G.C.E. (A/L) Examination
2004 April
Chemistry II / Three hours

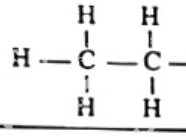
- *Periodic Table is also provided.*
- *Use of calculators is not allowed.*

PART A - STRUCTURED ESSAY (Pages 02-08)

Answer all the questions.
Write your answer in the space provided below each question. Please note that the space provided is sufficient for the answer and that etensive answers are not expected.

N.B. INSTRUCTION BOX

In answering questions 3 and 4, you may represent alkyl groups in a condensed manner.

e.g.  may be shown as $CH_3 - CH_2 -$

PART B and PART C - Essay
(pages 09-13)

Answer **four** questions selecting not more than two questions from each part. Use the paper supplied for this purpose.

At th end of the time allotted for this paper, tie the answers to three parts A, B and C together so that Part A is on top and hand them over to the Supervisor.

You are permitted to remove only Part B and C of the question paper from the Examination Hall.

Universal gas constant, R = 8.314 $JK^{-1} mol^{-1}$
Avogadro constant N_A = 6.022 x 10^{23} mol^{-1}

PART A - STRUCTURED ESSAY

Answer all four questions. Each question carries 10 marks.

1. (a) Complete the following statements by filling the blanks with an element/ elements from the list H, Cl, N, S, O, Cr, Zn and P.

(i) The element(s) showing both the +5 and -3 oxidation states is/are .....

(ii) The element with the lowest boiling point is .....

(iii) The element(s) forming oxides which are coloured at room temperature is/are .....

(iv) The strongest reducing agent in the elemental form is .....

(v) The strongest oxidising agent in the elemental form is .....

(vi) The element(s) showing allotropy is/are .....

(vii) The element(s) giving both an acidic oxide and an acidic hydride is/are .....

(2.6 marks)

(b) X and Y are two elements with atomic number less than 18. X reacts with water at room temperature liberating a gas Z and forming a solution A. Y does not react with water but reacts with solution A, liberating the same gas Z and forming a solution B

(i) Using chemical symbols **only**, write all the possibilities for X, Y and Z.
X = ... Y = ... Z = ...

(ii) What observations can be made when excess dilute HCl is added dropwise to solution B?

.....

.....

(iii) Using chemical symbols **only** write the balanced chemical equation for the reaction between A and Y.

.....

(4.4 marks)

(c) The molecules of a gaseous compound L are triatomic and angular. When L is oxidised M is formed as the only product. L and M are both gases at room temperature. Molecules of M are trigonal planar. M reacts with water forming the acid N. N forms a tetrahedral anion. Write the molecular formulae of L, M and N.

L= ..... M = ... N = ...

(3.0 marks)

2. (a) (i) $CrO_3(s)$ when heated decomposes to give $Cr_2O_3(s)$ and $O_2(g)$ as the only products. 0.4000 g of a sample of CrO_3 contaminated with Cr_2O_3 when heated gave 0.3184 g of Cr_2O_3. Calculate the mass percentage of CrO_3 in the sample. (Cr = 52.0, O = 16.0)

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(4.0 marks)

(ii) Write a balanced equation for the ionic half reaction corresponding to the conversion of Cr_2O_3 to CrO_4^{2-} in basic medium.

.....

(1.0 marks)

(b) Recall thr experiment to determine the order with respect to Fe^{3+} (aq), in the reaction between Fe^{3+}(aq) and KI.

Table I gives the volumes (in cm^3) and concentration of the reagents used for four different measurements.

Table I

Experiment number	Water	0.100 mol dm^{-3} acidified Fe^{3+}(aq) solution	1 mol dm^{-3} KI solution	0.0001 mol dm^{-3} $Na_2S_2O_3$ solution containing starch
1	-	25.00	5.00	5.00
2	5.00	20.00	5.00	5.00
3	10.00	15.00	5.00	5.00
4	15.00	10.00	5.00	5.00

All experiments were carried out at room temperature by three groups of students A, B and C. The reagents were measured into two beakers before mixing. The way in which the three student groups measured the reagents in the two beakers is given in table II. The stopwatch was started at the

time the contents of the two beakers were mixed, to determine the time for a blue colour to appear

. Table II

Group	Beaker 1	Beaker 2
A	KI solution	all other solutions
B	$Na_2S_2O_3$ solution	all other solutions
C	Fe^{3+} (aq) solution	all other solutions

Answer the following questions

(i) Why is the same amount of $Na_2S_2O_3$ used in these experiments?

