FINAL EXAMINATION
Organic Chemistry, Chem 220a
9 A.M.; Saturday, December 12, 2009

NAME (print): _____

TA:_____ Section Day:_____ Section Time:_____

Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will **not** be graded. The exam is the length of two hour exams with an additional one hour for review. **STOP** writing when you are asked to do so. Put your name on the **cover sheet and subsequent pages** (except for Work Sheets) where indicated. There is a Periodic Table on page 15.

.**REMEMBER:** Neatness is to your advantage.

Have a GREAT winter break!

1. Spectroscopy/Structure I (30 pts) _____
2. Reactions I (30 pts; 5 of 6) _____
3. Potpourri (48 pts; 8 of 10) _____
4. Structure II (30 pts.) _____
5. Synthesis (30 pts.) _____
6. Reactions II (30 pts.; 5 of 6) _____
7. The Standard State/Structure (30 pts.) _____
8. Concepts (22 pts.; 1 of 3) _____

_____

Total (250 pts)

1. **Spectroscopy/Structure I:** (30 pts.) Compound **A** ($M^+ = 86$), whose infrared spectrum is shown (Fig. 1, pg. 3), reacts with one equivalent of Grignard reagent **B** (RMgBr) to form compound **C** (IR: Fig. 2, pg. 3), whose mass spectrum displays a molecular ion at $M^+ = 102$. Compound **C** reacts **readily** with catalytic H_2SO_4 to give three isomers (**D**, **E** and **F**), two of which are stereoisomers. Compounds **D** and **E** both form two products upon ozonolysis and dimethyl sulfide reduction, namely, **G** (C_4H_8O) and **H** (C_2H_4O). Compound G is inert to aqueous chromic acid. Compound **D** liberates less heat upon combustion than does **E**. Vigorous permanganate oxidation of **F** forms **A** and CO_2. What are the structures of **A – H**? Show your reasoning.

