Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

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

Wednesday 12 June 2013 – 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 ▶

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6/6/7/1/1/

P 4 2 9 8 4 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 An important step in the production of sulfuric acid is the oxidation of sulfur dioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -196 \text{ kJ mol}^{-1}$$

Which of the conditions below is best suited to produce a high yield of sulfur trioxide, SO_3?

☒ **A** 1 atm pressure and 800 °C.

☒ **B** 2 atm pressure and 800 °C.

☒ **C** 1 atm pressure and 400 °C.

☒ **D** 2 atm pressure and 400 °C.

(Total for Question 1 = 1 mark)

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2 Which of the following statements is true about **all** substances that form acidic solutions in water?

☒ **A** They are corrosive.

☒ **B** They are liquids.

☒ **C** They contain hydrogen atoms.

☒ **D** They form $H^+(aq)$ ions.

(Total for Question 2 = 1 mark)

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

P 4 2 9 8 4 A 0 2 2 4

3 Select the correct pH for each of the following solutions.

(a) Nitric acid, HNO_3, of concentration 2 mol dm^{-3}, assuming it is fully dissociated.

(1)

- ☒ **A** –0.3
- ☒ **B** 0.0
- ☒ **C** 0.3
- ☒ **D** 2.0

(b) Sodium hydroxide, NaOH, of concentration 2 mol dm^{-3}, using $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

(1)

- ☒ **A** –13.7
- ☒ **B** 13.7
- ☒ **C** 14.0
- ☒ **D** 14.3

(c) Ethanoic acid, CH_3COOH, of concentration 2 mol dm^{-3}, making the usual assumptions.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$$

(1)

- ☒ **A** 2.2
- ☒ **B** 2.4
- ☒ **C** 4.5
- ☒ **D** 4.8

(d) The mixture formed when 25 cm^3 of 2 mol dm^{-3} sodium hydroxide solution is added to 50 cm^3 of 2 mol dm^{-3} ethanoic acid, for which $K_a = 1.7 \times 10^{-5}$ mol dm^{-3}.

(1)

- ☒ **A** 2.2
- ☒ **B** 2.5
- ☒ **C** 4.5
- ☒ **D** 4.8

(Total for Question 3 = 4 marks)

4 A solution of 2,4-dinitrophenylhydrazine (Brady's reagent) is used as a test for organic functional groups.

(a) The positive result of the test is the formation of

(1)

☒ **A** a yellow solution.

☒ **B** an orange precipitate.

☒ **C** a red solution.

☒ **D** a green precipitate.

(b) Which of the following gives a positive result with a solution of 2,4-dinitrophenylhydrazine?

(1)

☒ **A** Only aldehydes

☒ **B** Only ketones

☒ **C** Only aldehydes and ketones

☒ **D** Any compound containing the C=O group

(c) The initial attack by 2,4-dinitrophenylhydrazine, when it reacts, is by

(1)

☒ **A** a free radical.

☒ **B** an electrophile.

☒ **C** a nucleophile.

☒ **D** a negative ion.

(d) The product of a positive test, a 2,4-dinitrophenylhydrazone, contains which of the following bonds?

(1)

☒ **A** N=N

☒ **B** C=N

☒ **C** C=C

☒ **D** C=O

(Total for Question 4 = 4 marks)

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Turn over for Question 5

5 This question is about the following isomeric compounds with the molecular formula C_4H_8O and molar mass 72 g mol^{-1}.

A $CH_3CH_2CH_2CHO$

B $(CH_3)_2CHCHO$

C $CH_3CH_2COCH_3$

D $CH_3CH{=}CHCH_2OH$

(a) Which compound would you expect to give a peak at *m/e* = 41 in its mass spectrum?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which compound would NOT react with an acidified solution of potassium dichromate(VI)?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which compound would give a pale yellow precipitate when reacted with iodine in alkaline solution?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) Which compound can be reduced to give a chiral product?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(e) Which compound would NOT react with hydrogen cyanide under suitable conditions to form a hydroxynitrile?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 5 = 5 marks)

6 Transesterification involves the conversion of

☒ **A** esters into different esters.

☒ **B** esters into carboxylic acids.

☒ **C** *cis* carbon-carbon double bonds to the *trans* arrangement.

☒ **D** *trans* carbon-carbon double bonds to the *cis* arrangement.

(Total for Question 6 = 1 mark)

7 Biodiesel is formed by transesterification. It is used as a fuel in preference to untreated vegetable oils because

☒ **A** on combustion, biodiesel produces less carbon dioxide than vegetable oils.

☒ **B** on combustion, biodiesel produces more energy than vegetable oils.