(ii) What is the role of starch in this experiment?

(iii) One of the three groups followed the correct procedure In the following table, write in the appropriate cage the word 'correct' to identify this group. In the other two cages give the main reasons for the method followed by the relevant group being unacceptable

A	
B	
C	

(iv) The group which followed the correct procedure found that the time taken for the appearance of the blue colour in experiment number 1, was too short to be measured Write **three** ways in which the time taken for the colour change may be increased

(5.0 marks)

3 Selecting appropriate chemicals and solvents for the chemical reactions **only** the following list, answer parts (a) and (b)

Conc HCl, aqueous NaOH, aqueous NH_4OH

Mg, Fe, Zn(Hg)

PBr_3, PCl_5, $AlCl_3$, Br_2

$KMnO_4$, $NaBD_4$, $NaBH_4$

Formaldehyde (HCHO), acetone (CH_3COCH_3)

Water, ethanol, ether CCl_4, D_2O

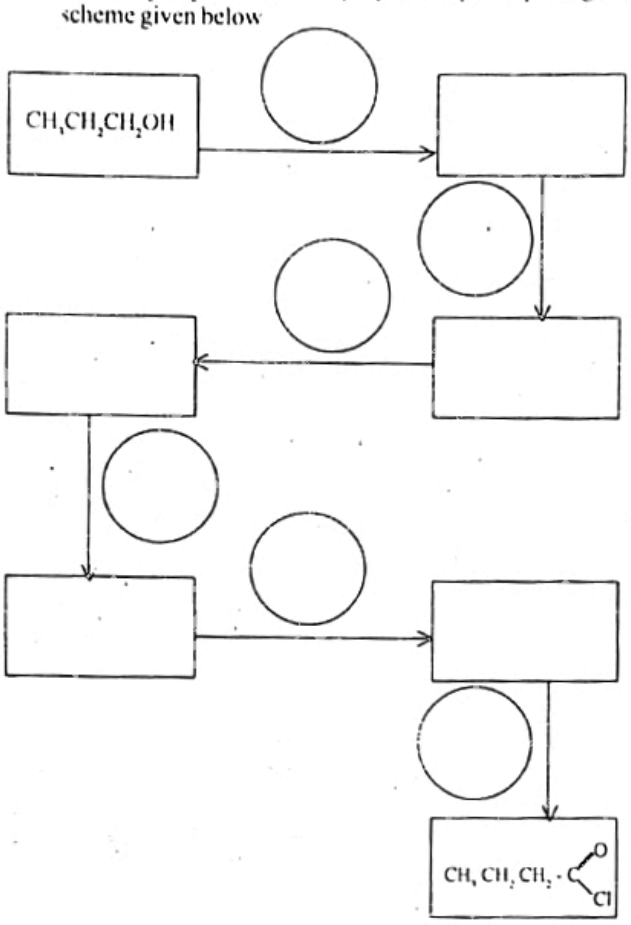
(D) - Deuterium

Note

(I) - In the following Schemes each arrow indicates a single reaction.

