Please check the examination details below before entering your candidate information			
Candidate surname	Other names		
Centre Number Candidate Number Pearson Edexcel International Advanced Level			
Wednesday 29 May 2024			
Morning (Time: 1 hour 45 minutes)	Paper reference WCH14/01		
Chemistry International Advanced Level UNIT 4: Rates, Equilibria and Further Organic Chemistry			
You must have: Scientific calculator, Data Booklet, rule	r Total Marks		

Instructions

- Use **black** ink or ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **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.
- Show all your working in calculations and include units where appropriate.

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.
- In the question marked with an **asterisk** (*) marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- There is a Periodic Table on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶



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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 \boxtimes . If you change your mind, put a line through the box \boxtimes and then mark your new answer with a cross \boxtimes .

1 Bromate(V) ions, BrO₃, react with bromide ions, Br⁻, in aqueous acid.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The rate equation for the reaction is shown.

rate =
$$k [BrO_3^-] [Br^-] [H^+]^2$$

(a) Which **continuous** monitoring method could be used to obtain kinetics data for this reaction?

(1)

- A colorimetry
- B mass change
- **C** titration with sodium thiosulfate
- **D** volume of gas evolved
- (b) What are the units of the rate constant, *k*, for this reaction?

(1)

- \triangle A moldm⁻³ s⁻¹
- \blacksquare **B** dm³ mol⁻¹ s⁻¹
- \square C dm⁶ mol⁻² s⁻¹
- \square **D** dm⁹ mol⁻³ s⁻¹
- (c) The concentrations of **all** reactants are halved.

By what factor does the rate of reaction change?

(1)

- \triangle A $\frac{1}{2}$
- \boxtimes B $\frac{1}{4}$
- \boxtimes c $\frac{1}{8}$
- \square D $\frac{1}{16}$



2

(d) The first four steps in the reaction mechanism are shown.

Step 1
$$BrO_3^- + H^+ \rightarrow BrO_3H$$

Step 2
$$BrO_3H + H^+ \rightarrow BrO_3H_2^+$$

Step 3
$$BrO_3H_2^+ + Br^- \rightarrow Br_2O_2 + H_2O$$

Step 4
$$Br_2O_2 + Br^- \rightarrow BrO_2^- + Br_2$$

Which is the rate-determining step?

(1)

- A Step 1
- ☑ B Step 2
- C Step 3
- D Step 4

(Total for Question 1 = 4 marks)

2 Some data on lattice energies are shown.

Compound Experimental lattice energy /		Theoretical lattice energy /
- Compound	kJ mol⁻¹	kJ mol⁻¹
NaI	- 705	-687
AgBr	-891	-816
Rb₂S	-1944	-1904
Li ₂ O	-2814	-2799

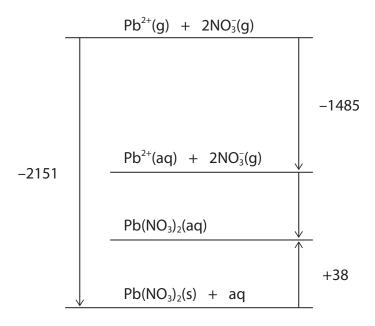
Which compound has the greatest degree of covalency within its ionic bonds?

- A NaI
- B AgBr
- \square **D** Li₂O

(Total for Question 2 = 1 mark)

3 An enthalpy cycle for lead(II) nitrate is shown.

All values are in kJ mol⁻¹. The cycle is **not** to scale.



(a) Which of these statements is **true**?

(1)

- A the enthalpy change of formation of lead(II) nitrate is -2151 kJ mol⁻¹
- **B** the enthalpy change of solution of lead(II) nitrate is exothermic
- **C** the enthalpy change of hydration of a lead(II) ion is more exothermic than that of a nitrate ion
- □ the entropy change of the surroundings for dissolving lead(II) nitrate is positive
- (b) Using the enthalpy cycle, it can be calculated that the enthalpy change of hydration of a nitrate ion, in kJ mol⁻¹, is

(1)

- **B** −1799
- **C** −628
- **■ D** -314

(Total for Question 3 = 2 marks)

4

4 Ammonia is produced from nitrogen and hydrogen in the presence of a solid catalyst in an equilibrium reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92 \text{ kJ mol}^{-1}$$

(a) $10 \text{ mol of } N_2(g)$ is heated with $30 \text{ mol of } H_2(g)$ in a sealed container. At equilibrium, $8.0 \text{ mol of } NH_3(g)$ is present.

