Department of Chemistry
Cumulative Examinations
August 27, 2005

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.

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

1. Any measurement that seeks to determine the concentration of an unknown via an instrumental technique such as electrochemistry, spectroscopy, mass spectrometry, etc., relies upon a relationship between the actual measured quantity (e.g., a voltage, a current, absorbance/transmittance) and concentration. The following questions relate to the error associated with the measured quantity and its relationship to the resulting error in concentration. We assume here that there is only random or indeterminate error.

a) A common means for determining the concentration of an analyte species in solution is to compare the radiant power of light transmitted through the analyte solution, P, with radiant power, P_0, transmitted through a solution with negligible analyte present (i.e., a blank solution) under otherwise identical conditions. What is the relationship between concentration, C, in the limit of low concentration, and P/P_0? Define all symbols that you provide. **(5 pts)**

b) Provide a mathematical relationship for the sensitivity associated with this measurement? **(10 pts)**

c) For a fixed error in the measurement of P/P_0 (i.e., $s_{P/P0}$ = constant) what is the relationship between the error in concentration, s_C, that arises from the error in P/P_0? **(10 pts)**

d) For $s_{P/P0}$ = constant with concentration, draw the shape of a plot of s_C/C versus C (i.e., a plot of the relative concentration error versus concentration). **(10 pts)**

e) Based on the dependence of relative concentration error on concentration in this type of measurement, where is the relative concentration error minimized? **(5 pts)**

   a) at low concentration
   b) at intermediate concentration
   c) at high concentration
   d) relative concentration is independent of concentration in this measurement

2. The titration of 50.00(±0.02) mL of a strong acid required 42.4(±0.2) mL of a 0.1034(±0.0002) M strong base to reach the equivalence point.

a) what is the concentration of the strong acid? **(5 pts)**

b) what is the error associated with the value of the acid determined by this titration? (Show how you arrived at the result) **(10 pts)**

3. The EPA monitors contract labs that analyze environmental samples. A standard sample containing lead at a concentration of 16.40 ppm was sent to the contract lab for analysis. The contract lab measured the standard sample 6 times and determined an average concentration of 16.23 ppm with a standard deviation of 0.1378 and a sum of the squares of deviation from the mean of 0.095. Does the contract lab's method show bias at the 95% confidence level? Show the work you use to justify your answer. **(10 pts)**

4. The behavior of an enzyme catalyzed reaction is often consistent with the generalized mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$$

where E is the enzyme, S is the substrate, ES is an enzyme-substrate complex, and P is the product.

a) Two scientists are associated with proposing this mechanism. What are their last names? **(5 pts)**

b) The relationship that gives the rate of product formation, v, (sometimes referred to as the velocity of the reaction) is given below:

$$v = \frac{v_{max}[S]}{K_M + [S]}$$

In terms of rate constants and concentrations, what is the relationship for the maximum rate, v_{max}? **(5 pts)**

c) What conditions will make the measured rate pseudo-first order in initial enzyme concentration? **(5 pts)**

5. The determination of an analyte of interest was accomplished by reacting it with excess iodide, I^-, to form triodide, I_3^-, with subsequent quantitation of triiodide. The determination of triiodide concentration can be accomplished via a variety of means, including potentiometrically.

$E^0_{I3-/I-} = 0.536$ V, $[I^-] = 0.202$ M, $I_3^- + 2e^- \rightarrow 3I^-$, RT/F = 0.0257 V-M^{-1}, $E_{SCE} = 0.244$ V

a) Write the expected relationship between cell potential, E_{cell}, and triiodide concentration if the potential of a platinum electrode placed into the analyte solution is measured against the standard calomel electrode (SCE). **(10 pts)**

b) What is the mathematical relationship between the random error associated with the cell potential measurement, s_{Ecell}, and the resulting error in concentration, s_C, assuming s_{Ecell} to be constant with concentration? **(10 pts)**

Useful relationships:

$$\frac{de^u}{dx} = e^u \frac{du}{dx} \qquad \frac{d \ln u}{dx} = \frac{1}{u}\frac{du}{dx}$$

TABLE 7-4

Critical Values of *F* at the 5% Probability Level (95% confidence level)