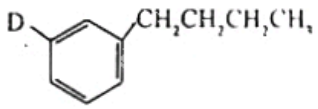
(II): Write in the boxes the structures of appropriate compounds and in the circles the appropriate reagents

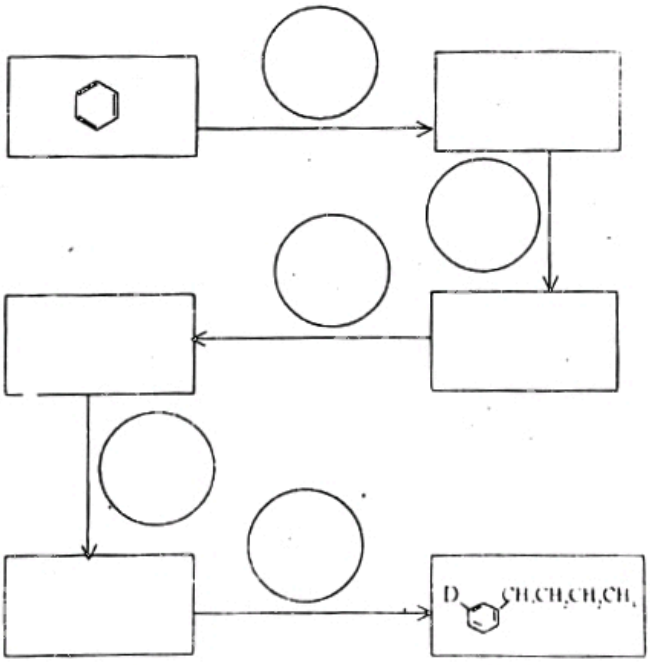
(a) Show how you would prepare butanoyl chloride ($CH_3CH_2CH_2COCL$) from propanol, by completing the scheme given below



(5 5 marks)

a) Using butanoyl chloride prepared in part (a) Show how you would synthesize the following compound from benzene





(4 5 marks)

4 (a) (i) The relative molecular mass of a hydrocarbon A is 58. Write the molecular formula of A. (c = 12.0, H = 1.0)

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(ii) Write possible structures for A.

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(iii) When one mole of the **acyclic** hydrocarbon **B** is subjected to complete catalytic hydrogenation, it reacts with 2 moles of hydrogen and gives one mole of **A**. What is the structure of **A**?

.....

.....

.....

.....

(iv) Write **four** possible stru tures for B.

(v) B reacts with ammoniacal Cu_2Cl_2 to give a red precipi tate What is the structure of B?

(vi) **C** an isomer of **B**, gives **D** in the presence of dilute H_2SO_4 and $HgSO_4$. **D** reacts with an acidified alcoholic solution of 2,4-dinitrophenylhydrazine to give an orange precipitate. **E**. Write down the structures of **C**, **D** and **E**.

C

D

E

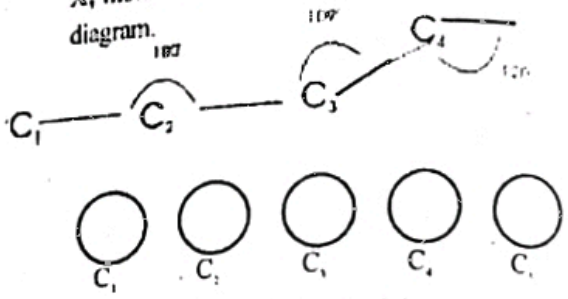
(4.8 marks)

(b) A molecule of the **acyclic** hydrocarbon **X**, contains 5 carbon atoms connected to each other as follows:

$$C_1 - C_2 - C_3 - C_4 - C_5$$

The bond angles $C_1C_2C_3$, $C_2C_3C_4$ and $C_3C_4C_5$ are 180° 109° and 120° respectively

(i) Write down the hybridization of each carbon atom of **X**, inside the corresponding circle in the following diagram.



(ii) Write the molecular formula of **X**

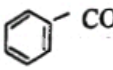
(1.6 marks)

(C) Consider the following reactions

(I) $CH_3 - C(=O) - CH_3 \xrightarrow[\text{ethanol}]{HCN, KCN}$ A

(II) $CH_3 - CH_2 - C(CH_3)_2 - Br \xrightarrow{\text{aq. NaOH}}$ B

(III) $CH_3 - CH = CH_2 \xrightarrow[CCl_4]{Br_2}$

(IV)  $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3}$ D

(i) Write the structures of the products **A**, **B**, **C** and **D** in the cages provided.

