Department of Chemistry
Cumulative Examinations
January 14, 2006

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains ***five*** examinations.

1) Analytical Cumulative Examination, Page 1
2) Biochemistry Cumulative Examination, Page 2
3) Inorganic Cumulative Examination, Pages 3-4
4) Organic Cumulative Examination, Pages 5-6
5) Physical Cumulative Examination, Pages 7-8

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: _____
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
UNIVERSITY

ANALYTICAL CHEMISTRY CUME **JANUARY 14, 2006**

Demonstrate your understanding of the importance of mass spectrometry in chemical analysis by answering the following questions.

1) Give three examples of analyses where mass spectrometry (or MS/MS) is superior over spectroscopy, separations (with no MS), or NMR. Justify by considering the limitations of each of the other methods. Also give three examples of analyses where mass spectrometry would be inferior to one of the other methods.

2) Describe in detail four different methods used to ionize molecules in mass spectrometry. Show chemical equations where relevant. Discuss the energetics associated with each method, and explain what are the strengths and weaknesses of each method.

3) The two commonly used methods to probe the structures of ionized analytes by using MS/MS are collision-activated dissociation (CAD) and ion-molecule reactions. Compare these methods, and discuss the strengths and weaknesses of each, including energetics. Give an example analysis wherein CAD performs better than ion-molecule reactions, and an example wherein ion-molecule reactions must be used.

4) Draw a typical potential energy surface (mark x- and y-axis) for unimolecular dissociation of an ionized analyte (propanol molecular radical cation) to give two ionic products, one via a direct bond cleavage (protonated formaldehyde) and one via a rearrangement reaction (cyclopropane radical cation). Show all the chemical structures in your potential energy surface. Be as quantitative as you can – give reasonable values for the different energy levels in your diagram. Based on your diagram, which reaction is more likely to dominate (consider different internal energy regimes)?

5) Draw a typical potential energy surface (mark x- and y-axis) for an ion-molecule reaction between an ionized analyte (protonated propanol) and a neutral reagent molecule (propyl amine) to give two ionic products, one via proton transfer and one via second-order nucleophilic substitution (S_N2). Show all the chemical structures in your potential energy surface. Be as quantitative as you can – give reasonable values for the different energy levels in your diagram. Which reaction is more likely to be dominant?

Cumulative Exam
Biochemistry
January 14, 2006
20 points/question
100 points total

1. In the seminar by Dr. Candice Klug, she described the technique of **site-directed spin labeling**. Design and describe an experiment that uses this technique for your protein of interest. Briefly describe **three** types of information that you can extract from a site-directed spin labeling experiment.

2. In the seminar by Dr. David Cafiso, a substrate-dependent structural change in a transport protein was seen by spectroscopic techniques. However, this structural change was not seen in the crystal structure of this protein. What was the reason for this discrepancy? Do you believe this effect will be generalizable for other proteins? Why or why not? Give an example.

3. In the seminar by Dr. Lee, what did he describe as the major mechanism of blood clearance and solid tumor distribution of liposomes and what surface modification strategy has been used to extend the circulation time of liposomes in the blood stream?

4. These questions pertain to the seminar by Dr. Charles Sanders:

   a. For inherited mutations that cause disease, what is the most common class in terms of both the nature of the mutation and the molecular consequences?

   b. What was the most important outcomes of his lab's studies of the folding of diacyglycerol kinase?

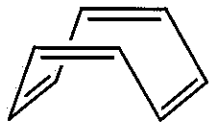
   c. What did the pH dependency of the NMR spectrum of the vasopressin receptor suggest about how the structure of the receptor changes during internalization into endosomes under cellular conditions?

5. In Dr. Hrycyna's seminar, she described the biochemistry of the isoprenylcysteine carboxylmethyltransferase (Icmt) enzymes from yeast and humans. In what posttranslational pathway does this enzyme function, what signals this enzyme to methylate a substrate and why is this enzyme a good target for some cancer chemotherapies?

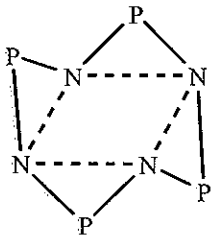
Inorganic Cumulative Exam

January 14, 2006

1. (20 pt) Identify point symmetry group for each of the following molecules/ions.