Degrees of Freedom (Denominator)	Degrees of Freedom (Numerator) 2	3	4	5	6	10	12	20	∞
2	19.00	19.16	19.25	19.30	19.33	19.40	19.41	19.45	19.50
3	9.55	9.28	9.12	9.01	8.94	8.79	8.74	8.66	8.53
4	6.94	6.59	6.39	6.26	6.16	5.96	5.91	5.80	5.63
5	5.79	5.41	5.19	5.05	4.95	4.74	4.68	4.56	4.36
6	5.14	4.76	4.53	4.39	4.28	4.06	4.00	3.87	3.67
10	4.10	3.71	3.48	3.33	3.22	2.98	2.91	2.77	2.54
12	3.89	3.49	3.26	3.11	3.00	2.75	2.69	2.54	2.30
20	3.49	3.10	2.87	2.71	2.60	2.35	2.28	2.12	1.84
∞	3.00	2.60	2.37	2.21	2.10	1.83	1.75	1.57	1.00

TABLE 7-5

Critical Values for the Rejection Quotient, *Q***

Number of Observations	Q_{crit} (Reject if $Q > Q_{crit}$) 90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

*Reprinted with permission from D. B. Rorabacher, *Anal. Chem.*, **1991,** *63,* 139. Copyright 1991 American Chemical Society.

TABLE 7-3

Values of *t* for Various Levels of Probability

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

TABLE 7-1

Confidence Levels for Various Values of *z*

Confidence Level, %	*z*
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

Biochemistry Cumulative Examination

Title: Signal Transduction

August 27, 2005

1. **(15 pts)** Provide brief general definitions for the following terms.

   (i) RNAi
   (ii) Antagonists
   (iii) Desensitization
   (iv) GTPase activating protein
   (v) SH3 domain

2. **(40 pts)** Provide concise answers to the following questions.

   (i) Why receptor tyrosine kinases possess multiple autophosphorylation sites, compared to cytoplasmic kinases like Src and Abl, which have only one autophosphorylation site?
   (ii) What is senescence?
   (iii) Src kinase gets phosphorylated at Y416, is this event stimulatory or inhibitor. Explain the mechanism.
   (iv) Mutations in G proteins active sites are often oncogenic. Explain a plausible mechanism.
   (v) What are the main kinases that constitute the MAP kinase cascade?
   (vi) If rasGAP protein is degraded by RNAi, predict the effect on G protein signaling pathway when it is specifically activated?
   (vii) Define the functional consequences of activating Ras with GTPγS versus GTPαS.
   (viii) What is the molecular target of Gleevec?

3. **(15 pts)** Explain briefly.

   (i) Define WW domain.
   (ii) What is the function of islets of Langerhans?
   (iii) What is the function of a PLCβ?
   (iv) How are PLCβ and PLCγ activated?
   (v) What are the hallmarks of cancer?

4. **(30 pts)** Provide concise answers to the following questions.

(i) Explain the molecular mechanism that leads to bubonic plaque.

(ii) EGTA is a chelating agent with high specificity and affinity towards calcium. How would EGTA microinjection affect a cell's response to (a) vasopressin (b) glucagon?

(iii) Explain two key differences between Jak/Stat and Receptor Tyrosine Kinase pathways?

(iv) Both kinases and ATPases require ATP as a cofactor, how do they differ?

(v) What is the key difference between PTP and PTEN?

Inorganic Chemistry Cumulative Exam
Purdue University
August 27, 2005

Question 1: (17 points)

One fun aspect of inorganic chemistry is all the pretty colors. The compound $[Ti(OH_2)_6]^{3+}$ is a nice red-violet color. Explain why $[Ti(OH_2)_6]^{3+}$ is colored. You need not explain the color specific to this complex. But you must provide the general origin of color in this compound.

Question 2: (16 points)

The compound $[Co(NH_3)_5Cl]^{2+}$ is pink and the compound $[Co(NH_3)_5I]^{2+}$ is purple. Why do these very similar compounds have different colors?

Question 3: (16 points)

The compound TiF_4 is colorless and the compound $TiBr_4$ is orange. Why does $TiBr_4$ have any color at all?

Question 4: (16 points)

What is EDTA? Provide the full name and structure of this molecule. What is this molecule very good at doing and often used for?

Question 5: (17 points)

Define what the terms "paramagnetic" and "diamagnetic" mean, when used to describe metal ions. Your answer should be brief, no more than one paragraph in total.

Question 6: (18 points)

What is the chelate effect in inorganic chemistry? Provide a brief explanation of:

A) What the chelate effect is

B) Why the chelate effect exists

Try to keep your answer to a maximum of two paragraphs.

