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)

Wednesday 10 June 2015 – 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.

Turn over ▶

P45075A

6/6/7/6/3/1/

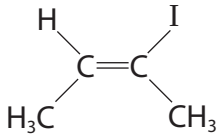
P 4 5 0 7 5 A 0 1 2 8

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 What is the name of the compound below?



☒ **A** *E*-2-iodobut-2-ene

☒ **B** *E*-3-iodobut-2-ene

☒ **C** *Z*-2-iodobut-2-ene

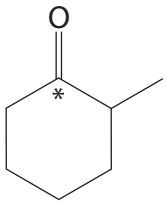
☒ **D** *Z*-3-iodobut-2-ene

(Total for Question 1 = 1 mark)

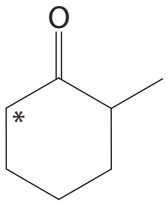
Use this space for any rough working. Anything you write in this space will gain no credit.

2 Which of the carbon atoms marked with an asterisk (*) is the chiral centre?

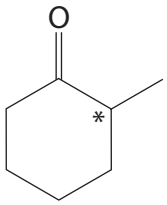
☒ **A**



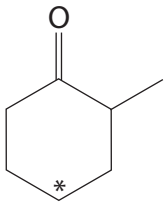
☒ **B**



☒ **C**



☒ **D**



(Total for Question 2 = 1 mark)

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

3 Calculate the pH of an aqueous solution of hydrochloric acid, HCl, of concentration 0.40 mol dm^{-3}.

☒ **A** 0.40

☒ **B** –0.40

☒ **C** –0.92

☒ **D** 0.92

(Total for Question 3 = 1 mark)

4 Which of the following is the most suitable carrier gas in gas chromatography?

☒ **A** Oxygen

☒ **B** Ammonia

☒ **C** Carbon dioxide

☒ **D** Water vapour

(Total for Question 4 = 1 mark)

5 What are the units of the equilibrium constant K_p for the general reaction shown below?

$$P(g) + 3Q(g) \rightleftharpoons 8R(g)$$

☒ **A** atm^2

☒ **B** atm^{-2}

☒ **C** atm^4

☒ **D** atm^{-4}

(Total for Question 5 = 1 mark)

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

6 This question is about the reversible reaction below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(a) A chemist investigating this reaction started with 5 mol of N_2O_4 and allowed the system to reach equilibrium. If 2 mol of NO_2 forms, the amount of N_2O_4 at equilibrium is

(1)

☒ **A** 1 mol

☒ **B** 1.5 mol

☒ **C** 3 mol

☒ **D** 4 mol

(b) Under different conditions, 25% of the moles of gas present at equilibrium is N_2O_4. If the total pressure of the system is 3 atm, the numerical value of the equilibrium constant K_p is

(1)

☒ **A** 9.00

☒ **B** 6.75

☒ **C** 3.00

☒ **D** 0.15

(Total for Question 6 = 2 marks)

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

7 Carbon monoxide and chlorine react together and reach equilibrium:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If the pressure of the system is then **decreased** at constant temperature, which of the following statements is correct?

☒ **A** The equilibrium moves to the left hand side, then back to the right hand side and K_p remains the same.

☒ **B** The equilibrium moves to the left hand side and K_p remains the same.

☒ **C** The equilibrium moves to the right hand side and K_p increases.

☒ **D** The equilibrium moves to the left hand side and K_p decreases.

(Total for Question 7 = 1 mark)

8 The table shows some data about metal ions, non-metal ions and their compounds.

Ion	Enthalpy change of hydration / kJ mol^{-1}	Compound	Lattice energy / kJ mol^{-1}
$Sr^{2+}(g)$	–1443	$SrF_2(s)$	–2492
$F^-(g)$	–483		
$Rb^+(g)$	–297	RbCl(s)	–685
$Cl^-(g)$	–340		

Use the data in the following calculations.

(a) What is the standard enthalpy change, in kJ mol^{-1}, for the following process?

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

(1)

☒ **A** –477

☒ **B** –960

☒ **C** –1926

☒ **D** –2409

(b) What is the standard enthalpy change of solution, in kJ mol^{-1}, for rubidium chloride, RbCl?

