FIRST NAME(S):____________________ LAST NAME:___________________

STUDENT NUMBER:_________________ SIGNATURE:___________________

The University of British Columbia
Chemistry 333 - Section 288
"Spectroscopic Techniques in Organic Chemistry"
MIDTERM EXAM

March 17th, 2011 Lecturer: Dr. Juergen Kast

Time: 60 minutes

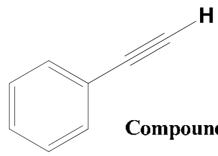
This paper consists of 10 pages including this title page.
The last page contains reference information and can be removed.

Ensure that you have a complete examination.

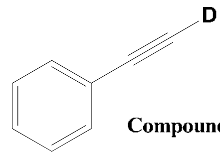
Question	Max	Grade
1	2	
2	4	
3	3	
4	2	
5	4	
6	2	
7	8	
8	10	
9	6	
10	6	
11	3	
Total	50	

Question 1

Reflect on what you know about infrared spectrometry. Will compound A have a stretching absorption in the terminal bond of greater or less wavenumber value than compound B? and why? **(2 marks)**



Compound A



Compound B

A has decreased reduced mass compared to B. wavenumber is inversely proportional to reduced mass. Therefore the wave number of A is greater than that of B.

Question 2

How could IR spectroscopy be used to distinguish between the following pair of compounds? **(4 marks)**

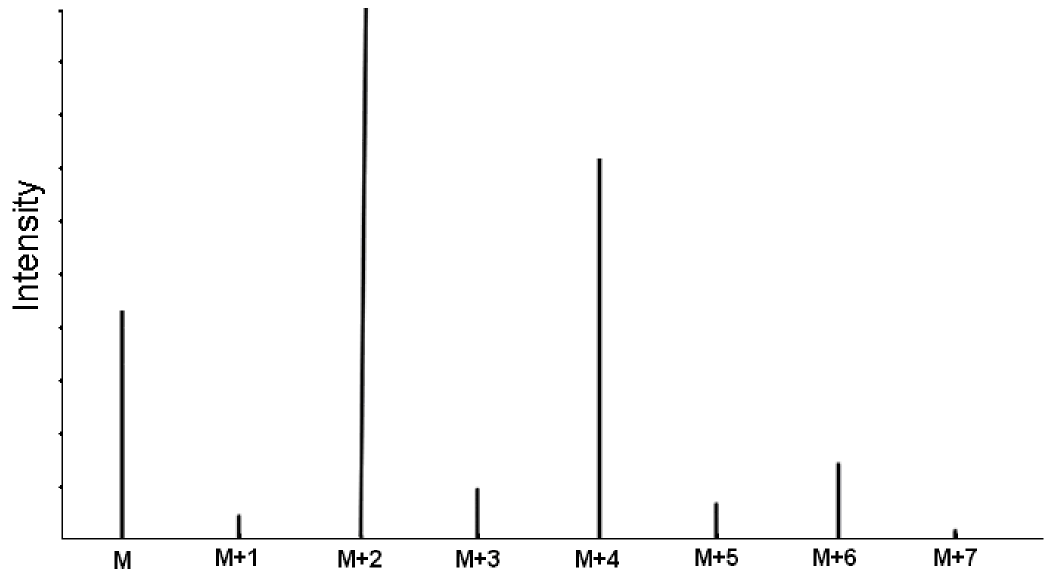
(a) $CH_3C(=O)CH{=}CHCH_2CH_3$ (**I**) **and** $CH_3C(=O)CH_2CH_2CH{=}CH_2$ (**II**)

The introduction of a C=C adjunct to a carbonyl group results in delocalization of the π electrons. This conjugation increases the single-bond character of the C=C and C=O bonds and hence lowers their force constants. Thus C=O absorption in conjugated carbonyl (compound **I**) appears at lower wavenumber compared with that of compound **II**.

(b) $CH_3CH_2C{\equiv}CH$ (**I**) **and** $CH_3C{\equiv}CCH_3$ (**II**)

Compound **I** will show C≡C stretch near 2150cm-1, while symmetrically substituted compound **II** will not give absorption or only give weak absorption at this region. Also compound I will show a ≡C-H stretch band at 3300 cm^{-1}, which will be absent in the spectrum of compound **II**.

