NZ Chemistry Olympiad

Training Group

Selection Examination

ANSWERS INCLUDED

Thursday 1 November 2012

TIME ALLOWED: 120 minutes

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **ten** (10) questions sum to **80**

A periodic table with atomic masses is also provided on the back page.

STUDENT'S NAME: _____

EMAIL: _____

SCHOOL: _____

CONTACT TEACHER: _____

Question	1 /7	2 /10	3 /8	4 /11	5 /7	6 /8	7 /8	8 /8	9 /6	10 /7	Total /80
Mark											

When completed post to:

Dr David Salter
School of Chemical Sciences
University of Auckland
Private Bag 92019
Auckland 1142

Make sure the *Student Application form* and the *School Report on Candidate form* are enclosed.

QUESTION 1: [7 marks]

A mining company carried out an analysis of an ore sample to find out how much copper was present. The analysis of an ore containing copper sulfide and other components involved the steps shown below.

Stage 1) Roasting the ore:	$2CuS + O_2 \rightarrow 2CuO + 2SO_2$	*Reaction 1*
Stage 2) Leaching out the copper:	$CuO + 2NH_4^+ \rightarrow Cu^{2+} + 2NH_3 + H_2O$	*Reaction 2*
	$Cu^{2+} + 4NH_3 \rightarrow Cu(NH_3)_4^{2+}$	*Reaction 3*

Stage 3) Filtering

Stage 4) Acidifying the filtrate

Stage 5) Displacing the copper using zinc

(a) Which reaction(s) from 1, 2 and 3 are redox reactions? *Justify your answer using oxidation numbers.* [2 marks]

Reaction 1**: The oxidation number of **oxygen goes from 0 to -2** and that of **S goes from -2 to +4

(b) Which reaction(s) from 1, 2 and 3 are acid-base reactions? *Justify your answer, including identifying the acid and the base.* [2 marks]

***Reaction 2**: **CuO** is the base and **NH_4^+** is the acid.*

(c) What is the purpose of the filtration? [1 mark]

*To **remove insoluble non-copper components** mixed with Cu in the ore – the copper is soluble as $Cu(NH_3)_4^{2+}$*

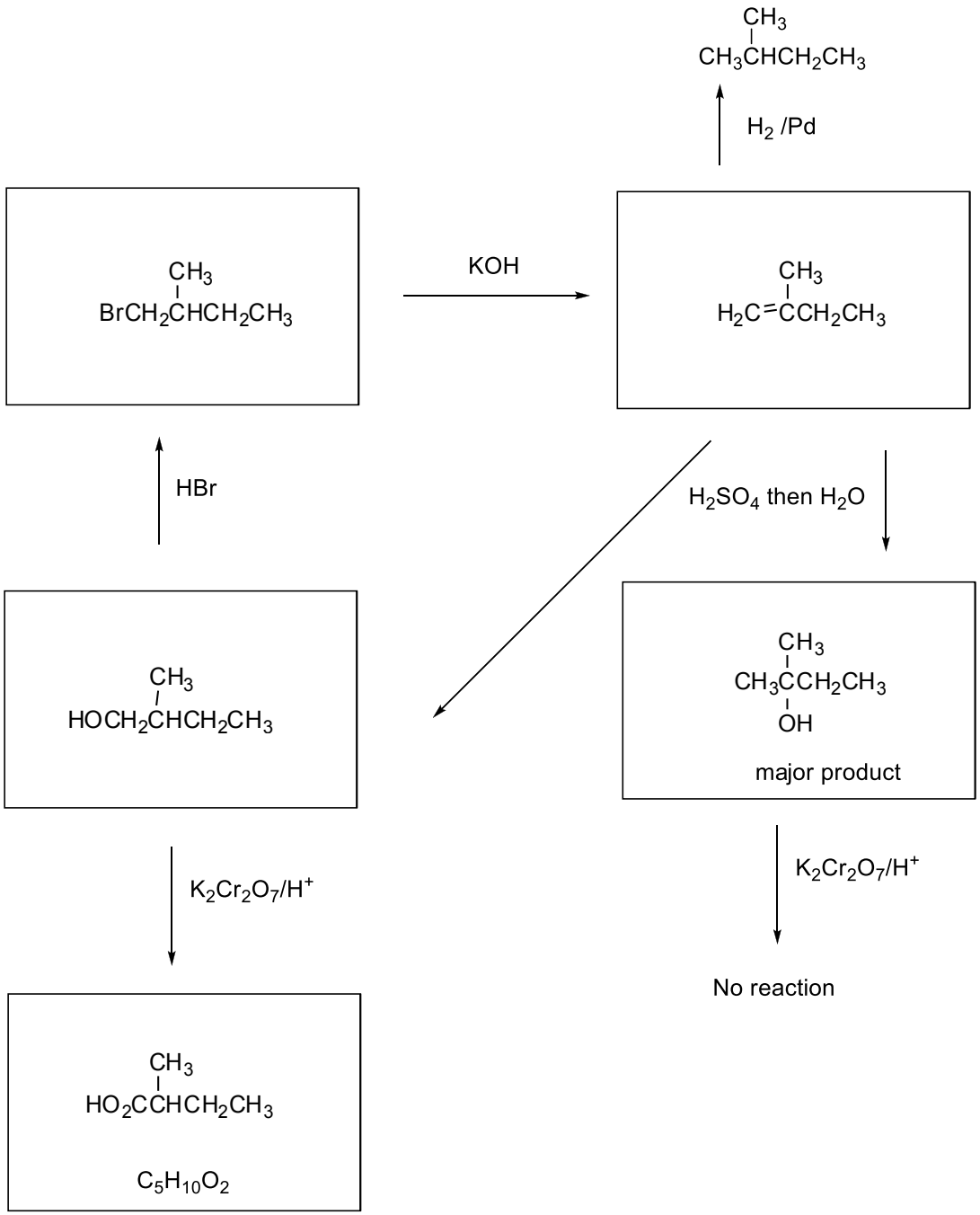
(d) Write the balanced equations for the reactions occurring in Stage 4 and Stage 5. [2 marks]