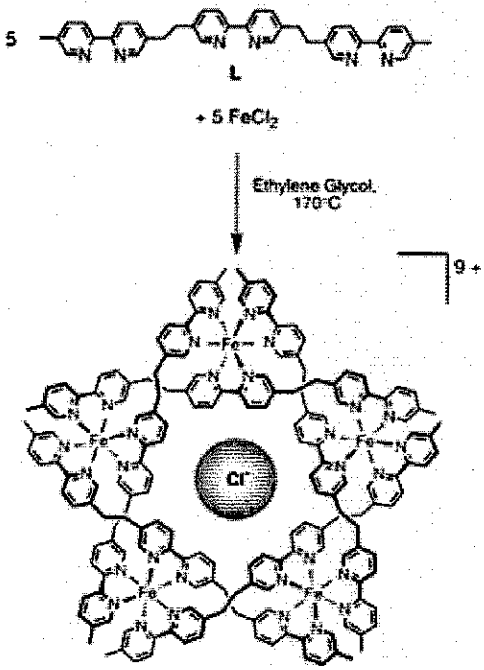


(a) cyclooctatetraene



(b)

(c) cyclopropane



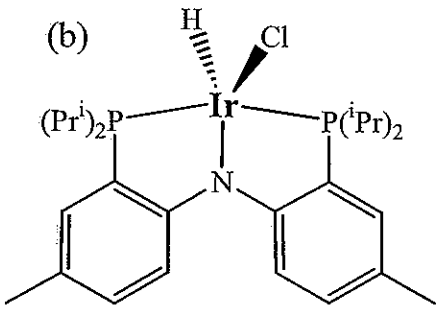
(d) Assign the complex ion at the bottom

2. (15 pt) (A) Predict the shape of the PF_5 molecule based on the VSEPR model. (B) The ^{19}F NMR spectrum of PF_5 recorded at the ambient temperature exhibits one doublet (each chemically distinct F nucleus gives arise to a doublet), but that recorded below -150 °C displays two doublets. Explain (including necessary structural sketches to support your argument).

3. (20 pt) Aqueous solutions of $MnSO_4$ are almost colorless. Please provide a detailed explanation on the basis of what you have learned from CHM641.

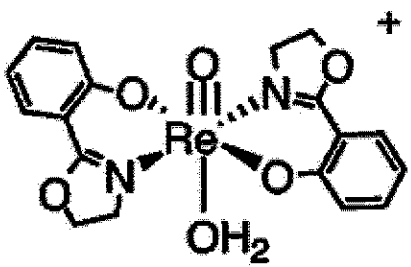
4. (15 pt) Give the valence electron count for the metal center in each of following that appeared in recent issues of *JACS*, and explain your reasoning briefly if necessary.
(a) $Ba(\eta^9\text{-}C_9H_9)_2$ (Sitzmann *et al. JACS*, 17494)

(b)



Ozerov *et al.* JACS, 16772

(c)



JACS, 11939

5. (15 pt) *Cisplatin* (*cis*-$PtCl_2(NH_3)_2$) is the most celebrated inorganic antitumor drug. Please devise the synthetic routes with concise rationale for both *cis*- and *trans*-$PtCl_2(NH_3)_2$ assuming the availability of K_2PtCl_4, $[Pt(NH_3)_4]Cl_2$, and common laboratory reagents such as HCl(*aq*), NH_4OH, NaOH(*aq*) and HNO_3(*aq*).

6. (15 pt) Carbon-carbon bond formation reactions catalyzed by Pd-compounds, such as Suzuki and Sonogashira reactions shown below, are powerful tools for synthetic chemists. Show your understanding of basic organometallic reaction mechanism by (a) sketching the catalytic cycle (Tolman's loop) for *either* of these two reaction types; (b) discuss the substituent *electronic* effect of ArI on the reaction rate based on your mechanism.

