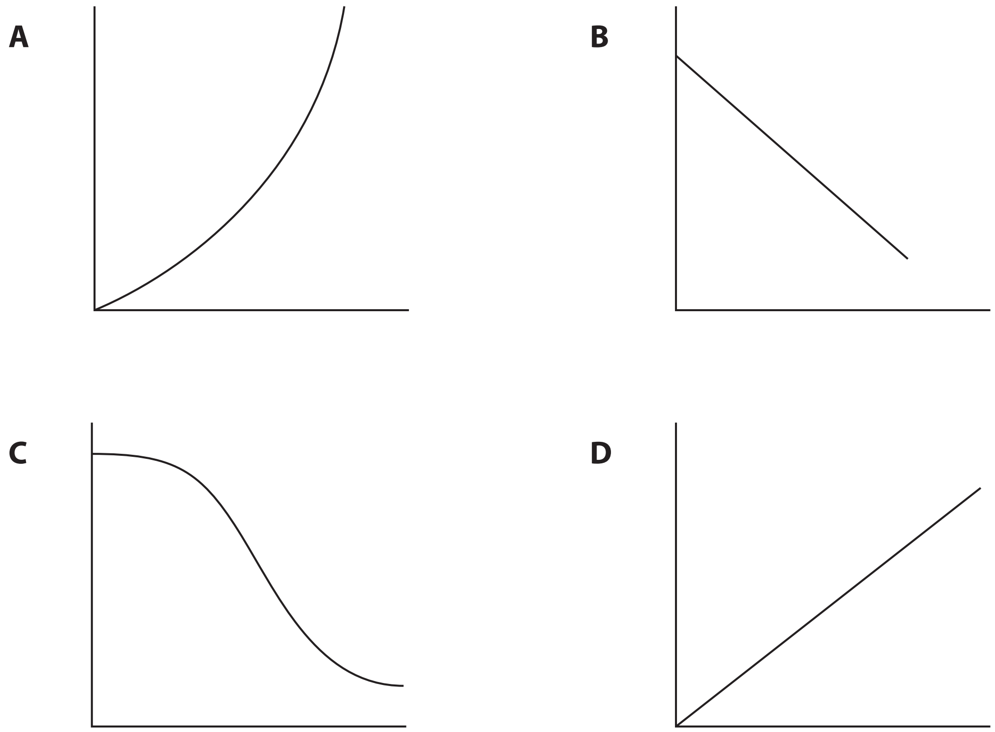
☒ **C**

☒ **D**

(Total for Question 1 = 4 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 the concentration of a reactant, on the vertical axis, against time 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 concentration of a reactant for a **first** order reaction?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) 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**

(d) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a reaction which is catalysed by a product?

(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 9 for use in a school laboratory?

☒ **A** Ethanoic acid and sodium ethanoate

☒ **B** Sodium chloride and sodium hydroxide

☒ **C** Hydrocyanic acid and sodium cyanide

☒ **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 Select the correct pH for each of the following solutions.

(a) 2 mol dm^{-3} nitric acid.

(1)

☒ **A** –2

☒ **B** –0.3

☒ **C** +0.3

☒ **D** +2

(b) 0.10 mol dm^{-3} barium hydroxide, $Ba(OH)_2$. $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}.

(1)

☒ **A** 13.0

☒ **B** 13.3

☒ **C** 13.7

☒ **D** 14.3

(c) A mixture of 20 cm^3 of 1.0 mol dm^{-3} hydrochloric 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 Ammonia reacts with water in a reversible reaction. Which are the Brønsted-Lowry bases?

☒ **A** H_2O and OH^-

☒ **B** NH_3 and OH^-

☒ **C** NH_4^+ and H_2O

☒ **D** NH_4^+ and NH_3

(Total for Question 5 = 1 mark)

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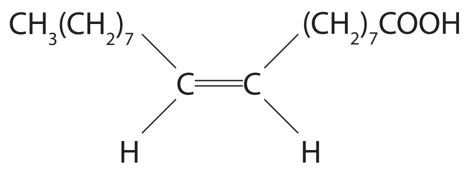
6 The formula for oleic acid, which is present in fingerprints, is shown below.