A B C D

(ii) Identify the mechanism type of the above reactions (I), (II), (III) and (IV) by writing I, II, III or IV in the appropriate cage in the second column of the following table. Also indicate the electrophile/nucleophile in the appropriate cage

Mechanism-type	Reaction No.	Electrophile	Nucleophile
Electrophilic addition			
Electrophilic substitution			
Nucleophilic addition			
Nucleophilic substiiution			

(iii) Write the structure of the intermediate in reaction (III)

(3.6 marks)

PART B - ESSAY

Answer two questions only. Each question carries 15 marks.

5. Answer all parts.

(a) State the Dalton's Law of partial pressures.

^{35}Cl and ^{37}Cl are the two naturally occurring isotopes of chlorine. The natural abundances of $^{35}Cl_2(g)$, $^{35}Cl\,^{37}Cl(g)$ and $^{37}Cl_2(g)$ are 70, 20 and 10 mole percent, respectively. A vessel contains 100 mol of naturally occurring chlorine gas at 300 K. The density of the gas in the vessel under these conditions is 2.36 g dm^{-3}.

Calculate the following :

(i) Volume of the vessel

(ii) the partial pressure of $^{37}Cl_2(g)$

($^{35}Cl = 35$, $^{37}Cl = 37$)

(4.5 marks)

(b) Using the standard enthalpyh of formation ($\Delta_f H^{\ominus}$) data at 25°C given below, determine by a suitable calculation, which of the compounds $SF_4(g)$ and $SF_6(g)$, has the stronger S-F bond.

	$SF_4(g)$	$SF_6(g)$	S(g)	F(g)
$\Delta_f H^{\ominus}$ / kJ mol^{-1}	-775	-1210	279	79

(4.5 marks)

(C) The standard enthalpies of formation of C (s), CO(g), $CO_2(g)$ and $H_2O(g)$ at 25°C are 0 kJ mol^{-1}, -110 kJ mol^{-1}, - 395 kJ mol^{-1} and -242 kJ mol^{-1} respectively. Calcuate the standard enthalpy changes of the following chemical reac tions at 25°C.

(i) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

(ii) $C(s) + O_2(g) \rightarrow CO_2(g)$

In the water gas reaction (reaction (i) above) steam is passed over heated C in the form of coal to produce water gas, an equimolar mixture of CO(g) and $H_2(g)$. In order to obtain water gas at a reasonable rate, it is necessary to maintain the temperature of the coal close to 400°C. In the industrial production of water gas the treatment of the heated coal with steam is alternated with treatment with air. Making reference to your calculations above and using your knowledge of chemical kinetics, explain why this is done in the industrial process.

(6.0 marks)

6. Answer all parts.

(a) Write down an expression for the solubility product of the ionic solid, M_2X_3

(1.0 makrs)

(b) A solution P was prepared by dissolving 0.12 mol of $[(Ag(NH_3)_2]NO_3$ and 2.0 mol of NH_3 in distilled water and diluting to 1000.0 cm^3 with distilled water. The equilibrium constant at 25°C for the reaction,

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$

is 1.7×10^7 $mol^2\ dm^{-6}$. Calculate the concentration of $Ag^+(aq)$ in the solution P at 25 °C

Show by calculation whether or not AgCl will precipitate when 500.0 cm^3 of P is mixed with 500.0 cm^3 of a 0 02 mol dm^{-3} aqueous solution of NaCl at 25 °C.

The solubility product K_{sp} of AgCl at 25°C = 1.8×10^{-10} $mol^2\ dm^{-6}$

(5.0 marks)

(C) All experiments given below are conducted at 25°C.

(i) A weedicide B is more soluble in $CHCl_3$ than in water. When a 4.65×10^{-2} mol dm^{-3} aqueous solution of B is shaken with an equal volume of $CHCl_3$ and the layers allowed to reach equilibrium, the concentration of B in the $CHCl_3$ layer is found to be 4.5×10^{-2} mol dm^{-3}. Calculate the partition coefficient for the partitioning of B between $CHCl_3$ and water.