Question 3
How many and what types of halogens are represented by the following partial mass spectrum. Show your entire work for full mark. (Hint: the molecule doesn't contain sulfur) **(3 marks)**



Contain **one** Cl and **two** Br

Question 4
In the EI mass spectrum of an unsaturated hydrocarbon, the molecular ion *M* peak has a relative intensity of 54.0, the *M+1* peak 4.8, and the base peak a relative intensity of 100. How many carbon atoms are there in the hydrocarbon per molecule? **(2 marks)**

Number of C atoms × 1.1% = (Intensity of M+1 peak) / (Intensity of M^+ peak)

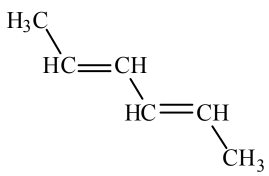
Number of C atoms = (Intensity of M+1 peak) / [(Intensity of M^+ peak) × 1.1%]
= 4.8 / (54× 1.1%) = 8.08 ≈ 8

If using 1.11% #C= 4.8 / (54× 1.11%) = 8.008 ≈ 8
If using 1.08% #C= 4.8 / (54× 1.08%) = 8.23 ≈ 8

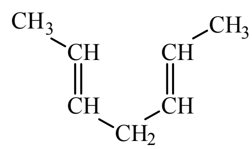
Question 5

How would you distinguish the following pairs of compounds using UV-Vis Spectroscopy? Select the structure that shows the higher λ_{max}, and briefly explain your answer by discussing both structures. **(4 marks)**

(a)



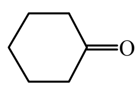
I **and**



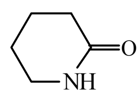
II

Diene **I** is conjugated and therefore should absorb longer wavelength light than does the diene **II**, which is not conjugated.

(b)



I **and**



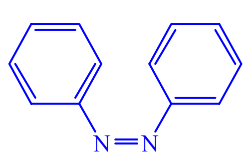
II

The n→π* absorption of ketone (**I**) appears near 290 nm, but in the amide (**II**) it appears near 210 nm. This is due primarily to the inductive effect of the nitrogen. It withdraws electrons from the carbonyl carbon, causing the lone pair of electrons of oxygen to be held more firmly than they would be in the absence of the inductive effect.

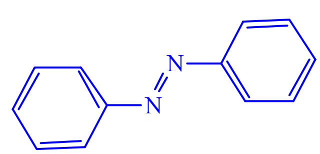
Question 6

Following is the UV-Vis spectroscopic data for azobenzene (C_6H_5-N=N-C_6H_5) in isooctane. Explain the λ_{max} and ε_{max} differences between the trans and cis isomers. **(2 marks)**

trans (anti)	λ_{max} = 318 nm	ε_{max} = 22,600
cis (syn)	λ_{max} = 282 nm	ε_{max} = 5,200



cis



trans

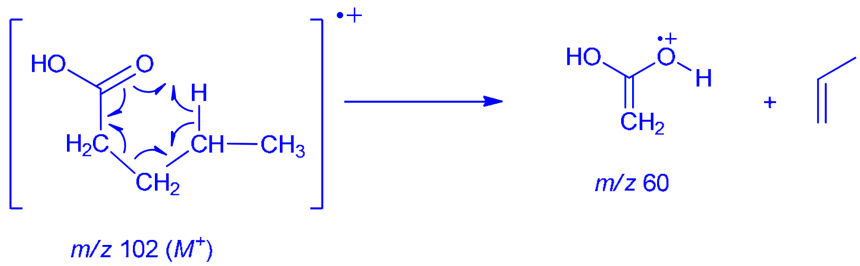
In cis isomer, steric hindrance inhibits mutual coplanarity of the two phenyl rings. The trans isomer can adopt a conformation easily with maximum coplanarity between the aromatic ring π system and the N=N double bond. Consequently, one expects a greater λ_{max} and ε_{max} of the trans isomer.