(a) The systematic name for oleic acid is **(1)**

☒ **A** *E*-octadec-9-enoic acid.

☒ **B** *Z*-octadec-9-enoic acid.

☒ **C** *E*-octadec-8-enoic acid.

☒ **D** *Z*-octadec-8-enoic acid.

(b) Which intermolecular forces are present between oleic acid molecules? **(1)**

☒ **A** Hydrogen bonds only.

☒ **B** Hydrogen bonds and permanent dipole-dipole forces only.

☒ **C** Hydrogen bonds, permanent dipole-dipole forces and London forces.

☒ **D** Hydrogen bonds and London forces only.

(c) Which of the following species is most likely to cause a peak at *m/e* = 45 in the mass spectrum of oleic acid? **(1)**

☒ **A** CH_2CH_2OH

☒ **B** $CH_2CH_2OH^+$

☒ **C** COOH

☒ **D** $COOH^+$

(d) What would you expect to see if oleic acid is tested separately with bromine water and with phosphorus(V) chloride, PCl_5? **(1)**

	Bromine water	Phosphorus(V) chloride, PCl_5
☒ **A**	Decolorises	Steamy fumes
☒ **B**	No colour change	No visible change
☒ **C**	Decolorises	No visible change
☒ **D**	No colour change	Steamy fumes

(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 **increase** the equilibrium yield of methane?

(1)

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

☒ **B** Decreasing both the temperature and the pressure.

☒ **C** Increasing both the temperature and the pressure.

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

(b) Which of the following would **decrease** 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)

---

8 When one optically active isomer of 3-chloro-3-methylhexane reacts with hydroxide ions to form 3-methylhexan-3-ol, a racemic mixture forms because

☒ **A** 3-chloro-3-methylhexane forms a carbocation intermediate.

☒ **B** the reaction is a nucleophilic substitution.

☒ **C** 3-chloro-3-methylhexane forms a five-bonded transition state.

☒ **D** 3-methylhexan-3-ol contains a chiral carbon.

(Total for Question 8 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

9 This question is about magnesium chloride, $MgCl_2$.

It can be formed by burning magnesium in chlorine.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s) \qquad \Delta S^{\ominus}_{surroundings} = +2152 \text{ J mol}^{-1}\text{ K}^{-1}$$

Remember to 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 mol chlorine molecules, Cl_2, is $+165 \text{ J mol}^{-1}\text{ K}^{-1}$. Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, 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 $\text{J mol}^{-1}\text{ K}^{-1}$, 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) 0.0300 mol of magnesium chloride, prepared by burning magnesium in chlorine, is added to 51.5 cm^3 of water.
50.0 cm^3 of 1.00 mol dm^{-3} solution is formed, and the temperature rise, ΔT, is 22.5°C.

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

Energy transferred in joules = volume of **solution** $\times$ 4.2 $\times$ ΔT

(1)

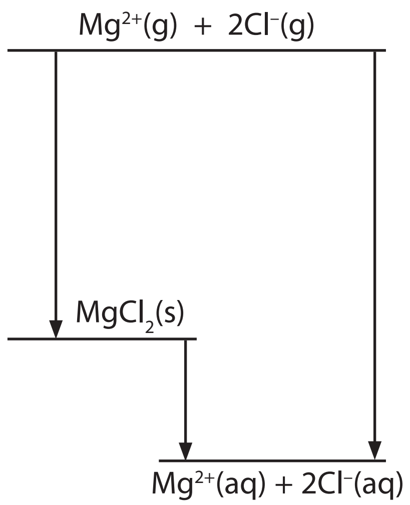
(ii) Calculate the enthalpy change of solution, $\Delta H_{solution}$, of magnesium chloride in kJ mol^{-1}.