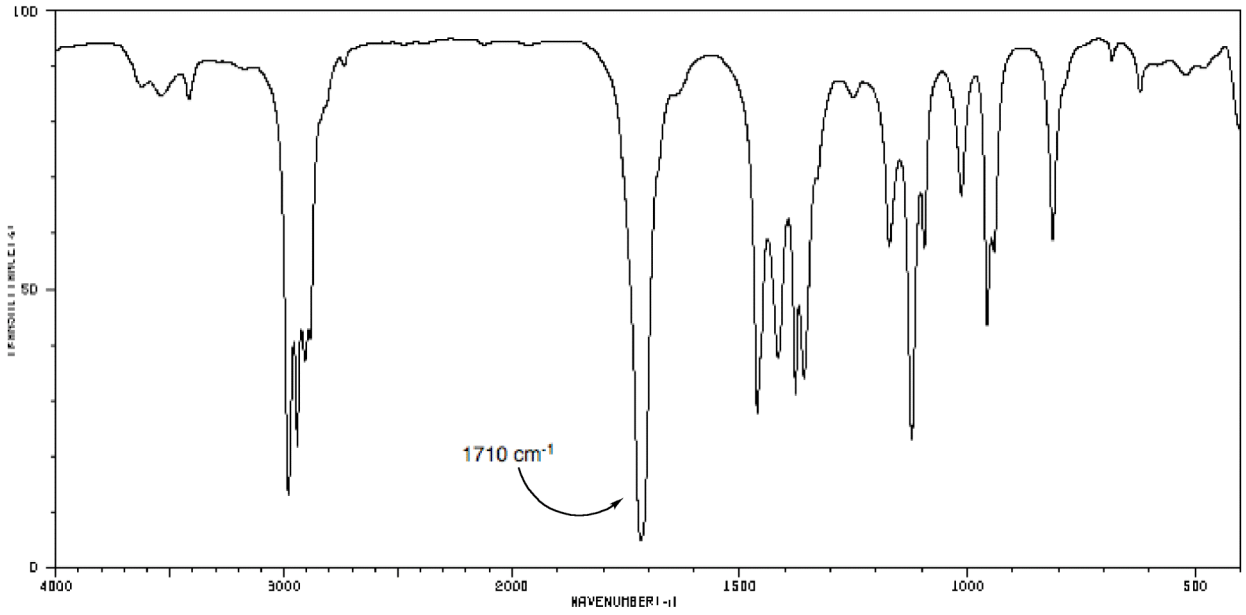

100
50
0
4000
3000
2000
1500
1000
500
1710 cm-1

Fig. 1

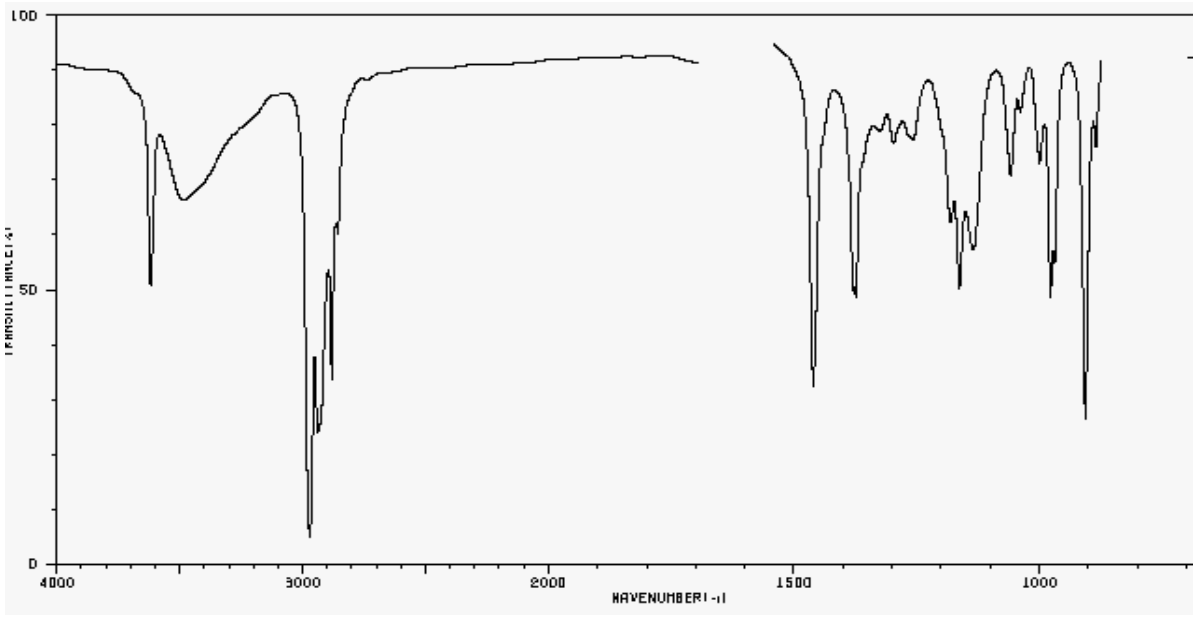
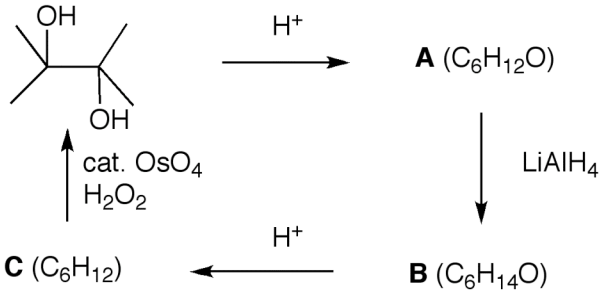

100
50
0
4000
3000
2000
1500
1000

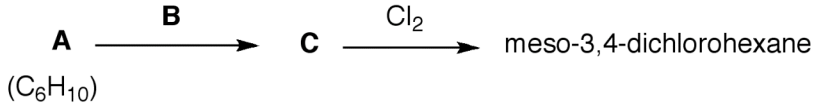
Fig. 2

2. **Reactions I:** (5 x 6 pts. = 30 pts.) **Do 5 of 6.** Provide structures for the unknown compounds. Be explicit about stereochemistry, optical activity, racemates, etc. No mechanisms required! **If you do more than five problems, cross out (with a large X through the solution) the one that you do not want graded**.

