New Zealand Chemistry Olympiad Trust

New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Monday 25 September 2017

TIME ALLOWED: 120 minutes

Answer **ALL** questions on this examination booklet.

Calculators may be used.

A periodic table with atomic masses is also provided.

NOTE - This paper is in two sections. Complete both sections.

Section A Multichoice: Total marks 50/100

There are 25 questions. **EACH answer is worth 2 marks**

Answer ALL questions — circle the letter of the correct answer.

Section B Long Answers: Total marks 50/100

The mark value for each question is shown.

All answers must be written in the space provided.

In questions involving numerical calculations show all reasoning and work.

STUDENT'S NAME: ____

STUDENT'S EMAIL: ____

SCHOOL: ____

	Section A Multichoice	Section B Long Answers					Total /100
	/2 × 25= 50	/7	/10	/18	/8	/7	
Mark							

SECTION A - Multichoice

For each question circle the correct answer.

Question One

What is the concentration of KI in a solution that is 5.00% KI by mass and has a density of 1.038 g/cm^3? M(KI) = 166 g mol^{-1}

A. 0.0301 mol L^{-1} **B.** 0.313 mol L^{-1} **C.** 0.500 mol L^{-1} **D.** 0.625 mol L^{-1}

Question Two

A compound with the formula X_2O_5 contains 34.8% oxygen by mass. Identify element X.

A. arsenic **B.** carbon **C.** phosphorous **D.**samarium

Question Three

Which is the composition of the solution that results from mixing 40.0 mL of 0.200 mol L^{-1} HCl with 60.0 mL of 0.100 mol L^{-1} NaOH?

A. 0.150 mol L^{-1} NaCl

B. 0.0200 mol L^{-1} NaCl and 0.0200 mol L^{-1} HCl

C. 0.0200 mol L^{-1} NaCl and 0.0600 mol L^{-1} HCl

D. 0.0600 mol L^{-1} NaCl and 0.0200 mol L^{-1} HCl

Question Four

An unknown anion in solution can be identified by adding Ag^+ and Ba^{2+} ions to separate samples. Which anion would produce the results listed for it? (+ indicates precipitate observed; - indicates no precipitate): Ag^+ Ba^{2+}

A. carbonate + – **B.** hydroxide – + **C.** iodide + – **D.** nitrate + +

Question Five

The preparation of bromobenzene can be represented by the equation shown.

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

A student reacted 20.0 g of C_6H_6 with 0.310 mol of bromine. If 28.0 g of C_6H_5Br was obtained, what was the percentage yield?

A. 31.5 **B.** 40.3 **C.** 57.6 **D.** 69.7

Question Six

Which of the following species has only one nonbonding pair of electrons on the central atom?

A. NH_3 **B.** H_2CO **C.** H_2O **D.** CH_4

Question Seven

The iodate ion (IO_3^-) can oxidize Fe^{2+} to Fe^{3+} in acid solution. IO_3^- is reduced to iodide (I^-) in this reaction. Which is the amount in moles of Fe^{2+} that can be oxidized by 1 mole of IO_3^- ?

A. 3 **B.** 4 **C.** 5 **D.** 6

Question Eight

Flutamide is an important organic compound containing three fluorine atoms in each molecule. It is used in the treatment of prostate cancer. An analytical chemist extracted flutamide from a commercial tablet weighing 203.21 mg leaving a residue (containing non-medicinal ingredients) that weighed 128.23 mg. Elemental analysis of the extracted flutamide revealed the presence of 15.47 mg of fluorine. What is the molar mass (in g mol^{-1}) of flutamide?

A. 232.8 **B.** 254.5 **C.** 276.3 **D.** 286.9

Question Nine

Consider the following reactions at equilibrium:

I) $C(graphite) + S_2(g) \leftrightarrows CS_2(g)$

II) $CO_2(g) + C(graphite) \leftrightarrows 2CO(g)$

III) $CH_4(g) + 2S_2(g) \leftrightarrows CS_2(g) + 2H_2S(g)$

IV) $CO(g) + 3H_2(g) \leftrightarrows CH_4(g) + H_2O(g)$

For which pair would there be NO change in compositon when the pressure is increased by reducing the volume, at constant temperature.