(2)

*(iii) The enthalpy change of hydration of $Mg^{2+}(g)$ is –1920 kJ mol^{-1}.

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

(3)



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

(iv) Draw a diagram to represent a hydrated chloride ion.

(1)

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

(2)

Temperature increases ....

....

....

Volume decreases ....

....

....

(Total for Question 9 = 17 marks)

10 A flow chart for making 2-hydroxy-2-methylbutanoic acid from butan-2-ol is shown below.

$CH_3CH_2CH(OH)CH_3$

↓ **Step 1**

$CH_3CH_2COCH_3$

↓ **Step 2**

$CH_3CH_2C(CH_3)(OH)CN$

↓ **Step 3**

$CH_3CH_2C(CH_3)(OH)COOH$

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

(2)

....

....

....

(ii) Butanone is formed in **Step 1**.
Give a chemical test to identify the carbonyl group and a further test to show the presence of the $H_3C–C(=O)–$ group.

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

(4)

Carbonyl group ....

....

....

....

$H_3C–C(=O)–$ group ....

....

....

....

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

Give the mechanism for this reaction.

(3)

*(ii) By considering the mechanism of the reaction, explain why the addition of hydrogen cyanide to butanone gives a solution which has no effect on the plane of polarization of plane-polarized light.

(3)

....

....

....

....

....

....

(c) (i) 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-methylbutanoic acid.

(1)

....

....

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

Give the chemical shift you would expect for this peak.

(1)

....

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

(1)

....

....

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

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

(2)

(Total for Question 10 = 18 marks)

11 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 persulfate 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 the 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 persulfate, but the same volumes and concentrations of sodium thiosulfate solution and potassium iodide 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 happen 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)

....

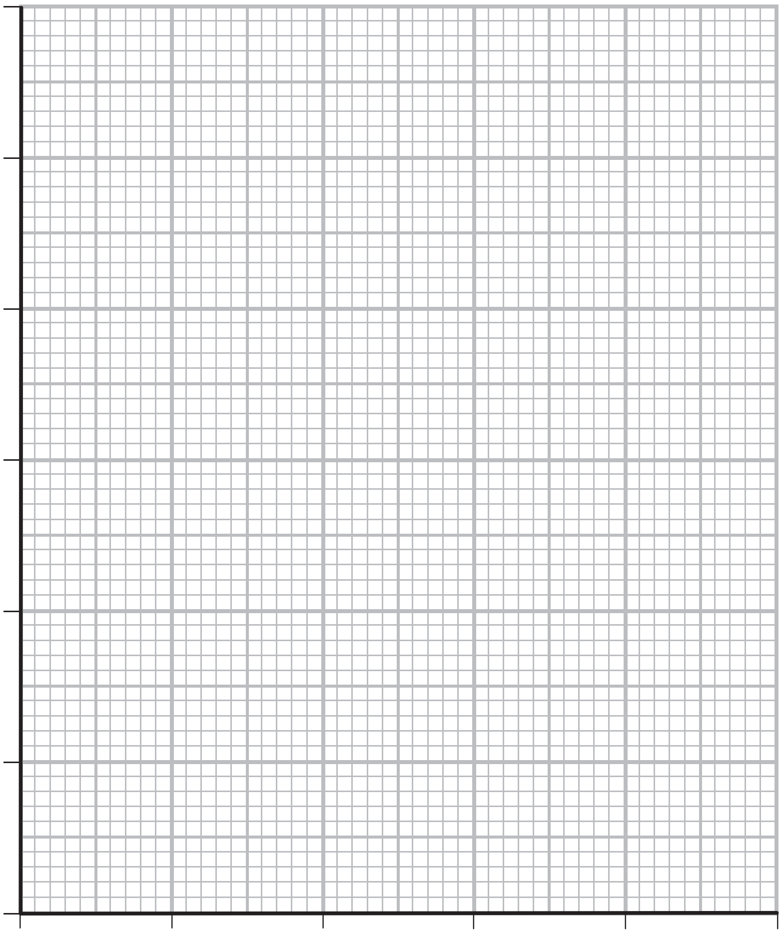
....