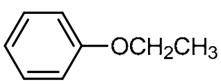
Question 7

Draw the fragmentation mechanisms that will lead to the appearance of the fragment ions at indicated m/z in the mass spectra of the following compounds: **(8 marks)**

(a) $CH_3CH_2CH_2CH_2COOH$ (MW=102), at *m/z* 60

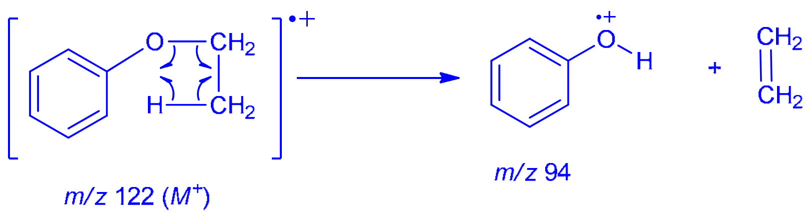
McLafferty Rearrangement:



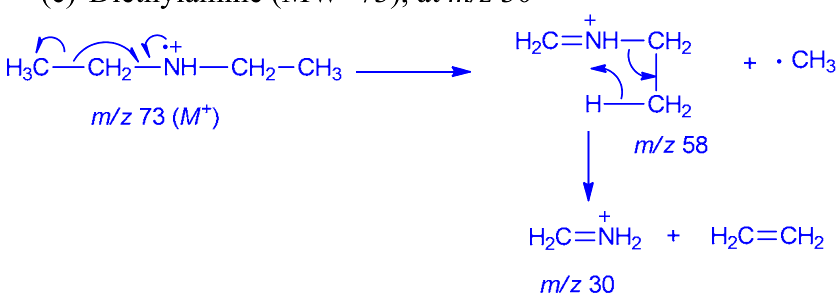
(b) 

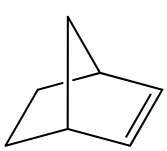
(MW=122), at *m/z* 94

Hydrogen Rearrangement:

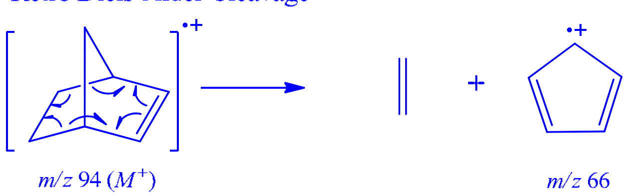


(c) Diethylamine (MW=73), at *m/z* 30

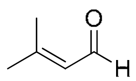


(d) 
(MW=94), at m/z 66

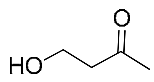
Retro Diels-Alder Cleavage



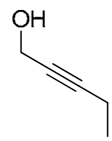
Question 8
Match the following compounds with their IR spectrum. Assign the band indicated by the arrows.
(10 marks)