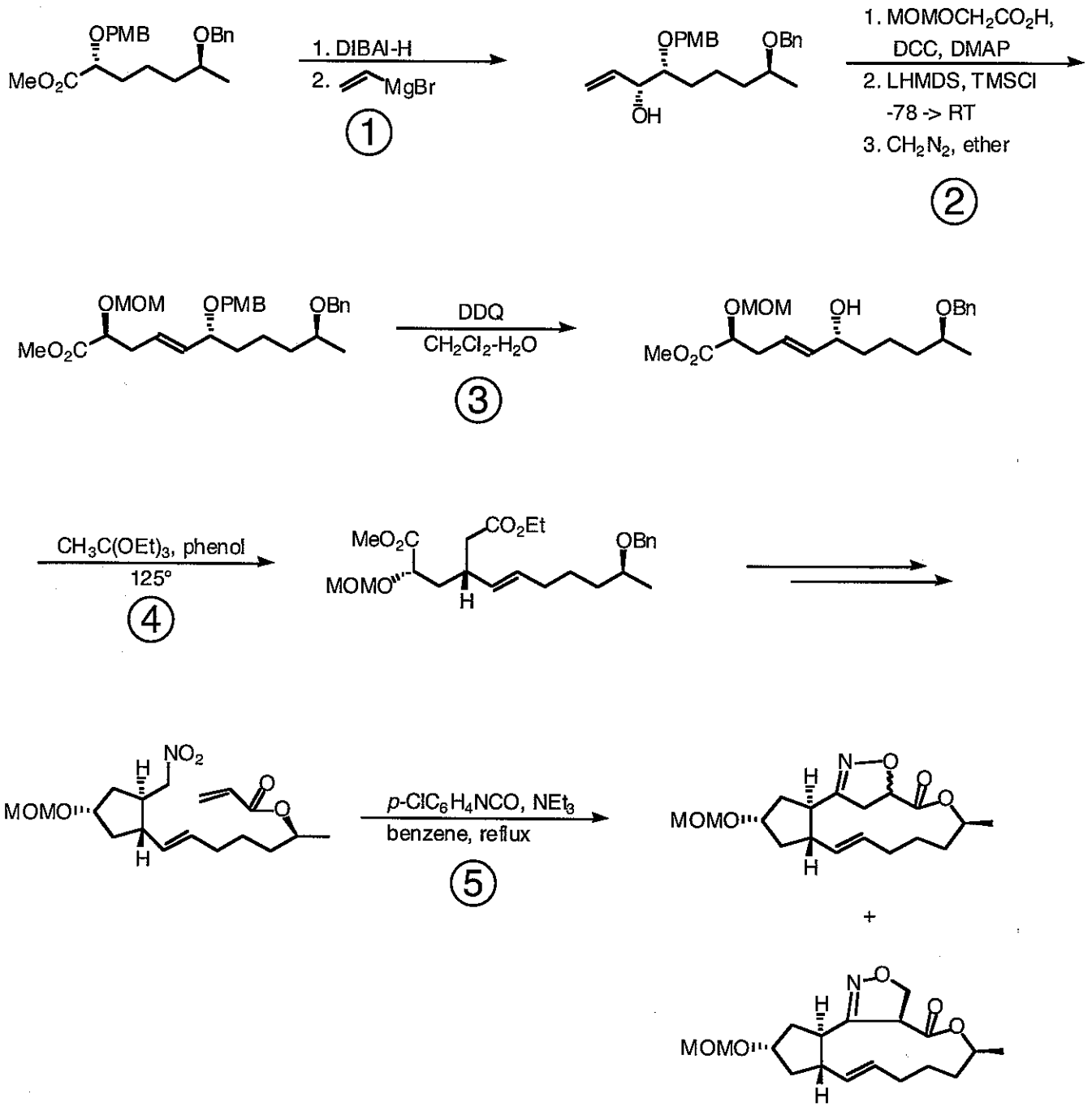
$$\text{ArI} + \text{PhB(OH)}_2 \xrightarrow[\text{Cs}_2\text{CO}_3]{\text{Pd(OAc)}_2} \text{Ar-Ph} \qquad \text{Suzuki type}$$

$$\text{ArI} + \text{HCCSiMe}_3 \xrightarrow[\text{Et}_2\text{NH}]{\text{PdCl}_2(\text{PPh}_3)_2} \text{Ar-CCSiMe}_3 \qquad \text{Sonogashira type}$$

Organic Cumulative Examination

January 14, 2006

Answer the questions on p. 2 concerning the scheme shown below:



Abbreviations:

PMB: *para*-methoxybenzyl
DMAP: 4-*N,N*-dimethylaminopyridine
DCC: dicyclohexylcarbodiimide
LHMDS: lithium hexamethyldisilazide
MOM: methoxymethyl
Bn: benzyl
DIBAL-H: diisobutylaluminum hydride
TMS: trimethylsilyl