(c) The results obtained from the experiment in part (b) were tabulated as follows.

$[S_2O_8^{2-}]$ /mol dm^{-3}	Time /s	1/time /s^{-1}
0.0100	40.0	0.0250
0.0090	44.4	0.0225
0.0075	53.3	0.0188
0.0060	66.7	0.0150

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

(2)



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

Deduce the order of the reaction with respect to persulfate ions.

Justify your answer.

(2)

....

....

....

....

(iii) The reaction is first order with respect to iodide 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	0.0250	3.41×10^{-3}	−3.69
303	0.0500	3.30×10^{-3}	−3.00

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

(3)

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

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

(1)

....

....

....

(Total for Question 11 = 14 marks)

TOTAL FOR SECTION B = 49 MARKS

SECTION C

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

12 This question is about an experiment to determine the equilibrium constant, K_c, for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water.

Two sealed test tubes were prepared.

The first test tube contained 0.0400 mol ethanoic acid, 0.0400 mol of ethanol and 0.20 cm^3 of concentrated hydrochloric acid.

The second test tube contained 0.0400 mol ethyl ethanoate, 0.0400 mol of water and 0.20 cm^3 of concentrated hydrochloric acid.

After standing at 25°C for two weeks, to ensure equilibrium is reached, the contents of each test tube were separately titrated with 0.200 mol dm^{-3} sodium hydroxide solution.

0.20 cm^3 of concentrated hydrochloric acid was also titrated with the same sodium hydroxide solution.

(a) (i) Using data from the Data Booklet, calculate the volume, in cm^3, of 0.0400 mol of ethanoic acid.

(2)

(ii) What would be the best piece of apparatus to measure out the volumes of the liquids for the sealed test tubes?

(1)

....

(iii) Suggest a reason why the test tubes were sealed.

(1)

....

....

(iv) Suggest a suitable indicator for the titration of the equilibrium mixture in either test tube, with the expected colour change. Justify your suggestion.

(3)

Indicator ....

Colour change from .... to ....

Justification ....

....

(b) In this experiment, the following titres were obtained.

Titration	Volume of 0.200 mol dm^{-3} sodium hydroxide solution/cm^3
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm^3 concentrated hydrochloric acid	11.70

(i) Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae. State symbols are not required.

(1)

(ii) Calculate the number of moles of ethanoic acid present at equilibrium in the first test tube.

(2)

(iii) Deduce the number of moles of ethanol present at equilibrium in the first test tube.

(1)

(iv) Calculate the number of moles of ethyl ethanoate formed at equilibrium in the first test tube.

(1)

(v) Write an expression for the equilibrium constant, K_c, for the reaction. Assuming the number of moles of water and ethyl ethanoate present at equilibrium are the same, calculate the equilibrium constant, K_c.

(2)

(vi) Explain why the equilibrium constant for this reaction has no units.

(1)

....

....

(vii) Why, in fact, is the number of moles of water present in the equilibrium mixture greater than the number of moles of ethyl ethanoate?

(1)

....

....

(c) (i) What is the type of reaction that took place in each test tube?

(2)

First test tube ....

Second test tube ....

*(ii) Comment on the value of the titre for the equilibrium mixture in the second test tube compared to the first test tube.

What characteristic feature of equilibrium reactions is demonstrated by the values of these titres?

(2)

....

....

....

....

(iii) State the role of the concentrated hydrochloric acid in the equilibrium reaction.

(1)

....

....

(Total for Question 12 = 21 Marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

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P 4 2 9 7 2 A 0 2 3 2 4

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

* 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