$Cu(NH_3)_4^{2+} + 4H^+ \rightarrow Cu^{2+} + 4NH_4^+$

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

QUESTION 2: [10 marks]

Draw the structures for the five missing compounds in the scheme below. [2 marks each]



QUESTION 3: [8 marks]

Two solutions of different acids (HA and HB) have the same concentration (0.100 mol L^{-1}) but the pH of the solution of acid HA is 1.00, and the pH of the solution of acid HB is 2.87. 1 mL of each of the solutions is diluted to 10 mL with pure water.

(a) Calculate the pH of the diluted solution of acid HA and justify your answer. [2 marks]

pH = -log(0.01) = ***2.00***

This ***acid is strong*** *because the hydronium ion from the pH is equal to the concentration of the acid on the label. It is* ***totally dissociated*** *in both solutions.*

(b) Explain in terms of equilibrium principles why the *change* in the pH of the solution of acid HB on dilution is less than the change in the pH of the solution of acid HA. [2 marks]

HB is a weak acid, will dissociate more on addition of water, so the increase in pH is smaller
HB is weak and is not totally dissociated. Addition of water causes it to reach a new equilibrium state where it is dissociated to a greater extent. This is because H_2O is a reactant in the dissociation equation. This increase in dissociation will decrease the pH and to some extent counter the increase in pH due to the dilution.

The pH of the blood of a healthy person is in the range 7.35-7.45.

(c) What is the maximum concentration of H_3O^+ in healthy blood? [1 mark]

$10^{-7.35}$ = ***4.47×10^{-8} mol L^{-1}***

K_w at body temperature (37 ˚C) is 2.34×10^{-14} pK_w =13.63.