☒ **C** biodiesel vaporises more easily than vegetable oils.

☒ **D** biodiesel is less volatile than vegetable oils.

(Total for Question 7 = 1 mark)

8 The main reason for hardening vegetable oils when producing low-fat spreads is to

☒ **A** prevent oxidation.

☒ **B** make the oil less viscous.

☒ **C** increase the melting temperature.

☒ **D** decrease the cholesterol content.

(Total for Question 8 = 1 mark)

9 Which atoms are not detected by X-rays but are detected by nuclear magnetic resonance imaging which also shows their environments?

☒ **A** Carbon

☒ **B** Hydrogen

☒ **C** Nitrogen

☒ **D** Oxygen

(Total for Question 9 = 1 mark)

10 In one type of high-performance liquid chromatography (HPLC), the stationary phase is non-polar and a polar solvent is used as the eluent. Which of the following would travel through the chromatography column most quickly?

☒ **A** Tetrachloromethane

☒ **B** Chloromethane

☒ **C** Iodomethane

☒ **D** Hexane

(Total for Question 10 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

11 This question is about the equilibrium reaction below.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

The equilibrium is reached slowly.

*(a) Describe the changes you would see if aqueous solutions of iron(II) sulfate and silver nitrate were mixed and allowed to stand for a few hours.

(2)

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(b) The concentration of silver ions in the equilibrium mixture can be found by titration with potassium thiocyanate. Silver thiocyanate precipitates.

$$Ag^{+}(aq) + CNS^{-}(aq) \rightleftharpoons AgCNS(s)$$

When all the silver ions have reacted, a deep red complex ion of iron(III) thiocyanate forms.

In an experiment, 25.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution was added to 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) sulfate solution, mixed thoroughly, and allowed to stand overnight in an air-tight container.

10.0 cm^3 samples of the reaction mixture were then titrated with 0.0200 mol dm^{-3} potassium thiocyanate solution. The average titre was 5.60 cm^3.

(i) The initial concentrations of silver ions and iron(II) ions **in the reaction mixture** are the same.

Calculate this initial concentration in mol dm^{-3}.

(1)

(ii) Calculate the number of moles of silver ions in the 10.0 cm^3 sample at equilibrium and hence calculate the equilibrium concentration of silver ions in the mixture.

(2)

(iii) Deduce the equilibrium concentration of iron(II) ions.

(1)

(iv) Hence calculate the equilibrium concentration of iron(III) ions.

(1)

(v) Write the expression for the equilibrium constant, K_c, for the reaction

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Calculate its value and give your answer, with appropriate units, to **three** significant figures.

(4)

(c) (i) The relationship between the total entropy change for a reaction and the equilibrium constant is

$$\Delta S^{\ominus}_{total} = R \ln K$$

Calculate the total entropy change for this reaction, giving a sign and appropriate units.

[R = 8.31 J mol^{-1} K^{-1}]

(2)

(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

$\Delta S^{\ominus}_{system}$ for this reaction is –208.3 J mol^{-1} K^{-1}

Use ideas about entropy to explain why this value is negative.

(2)

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(iii) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$.

(1)

(iv) Use your answer to (c)(iii) to calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction at 298 K.

Hence state and explain the effect of increasing temperature on the value of ΔS_{total}.

(3)

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*(d) After the samples from the original mixture for the titration are taken, the remainder was filtered and then allowed to stand overnight, in an air-tight container at the same temperature. Another 10.0 cm^3 sample was taken and titrated. How, if at all, would you expect the titre to change?

Justify your answer. A calculation is not required.

(2)

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(Total for Question 11 = 21 marks)

12 This question is about the reactions of butanoic acid, $CH_3CH_2CH_2COOH$. It has a foul smell and behaves like a typical carboxylic acid.

(a) (i) The addition of sodium carbonate solution is often used as a chemical test to distinguish carboxylic acids, like butanoic acid, from other compounds, such as aldehydes.

Explain why old stocks of aldehydes often react with sodium carbonate solution.

(1)

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(ii) How would the result of this test distinguish between a carboxylic acid and an old stock of an aldehyde?

(1)

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....

(iii) Write the balanced chemical equation, including state symbols, for the reaction of sodium carbonate solution with butanoic acid.

(2)

*(iv) Infrared spectroscopy is a good physical method to distinguish carboxylic acids from other organic compounds. Give the wavenumbers of **two** characteristic absorptions for a carboxylic acid. Indicate the bond responsible for each absorption. Suggest why one of the absorptions is broad.