(1)

☒ **A** –1322

☒ **B** –48

☒ **C** +48

☒ **D** +1322

(Total for Question 8 = 2 marks)

9 Which of these solvents would **not** be warmed by microwave radiation?

☒ **A** water, H_2O

☒ **B** tetramethylsilane (TMS), $Si(CH_3)_4$

☒ **C** cyclohexanol, $C_6H_{11}OH$

☒ **D** trichloromethane, $CHCl_3$

(Total for Question 9 = 1 mark)

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

10 Some chemical tests are described below.

A Warm with Fehling's (or Benedict's) solution

B Warm with iodine dissolved in alkali

C Add sodium carbonate solution

D Add 2,4-dinitrophenylhydrazine solution

(a) Which test would result in effervescence with the compound $CH_3CH{=}CCl(COOH)$?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test can be used to distinguish between aldehydes and ketones?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test results in an orange-yellow precipitate with CH_3COCH_3?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 10 = 3 marks)

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

11 Consider the four compounds shown below.

A $HCOOCH_2CH_3$

B CH_3COOH

C CH_3CONH_2

D CH_3COCl

Which of these compounds

(a) forms the **most** acidic solution when equimolar amounts of each compound are separately dissolved in 10 cm^3 of water?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) has a peak at 3348 cm^{-1} in its infrared spectrum? Use your Data Booklet.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) is most likely to be used as a fruit-flavoured food additive?

(1)

☒ **A**

☒ **B**

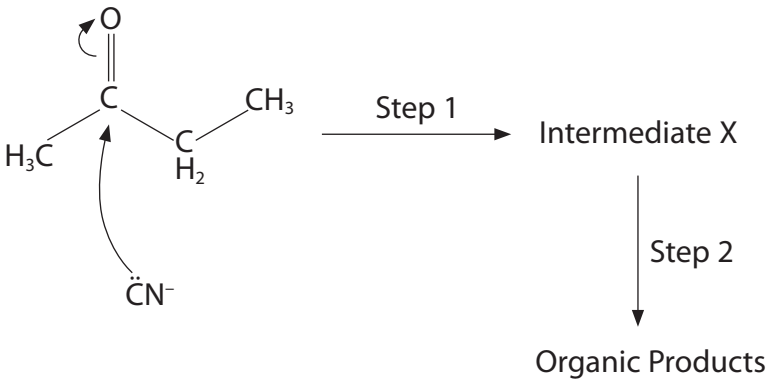
☒ **C**

☒ **D**

(Total for Question 11 = 3 marks)

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

12 This question is about the nucleophilic addition of hydrogen cyanide to butanone.
The diagram below shows part of the mechanism for this reaction.



(a) Consider the dissociation of the weak acid HCN.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

Which of the following reagents would lower the concentration of the nucleophile, CN^-, by the greatest extent?

(1)

☒ **A** CH_3COOH

☒ **B** HCl

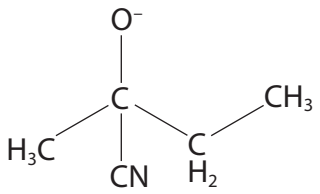
☒ **C** NH_3

☒ **D** KOH

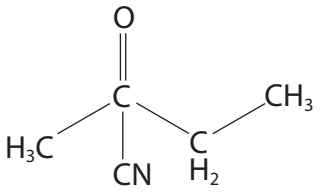
(b) The intermediate X is

(1)

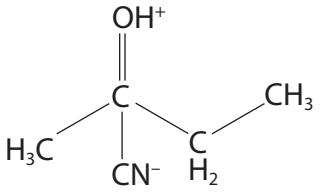
☒ **A**



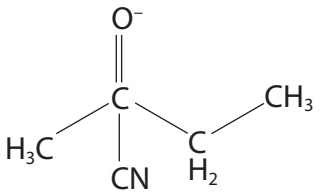
☒ **B**



☒ **C**



☒ **D**



(c) Which statement about the mixture of organic products formed is **not** correct?
The mixture

(1)

☒ **A** contains products with one more carbon atom than the ketone.

☒ **B** rotates the plane of plane-polarized light.

☒ **C** contains products with the nitrile functional group.

☒ **D** contains products with chiral molecules.