(d) What is the maximum concentration of hydroxide ion in healthy blood? [2 marks]

Maximum OH^- for minimum H_3O^+ *Minimum H_3O^+ = $10^{-7.45}$*

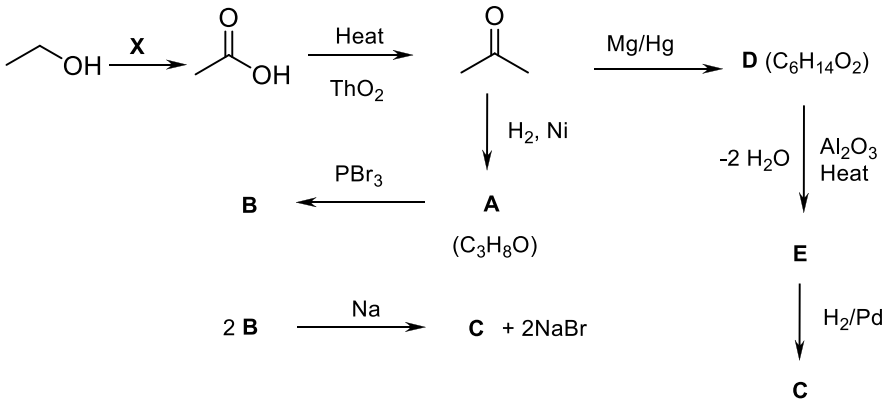
$[OH^-] = 2.34 \times 10^{-14} / 3.55 \times 10^{-8}$ = ***6.60×10^{-7} mol L^{-1}***

(e) For the dissociation of water into H_3O^+ and OH^- ions the reaction enthalpy is 55.8 kJ mol^{-1}. Predict with reasoning whether K_w will be greater or smaller than 2.34×10^{-14} when the temperature is 50 ˚C. [1 marks]

At higher temperature position of equilibrium shifts in ***favour of reaction in the endothermic direction****. In this case it will favour formation of ions which means there will be an* ***increased concentration of products*** *compared to reactants and* ***K_w will increase****.*

QUESTION 4: [11 marks]

The scheme below shows how ethanol (CH_3CH_2OH) can be converted by a series of reactions into compounds containing six carbon atoms. Note that one of the reactions causes a rearrangement, namely, the product of the reaction has a different arrangement of carbons than the reactant.

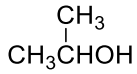
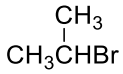
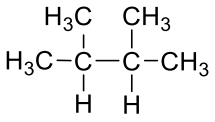
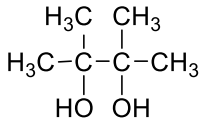
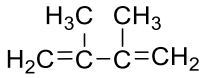


Additional information:

D has several methyl groups in equivalent environments.

Neither **D** nor **E** is susceptible to oxidation with $K_2Cr_2O_7/H^+$.

Give the structures of compounds **A**, **B**, **C**, **D**, and **E**, **and** the formula for reagent **X**.

A 	**B** 	**C** 
D 	**E** 	**X** $K_2Cr_2O_7/H^+$

QUESTION 5: [7 marks]

The structures of the amines having the formula C_3H_9N are given below. These compounds have boiling points that range from -3 °C to 49 °C

Compound:	**A**	**B**	**C**	**D**
Structure:	$CH_3CH_2CH_2NH_2$	CH_3CHNH_2 | CH_3	$CH_3CH_2NHCH_3$	$H_3C-N(CH_3)-CH_3$
Boiling Point:	49 °C	33 °C	36 °C	-3 °C

The boiling point of molecular substances, such as the amines shown, depends on the strength of attractive forces between the molecules of the substance. The strength of these attractive forces depends both on the polarity, the shape, and the size, of the molecule.

Electronegativities: C = 2.6; N = 3.0; O = 3.4; H = 2.2

(a) In a mixture of which two of the amines above would the attractive forces between the molecules due to polar bonds be the greatest? *Justify your answer including describing the nature of the attractive forces* [2 marks]

A and B. A and B have strong inter-molecular **hydrogen bonds** between the N lone pair and a H on the other molecule. **Primary amine** ($R\text{-}NH_2$) groups have more partial negative charge on the N and positive charge on the H than secondary (R_2–NH) or tertiary (R_3-N) because more N-H bonds with **high N-H electronegativity difference**.