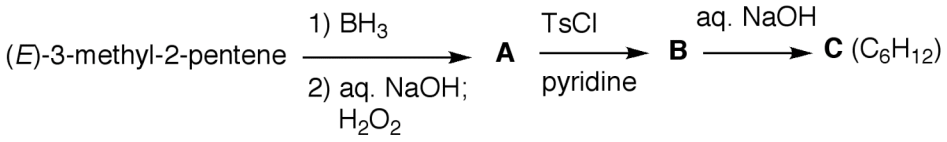
a)



b)



c)



…continued

d) (*Z*)-**A** $\xrightarrow{\text{cat. } OsO_4/HIO_4}$ **B** (C_4H_8O) + **C** (C_2H_4O)

B (C_4H_8O) $\xrightarrow{\text{aq. } CrO_3}$ no reaction

e) **A** ($C_5H_{12}O$) $\xrightarrow{HBr}$ **B** ($C_5H_{11}Br$) $\xrightarrow{\text{aq. NaOH}}$ **C** (C_5H_{10})

A ($C_5H_{12}O$) $\xrightarrow{CH_3MgBr}$ CH_4 evolved

A ($C_5H_{12}O$) $\xrightarrow{\text{excess } H_2Cr_2O_7}$ **E** ($C_5H_{10}O$)

C (C_5H_{10}) $\xrightarrow{\text{1) } O_3 \text{ 2) } (CH_3)_2S}$ **D** (C_2H_4O) + acetone

f) **A** (C_6H_{12}) $\xrightarrow{Cl_2/H_2O}$ **B** ($C_6H_{13}ClO$) $\xrightarrow{\text{aq. KOH}}$ **C** ($C_6H_{12}O$)

C ($C_6H_{12}O$) $\xrightarrow{CH_3MgBr}$ 3-ethyl-3-pentanol

3. **Potpourri:** (8 x 6 pts. = 48 pts.) **Do 8 of 10 problems. If you do more than eight problems, cross out (with a large X through the solution) the ones that you do not want graded**.

a) **Circle** the reagent(s) that will efficiently convert 3-hexene into propionaldehyde.

cat. OsO_4/H_2O_2 HIO_4 OsO_4/cat. HIO_4 cat. OsO_4/ HIO_4 $O_3/(CH_3)_2S$

b) Given the ΔH_f^o of CO_2 (-94.05 kcal/mol), H_2O (-68.3 kcal/mol) and acetylene (+54.5 kcal/mol), determine the heat of combustion of acetylene (C_2H_2). **Show work**.

c) Provide a sketch of the molecular ion(s) in the mass spectrum of 1,2,3-tribromobutane. Include the masses and intensities of the peaks. **Show work**.

d) The heat of combustion of n-octane is –1308 kcal/mol. Predict the heat of combustion of n-decane. **Show work.**

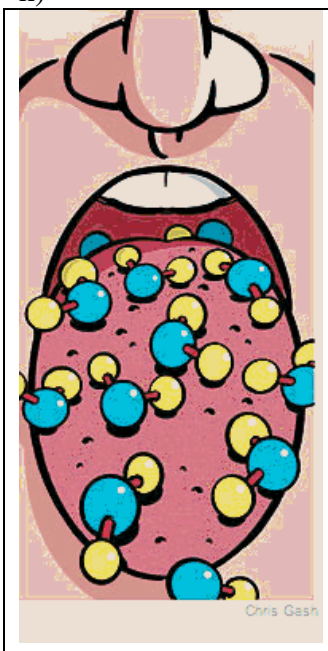
e) **Circle** the functional group that has the lowest energy carbonyl frequency (cm^{-1}) in its infrared spectrum.