(ii) A soil sample is contaminated with B. The content of B in this soil sample was determined as follows. 100.0 g of the contaminated soil containing 10% by mass of water, is shaken well with 90.0 cm^3 of distilled water. All B in the wet soil sample dissolves in the water to give an aqueous phase. The concentration of B in this aqueous phase is X mol dm^{-3}. The aqueous suspension is then shaken with 10.0 cm^3 of $CHCl_3$ and at equilib- rium the concentration of B in the aqueous and $CHCl_3$ phases are Y mol dm^{-3} and Z mol dm^{-3} respectively. Express Z in terms of X and Y and calculate the ratio Y/X. Volume of 1.0 g of water = 1.0 cm^3)

(iii) The relative molecular mass of B is 125.0. If 1.0 g of the above moist soil sample contained 4×10^{-4} g of B. calculate the values of X, Y and Z.

(iv) The aqueous suspension after extraction with $CHCl_3$ in (ii) above, is separated and extracted twice more, using 10.0 cm^3 of $CHCl_3$ for each extraction. Calculate the concentration of B in the aqueous phase after the third extraction in,

(I) mol dm^{-3} (II) ppm (1 ppm = 1 mg dm^{-3})

(9.0 marks)

7. Answer both parts.

(a) You are provided with two labelled rods of the pure metals A and B and two unlabelled bottles one containing a 1.0 mol dm^{-3} aqueous solution of A^{m+} and other containing a 1.0 mol dm^{-3} aqueous solution of B^{n+}. A and B do not form other ionic species in aqueous media. Giving reasons describe how you would,

(i) identify which of the metals A and B is more reducing.

(ii) identify each of the two solutions.

(6.0 marks)

(b) A, B, D, P, Q and R are gaseous compounds which behave ideally. In the temperature range from 100 °C to 800 °C. A(g) dissociates giving the equilibrium.

$A(g) \rightleftharpoons P(g) + Q(g)$

In the same temperature range B(g) reacts with D(g) to give the equilibrium

$B(g) + D(g) \rightleftharpoons R(g)$

No other reactions occur among these six compounds.

X, Y and Z are three identical rigid vessels each with a volume of 8.314 dm³. Their volumes are unchanged on heating X is filled with 0.2 mol of A(g), Y with 0.2 mol each of B(g) and D(g) and Z with 0.2 mol each of A(g), B(g) and D(g). The three vessels are placed in an oven at 127°C, until equilibrium is reached in all vessels. At equilibrium the total pressures inside X and Y are 1.2×10^5 Pa and 1.4×10^5 Pa respectively

(i) Calculate for the equilibria in X, Y and Z at 127°C.

(I) the partial pressures of A(g), P(g) and Q(g) in X. and the equilibrium constant K_p, for the equilibrium in X

(II) the partial pressures of B(g), D(g) and R(g) in Y and the equilibrium constant K_p, for the equilibrium in Y

(III) the total pressure inside Z.

(IV) the ratio of the partial pressures of B(g) and A(g) in Z, P_B/P_A

(ii) At 25 °C the standard enthalpy of formation $\Delta_f H^\ominus$ of the above compounds are given below.

	A(g)	B(g)	D(g)	P(g)	Q(g)	R(g)
$\Delta_f H^\ominus$ /kJ mol⁻¹	50	35	45	40	30	60

Predict whether the ratio P_B/P_A in Z will decrease, increase or remain unchanged when the temperature of the oven is raised to 227 C Give reasons for your answer

(9.0 marks)

PART C - ESSAY

Answer two questions only. (Each question carries 15 marks.)

8 Answer all parts

(a) When the carbonate of a d-block element X reacts with dil HCl, a pink solution is formed This so turns blue upon the addition of conc HCl

(i) Identify X

(ii) Write down the complete electronic configuration of X

(iii) Identify the species responsible for the pink and blue colours, and name their shapes

(iv) What types of bonds are found in the pink species?

(v) Why is the blue coloured species not formed when X is treated with dil HCl?

(vi) What can be observed when the blue solution is diluted with water?