(3)

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(v) High resolution nuclear magnetic resonance spectroscopy is a suitable physical method to use alongside infrared spectroscopy to identify butanoic acid. State the total number of peaks and suggest the splitting pattern for each peak that you would expect for butanoic acid, $CH_3CH_2CH_2COOH$.

(3)

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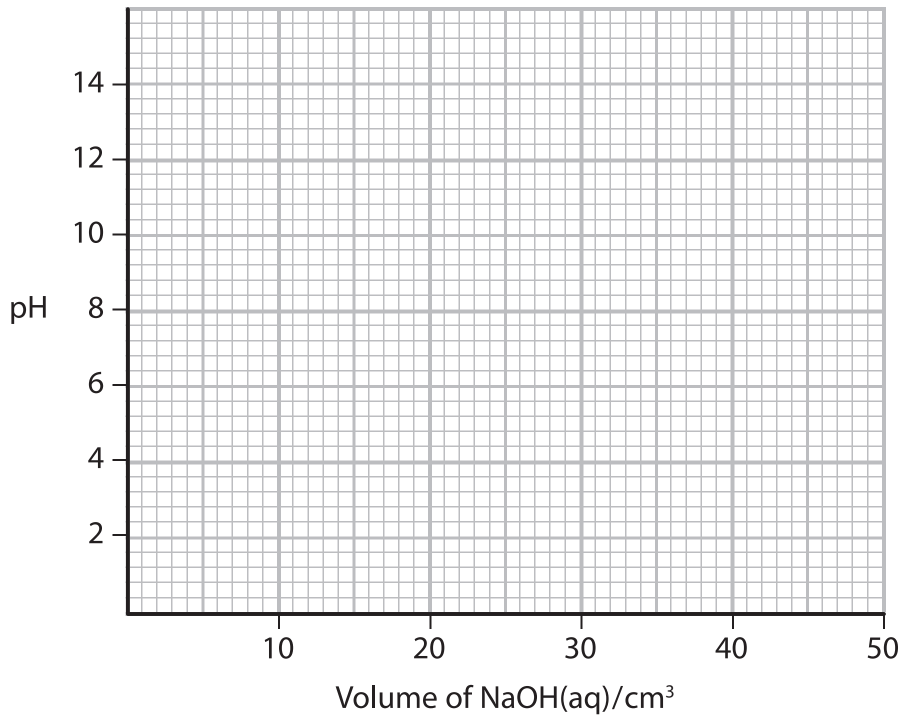
(b) Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

(4)



(c) (i) What would you see when phosphorus pentachloride, PCl_5, reacts with butanoic acid?

(1)

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(ii) Give the structural formula and name of the organic product of this reaction.

(2)

Structural formula

Name ....

(d) (i) Give the name or formula of the organic product of the reaction between butanoic acid and lithium tetrahydridoaluminate (lithium aluminium hydride).

(1)

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(ii) Water cannot be used as the solvent in this reaction because it reacts with lithium tetrahydridoaluminate. Suggest a suitable solvent.

(1)

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(iii) State the type of reaction that takes place between butanoic acid and lithium tetrahydridoaluminate. Justify your classification.

(2)

Type ....

Justification ....

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(e) (i) Butanoic acid can be reacted with methanol to make methyl butanoate. State **two** conditions that help to speed up this reaction.

(2)

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(ii) Draw the **displayed** formula of methyl butanoate.

(1)

(iii) Identify another chemical, by name or formula, which could be added to methanol to make methyl butanoate.

(1)

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*(iv) Give **two** advantages and **one** disadvantage of using the reaction occurring in (e)(iii), compared to the reaction in (e)(i), when making methyl butanoate.

(3)

Advantages ....

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Disadvantage ....

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(Total for Question 12 = 28 marks)

TOTAL FOR SECTION B = 49 MARKS)