RCOCl RCO_2R RCHO R_2CO $RCONH_2$

f) Cholesterol contains 27 carbons, a secondary alcohol, a double bond and four rings. What is its molecular formula? **Show work**.

g) A solution of a 2:1 mixture of meso- and (*R, R*)-tartaric acid ($[\alpha]_D = +12^o$) will display what specific rotation? **Show work**.

h)



New York Times, Science Times, 10/19/09

How Tongues Taste the Carbonation in a Fizzy Beverage

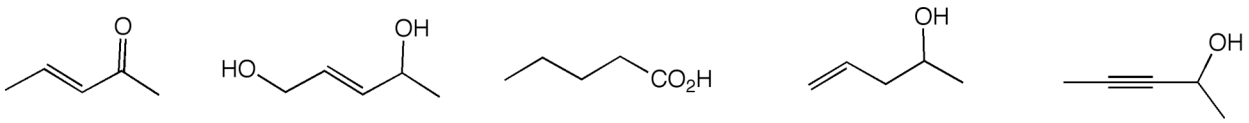
By HENRY FOUNTAIN
Published: October 19, 2009

"Aside from the natural and artificial flavors and sweeteners, soda and other fizzy beverages have a distinct carbonated taste. It is difficult to describe, but you know it is there when tiny bubbles of carbon dioxide go crazy all over your tongue."

What's wrong with this picture? What can you tell the author and graphic artist about CO_2 to improve the presentation?

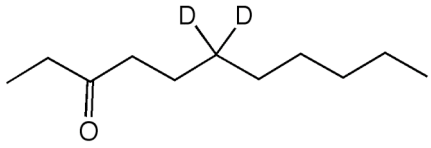
continued …

i) **Circle** the greatest number of structures that are at the same oxidation level.



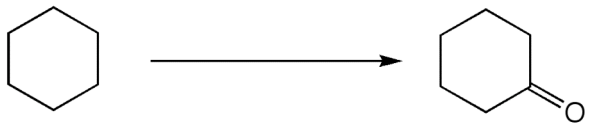
j) The compound $C_{17}H_{26}Br_2ClN_3O_3S$ absorbs four equivalents of hydrogen. How many rings are present in the compound? **Show work.**

4. **Structure II:** (30 pts.) Optically active ester **A**, $C_{10}H_{20}O_2$, reacts with excess Grignard reagent **B** (RMgBr) to form (*R*)-**C** ($C_9H_{20}O$) and (*S*)-**D** ($C_5H_{12}O$). Compound **C** is inert to PCC oxidation but **D** forms **E** ($C_5H_{10}O$) with this reagent. Exposure of compound C to catalytic H_2SO_4 **readily** leads to optically inactive **F** (C_9H_{18}), the major E_1 product. Reduction of **A** with $LiAlH_4$ affords (±)-**D**. What are the structures of **A**-**F**? Explain and illustrate.

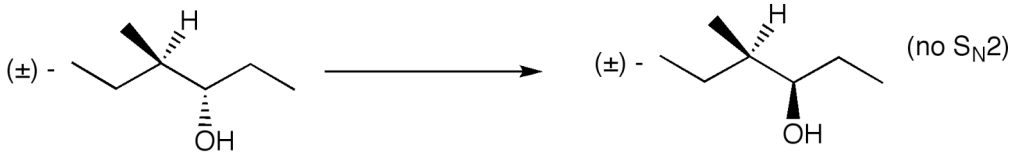
5. **Synthesis:** (30 pts.) A chemist wishes to synthesize 3-undecanone specifically labeled with deuterium at C_6 to study the fragmentation pattern of alkyl ketones in the mass spectrometer. She has at her disposal 1-hexanol, ethylene, and 1-propanol as sources of carbon to become incorporated into 3-undecanone. She also has available D_2O and $LiAlD_4$ as deuterium sources and all other necessary reagents. She designs a synthesis of 3-undecanone-d_2. What is her strategy?	