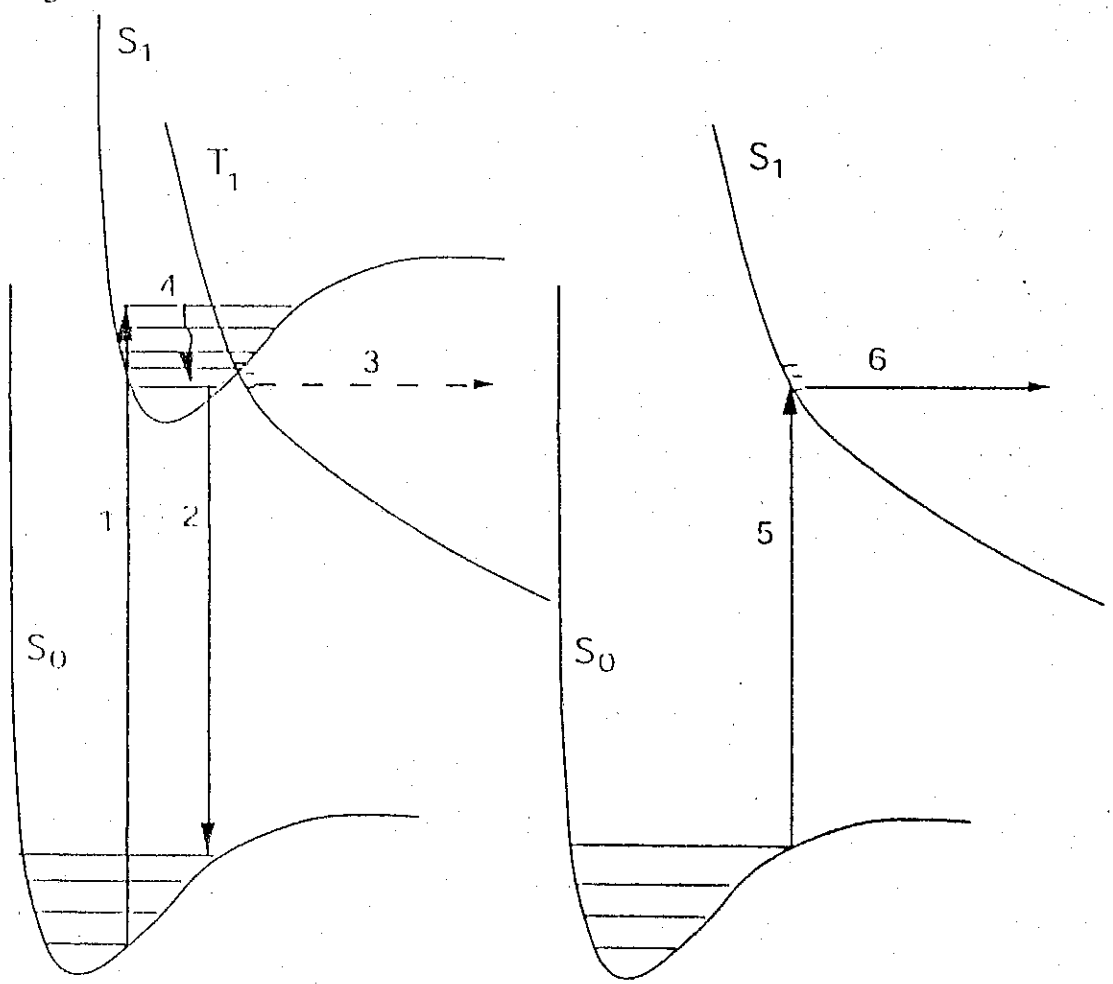
1. (60 points)Provide mechanisms for the reactions involved in steps **1-5**. Use curved arrow formalism and show all likely intermediates. Assume an aqueous workup after each reaction. Your mechanism in step **5** should account for the formation of <u>both</u> products.

2. (40 points) Provide <u>detailed</u> explanations for the stereoselectivities observed in steps **1** and **2**.

Physical Chemistry Cumulative Examination

1. A diatomic molecular A_2 in electronic state S_0, with v = 0 and J = 0 strongly absorbs ultraviolet light. The resulting spectrum is structured (no continuous absorption) but it is observed that after a while (that is, not quickly) the molecule is dissociated. Sketch a set of potential energy curves and rotational, vibrational levels to describe this process. Explicitly describe all processes that change the electronic state. Explicitly indicate any nonadiabatic processes.

2. For the two diagrams presented below ***identify*** and ***define*** the processes corresponding to the numbered arrows. Be sure to state whether the process involves a photon or is radiationless, and if it is radiationless whether it is adiabatic or nonadiabatic. If the process involves a photon, state whether the spectrum will be structured (line spectrum) or continuous. Note S_0 = lowest singlet state, S_1 = first excited singlet state, and T_1 = first triplet state. The rotational quantum numbers are ignored here.



Arrow 1: S_0, v=0 to S_1, v=4
Arrow 2: S_1, v=0 to S_0, v=3
Arrow 3: S_1, v=0 to an isoenergetic (same energy) T_1 state
Arrow 4: S_1, v=4 to S_1 v=0. You need not consider whether or not this process involves a photon.
Arrow 5: S_0, v=3 to S_1
Arrow 6: an S_1 process

3. Find and **carefully explain** the mistakes in the following statements.

Radiation from the sun is absorbed over a continuous range at wavelengths shorter than 200 nm by vibration-rotational transitions in O_2.

A spectroscopist can determine methane's (CH_4's) force constants by measuring its pure rotational spectrum (only the rotational quantum number changes).

Because N_2 and O_2 are the principal atmospheric gases their pure rotational absorption is the principal mechanism of preventing the escape of the earth's blackbody radiation, resulting in the greenhouse effect.

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

*1995 IUPAC masses and Approved Names from http://www.chem.qmw.ac.uk/iupac/AtWt/
masses for 107-111 from C&EN, March 13, 1995, p. 35
112 from http://www.gsi.de/z112e.html