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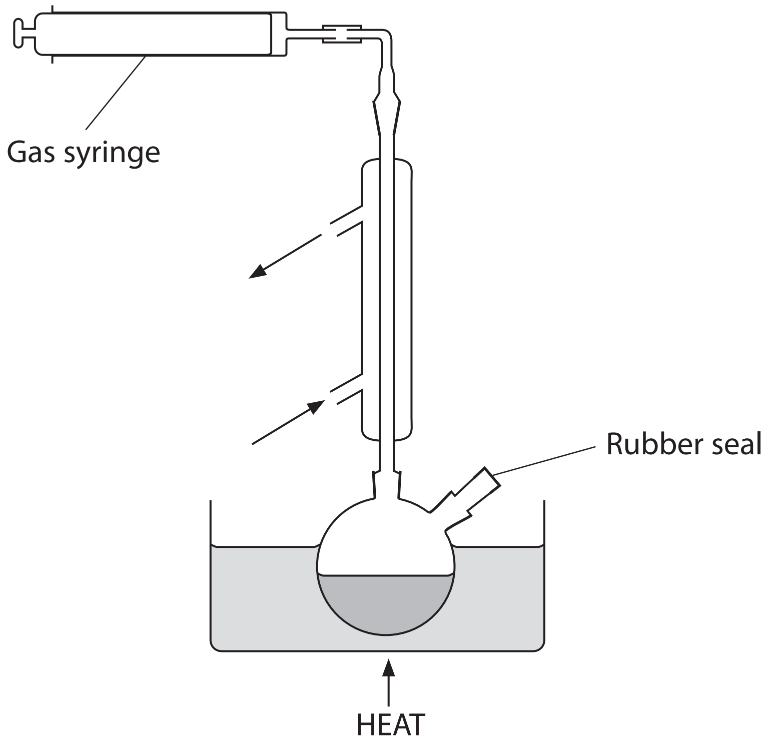
SECTION C

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

13 This question is about the elimination of hydrogen bromide from bromoalkanes by reaction with alcoholic potassium hydroxide.

$$C_4H_9Br + KOH \rightarrow C_4H_8 + KBr + H_2O$$

To investigate the kinetics of this reaction the following apparatus was used:



A solution of concentrated potassium hydroxide in ethanol was refluxed and the gas syringe connected as shown.

0.6 cm^3 of 1-bromobutane was added to the solution with a hypodermic syringe through a rubber seal.

A stop clock was started and the volume of gas, V_t, measured at 2 minute intervals, for 12 minutes. When there was no further evolution of gas the volume of gas, V_{final}, was 76.5 cm^3.

(a) (i) Calculate the number of moles of 1-bromobutane used. You will need the values of the density and molar mass of 1-bromobutane from your Data booklet.

(2)

(ii) Calculate the maximum volume of gaseous but-1-ene, in cm^3, that could form.

[Molar volume of a gas 24 000 cm^3 under reaction conditions]

Suggest **two** reasons why this volume is unlikely to form.

(3)

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(b) The results obtained are shown in the table below.

Time t/min	Volume of but-1-ene V_t/cm^3	$(V_{final} - V_t)/cm^3$
0	0	76.5
2	31.5	45.0
4	51.0	25.5
6	62.5	14.0
8	68.5	8.0
10	72.0	4.5
12	74.0	2.5

(i) Explain why a large excess of potassium hydroxide is used in this experiment.

(1)

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(ii) Plot a graph of $(V_{final} – V_t)$/cm^3 against t/min.

(3)

(iii) Suggest why the value of $(V_{final} – V_t)$ was plotted on your graph.

(1)

(iv) Measure two successive half lives from your graph.

(2)

First half life .... min

Second half life .... min

(v) Deduce the order of reaction with respect to 1-bromobutane.

Justify your answer.

(2)

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(c) In another experiment, an excess of 1-bromobutane is reacted with varying concentrations of hydroxide ions. The results for the initial rate of the reaction are shown in the table below.

Experiment Number	$[C_4H_9Br]$ $/10^{-2}$ mol dm^{-3}	$[OH^-]$ $/10^{-3}$ mol dm^{-3}	Initial rate $/10^{-5}$ mol dm^{-3} min^{-1}
1	2.50	2.50	5.00
2	2.50	1.25	2.50
3	2.50	0.50	1.00

(i) Deduce the order of reaction with respect to hydroxide ions. Justify your answer using the data in the table.

(2)

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(ii) Write the rate equation for the reaction using your answers to parts (b)(v) and (c)(i).

(1)

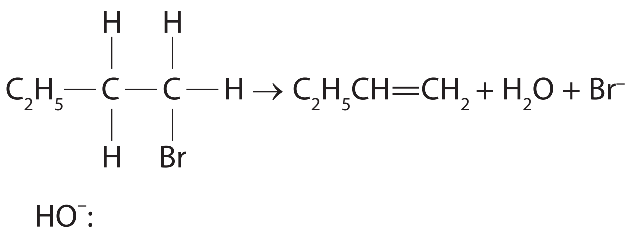
(iii) Give the units of the rate constant.

(1)

*(iv) It is suggested that the reaction begins with the slow attack by a hydroxide ion on a hydrogen atom in the 1-bromobutane, as shown below.

Complete the electron pair movement for this reaction using curly arrows and explain why this step is consistent with the rate equation for the reaction you have given in (c)(ii).

(3)



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(Total for Question 13 = 21 marks)

TOTAL FOR SECTION C = 21 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

* 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