Organic Cumulative Exam
August 27, 2005

1) (5 points) For each of the biological molecules listed on the left, identify the components that they contain listed on the right. Chose only the ***single best answer*** for each of 1 - 5, but you can use each option (A - E) more than once or not at all.

1. ______	polypeptides	A. alkyl amines
2. ______	DNA	B. amino acids
3. ______	oligosaccharides	C. carbohydrates
4. ______	lipids	D. nucleotides
5. ______	alkaloids	E. fatty acids

2) (12 points)
a) What is the difference, chemically, between animal fat, vegetable oil, and tropical oils?
b) What is the difference between butter and margarine?

3) (25 points) Hammett parameters σ for substituents and ρ reactions are defined by the equation

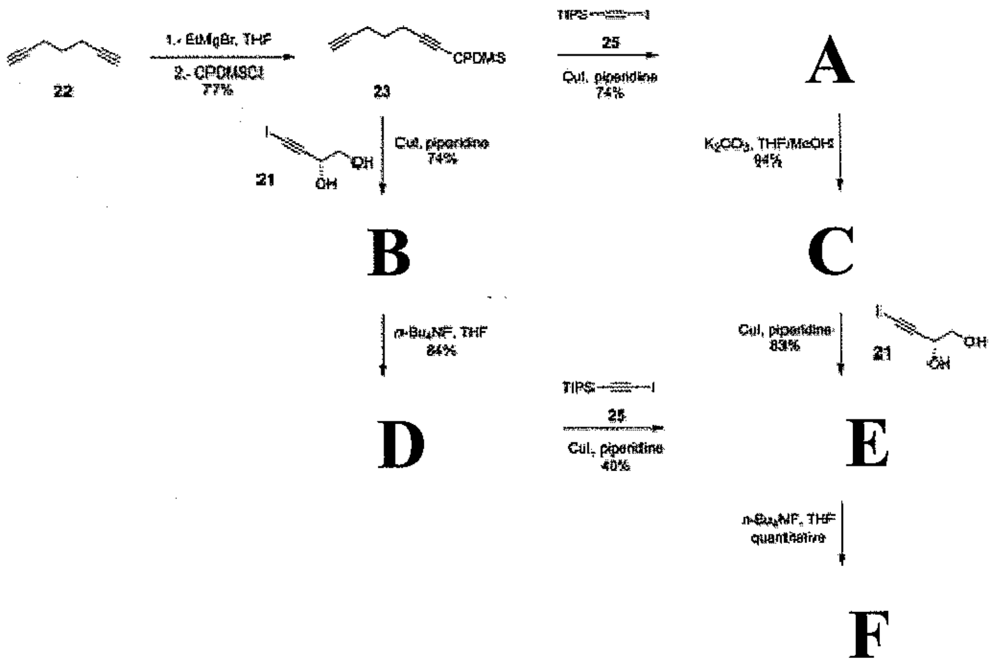
$$\log(K/K_H) = \sigma\rho$$

where K is the equilibrium constant for the substituted system and K_H is the constant for the unsubstituted system. As can be seen in the attached table, the convention is that the σ parameters for electron-attracting substituents are positive, whereas those for electron releasing substituents are negative. When interpreting reaction constants, a reaction with a positive ρ value is assisted by electron-attracting substituents and adversely affected by electron-donating substituents. The converse is true for reactions with negative ρ values.

A Hammett plot the reaction of *meta-* and *para-*substituted benzoic acids with diphenyldiazomethane in methanol solution had a ρ value of 0.844. When the same reaction was toluene solution, the value of ρ was 2.20. Write mechanisms for the reaction that are consistent the signs of ρ, and explain the dependence of the values on ρ on the nature of the solvents.

4) (25 points) Many recent articles in the literature have discussed the formation of poly-acetylene molecules. For example, a synthesis of (-)-Siphondiol, a tetra-yne with propargylic and homo-propargylic alcohol groups, has recently been reported by López and co-workers. The synthesis started from 1,6-heptadiyne, **1**. A key feature of the process is the lengthening of both sides of the diyne through Cadiot-Chodkeiwicz cross-coupling using CuI. The two sides were treated sequentially, such that there were two routes available for this process that converged to the same product.