(b) For which two of the amines above would the attractive forces between molecules be weaker due to the shape of the molecules? *Justify your answer* [2 marks]

***B and D**. The **branching groups** around the N **prevent close approach** necessary for H-bonds.*

(c) Place the following molecules in order of increasing boiling point: Butan-1-ol; butan-1-amine; propan-1-amine; butan-1,4,-diamine; butan-1,4-diol; pentan-1,5-diol. *Explain your reasoning* [3 marks]

propan-1-amine < butan-1-amine < [Butan-1-ol; butan-1,4,-diamine] < butan-1,4-diol < pentan-1,5-diol.

[N.B.; evidence insufficient to determine order of butanol/butan-diamine, accept either]

Propyl < butyl < pentyl; amine < alcohol; monofunctional < difunctional.

QUESTION 6: [8 marks]

Titanium in nature occurs in the form of the mineral *rutile*, TiO_2. Rutile can be converted to titanium chloride, $TiCl_4$, a colourless liquid which boils at 136 ˚C and fumes in moist air. The $TiCl_4$ is heated with magnesium and the mixture from the reaction is washed with very dilute acid to leave titanium metal.

Titanium is resistant to corrosion by acid and seawater, but will react if heated in oxygen in the presence of fused alkali (KOH), to give K_2TiO_3, potassium titanate.

Titanium is used in the aerospace industry and in chemical and marine engineering. Titanium carbide, TiC, is harder even that carborundum, SiC, and has many industrial uses.

(a) Using the evidence above, what type of bonding exists in titanium chloride? Justify your answer. [1 mark]

Covalent bonding *between Ti and Cl to form $TiCl_4$ molecules. In addition there are weak intermolecular forces between the molecules.*
Evidence: ***liquid*** *below 136 ˚C,* ***boils to vapour*** *not decomposes.*

(b) Give a possible explanation for the fuming of titanium chloride in moist air. [1 mark]

Reaction between $TiCl_4$ and water *will produce HCl vapour.*

(c) Identify the products from the reaction of titanium chloride with magnesium. What is the position of Ti relative to magnesium in the activity series of metals? [2 marks]

$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

Mg is more reactive than Ti *and displaces the Ti metal from the $TiCl_4$ compound.*

(d) Write a balanced equation for the formation of potassium titanate [2 marks]

$$Ti\ (s) + O_2\ (g) + 2KOH\ (s) \rightarrow K_2TiO_3\ (s) + H_2O\ (l)$$

(e) Suggest a likely type of structure and bonding for titanium carbide. [2 marks]

Covalent network solid *with* ***covalent bonding*** *between all Ti and C atoms forming a 3D* ***diamond-like lattice***.

QUESTION 7: [8 marks]

Calcium hypochlorite, $Ca(OCl)_2$, is a chemical product which can be used to kill bacteria in water supplies. It can be prepared in the following sequence of reactions.

130.5 g of manganese dioxide is reacted with excess hydrochloric acid

Reaction 1: $MnO_2\,(s) + 4HCl\,(g) \longrightarrow MnCl_2\,(s) + 2H_2O\,(l) + Cl_2\,(g)$

The Cl_2 from the above reaction is absorbed in 148 g of $Ca(OH)_2$.

Reaction 2: $2Cl_2\,(g) + 2Ca(OH)_2\,(s) \longrightarrow CaCl_2\,(s) + Ca(OCl)_2\,(s) + 2H_2O\,(l)$

The solid products formed are dissolved in 1.000×10^3 L of water.

(a) The anti-bacterial effect depends on the concentration of OCl^- ion. Assuming that the OCl^- does not react with the water, calculate the concentration of OCl^- (in mol L^{-1}) in the solution formed above. [3 marks]

$M(MnO_2) = (24.9 + 2 \times 16)\ g\ mol^{-1} = 86.9\ g\ mol^{-1}$

$n(MnO_2) = 130.5\ g / 86.9\ g\ mol^{-1} = 1.502\ mol = n(Cl_2)$
$n(OCl^-) = 2 \times n(Ca(OCl)_2) = n(Cl_2) = 1.502\ mol$

$V = 1.00 \times 10^3$ L *$[OCl^-] = 1.502\ mol / 1 \times 10^3\ L =$* ***$1.50 \times 10^{-3}\ mol\ L^{-1}$***

(b) Suggest a chemical method by which the OCl^- might kill bacteria. [1 mark]

Accept any reasonable answer: e.g., oxidation of enzymes/membrane/bacteria/DNA; blocking enzyme action; "poison" or "toxic" without any sort of mechanism no mark.