6) **Reactions II:** (5 x 6 pts. = 30 pts.) **Do 5 of 6.** Provide reagents for the chemical transformations. Several steps may be required. Additional sources of carbon may be required. **If you do more than five problems, cross out (with a large X through the solution) the one that you do not want graded**.

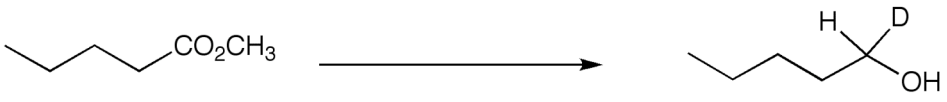
a)



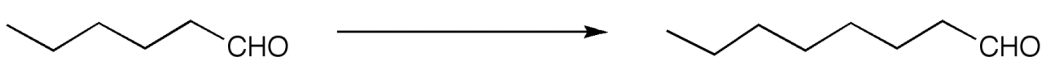
b)

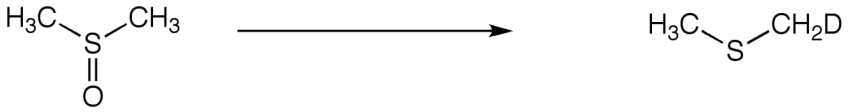


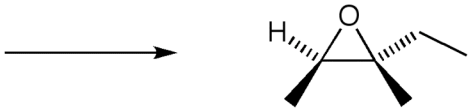
c)



…continued

d) 

e) 

f) (2*S*, 3*R*)-3-methylpentane-2,3-diol 

opt. act.