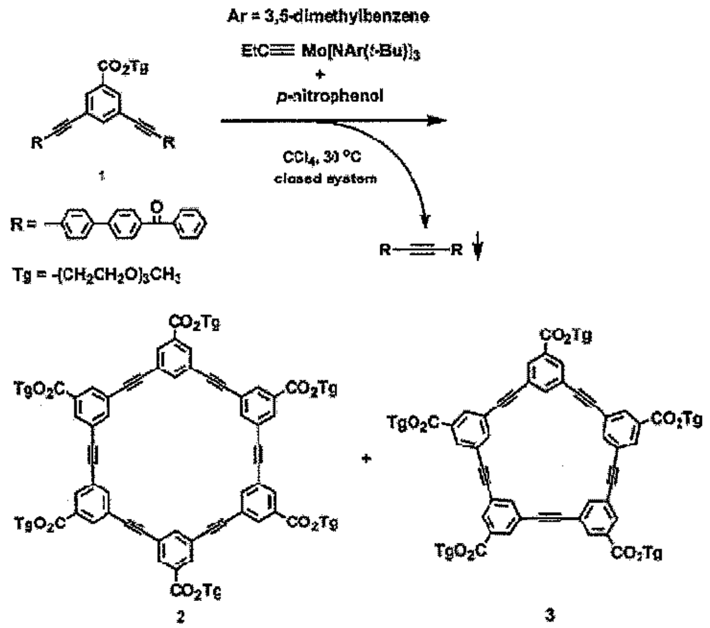
a) Given the reaction conditions and reagents, give the structures of products **A**, **B**, and **C**, **D**, and **E**:



b) What is the structure of (-)-Siphondiol, **F**?

c) At the beginning of the synthesis, the authors use a CPDMS protecting group. What does CPDMS stand for?

5) (25 points) Zhang and Moore have reported that metathesis of diethynylbenzene, **1**, in CCl_4, mostly to formation of the hexacycle, **2**, and smaller amounts of the pentacycle, **3**, without forming rings of other sizes.



(eq 1)

Force field calculations of free energies are in agreement with experimental observations. Relative ΔG values between the hexacycle and the other size rings are the following:

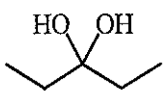
ring size	ΔG (kcal/mol at 303 K)
4	15.6
5	0.54
6	0.0
7	3.53
8	5.81

Thus, the hexacycle has the lowest free energy, the pentacycle is slightly higher, followed by the heptacycle, octacycle, and tetracycle.

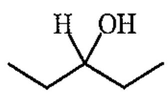
a) Provide a justification for the free energy ordering of these rings (HINT: it might be easiest to deconstruct the free energy into its enthalpy and entropy components)

b) It is tempting to see these macrocycles as building blocks for carbon nanotubes. One type of carbon nanotube is known as a "single-walled nanotube" (SWNT), which, as the name implies, has only a single wall of carbon atoms. The diameter of SWNTs is generally around 1 nm. Assuming that the wall of a nanotube is just a sheet of graphite (and not a arylene ethynylene macrocycle like above), estimate the number of carbon atoms in a SWNT that is 1 μm long.

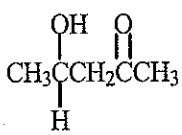
6) (8 points) For the products on the left, supply the reactants and reaction conditions on the right that would lead their formation. Note that there can be more than one set of conditions that lead to a given product. None of the reactions on the right are used more than once, but they might not be used at all.

I. 

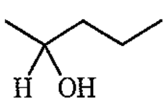
____

II. 

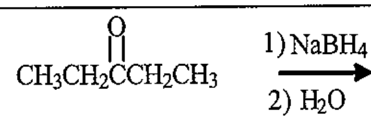
____

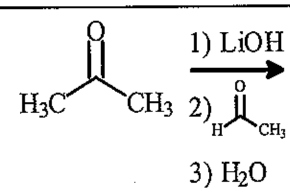
III. 

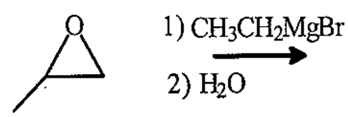
____

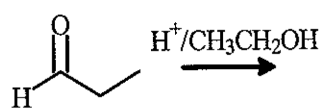
IV. 

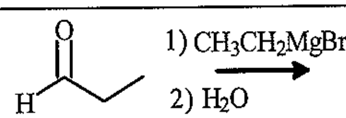
____

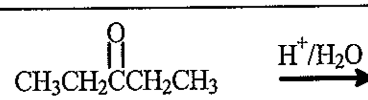
a. 

b. 

c. 

d. 

e. 

f. 