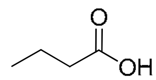
A



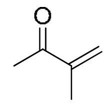
B



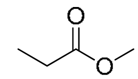
C



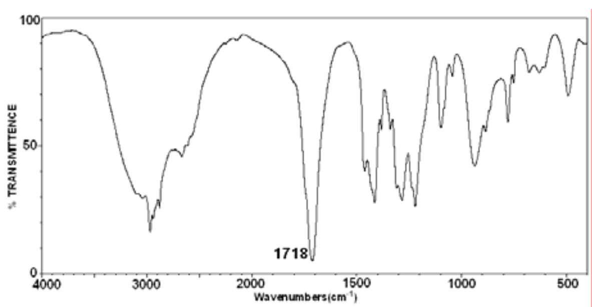
D



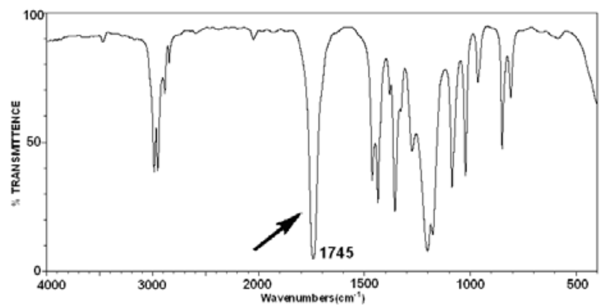
E



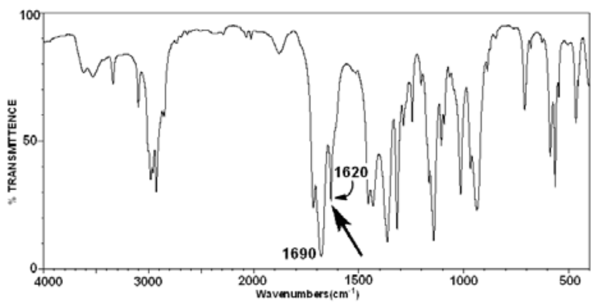
F



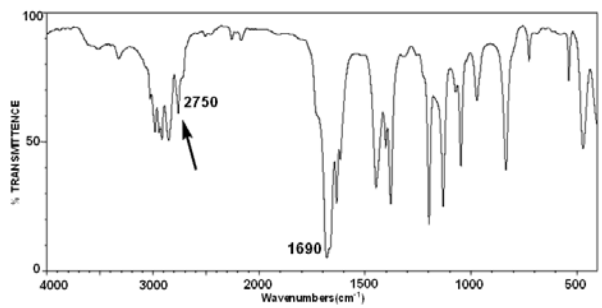
Structure: **D**



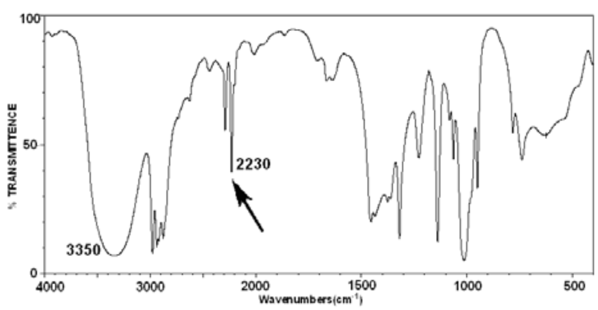
Structure: F **C=O (ester)**



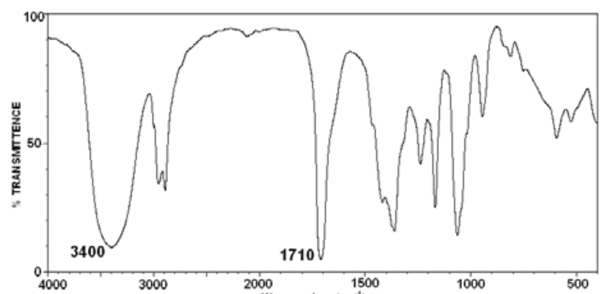
Structure: **E** **C=C**



Structure: **A** **C-H (aldehyde)**



Structure: **C** **C≡C**



Structure: **B**

Question 9

The molar extinction coefficient of a carbonyl compound (MW=122.1) in ethanol at 273 nm is about 2000 L mol^{-1} cm^{-1}.

(a) If an absorbance of smaller than 1.35 is desired, what is the maximum allowable concentration in **g L^{-1}** that can be used in a 20.0 mm cell? **(3 marks)**

A = εlc

c = A/εl = 1.35/(2000×2.00 cm) =3.375×10^{-4} mol L^{-1}

=$3.375\times10^{-4}\times122.1$ g L^{-1} = 4.12×10^{-2} g L^{-1}

(b) Based on the Franck-Condon Principle, one would assume that for the UV/Vis absorption observed at λ_{max}=273 nm, the electronic transition also started a C=O stretching vibration in this compound (co-excitation of vibrations). Hypothetically, if the electronic transition did not start any vibrations, the λ_{max} would be expected to show at 286.5 nm (assume the amounts of energy of electronic transition and vibration to be additive).

Estimate the wavenumber for this C=O stretching vibration by calculating the energy change. **(3 marks)**