What is the total amount of gas, in mol, in the equilibrium mixture?

(1)

- **A** 8.0
- B 20

- (b) What is the expression for the equilibrium constant, K_p , for this reaction?

(1)

- **A** $\frac{p(N_2) + p(H_2)^3}{p(NH_3)^2}$
- $\square \qquad \mathbf{C} \qquad \frac{p(\mathsf{NH}_3)^2}{p(\mathsf{N}_2) \times p(\mathsf{H}_2)^3}$
- $\square \quad \mathbf{D} \quad \frac{p(\mathsf{N}_2) \times p(\mathsf{H}_2)^3}{p(\mathsf{NH}_3)^2}$
- (c) Which change would increase the value of K_p for this reaction?

(1)

- A decreasing the temperature
- **B** decreasing the particle size of the catalyst
- C increasing the total pressure
- D increasing the concentration of hydrogen molecules

(Total for Question 4 = 3 marks)

5 For all chemical reactions, the equilibrium constant, K, is related to the total entropy change, ΔS_{total} , by the expression shown.

$$\Delta S_{\text{total}} = R \ln K$$

 ΔS_{total} for a reaction is negative.

Which statement is true?

- \triangle **A** the value of *K* is less than 1
- **B** the value of *K* is greater than 1
- \square **C** the value of *K* is negative
- **D** the position of equilibrium lies to the right

(Total for Question 5 = 1 mark)

6 A buffer solution contains CH₃COOH and CH₃COONa in the ratio, 1:4.

What is the pH of this buffer solution?

$$[K_a(CH_3COOH) = 1.7 \times 10^{-5} \, \text{mol dm}^{-3}]$$

- **■ A** 2.4
- **■ B** 4.2
- **C** 4.8
- **D** 5.4

(Total for Question 6 = 1 mark)

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

7 The accumulation of carbon dioxide during exercise reduces the pH in cells and in blood.

Which of these reactions is **most** important in buffering the decrease in pH that occurs?

- \square A $H_2CO_3 \rightarrow H^+ + HCO_3^-$
- \square **B** HCO $_3^-$ + H $^+$ \rightarrow H $_2$ CO $_3$
- \square C $HCO_3^- \rightarrow H^+ + CO_3^{2-}$
- \square **D** $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

(Total for Question 7 = 1 mark)

8 How many chiral centres are in the molecule shown?

- A 4
- **B** 5
- □ 7

(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 rate equation for the hydrolysis of a halogenoalkane, RX, in aqueous alkali is shown.

$$rate = k [RX]$$

Which of these statements is true?

- A the mechanism involves a carbocation intermediate
- \square **B** the reaction has an $S_N 2$ mechanism
- C the halogenoalkane could be 1-bromobutane
- ☑ D the main nucleophile in this reaction is H₂O

(Total for Question 9 = 1 mark)

10 Propanone reacts with HCN in the presence of KCN.

Which of these statements is **incorrect**?

- A CN⁻ acts as a nucleophile in the reaction
- **B** a racemic mixture is formed
- C the product is **not** optically active
- **D** the product is 2-hydroxy-2-methylpropanenitrile

(Total for Question 10 = 1 mark)

11 Which statement(s) is/are correct?

CH₃CH₂COCl reacts with

- 1 CH₃NH₂ to form CH₃CH₂CONHCH₃
- 2 (CH₃)₂NH to form CH₃CH₂CON(CH₃)₂
- 3 (CH₃)₃N to form CH₃CH₂CON(CH₃)₃

 - B 1 and 2 only
 - C 2 and 3 only
 - **D** 1 only

(Total for Question 11 = 1 mark)

8

12 An ester is hydrolysed in excess dilute hydrochloric acid to form ethanol and propanedioic acid.

What is the skeletal formula of this ester?

- B 0
- □ c 0
- D 0

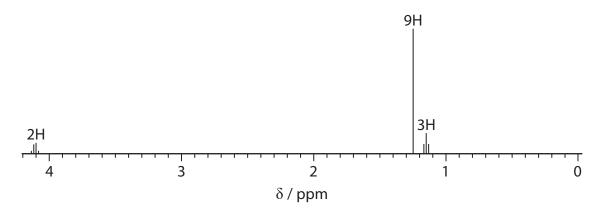
(Total for Question 12 = 1 mark)

- **13** Which compound has **most** peaks in its ¹³C NMR spectrum?
 - A CH₃COCH₃
 - B CH₃COCH₂CH₃
 - C CH₃CH₂COCH₂CH₃
 - ☑ D CH₃COCH₂CH₂COCH₃

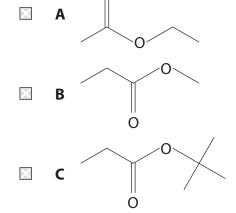
(Total for Question 13 = 1 mark)

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

14 The high resolution ¹H NMR spectrum of an ester is shown.



What is the skeletal formula of this ester? Use the Data Booklet as a source of information.



(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

- **15** This question is about some compounds of silicon.
 - (a) Silicon dioxide and magnesium react when heated strongly.

Reaction 1

$$SiO_2(s) + 4Mg(s) \rightarrow Mg_2Si(s) + 2MgO(s)$$

(i) Complete the table, indicating the type of bonding in the reactants and products of this reaction.

(2)

Substance	SiO ₂	Mg	Mg₂Si	MgO
Bonding type			covalent	

(ii) The entropy change of the system, ΔS_{system} , for Reaction 1 is -43.8 J K⁻¹ mol⁻¹.

Suggest, with reference to the equation, why $\Delta \textit{S}_{\text{system}}$ for this reaction is negative.

(2)

(iii) The enthalpy change, ΔH , for Reaction 1 is $-370 \, \text{kJ} \, \text{mol}^{-1}$.

Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, in JK⁻¹ mol⁻¹, for Reaction **1** at 23.0 °C.

(2)



(iv) Calculate the total entropy change, ΔS_{total} , for Reaction 1 at 23.0 °C.

Give your answer to an appropriate number of significant figures, and in units of $JK^{-1}mol^{-1}$.

(2)

(v) Reaction **1** does not occur at room temperature due to its very high activation energy.

Suggest why the activation energy for Reaction 1 is very high.

(1)

- (b) Magnesium silicide, Mg₂Si, reacts with hydrochloric acid forming silane, SiH₄, and magnesium chloride.
 - (i) Write an equation for this reaction.

State symbols are **not** required.

(1)

(ii) Silane has a molecular structure.

Complete the table, giving the shape of a molecule of SiH₄ and its bond angle.

(2)

Name of shape	
Bond angle	



(c) Silane spontaneously combusts in air at room temperature.

$$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(l)$$

Entropy data for this reaction are shown.

Species	SiH₄(g)	O ₂ (g)	SiO ₂ (s)	H ₂ O(I)
S°/JK ⁻¹ mol ⁻¹	204.5	205.0	41.8	69.9

(i) Calculate the entropy change of the system, ΔS_{system} , in J K⁻¹ mol⁻¹, for Reaction **2**.

(2)

(ii) State why the entropy change of the surroundings for Reaction **2** is highly positive, in terms of the bond strengths of the reactants and products.

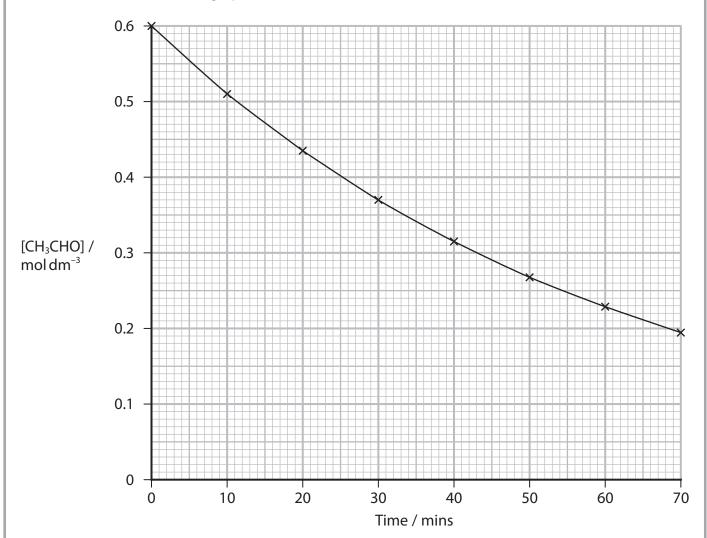
(1)

(Total for Question 15 = 15 marks)

16 This question is about the kinetics of the gas phase decomposition of CH₃CHO.

$$CH_3CHO \rightarrow CH_4 + CO$$

(a) A concentration-time graph for this reaction at 1000 K is shown.



(i) Calculate the initial rate of reaction, in $mol dm^{-3} s^{-1}$, at 1000 K.

You must show your working on the graph.

(3)

(ii) Deduce the rate equation for this reaction at 1000 K, by determining two half-lives.

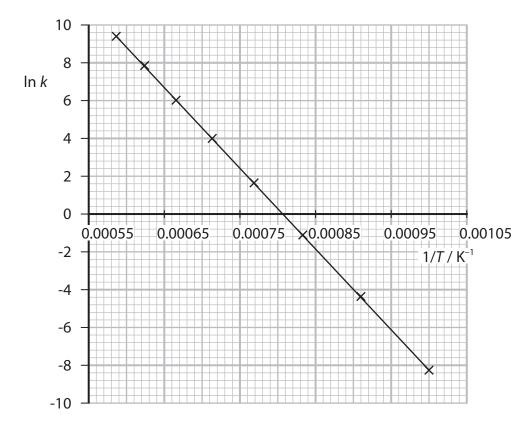
You must show your working on the graph.

(2)



(b) The rate constant, k, for the decomposition of CH $_3$ CHO was determined between 1000 K and 1700 K.

The results are plotted on the graph of $\ln k$ against 1/T.



Determine the activation energy, $E_{\rm a}$, for this reaction.

Give your answer to **three** significant figures and include units.

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

(4)

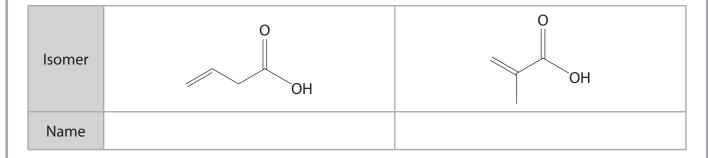
(Total for Question 16 = 9 marks)

- 17 This question is about carboxylic acids and their derivatives.
 - (a) There are five carboxylic acids with the formula $C_4H_6O_2$. Four are structural isomers.

One of these structural isomers has two stereoisomers.

(i) Name the two structural isomers shown.

(2)



(ii) The third structural isomer has two stereoisomers.

Draw these stereoisomers.

(2)

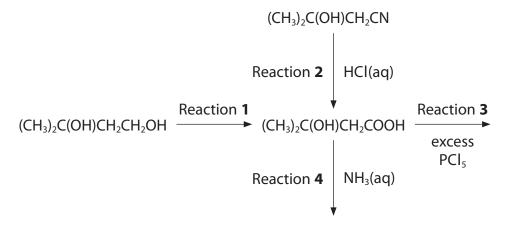
Stereoisomer 1	Stereoisomer 2

(iii) Draw the fourth structural isomer.

(1)



(b) Some reactions involving 3-hydroxy-3-methylbutanoic acid, (CH₃)₂C(OH)CH₂COOH, are shown.



(i) Give the reagents and conditions for Reaction 1.

(1)

(ii) Write the equation for Reaction 2. State symbols are **not** required.

(2)

(iii) Give the structure of the organic product formed in Reaction 3.

(2)

(iv) Give the structure of the organic product formed in Reaction 4.

(1)

(Total for Question 17 = 11 marks)



- **18** This question is about some reactions of propanal, CH₃CH₂CHO, and propanone, CH₃COCH₃.
 - (a) Propanal and propanone react similarly with lithium tetrahydridoaluminate(III).

Complete the table about these reactions.

(4)

Formula of lithium tetrahydridoaluminate(III)	
Essential reaction conditions	
Type of reaction	
Name of organic product with propanal	
Name of organic product with propanone	

(b)	State what would be seen when separate samples of propanal and propanon
	are warmed with Tollens' reagent.

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(c)	When propanone reacts with iodine in the presence of aqueous sodium hydroxide
	a yellow precipitate is observed.

Write an equation for this reaction.

Include state symbols.