Appendix: Table of some Hammett σ parameters

Substituent	σ_{para}	σ_{meta}
NO_2	0.78	0.71
CN	0.66	0.56
Cl	0.28	0.39
F	0.06	0.34
CH_3	-0.17	-0.07
OH	-0.37	0.12
NH_2	-0.66	-0.16
S^-	-1.21	-0.36

1. The time-dependent Schrodinger equation (TDSE) in one dimension has the form:

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t)$$

where H is the Hamiltonian operator. If H is independent of time, we can use separation of variables to simplify this partial differential equation into two ordinary differential equations in x and t, respectively.

Assume that $\Psi(x,t) = \psi(x)\cdot f(t)$, and plug this form into the TDSE to show that for time-independent Hamiltonians:

$$\Psi_n(x,t) = \psi_n(x)\cdot e^{iE_nt/\hbar} \quad \text{and} \quad H\psi_n(x) = E_n\psi_n(x).$$

2. Any physically realizable wave function $\Psi(x,t)$ for our system can always be written as a linear combination of the basis functions $\Psi_n(x,t)$; that is,

$$\Psi(x,t) = \sum_n c_n \cdot \Psi_n(x,t).$$

a) What is the expectation value of the Hamiltonian for a system with wave function $\Psi(x,t)$?

b) If you made repeated measurements of the total energy E for this system, what is the probability of obtaining the answer E_n?

3. Now consider a particle in a one-dimensional box of length L.

Suppose that at t=0, $\Psi(x,t=0) = \frac{1}{\sqrt{2}}\cdot\psi_{n=1}(x) + \frac{1}{\sqrt{2}}\cdot\psi_{n=2}(x)$.

a) Plot the probability density at t=0, $|\Psi(x,t=0)|^2$.

b) Comment on the effect of taking a linear combination of eigenfunctions on the extent of localization or delocalization of the wave function relative to the eigenfunctions themselves.

c) Determine an expression for the probability density, $|\Psi(x,t)|^2$ as a function of time.

d) Show that it oscillates with period $T = \frac{8mL^2}{3h}$. In what way does this recover some of our classical intuition regarding a classical particle moving in a one-dimensional box?

4. *Without doing any calculations,* determine the following expectation values for a system in the n=1 state with energy $E_{n=1} = \frac{h^2}{8mL^2}$:

a) <p>, the momentum b) <KE>, the kinetic energy

c) <x>, the position.

In each case, briefly defend your answer.

Formula sheet for the P-Chem cume

Quantum mechanical particle of mass 'm' confined to a one-dimensional box of length L:

Assume that V(x)=0 for $0 \le x \le L$ and $V(x) = +\infty$ for x<0 and x>L.

$$H\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi_n(x)}{\partial x^2} = E_n\psi_n(x) \text{ inside the box.}$$

Energy eigenfunctions: $\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right)$.

Energy eigenvalues: $E_n = \frac{n^2h^2}{8mL^2}$

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII	VIII	VIII	I B	II B	III A	IV A	V A	VI A	VII A	O
1 **H** 1.00797																	2 **He** 4.0026
3 **Li** 6.939	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.01115	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.183
11 **Na** 22.9898	12 **Mg** 24.312											13 **Al** 26.9815	14 **Si** 28.086	15 **P** 30.9738	16 **S** 32.064	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.102	20 **Ca** 40.08	21 **Sc** 44.956	22 **Ti** 47.90	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.909	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.905	40 **Zr** 91.22	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (99)	44 **Ru** 101.07	45 **Rh** 102.903	46 **Pd** 106.4	47 **Ag** 107.870	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9044	54 **Xe** 131.30
55 **Cs** 132.905	56 **Ba** 137.34	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.09	79 **Au** 196.967	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.980	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac†** (227)															

***Lanthanides**	58 **Ce** 140.12	59 **Pr** 140.907	60 **Nd** 144.24	61 **Pm** (147)	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.924	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.934	70 **Yb** 173.04	71 **Lu** 174.97
†Actinides	90 **Th** 232.038	91 **Pa** (231)	92 **U** 238.03	93 **Np** (237)	94 **Pu** (242)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (249)	99 **Es** (254)	100 **Fm** (253)	101 **Md** (256)	102 **No** (256)	103 **Lw** (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)