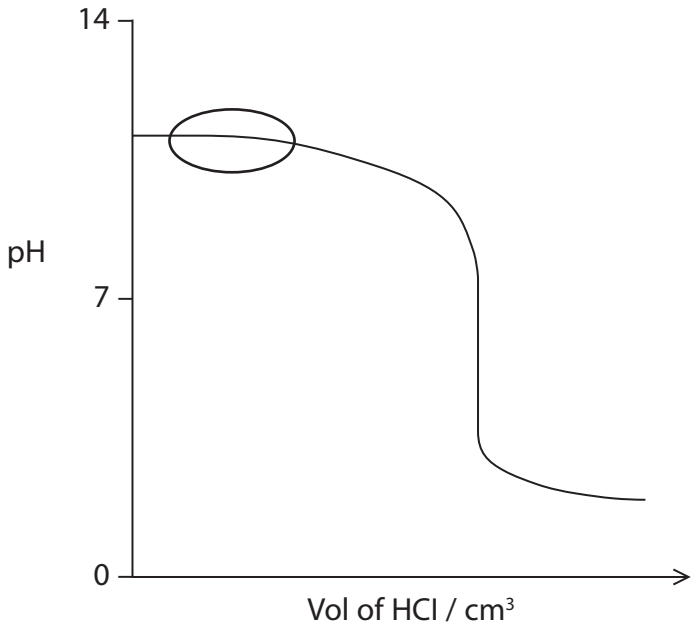
(Total for Question 12 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

13 A student carried out a titration by adding 0.0540 mol dm^{-3} hydrochloric acid to 25.0 cm^3 of 0.0240 mol dm^{-3} ammonia solution. A sketch graph of pH against volume of hydrochloric acid added is shown below.



(a) *(i) Name the type of solution formed in the region ringed on the sketch graph and explain its chemical behaviour.

(3)

*(ii) Explain why the pH at the equivalence point of this titration is less than 7. Include an ionic equation in your answer.

(3)

(iii) By considering the amount of excess acid remaining, calculate the pH of the solution formed when 40.0 cm^3 of 0.0540 mol dm^{-3} hydrochloric acid has been added to 25.0 cm^3 of 0.0240 mol dm^{-3} ammonia solution.

(4)

(b) (i) Show, using the data below, that the pH of water at 373 K is 6.13.

- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- $K_w = 5.50 \times 10^{-13}$ mol^2 dm^{-6} at 373 K

(2)

(ii) At 373 K, is water neutral, acidic or alkaline? Explain your answer.

(2)

(Total for Question 13 = 14 marks)

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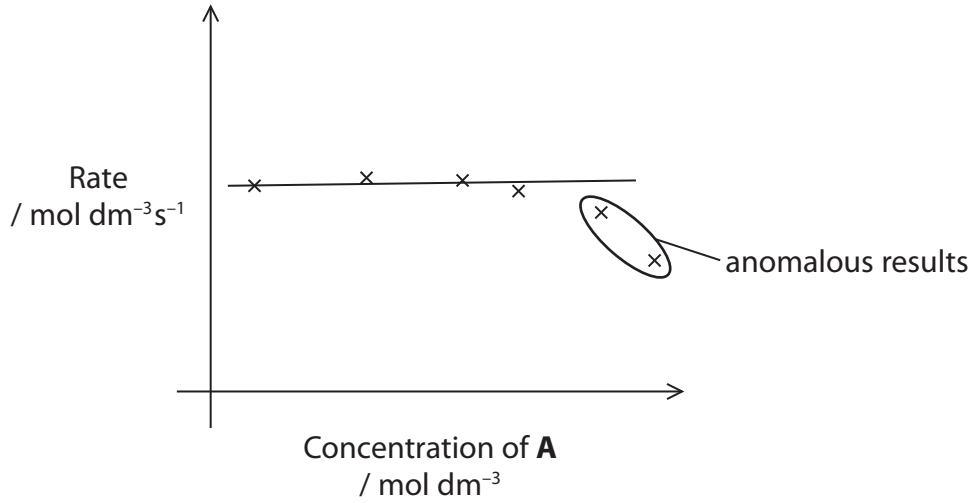
14 The kinetics of the reaction below was investigated in a series of experiments.

$$\mathbf{A} + \mathbf{B} \xrightarrow{\text{catalyst } \mathbf{X}} \mathbf{C} + \mathbf{D} \quad \Delta H \text{ is positive}$$

(a) Compound **C** is a gas, whereas compounds **A**, **B** and **D** are in solution. Outline a method that could be used to investigate the rate of the reaction. You may wish to draw a diagram.

(3)

(b) The rate of the reaction was measured at several different initial concentrations of **A** in the presence of a large excess of compound **B** and a constant amount of catalyst **X**, to find the order of reaction with respect to **A**. The results are shown on the graph below.



(i) Suggest an explanation, other than experimental error, for the two anomalous results ringed.

(2)

.....

.....

.....

.....

(ii) What is the order of reaction with respect to **A**? Justify your answer.

(2)

.....

.....

.....