(c) $Ca(OCl)_2\,(s)$ is unstable to heat, and will decompose by disproportionation to form $Ca(ClO_3)_2\,(s)$ and $CaCl_2\,(s)$. Give a balanced equation for this reaction. [2 marks]

$3\ Ca(OCl)_2\,(s) \rightarrow Ca(ClO_3)_2\,(s) + 2\ CaCl_2\,(s)$

(d) Write a balanced equation for the following reaction. [2 marks]

$ClO_3^-\,(aq) + MnO_4^-\,(aq) + H_3O^+\,(aq) \rightarrow MnO_2\,(s) + ClO_4^-\,(aq) + H_2O\,(l)$

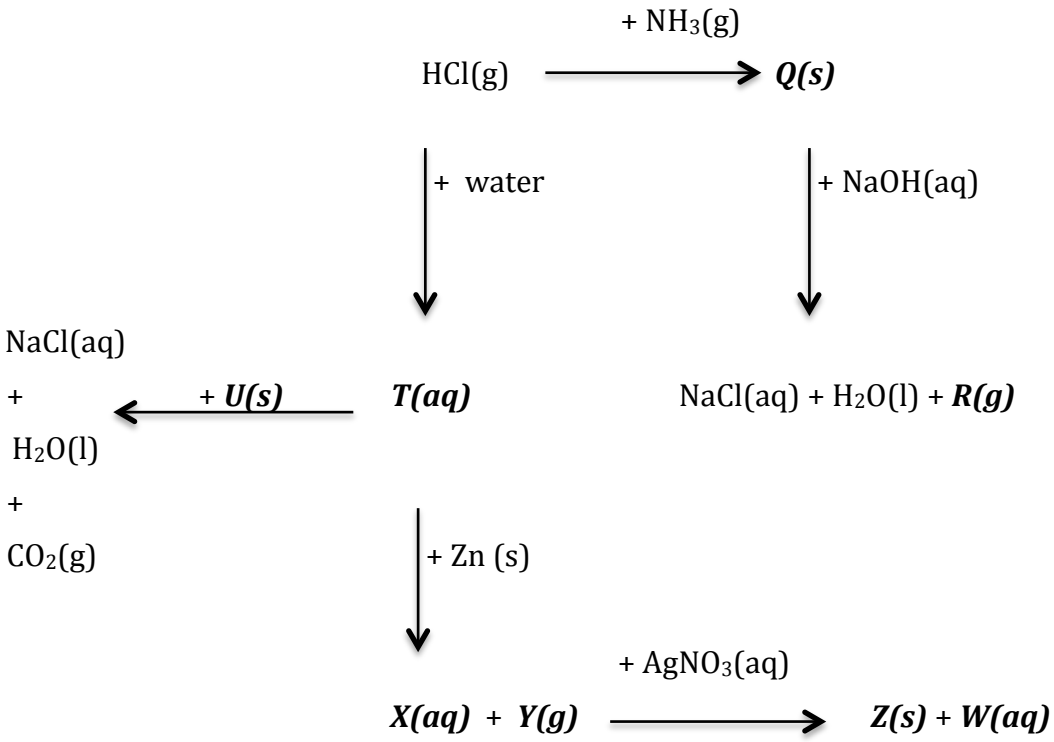
$H_2O + ClO_3^- \rightarrow ClO_4^- + 2H^+ + 2e^-$

$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$

$2MnO_4^- + 3ClO_3^- + 2H^+ \rightarrow 3ClO_4^- + 2MnO_2 + H_2O$

QUESTION 8: [8 marks]

Identify the substances ***Q***, ***R***, ***T***, ***U***, ***X***, ***Y***, ***Z*** and ***W*** in the reaction scheme below.



Answers (1 mark each):

Q = NH_4Cl **R** = NH_3

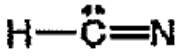
T = HCl(aq) **U** = Na_2CO_3

X = $ZnCl_2$ **Y** = H_2

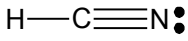
Z = AgCl **W** = $Zn(NO_3)_2$

QUESTION 9: [6 marks]

The following Lewis structures are incorrect. Explain what is wrong with each one and draw a correct Lewis structure for the molecule.