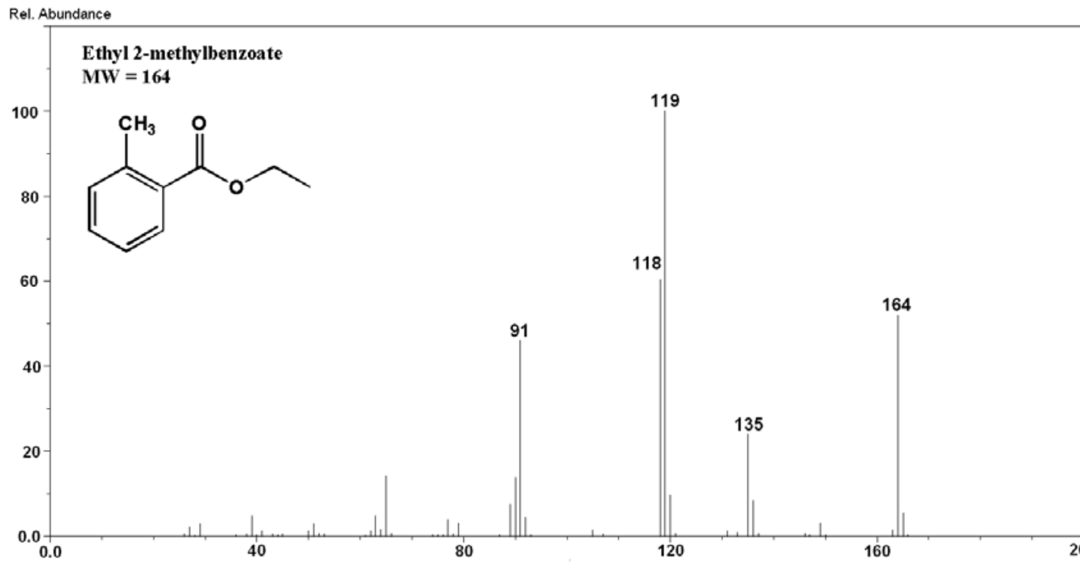
$\Delta E = \Delta E_{elec} + \Delta E_{vib}$

$$\Delta E_{vib} = \Delta E - \Delta E_{elec} \qquad h\frac{c}{\nu_{vib}} = h\frac{c}{\nu} - h\frac{c}{\nu_{elec}}$$

$$\frac{1}{\upsilon_{vib}} = \frac{1}{\upsilon} - \frac{1}{\upsilon_{elec}} \qquad wavenumber\left(cm^{-1}\right) = \frac{1}{\upsilon_{vib}} = \frac{1}{273\times10^{-7}\,cm} - \frac{1}{286.5\times10^{-7}\,cm}$$

= 1726 cm^{-1}

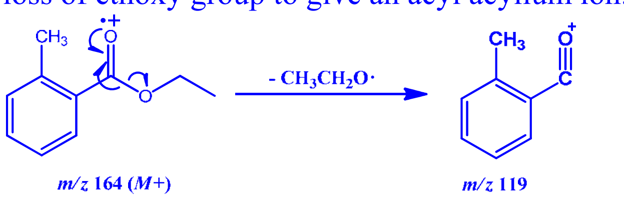
Question 10 (6 marks)
The EI mass spectrum of ethyl 2-methylbenzoate is shown below.



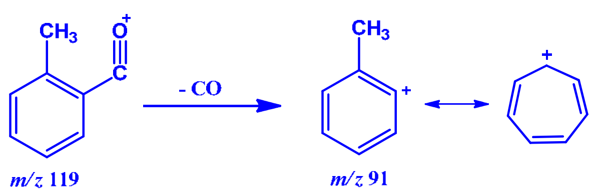
Draw the charge-localized structures of each fragment ion, as well as the fragmentation mechanisms that will lead to the appearance of the fragment ions with:

(a) *m/z* 119

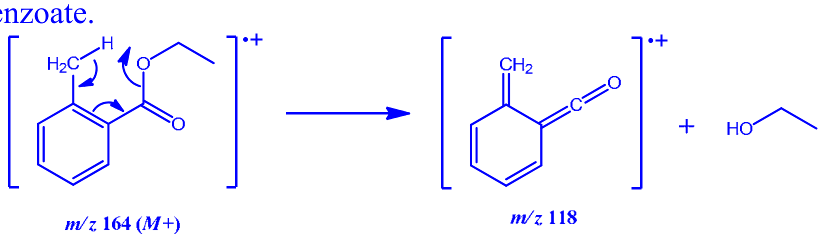
loss of ethoxy group to give an acyl acylium ion.