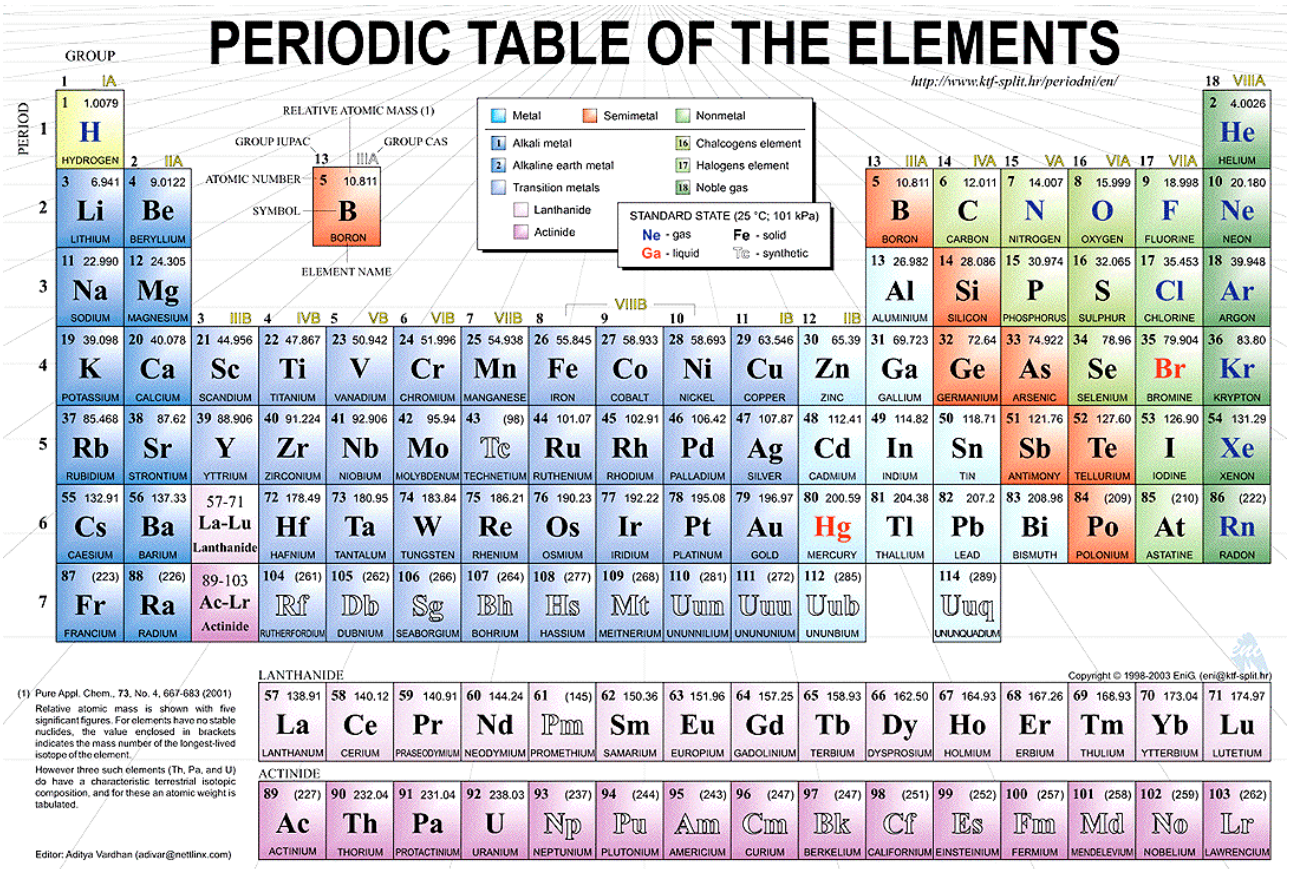
7. **Standard State/Structure:** (30 pts.) Three **achiral and non-racemic** isomers **A**, **B** and **C**, two of which (**A** and **B**) are stereoisomers, **all** give the same alkane **D** ($M^+ = 86$) upon the uptake of one equivalent of hydrogen. The absolute difference in the heat of combustion of **A** and **B** is 0.6 kcal/mol (**not 1.0 kcal/mol,** which will eliminate two possible carbon skeletons) with **A** liberating more heat than **B** upon hydrogenation. The acid-catalyzed isomerization of **C** to **B** liberates -2.0 kcal/mol of heat. The heats of formation of **C** and **D** are -13.4 kcal/mol and -41.0 kcal/mol, respectively: a) Draw a Standard State diagram that employs the data given and shows the structures of **A-D**. b) Determine the heats of formation of **A** and **B**. c) What are the heats of hydrogenation of **A** and **B**? Show work. [**Hint:** What are the possible carbon skeletons for **D**? Which one, working backwards, can only be derived from **A**, **B** and **C** given the information provided?]

8. **Concepts:** (22 pts.) Do 1 of 3**. If you do more than one problem, cross out (with a large X through the solution) the ones that you do not want graded**.

a) Explain and illustrate an example of the role that isotopic labeling plays in establishing the mechanism of a chemical reaction we have studied.

b) Using energy diagrams and commentary, distinguish between a kinetic (E_2) and a thermodynamically (E_1) controlled reaction. Be sure to indicate which energy differences are relevant. Use an example of your choosing.

c) Explain and illustrate an example of a stereospecific reaction. How does it differ from one that is stereoselective?


PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
Metal
Semimetal
Nonmetal
Alkali metal
Alkaline earth metal
Transition metals
Lanthanide
Actinide
Chalcogens element
Halogens element
Noble gas
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9
10
VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.922 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
Editor: Aditya Vardhan (adivar@netlinx.com)
Copyright © 1998-2003 EniG. (eni@ktf-split.hr)

Work Sheets

Work Sheets

Work Sheets

Work Sheets