.....

.....

(c) In a second series of experiments, further data were collected using a different method. These results are summarised in the table below.

Experiment	Initial concentration / mol dm^{-3}			Rate / mol dm^{-3} s^{-1}
	A	**B**	**X**	
1	0.010	0.025	0.100	0.0025
2	0.010	0.075	0.100	0.0225
3	0.010	0.100	0.200	0.0800
4	0.020	0.100	0.200	0.0800

(i) Give **one** reason why obtaining these further data may be considered useful.

(1)

(ii) State the order with respect to **B** and hence deduce the order with respect to **X**. Explain how you arrived at your answers. Include appropriate experiment numbers in your explanation.

(4)

(iii) Use your answers to (b)(ii) and (c)(ii) to give the rate equation for the reaction.

(1)

(iv) Use your answer from (c)(iii) and appropriate data from **Experiment 3** in the table, to calculate the value of the rate constant, *k*.
Include units in your answer.

(2)

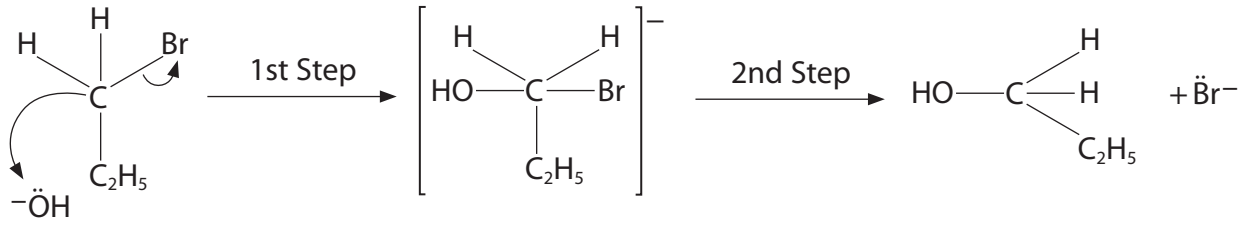
(d) A student carried out an investigation into the kinetics of the reaction between 1-bromopropane and hydroxide ions. A summary of the student's findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is second order overall and is known as S_N2.
Both 1-bromopropane and the hydroxide ions are involved in the slow step of this two-part reaction.

Suggested Mechanism

The hydroxide ions react with the 1-bromopropane as below.



Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest **two** features of the summary, including the student's mechanism, that you think are correct and **two** features you think are incorrect.

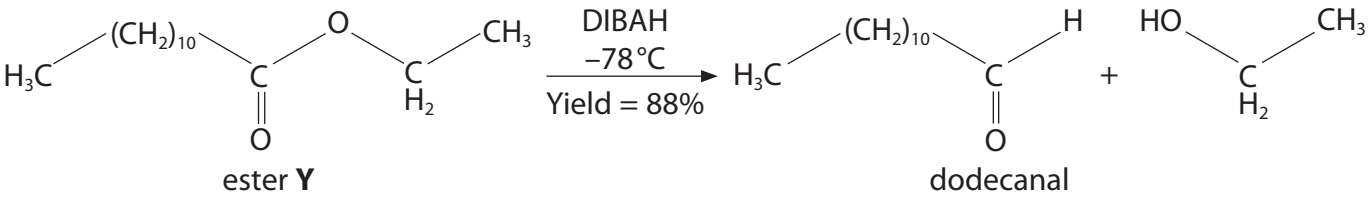
(4)

Two features you think are correct.

Two features you think are incorrect.

(Total for Question 14 = 19 marks)

15 Aldehydes can be synthesised in the laboratory by the reaction of esters with the reagent diisobutylaluminiumhydride (DIBAH), which acts as a source of hydride ions. An example is shown below.



ester **Y** dodecanal

(a) Give the systematic name of ester **Y**.

(1)

.....

(b) DIBAH acts as a source of hydride ions. What type of reagent is DIBAH?

(1)

.....

(c) Suggest why the reaction is kept at −78 °C.

(1)

.....

.....

(d) The overall yield for this process is 88%.

Calculate the mass, in g, of dodecanal that would be formed from 5.26 g of the ester **Y**.

[Molar masses / g mol^{-1}: ester **Y** = 228; dodecanal = 184]

(3)

(Total for Question 15 = 6 marks)

16 Chemists in Asia have been investigating the use of a range of non-edible seeds to produce oil for bio-diesel production, instead of using edible oils. The oils are obtained by pressing the seeds to release the oil. The relatively impure oil is filtered, and then purified using an industrial version of a standard laboratory technique. The oil can then be converted to bio-diesel by the reaction with methanol in the presence of a suitable catalyst.