(3)



(d)	Propanal and propanone both react with 2,4-dinitrophenylhydrazine.	
	The products of these reactions may be used to distinguish between separate samples of propanal and propanone.	
	Describe, in outline, the laboratory procedure for doing this.	
		(3)

(4)

(e) Propanone, CH₃COCH₃, reacts with hydroxylamine, NH₂OH, under mildly acidic conditions.

The first stage of the reaction is a nucleophilic addition.

Add curly arrows to complete the mechanism for this reaction.

Н Н НО НО HO Η N^{+} H_3C H^{+} H_3C H_3C 0: = O H_3C H_3C $\boldsymbol{H}^{\scriptscriptstyle +}$ H_3C Н НО HO H^{+} НО N: Ν H_3C H_3C Η CH₃ H_3C CH₃ H_3C

 H_2O

(Total for Question 18 = 16 marks)

Η

TOTAL FOR SECTION B = 51 MARKS

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SECTION C

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

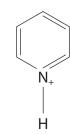
- **19** This question is about acids and bases.
 - (a) Some K_a and pK_a values for several weak acids are shown.

Weak acid	K_a / mol dm ⁻³	p <i>K</i> _a
C₅H₅NH⁺		5.25
CH₃CH₂COOH	1.3×10^{-5}	4.88
НСООН	1.8×10^{-4}	3.75
CH₂CICOOH	1.4×10^{-3}	2.85
CHCl₂COOH	4.5×10^{-2}	

(i) Complete the table.

(2)

(ii) The structure of $C_5H_5NH^+$ is shown.



Write the K_a expression for this weak acid.

(1)



24



(iii) When methanoic acid is added to propanoic acid, an equilibrium is set up containing two acid-base pairs.

Complete the equilibrium, labelling the acid-base pairs as A1, B1 and A2, B2.

(2)

 $CH_3CH_2COOH + HCOOH \rightleftharpoons$

......

*(iv) A student measured the pH of separate 0.050 mol dm⁻³ solutions of CH₂CICOOH and of CHCl₂COOH, using a pH meter.

The student also calculated the pH of these solutions, making two assumptions:

- $[H^+] = [A^-]$
- [HA]_{equilibrium} = [HA]_{initial}

The measured and calculated pH values are shown.

	0.050 mol dm ⁻³ CH ₂ CICOOH	0.050 mol dm ⁻³ CHCl₂COOH		
Measured pH value	2.11	1.52		
Calculated pH value	2.08	1.32		

Discuss the differences between the student's measured and calculated pH values.

(6)

In your answer, you should

show how the student calculated their pH values

$$[K_a(CH_2CICOOH) = 1.4 \times 10^{-3} \text{ mol dm}^{-3};$$

 $K_a(CHCI_2COOH) = 4.5 \times 10^{-2} \text{ mol dm}^{-3}]$

- explain, with reference to the assumptions made, why there is a difference between the calculated and measured pH values
- suggest why the measured pH values are higher than the calculated pH values.





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(b) 4-Hydroxybenzoic acid, HOC_6H_4COOH , is a diprotic acid, which dissociates in two stages. Each stage has a different pK_a value.

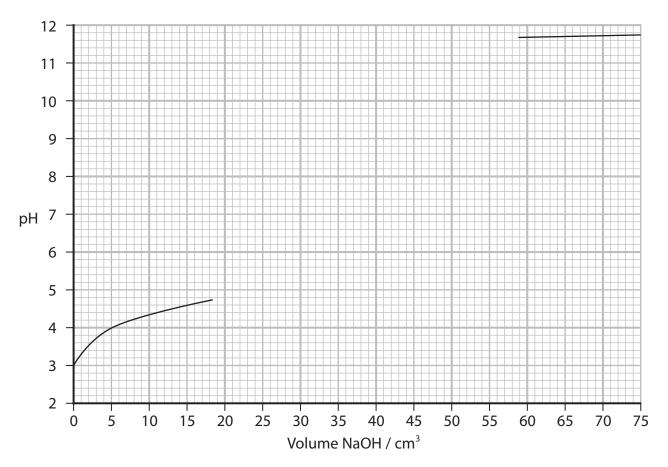
Stage 1
$$HOC_6H_4COOH \rightleftharpoons H^+ + HOC_6H_4COO^ pK_{a1} = 4.5$$

Stage **2**
$$HOC_6H_4COO^- \rightleftharpoons H^+ + {}^-OC_6H_4COO^ pK_{a2} = 9.3$$

In a titration, 75.0 cm 3 of 0.025 mol dm $^{-3}$ NaOH was added to 25.0 cm 3 of 0.025 mol dm $^{-3}$ HOC $_6{\rm H_4COOH}.$

Complete the titration curve.