A. I and II **B.** I and III **C.** I and IV **D.** II and III

Question Ten

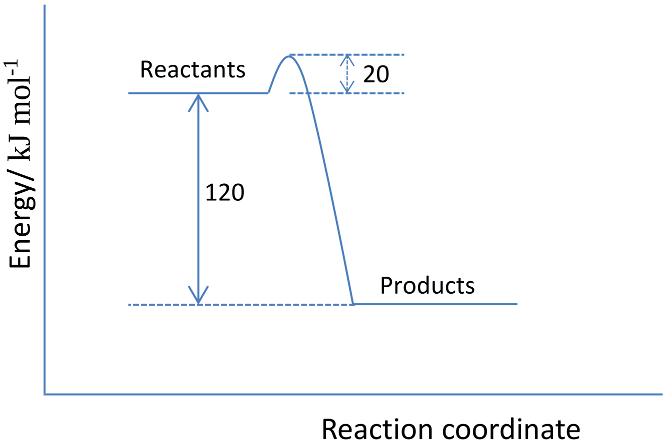
Use the thermochemical data given to calculate $\Delta_f H°$ for $N_2O_5(g)$ in kJ mol^{-1}.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H° = +180.5 \text{ kJ}$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H° = -114.1 \text{ kJ}$$
$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g) \qquad \Delta H° = -110.2 \text{ kJ}$$

A. −332.8 **B.** −43.8 **C.** 11.3 **D.** 22.

Question Eleven

Consider the energy profile diagram for a chemical reaction



Which of the following statements **must** be correct?

A. The activation energy of the forward reaction is 120 kJ mol^{-1}

B. The activation energy of the reverse reaction is 140 kJ mol^{-1}

C. The energy change (ΔE) of the forward reaction is – 100 kJ mol^{-1}

D. The forward reaction is spontaneous

Question Twelve

What is the oxidation number of vanadium in ammonium orthovanadate, $(NH_4)_3VO_4$?

A. +2 **B.** +3 **C.** +4 **D.** +5

Question Thirteen

When the equation $ClO_2(aq) + OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O$

is balanced, what is the ratio of the stoichiometric coefficient of ClO_2 to that of ClO_3^-?

A. 1:1 **B.** 2:1 **C.** 3:1 **D.** 3:2

Question Fourteen

What is the formula of the most stable oxide of francium, Fr, an element in Group 1 of the periodic table

A. Fr_2O **B.** FrO **C.** Fr_2O_3 **D.** FrO_2

Question Fifteen

Ammonium nitrate, NH_4NO_3 can decompose explosively when heated to give the products shown below.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

What are the changes in the oxidation numbers of the two nitrogen atoms in NH_4NO_3?

A. -2, -4 **B.** +2, +6 **C.** +4, -6 **D.** +4, -4

Question Sixteen

What is the geometry of the ClO_3^- anion?

A. Trigonal planar **B.** Trigonal pyramidal **C.** bent **D.** Tetrahedral

Question Seventeen

How many structural (constitutional) isomers are possible for C_6H_{14}?

A. 2 **B.** 3 **C.** 4 **D.** 5

Question Eighteen

How many geometric isomers are possible for $CH_3CH{=}CHCH_2CH{=}CHCH_3$?

A. 0 **B.** 2 **C.** 3 **D.** 4

Question Nineteen

Which isomer of $C_4H_{10}O$ forms three isomeric alkenes on dehydration?

A. butan-1-ol **B.** butan-2-ol

C. 2-methylpropan-1-ol **D.** 2-methylpropan-2-ol

Question Twenty

Quinaldine red is a useful acid-base indicator which is red in solutions of pH higher than 3.5, but colourless below pH 1.5. Which of the following solutions would turn red if a few drops of quinaldine red were added?

(i) 0.1 mol L^{-1} HCl (ii) 0.05 mol L^{-1} NH_3 (iii) 0.0005 mol L^{-1} CH_3COOH

A. **(**i)and (ii) only **B.** **(**i) and (iii) only **C.** **(**ii) and (iii) only **D.** (ii) only

Question Twenty One

Which is the conjugate acid of Na_2HPO_4?

A. H_3PO_4 **B.** $H_2PO_3^-$ **C.** $H_2PO_4^-$ **D.** PO_4^{3-}

Question Twenty Two

Element **X**, a grey solid, reacts with element **Z**, a colourless gas, to form a compound in which there are twice as many atoms of **X** as there are of **Z**. Which of the following statements about the ground-state electron configurations of these atoms is most likely to be true?

A. **X** has one valence electron and **Z** has six.
B. **X** has one valence electron and **Z** has five.
C. **X** has two valence electrons and **Z** has one.
D. **X** has two valence electrons and **Z** has five.

Question Twenty Three

What is the pH of a solution made by mixing 15 mL of 0.1 mol L^{-1} $Ca(OH)_2$ with 12 mL of 0.15 mol L^{-1} HCl?

A. 1.35 **B.** 12.65 **C.** 12.35 **D.** 11.08

Question Twenty Four

Nitrous acid, HNO_2, is a weak monoprotic acid. It can be concluded from this that nitrite ion, NO_2^- is

A. unreactive towards acids **B.** a strong base
C. a stronger base than hydroxide ion, OH^- **D.** a weak base

Question Twenty Five

At 50 °C K_w is equal to 5.5.x.10^{-14}. What is the pH of a neutral aqueous solution at 50 °C?

A. 7.00 **B.** 13.26 **C.** 2.3×10^{-7} **D.** 6.63

SECTION B – Long Answers

QUESTION ONE (7 marks)

The percentage purity of a commercial sample of potassium nitrite can be established by titration. The determination involves reaction of a nitrite solution with excess standard acidified cerium(IV) sulfate followed by titration of the excess cerium(IV) sulfate with a standard iron(II) solution.

$$Ce^{4+} + NO_2^- \rightarrow Ce^{3+} + NO_3^- \text{ (not balanced)}$$

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

0.4911 g of impure potassium nitrite is dissolved in water and made up to 100 mL. 10.00 mL of this solution is added to 25.00 mL of an acidified 0.1105 mol L^{-1} solution of cerium(IV) sulfate. It is found that 16.24 mL of 0.1007 mol L^{-1} iron(II) ammonium sulfate is required to consume the excess cerium(IV) sulfate. Calculate the percentage purity of the potassium nitrite sample.

$n(Fe^{2+})$ = 0.1007 mol x 0.01624 L = 0.001635 mol = $n(Ce^{4+})_{excess}$ 1 mark

Total $n(Ce^{4+})_{added}$ = 0.1105 mol x 0.025 L = 0.002763 mol 1 mark

$n(Ce^{4+})_{reacted}$ = $n(Ce^{4+})_{added}$ - $n(Ce^{4+})_{excess}$ = 0.001128 mol 1 mark

Ce^{4+} reacts with NO_2^- in 2:1 ratio so $n(NO_2^-)_{reacted}$ = 0.0005638 mol in 10.00 mL 1 mark

$n(NO_2^-)$ in 100 mL = 0.005638 mol 1 mark

$m(NO_2^-)$ = 0.005638 mol x 85.1 g mol^{-1} = 0.4798 g 1 mark

% purity = (0.4798 / 0.4911) x100/1 = 97.69 % 1 mark

QUESTION TWO (10 marks)

a) Nitric oxide (NO) can be formed by the action of dilute nitric acid on copper. Commercially, it is prepared by reacting ammonia with O_2 at about 850 °C in the presence of a catalyst (to give NO and water).

(i) Write a balanced equation for the reaction.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ 1 mark

(ii) Nitric oxide (NO) can be further reacted with O_2 give nitrogen dioxide. Write a balanced equation for the reaction.

$2NO + O_2 \rightarrow 2NO_2$ 1 mark

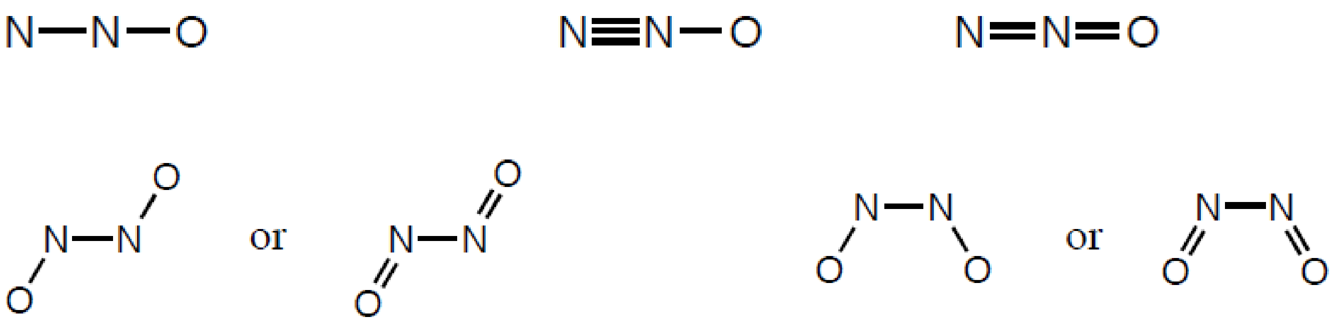
b) The reaction in (a)(ii) is believed to involve two steps. The first step is a reaction in which two molecules of NO react to form an unstable oxide of nitrogen, N_2O_2. Once the system is at equilibrium N_2O_2 reacts with O_2 in a second step to form nitrogen dioxide.

Overall the reaction is exothermic and in the commercial process it is cooled to 25 °C because the yield of NO_2 **decreases** with increasing temperature.

Explain why the yield of NO_2 decreases with increasing temperature.

The equilibrium $2\,NO \leftrightarrows N_2O_2$ is exothermic. An increase in the temperature shifts the equilibrium to the left lowering the $[N_2O_2]$ available to react with O_2 to form NO_2. 1 mark

Draw the Lewis structures of N_2O and N_2O_2. Show the shapes of these molecules and include the bond angles around the inner atoms. 1 mark each structure (2 marks)
1 mark each shape with bond angle (2 marks)



d) Nitrogen dioxide, NO_2, is an acidic oxide that reacts with water to form nitric acid, HNO_3. Nitric oxide, NO, is also produced in the reaction and recycled in the process.

(i) Write balanced **half** equations for the reaction of NO_2 with water. Clearly show the oxidation number of each nitrogen atom in the equation and then indicate whether the half reaction is an oxidation or a reduction process.

$2e + 2H^+ + NO_2 \rightarrow NO + H_2O$ (reduction: N(+4) goes to N(+2) 1 mark

$H_2O + NO_2 \rightarrow HNO_3 + H^+ + 1e$ (oxidation N(+4) goes to N (+5) 1 mark

(ii) Write the overall balanced equation

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ 1 mark

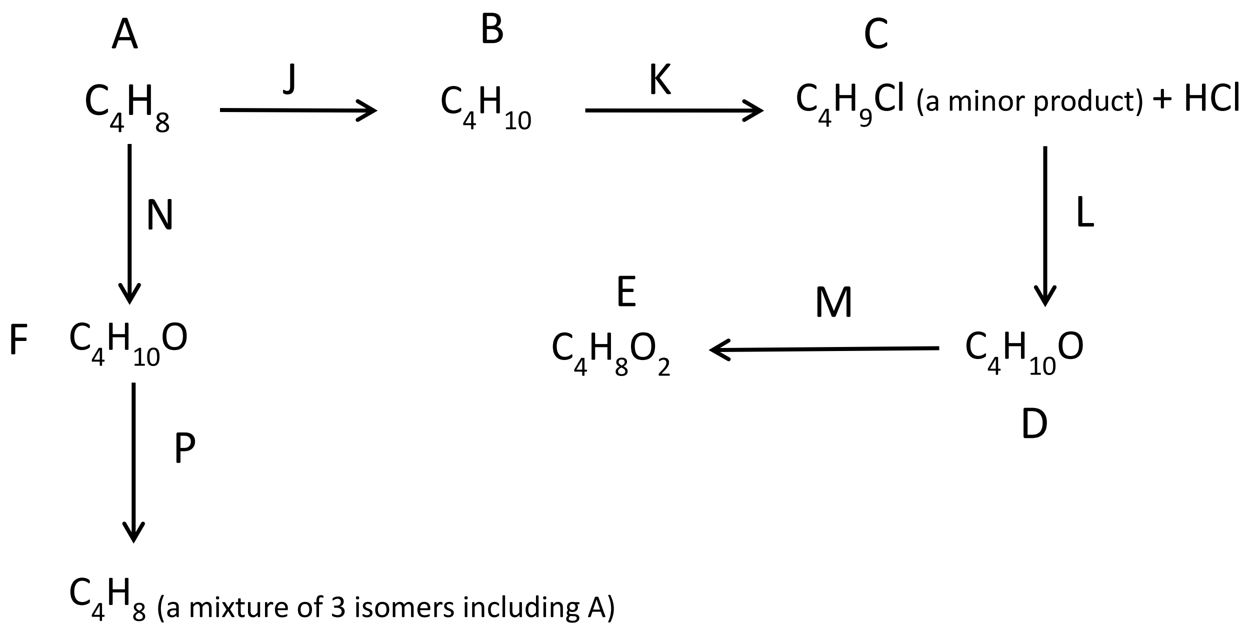
QUESTION THREE (18 marks)

a) (3 marks) Draw the organic products of the following reaction and clearly identify which is the major product.

$HBr + (CH_3)_2C{=}CHCH_3 \rightarrow$

1 mark for each product and 1 mark for identifying the major product as structure of 2-bromo-2-methyl butane (name not needed)

b) The flow diagram below shows some reactions involving organic substances starting with the unbranched compound A which has geometric isomers.



In the table on the next page

(i) draw the structures of all the organic products and name them.

(ii) identify the reagents (by name or formula) that can be used to carry out each of these reactions.

Marking = 1 mark for each of compounds A to F and ½ mark for each name that correctly matches structure (allow follow on marking)

1 mark for each reagent

Total 15 marks

Compound A **Name:**	**Compound B** **Name:**
Compound C **Name:**	**Compound D** **Name:**
Compound E **Name:**	**Compound F** **Name:**
Reagent J	**Reagent K**
Reagent L	**Reagent M**
Reagent N	**Reagent P**

QUESTION FOUR (8 marks)

Methyl orange can be used as an acid-base indicator. It is pink in solutions with a pH lower than 3 and yellow in solutions with a pH higher than 4.

Four beakers are known to contain one each of:

- 0.1 mol L^{-1} HCl
- 0.01 mol L^{-1} HCl
- distilled water
- 0.1 mol L^{-1} NaOH

(a) Complete the following table.

½ mark each pH

½ mark each correct colour = total 4 marks

	pH	Colour of methyl orange
0.1 mol L^{-1} HCl	1	pink
0.01 mol L^{-1} HCl	2	pink
distilled water	7	yellow
0.1 mol L^{-1} NaOH	13	yellow

(b) Using **only** the methyl orange indicator, **additional** water, test tubes and a **measuring cylinder**, discuss how a student could identify each of the four solutions.

Answer

Both HCl solutions – add indicator and slowly add the same volume of water to each solution. The solution that turns the indicator from pink to yellow first is the more dilute acid, ie 0.01 mol L^{-1} HCl.

Water / NaOH solution – take 1 mL samples of the 0.1 mol L^{-1} HCl solution and add indicator. Add the same volume of water and NaOH, eg 100 mL. The indicator will remain pink for the water sample, and the NaOH will cause the indicator to turn from pink to yellow.

4 marks

QUESTION FIVE (7 marks)

To launch the space shuttle, two propulsion systems are used. Most of the thrust for the first two minutes of flight comes from the two reusable solid rocket boosters. The solid rocket boosters use a mixture of aluminium powder and ammonium perchlorate, NH_4ClO_4, together with an iron oxide catalyst.

The external tank is filled with liquid hydrogen and liquid oxygen which react to form water.

The enthalpy of reaction ($\Delta_r H$) can be calculated from standard enthalpies of formation as shown below.

$$\Delta_r H^o = \sum \Delta_f H_{\text{products}} - \sum \Delta_f H_{\text{Reactants}}$$

The reaction that takes place during the combustion of the solid rocket booster fuel has been summarized as:

$$10Al(s) + 6\,NH_4ClO_4(s) \rightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(l) + 3N_2(g)$$

a) (3 marks) Use the enthalpies of formation ($\Delta_f H$), to calculate the enthalpy of reaction at 298 K for this reaction. Note that $\Delta_f H$ for an element in its standard state is 0.00 kJ mol^{-1}

	$NH_4ClO_4(s)$	$Al_2O_3(s)$	$AlCl_3(s)$	$H_2O(l)$
$\Delta_f H$ / kJ mol^{-1}	−295.3	−1675.7	−704.2	−285.8

Answer 9,769 kJ

$\Delta_r H^o$ = (4 x -1675.7 + 2 x -704.2 + 12x-285.8) – (6x-295.3) 1 mark

= -11540.8 kJ + 1771.8 kJ 1 mark

= 9769 kJ 1 mark

Note may not show working but 2 marks for working and 1 mark for final answer. Accept unit kJ or kJ mol^{-1}

b) (4 marks) 450 tonnes (4.50 x 10^5 kg) of solid propellant are used in the solid rocket boosters in total, and that aluminium is the limiting reagent present at 16% in the mixture, calculate the energy released when this is reacted according to the above equation.

m(Al) = 0.16 x 4.50 x 10^5 kg = 72 x 10^3 kg 1 mark

n(Al) = 72 x 10^6 g/27 g mol^{-1} = 2.66 x 10^6 mol 1 mark

n(reaction) = 2.66 x 10^5 mol 1 mark

Heat released = 2.66 x 10^5 mol x 9,769 kJ mol^{-1} = 2.6 x 10^9 kJ 1 mark

PERIODIC TABLE OF THE ELEMENTS

Atomic Number	1 **H** 1.0	Molar Mass / g mol^{-1}

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
																	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											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.	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 Lanthanide 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