(a) (i) Suggest a 'standard laboratory technique' that could be used to purify the oil.

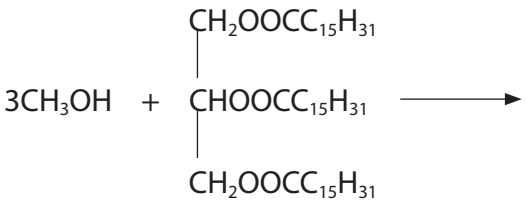
(1)

.....

.....

(ii) Complete the equation below for the formation of a bio-diesel from the reaction of an oil with methanol.

(2)



(iii) Suggest a suitable catalyst for the reaction in (a)(ii).

(1)

.....

*(b) Another source of oil currently being investigated for bio-diesel production is the edible plant known as samphire. It can be grown in marshy areas close to coastlines and is tolerant of salt.

Consider the advantages and disadvantages of growing both samphire and non-edible seeds as sources of vegetable oil.

Suggest, giving your reasons, which of the two sources would provide a potentially greener, more sustainable supply of bio-diesel.

(4)

(Total for Question 16 = 8 marks)

TOTAL FOR SECTION B = 47 MARKS

SECTION C

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

17 Ethanoic acid, CH_3COOH, is a carboxylic acid with many uses, including as a food additive. It can be made by the reaction of butane with oxygen.

$$2CH_3CH_2CH_2CH_3(g) + 5O_2(g) \rightleftharpoons 4CH_3COOH(l) + 2H_2O(l)$$

(a) (i) Use the Data Booklet to complete the table below.

(3)

	$CH_3CH_2CH_2CH_3(g)$	$O_2(g)$	$CH_3COOH(l)$	$H_2O(l)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}		0		
$S^{\ominus}$ / J mol^{-1} K^{-1}		205		

(ii) Use data from your table to calculate the standard enthalpy change, in kJ mol^{-1}, for this reaction.

$$2CH_3CH_2CH_2CH_3(g) + 5O_2(g) \rightarrow 4CH_3COOH(l) + 2H_2O(l)$$

(2)

(iii) Use data from your table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, for the same reaction.

$$2CH_3CH_2CH_2CH_3(g) + 5O_2(g) \rightarrow 4CH_3COOH(l) + 2H_2O(l)$$

(2)

(iv) Use your answer to (a)(ii) to calculate $\Delta S_{surroundings}$ and use this and your answer to (a)(iii) to calculate ΔS_{total} for the reaction at 298 K.

(3)

(v) It was suggested that **increasing** the temperature of the reaction to more than 298 K would produce a greater yield of ethanoic acid.

Explain, in terms of the effect on ΔS_{system}, $\Delta S_{surroundings}$ and hence ΔS_{total}, whether this would be the case.

(3)

(b) Infrared spectroscopy can be used to follow the progress of reactions.

Using information from the Data Booklet, suggest one way this technique could be used to follow the progress of the reaction in (a) to produce ethanoic acid.

(1)

(c) Ethanoic acid is the food additive E260. Suggest the role it may have when added to foodstuffs.

(1)

.....

.....

(d) An organic compound, **Q**, is found to contain 52.5% carbon and 7.5% hydrogen by mass.

(i) Use these data to confirm its empirical formula is $C_7H_{12}O_4$.

(3)

(ii) Explain how the mass spectrum of **Q** could be used to confirm that its relative molecular mass is 160.

(1)

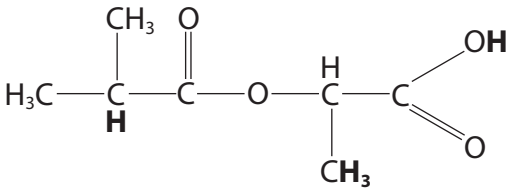
.....

.....

(iii) The table below summarises some information about parts of the nmr spectrum of compound **Q**.

Use the Data Booklet, and your knowledge of features in nmr spectra, to complete the table with respect to the features of compound **Q** shown in bold.

(4)



Feature of compound **Q**	Chemical shift / ppm for TMS	Splitting pattern	Relative area below peak
C**H**$_3$	0.1 – 1.9	doublet	
C**H**			1
COO**H**		singlet	1

(Total for Question 17 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
						1.0 H hydrogen 1											4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
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	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(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

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
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

* Lanthanide series

* Actinide series