(3)



(c) A student was given 50.0 cm³ of a solution of sodium hydroxide.

The pH of this solution was 12.43.

The student was asked to adjust the pH to 12.00, by dilution with deionised water. The student did **not** have access to a pH meter.

Calculate the volume of deionised water, **in cm**³, the student should add to the original solution.

(5)

(Total for Question 19 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS TOTAL FOR PAPER = 90 MARKS



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Md No Lr
n mendelenum nobelium lawrencium
101

5 96

95

94

93

92

5

06

protactinium [231] Pa

Thorium 232

U Np Pu Am uranium neptunium plutonium americium

69

68

67

99

65

2

63

62

9

9

59

28

[243]

[237]

The Periodic Table of Flements

1 2	(1) (2)	6.9 9.0 Li Be Hithium 3 4	23.0 24.3 Na Mg sodtum magnesium 11	39.1 40.1 K Ca potassium calcium sc 20	85.5 87.6 Sr Sr strontium y 37 38	132.9 137.3 1 Cs Ba caesium barium lan 55 56	[223] [226] Fr Fr Ra radium au 87 88	* Lanthanide series	
			(3)	Sc Scandium 21	88.9 ×	138.9 La* lanthanum 57	[227] Ac* actinium n 89		
negorbyn	relativ	relativ atoric	<i>(</i> 4)	47.9 Ti titanium 22	91.2 Zr zirconium 40	178.5 Hf hafmium 72	[261] Rf nutherfordlum 104	Ce 140	
		Key	relative atomic mass atomic symbol name atomic (proton) number	(5)	50.9 V vanadium 23	92.9 Nb niobium 41	180.9 Ta tantalum 73	[262] Db dubnium 105	141 Pr
	mass	mass bol umber	(9)	52.0 Cr chromium 24	95.9 Mo molybdenum 42	183.8 W tungsten 74	Sg seaborgium 106	141 144 [147] Pr Nd Pm	
			(2)	54.9 Mn manganese 25	[98] Tc technetium 43	186.2 Re rhenium 75	[264] Bh bohrium 107	[147] Pm	
	1.0 T hydrogen		(8)	55.8 Fe iron 26	Ru Ru ruthenium 44	190.2 Os osmium 76	[277] Hs hassium 108	150 Sm	
			(6)	S8.9 Co cobalt 27	102.9 Rh rhodfum 45	192.2 1r iridium 77	[268] Mt meitnerium 109	152 Eu	
			(01)	58.7 Ni nicket 28	106.4 Pd palladium 46	Pt Pt platinum 78	Ds damstadtium 110	157 Gd	
			(11)	63.5 Cu copper 29	107.9 Ag silver 47	197.0 Au gold 79	Rg noentgenium 111	159 T	
			(12)	55.4 Zn zinc 30	Cd Cadmium 48	200.6 Hg mercury 80		163 DV	
m	(13)	10.8 B boron 5	27.0 Al aluminium 13	Ga gallium 31	114.8 In indium 49	204.4 T1 thallium 81	Elements with atomic numbers 112-116 have been reported but not fully authenticated	165 H	
4	(14)	12.0 C carbon 6	Si Silicon 14	72.6 Ge germanium 32	118.7 Sn tin 50	207.2 Pb lead 82	atomic nu but not f	167 Er	
Ŋ	(15)	14.0 N nitrogen 7	31.0 P phosphorus 15	AS As arsenic 33	Sb Sh antimony 51	209.0 Bi bismuth 83	tomic numbers 112-116 hav but not fully authenticated	169 Tm	
9	(16)	16.0 O oxygen 8	32.1 S sulfur 16	Se selenium 34	127,6 Те теШитінт 52	Po Polonium 84	-116 have	173 Yb	
1	(17)	19.0 F fluorine 9	35.5 CL chlorine 17	79.9 Br bromine 35	126.9 I iodine 53	[210] At astatine 85	been repor	175 Lu	
0 (8)	(18) 4.0 He helium 2	20.2 Ne neon	39.9 Ar argon 18	83.8 Kr krypton 36	Xe xenon 54	[222] Rn radon 86	ted		