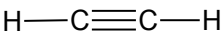
(a) 

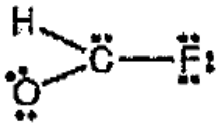
This has a total 8 valence electrons instead of 10. This means the N does not have a full octet of electrons in the outer shell

Correct: 

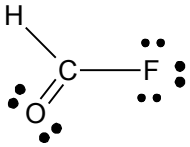
(b) 

This has total 12 electrons – should only be 10 valence electrons. In addition the H atoms should not be linked by double bonds to C.

Correct: 

(c) 

O and C atoms do not have the full octet of valence electrons. Correct total valence electrons

Correct: 

QUESTION 10: [7 marks]

The complexation of gold from minerals with cyanide ion (CN^-) is often used in the extraction of gold from naturally occurring sources. The complex reaction is strongly product-favoured, and the equation for the reaction is given below.

$$Au^+(aq) + 2CN^-(aq) \rightleftharpoons Au(CN)_2^-(aq) \qquad K_c = 2 \times 10^{38}$$

An ore containing 0.689 g of gold was treated with *aqua regia* (a mixture of concentrated nitric acid and sulfuric acid) to produce a 1.00 L solution containing Au(I) ions. This solution was mixed with 1.00 L of 0.040 mol L^{-1} KCN. The resultant solution contains a mixture of Au^+, K^+, $Au(CN)_2^-$, and CN^- ions.

(a) What is the concentration of $Au(CN)_2^-$ in the resultant solution? [2 marks]

*$n(Au) = 0.689\ g / 197\ g\ mol^{-1} = 3.497 \times 10^{-4}$ mol; c(*Au(all forms))*= 3.497 × 10^-4 mol / 2.00 L = 1.749 × 10^-4 mol L^-1*

Since equilibrium constant very large then essentially all will be converted to the complex ion so ***[Au(CN)$_2^-$] =1.749 × 10^{-4} mol L^{-1}***

(b) What is the concentration of CN^- in the resultant solution? [2 marks]

Initial $n(CN^-) = 0.040\ mol\ L^{-1} \times 1.00\ L = 0.040$ mol; Amount in complex = 2 × 3.497 × 10^-4 mol;

Final $c(CN^-) = (0.040\ mol - 6.994 \times 10^{-4}\ mol) / 2.00\ L =$ ***0.0197 mol L^{-1}***

(c) Determine the concentration of uncomplexed Au^+ in the resultant solution. [1 mark]

$K_c = 2 \times 10^{38} = [Au(CN)_2^-] / [Au^+] [CN^-]^2 = 1.749 \times 10^{-4} / [Au^+] \times (0.0197)^2$

$[Au^+] =$ ***2.25×10^{-39} mol L^{-1}***

{N.B., on average there are **no** *free gold ions in solution!}*

(d) The CN^- ion is highly toxic, because it will readily complex with many metal ions, including those in biological enzymes. Predict using the information below whether the presence of silver(I) ions in the same concentration as gold (I) ions would have a significant effect on the extraction of gold. [2 marks]

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) \qquad K_c = 3 \times 10^{21}$$

It would have ***no effect****; the K_c value for formation of the silver complex is10^{17} less than the value for the formation of the gold complex, so essentially* ***no silver complex forms until all the gold has been fully complexed****.*

PERIODIC TABLE OF THE ELEMENTS

Atomic Number

H 1.0 — Molar Mass / g mol^{-1}

1	2											13	14	15	16	17	2
1 **H** 1.0																	2 **He** 4.0
3 **Li** 6.9	4 **Be** 9.0											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3	3	4	5	6	7	8	9	10	11	12	13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 40.0
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.0	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** 98.9	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
55 **Cs** 133	56 **Ba** 137	**57–71** Lantha-nide series	72 **Hf** 179	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226	**89–103** Actinide series	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 262	108 **Hs** 265	109 **Mt** 266									

Lanthanide Series	57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175
Actinide Series	89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 255	103 **Lr** 262