(b) *m/z* 91

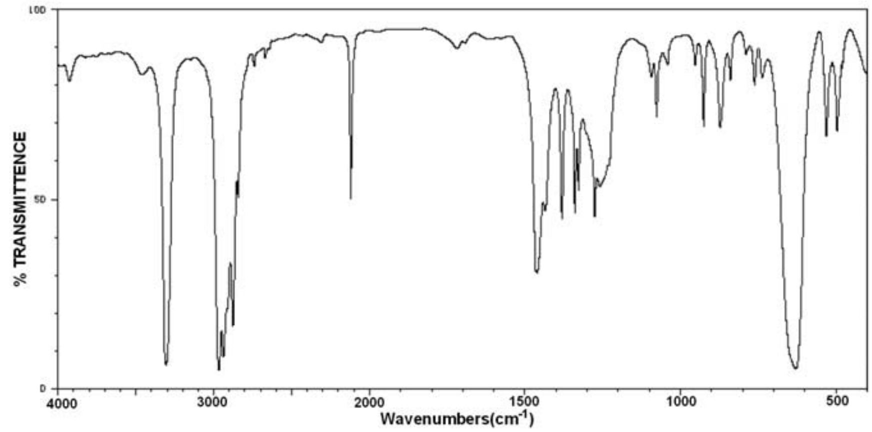


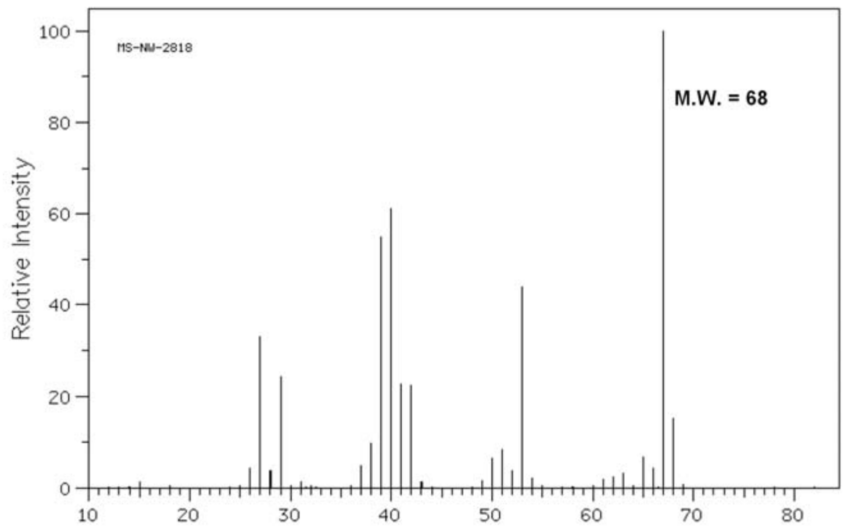
(c) In the EI spectrum of ethyl 3-methylbenzoate, the peak *m/z* 118 is absent. Explain why. Use fragmentation mechanism to rationalize your deduction.
The ion at *m/z* 118 requires the ortho effect and is not expected in the meta-isomer, ethyl 3-methylbenzoate.



Question 11

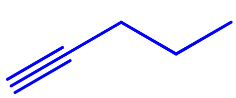
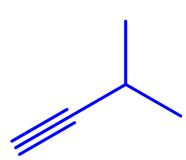
Determine the molecular formula and **all** the possible structures for the unknown based on the given spectra. Show your reasoning for the full mark. **(3 marks)**





IR (2100-2200 cm^{-1}): C≡C or C≡N. IR (3300 cm-1, sharp): C≡C-H.
Thus, it's C≡C NOT C≡N.
MW = 68, 68 – 25 (C≡C-H) = 43 (C_3H_7)

The molecular formula: C_5H_8. Unsaturation Number: 2

Possible structures:  or 

USEFUL ADDITIONAL INFORMATION

PERIODIC TABLE OF ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
11 Na 22.98977	12 Mg 24.035											13 Al 26.9815	14 Si 28.0855	15 P 30.9736	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.33	*57* - *71*	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.966	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	*89* - *103*	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)									

Lanthanide series (57 – 71)	57 La 138.905	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
Actinide series (89 – 103)	89 Ac 227.028	90 Th 232.038	91 Pa 231.046	92 U 238.029	93 Np 237.048	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 (259)	103 Lr (262)

PHYSICAL CONSTANTS

$h = 6.626 \times 10^{-34}$ J s
$c = 2.998 \times 10^{8}$ m s^{-1}