(vii) Give one medical use and one industrial use for X or its compounds

(5 5 marks)

(b) Catalysts are very often used in chemical industry

(i) Give three instances where transition metals or their compounds are used as catalysts

Clearly indicate the catalysts used in each instance

(ii) Write down balanced chemical equations for the reactions catalysed by each of the catalysts in (i) above

(iii) Give two ways in which catalysts reduce cost of production

(iv) Briefly explain why transition metals and their compounds are good catalysts for gas-phase

(5 5 marks)

(c) How would you identify the aqueous solutions in each of the following groups by using only the method material mentioned against each group?

(i) $(NH_4)_2CO_3$ solution $(NH_4)_2SO_4$ solution $Ba(OH)_2$ solution	By mixing solutions pair-wise and using dil HNO_3 as necessary
(ii) $Zn(CH_3COO)_2$ solution $Ba(OH)_2$ solution Na_2CO_3 solution	By adding each solution dropwise to portions of the others

(4 0 marks)

9. Answer all parts

(a) (i) Propose, giving only the essential chemical steps, industrial process for the production of acetylene from limestone.

(ii) Give five factors you would consider before starting such an industry

(iii) Considering your answer to (ii) above, do you think that production of acetylene from limestone is industry suitable for Sri Lanka? Give reasons for your answer.

(iv) How would you extend the process proposed in (i) above, to manufacture PVC, [poly (vinychloride)]? Give only the essential chemical steps

(v) Give three adverse effects that the processes mentioned in (i) and (iv) above can have on the environment?

(7 5 marks)

(b). (i) When an aqueous solution of Na_2CO_3 is titrated with dil. HCl using a mixture of phenolphthalein and methyl orange as indicator, the colour changes from the initial reddish-orange to orange and then to red on further titration with dil. HCl. Explain these colour changes in relation to the chemical changes taking place during the titration. (Each indicator behaves independently of the other)

(ii) An aqueous solution contains NaOH and Na_2CO_3 only. The concentration of Na_2CO_3 in the solution is 0.1 mol dm^{-3} CO_2 (g) is passed into 25.0 cm^3 of the solution containing phenolphthalein and methyl orange together as indicators, until the colour changes from reddish-orange to orange The solution is then titrated with 0.5 mol dm^{-3} HCl, until the end point orange to red is obtained.

The volume of HCl required is 28.0 cm^3. Calculate the concentration of NaOH in the original solution.

(7.5 marks)

10. Answer all parts.

(a) (i) Mention two sources of sulphur dioxide for the industrial production of sulphuric acid

(ii) The reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is exothermic

Using the Le chatelier's principle, predict the conditions of temperature and pressure (high low) that favour the reaction

(iii) "The conditions of temperature and pressure used in industry to carry out the above reaction a both not in keeping with the predictions based on the Le Chatelier's principle."

(iv) Sulphur and lead are present in some petroleum fuels Give one harmful effect of each of the

on (I) the combustion engine.

(II) the environment

(9.0 mnarks)

(b) Sulphites are used as bleaching agents in the paper industry. Therefore the effluent water from a paper industry contains SO_3^{2-} and SO_4^{2-} ions. It is necessary to determine the concentrations of these ions, so that they can be removed before the water discharged from the factory. A method to determine the concentrations of these ions is given below.

A 10.0 cm^3 sample of the effluent water was reacted with 25.0 cm^3 of a 0.10 mol dm^{-3} I_2 (in KI) solution. 30.0 cm^3 of a 0.10 mol dm^{-3} $Na_2S_2O_3$ solution was required to react with the I_2 remaining after the above reaction. Another 10.0 cm^3 of the effluent water sample was reacted with 25.0 cm^3 of 0.10 mol dm^{-3} I_2 (in KI) solution, acidified with dil. HNO_3 and reacted with excess aqueous $BaCl_2$ solution when a white precipitate was obtained. The precipitate when washed and heated to constant mass, had a mass of 0.932 g. Calculate the concentrations of SO_3^{2-} and SO_4^{2-} in the effluent water.

(Ba = 137 0. S = 32. O. O = 16 O)

(6.0 marks)

The Periodic Table

	1 H																2 He
	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	....				

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr