Department of Chemistry
Cumulative Examinations
April 30, 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.

1) Analytical Cumulative Examination, Page 1
2) Biochemistry Cumulative Examination, Pages 2-3
3) Inorganic Cumulative Examination, Pages 4-5
4) Organic Cumulative Examination, Pages 6-8
5) Physical Cumulative Examination, Pages 9-10

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

Methods to Determine the Identity and Coverage of Biomolecules on Surfaces
Analytical Cume, April 2005

Suppose that you would like to understand the adsorption behavior of a synthetic peptide (5-10 amino acid residues) to a hydrophilic substrate in-situ. Assume that you decided to use attenuated total reflection infrared spectroscopy (ATR-IR). Suppose that you have successfully cleaned or modified the ATR crystal to have a hydrophilic surface.

1) Sketch the spectrum that you expect to collect based on the presence of Amide I and Amide II bands.
2) Propose an experiment that will help you verify the band assignments.
3) Describe a method to follow the adsorption behavior of the peptide to the crystal surface if you assume Langmuirian behavior. Describe how you will determine coverage at a given concentration of peptide to which the surface was exposed. (Note you will not receive any points for simply stating the assumptions of the Langmuir adsorption isotherm).
4) Does the Langmuir adsorption isotherm work if a cooperative effect is taking place?

Biochemistry Cumulative Examination

Title: Signal Transduction

April 30 2005

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

   (i) Paracrine
   (ii) Agonists
   (iii) Desensitization
   (iv) GEFs
   (v) SH2 domain

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

   (i) Wild-type Akt kinase has a pH domain at the N-terminus, which is sensitive to phosphoinositides. If the pH domain is replaced by a myristoylation tag, how will that effect its kinase activity?
   (ii) What will happen if the pH domain of Akt is deleted by mutagenesis?
   (iii) Src kinase gets phosphorylated at Y527, is this event stimulatory or inhibitor. Explain the mechanism.
   (iv) Mutations in G proteins active sites are often oncogenic. Explain a plausible mechanism.
   (v) cAMP and cGMP are second messengers. How are these synthesized and degraded?
   (vi) If SOS protein is degraded by RNAi, predict the effect on G protein signaling pathway when it is specifically activated?
   (vii) Define the molecular mechanism of Whooping Cough.
   (viii) How does Gleevec acts as an anticancer drug?

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

   (i) Which class of signaling proteins constitutes the largest family of drug target candidates?
   (ii) What is the function of Calcitonin?
   (iii) What is the function of a GAP protein?
   (iv) What is the cause of goiter?

(v) What is the function of Nitric Oxide?

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

(i) Explain how mutations in the R or C subunit of c-AMP-dependent protein kinase (PKA) might lead to (a) a constitutively active PKA or (b) a constantly inactive PKA.

(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 G proteins coupled to GPCRs and Ras?

(iv) Post-translational Modifications (PTMs) play key role in signal transduction. Define the functions of any three enzyme classes responsible for PTMs in the cell.

(v) Why epinephrine is called a "flight or fight hormone?

Inorganic Chemistry Cume Exam

April 30, 2005

100 points will be assigned

Cyclopentadienyl (Cp) complexes of the transition metals constitute an extensive class of compounds that can display a variety of bonding modes for the Cp ligands. The structures and reactivities of these Cp complexes are often dependent upon the substituents that are present on the Cp rings and upon the transition metal and its oxidation state. The following questions relate to the synthesis, electronic and molecular structures, and reactivities of transition metal cyclopentadienyl complexes.

1.) Complexes of the types $(C_5R_5)MCl_3$ and $(C_5R_5)_2MCl_2$ (R = H or Me; M = Ti or Zr) are important complexes for the synthesis of the other Cp derivatives. Draw the structures and give the electron counts for the metals in complexes of these two types when M = Ti or Zr.

Draw the structures of the metal complexes that are the products of the following reactions and in each case give the metal count.

(i) $(C_5H_5)_2TiCl_2$ + excess $Na^+C_5H_5^-$
(ii) $(C_5H_5)_2TiCl_2$ + excess PMe_3 in the presence of Mg metal
(iii) $(C_5H_5)_2ZrCl_2$ + Mg metal + $ClCH_2C\equiv CCH_2Cl$ (1, 4-dichlorobut-2-yne)
(iv) $(C_5Me_5)TiCl_3$ + C_7H_8 (cycloheptatriene) in the presence of Mg metal.

2.) Draw the structures of the compounds of composition $M(C_5H_5)_2$ in the cases where M = V, Nb, Os, and Re. If more than one structure is known for any of these molecules, make sure you draw all known structures. Explain as best you can why structural differences exist within this set of compounds.

3.) Draw the structures of compounds **A** and **B** that are formed in the following reactions:

$$(C_5Me_4H)_2ZrCl_2 \xrightarrow[\text{Na/Hg}]{N_2} \mathbf{A} \xrightarrow[25°\text{C}]{H_2} \mathbf{B}$$

Discuss briefly the significance of these two reactions.

4.) Provide the synthetic details for the synthesis of $(C_5H_5)_2Ta(CH_3)_3$ and $(C_5H_5)_2Ta(CH_3)(CH_2)$ from $TaCl_5$. Draw very clearly the structures of both complexes and discuss the special significance of $(C_5H_5)_2Ta(CH_3)(CH_2)$.

5.) What is Tebbe's reagent? Give its synthesis, draw its structure, and explain what it is used for.

6.) Although the η^1- and η^5-bonding modes of C_5R_5 ligands are the ones most commonly encountered, examples of η^3-bonding are known. Give <u>one</u> such example for a cyclopentadienyl complex whose structure has been determined, draw its structure, and rationalize why a η^3-bond cyclopentadienyl ligand is present.

Cumulative Exam
Organic Chemistry
April 2005

1) a) Rank the following radicals in order of *increasing* stability (1 being least stable).

CH_3 C_2H_5 i-C_3H_7 t-C_4H_9

b) Propose a physical property that can be used *legitimately* to assess the stabilities of the radicals in part (a).

For the rest of the exam, refer to the attached paper by Houk and co-workers, where they compare the conjugation energy of diacetylene with that in butadiene. Their calculations find that the heat of hydrogenation of the first triple bond in diacetylene is the same as the second, indicating no resonance stabilization in the di-yne, in contrast with what is expected from simple molecular orbital models. The paper is an attempt to rationalize the discrepancy.

2) It can be seen in eq 2 that, experimentally, the heat of hydrogenation of the second olefin in butadiene is 3.8 more favorable than that for the first.
a) Draw a potential energy diagram for the hydrogenation of butadiene.
b) Indicate how the potential energy diagram would be different if butadiene were not stabilized by conjugation. Explain your reasoning.

3) According to Hückel theory, the 4 π MOs of butadiene have energies $\alpha + 1.618\beta$, $\alpha + 0.618\beta$, $\alpha - 0.618\beta$, and $\alpha - 1.618\beta$. Using these values, calculate the Hückel resonance energy of butadiene. Give the answer in β units, and estimate a numerical value using an appropriate value of β. (Hint: the energies of the π orbitals in ethylene are $\alpha \pm \beta$)

4) a) According to the paper, by how much energy does diacetylene benefit from conjugation?
b) In 25 words or less, explain why sequential heats of hydrogenation are insufficient to determine conjugation energies of diynes?

5) The use of heats of hydrogenations is called a "Kistiakowsky" approach, based on the work of the Harvard thermochemist. Outside of organic chemistry, Kistiakowsky is probably best known for his participation in the Manhattan Project, and for his term as President Eisenhower's Science Advisor in the early 1950s. Within organic chemistry, he is probably best known for his determination of the resonance energy of benzene. Describe Kistiakowsky's approach for determining the resonance energy of benzene, and the answer he obtained.

J|A|C|S
COMMUNICATIONS

How Large Is the Conjugative Stabilization of Diynes?

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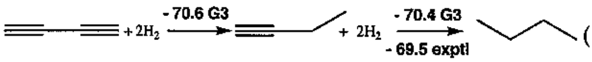
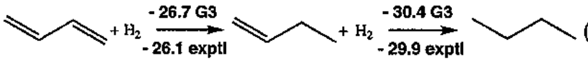
A recent paper by Rogers et al. reported, "The Conjugation Stabilization of 1,3-Butadiyne is Zero."[1] This conclusion was based upon unmodified energetic comparisons of conjugated species with nonconjugated analogues; a method first applied by Kistiakowsky in 1936 to assess the energetic consequences of conjugation in butadiene.[2a] Following this approach, Rogers et al.[1] computed the stepwise hydrogenation of 1,3-butadiyne first to 1-butyne and then to butane (eq 1) at the G3(MP2)[3] level. Both these steps were calculated to be equally exothermic, indicating an absence of conjugation energy for 1,3-butadiyne according to the Kistiakowsky method. Our higher-level G3[4] results (eq 1, in kcal/mol) confirm the hydrogenation data of ref 1, but we disagree with the interpretation.



(1)

The analogous stepwise hydrogenation of 1,3-butadiene[2a] (eq 2) reproduces the widely accepted empirical value of 3.7 kcal/mol,[5] typically ascribed to conjugative stabilization, derived from the difference between the first and second hydrogenation step.



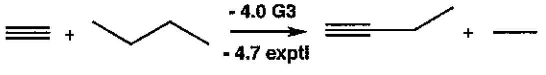
(2)

Rogers et al.'s evaluation led them to conclude that diyne conjugation is less stabilizing than diene conjugation.[1] All accepted theoretical models for conjugation would predict the opposite to be true.[5] Pauling,[5b−d] Dewar,[5e−f] Conn,[2c] and others[5g−k] have invoked resonance, hybridization, and nonbonded repulsion effects, respectively, to interpret the thermodynamically favorable consequences of conjugation. Kollmar[6] computed the resonance stabilization of 1,3-butadiyne (19 kcal/mol) to be nearly double that of 1,3-butadiene (9.7 kcal/mol), based upon comparison to hypothetical systems with nonresonating acetylene and ethylene units. In addition, the greater s-character of the central single bond and the lower coordination of the interacting carbon atoms would favor the conjugation of acetylene units over ethylene units. All these effects are manifested in the remarkably short (1.38 Å)[5a,d] carbon−carbon single bond of 1,3-butadiyne.[5a]

Conjugative stabilization, like many well-accepted constructs in chemistry, is a virtual thermodynamic quantity that depends on the choice of model systems and method of evaluation. The true conjugative stabilization is not a measurable quantity: it is the difference in energy between a conjugated molecule and its hypothetical energy (virtual state) if the entire contribution stemming from conjugation could be accounted for and excised. Kistiakowsky's hydrogenation evaluation gives only a rough approximation of this conjugation energy: comparisons of heats of hydrogenation evaluate not only conjugation effects but also other structural and electronic differences between the conjugated molecule and its hydrogenated products. More refined conjugative stabilization evaluations should eliminate or minimize these differences as much as possible. Specifically, 1-butyne, the reference compound for 1,3-butadiyne, is stabilized significantly by hyperconjugation,[7] which is not present in 1,3-butadiyne. Hyperconjugation also complicates the evaluation of the conjugative stabilization of 1,3-butadiene but was not considered in Kistiakowsky's[2] original work. We now propose modifications of the Kistiakowsky scheme, which take hyperconjugative interactions into account. Determined by this modified method, the conjugative stabilization of butadiyne and butadiene are both quite large, in accord with the well-based theoretical expectations.[5,6]

We have calculated the energies of hyperconjugation of substituted acetylenes and ethylenes using computational and experimental data. These quantities are applied to refine the evaluation of diyne and diene conjugation energies, not only using Kistiakowsky's method, but also isomerization reactions of diynes and dienes. Using the Gaussian 98 program,[8,9] we employed G3,[4] a well-established method for computing accurate thermochemical data. We also used G3(MP2),[3] which is a less computer intensive, but comparably accurate variation, for the larger systems employed for isomerization reactions. Data obtained from both theoretical methods agree very well with the experimentally available heats of formation and hydrogenation.[2,10−12] Data and their analyses are given in Supporting Information, Tables 1−4.

When evaluated by the conventional method, hyperconjugation involving alkynes is twice as large as alkenes; the stabilization of ethylene (in kcal/mol) by an ethyl substituent (2.4 G3; 2.2 G3(MP2); 2.7 expt) is based on the difference between the heats of hydrogenation of ethylene and 1-butene. Likewise, the hyperconjugative stabilization of acetylene by an ethyl group (4.9 G3; 4.8 G3(MP2); 4.7 expt)[14] is the difference between the heat of hydrogenation of acetylene and 1-butyne. Equivalently, the hyperconjugative stabilization can also be described by isodesmic reactions 3 and 4 that produce data consistent with the above evaluation:



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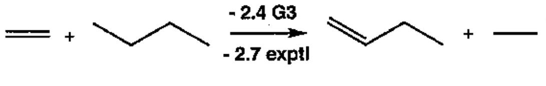

(4)

Deleting the hyperconjugative interactions evaluated conventionally gives the virtual states shown below. These states have energies that are 4.9 and 2.4 kcal/mol higher than those of 1-butyne and 1-butene, respectively.

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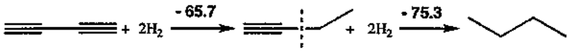
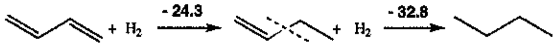
Employing these virtual states in a Kistiakowsky scheme (eq 5) results in a 9.8 (9.2 G3(MP2)) kcal/mol conjugative stabilization for 1,3-butadiyne. This is 1.3 (1.0 G3(MP2)) kcal/mol *more* than the 8.5 (8.2 G3MP2) kcal/mol stabilization obtained for 1,3-butadiene (eq 6).

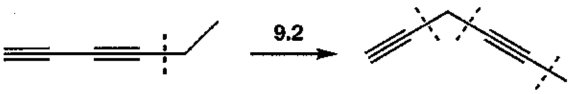


(5)

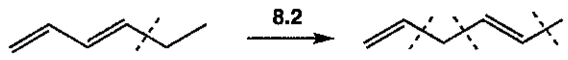


(6)

Isomerization reactions also yield conjugative stabilization energies. The directly computed G3(MP2)[3] heats of isomerization of 1,3-hexadiyne (4.0 kcal/mol)[15] and of 1,3-hexadiene (4.3 kcal/mol) to their respective 1,4-unsaturated isomers are nearly the same (note they are not zero). However, these equations are not hyperconjugation-balanced: the products are stabilized more than the reactants. When the hyperconjugation stabilization of each species is taken into account (Supporting Information, Table 4), the isomerization energies are 9.2 kcal/mol for the isomerization of 1,3-hexadiyne (eq 7) and 8.2 kcal/mol for the isomerization of 1,3-hexadiene (eq 8).

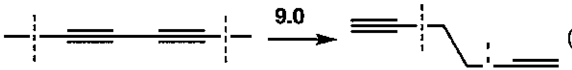


(7)



(8)

These agree with the directly computed energies of isomerization of species that are more nearly hyperconjugation-balanced: 11.3 kcal/mol for 2,4-hexadiyne and 8.6 kcal/mol for 2,4-hexadiene. After minor adjustments for subtle changes in hyperconjugation (Supporting Information, Table 4), the isomerization energies of eqs 9 and 10 are in near perfect agreement with our other conjugation stabilization evaluations, eqs 5 and 7, as well as eqs 6 and 8.



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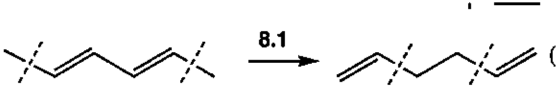

(10)

The conjugative stabilization for butadiene and butadiyne, as given by Kistiakowsky's scheme, is counterbalanced by the hyperconjugative stabilization by the ethyl groups in 1-butene and 1-butyne, respectively. These hyperconjugative interactions[7] are large enough to fully obscure the conjugative stabilization in 1,3-butadiyne and considerably diminish the analogous 1,3-butadiene value.

The results of Rogers et al.[1a] bring to light the limitations in Kistiakowsky's method. For 1,3-butadiene, the method gave results that seemed reasonable at the time, but for 1,3-butadiyne, the results defy well-founded theoretical models,[5] as well as the simple expectation (confirmed by the hyperconjugation evaluations) that the two double bonds in an alkyne should conjugate better than the single double bond in an alkene. In our view, Kistiakowsky's method substantially underestimates conjugative stabilization of dienes and of diynes to an even greater extent. Consideration of hyperconjugative interactions provides a more refined measure of conjugative stabilization. All the conjugation energies of the isomerization and hydrogenation reactions considered here agree superbly, 9.3 ± 0.5 kcal/mol for diynes and 8.2 ± 0.1 kcal/mol for dienes, only when this is done.

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Supporting Information Available: Tables 1−4 of computed and experimental thermodynamic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7564−7776.

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(9) Enthalpies, computed as the sum of the electronic energy and thermal corrections obtained from analytical harmonic vibrational frequencies at 298 K, are reported. All species are minima. Thermodynamic details are given in Supporting Information, Tables 1−4.

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(14) These magnitudes are close to the experimental isomerization energies of 1-butene to *trans*-2-butene, 2.4 kcal/mol (see ref 11), and 1-butyne to 2-butyne, 4.8 kcal/mol (see ref 10), which involve an increase of one hyperconjugative interaction.

(15) A 3.8 kcal mol^{-1} experimental isomerization energy of the conjugated 5,7-dodecadiyne to the nonconjugated 3,9-dodecadiyne has been reported (Benson, S. W.; Garland, L. J. *J. Phys. Chem.* **1991**, *95*, 4915).

JA046432H

Physical Cumulative Examination April 30, 2005

1. The surface tension of water is observed to decreases linearly with temperature (in experiments at constant p and a): $\gamma(T) = b - cT$, where T = temperature °C, $b = 75.6$ erg/cm^2 (the surface tension at 0 °C) and $c = 0.1670$ erg/(cm^2 deg)

(a) (10 points) If γ is defined by $dE = TdS - pdV + \mu dN + \gamma da$, where da is the area change of a pure material, give γ in terms of a derivative of the Gibbs free energy at constant T and p.

(b) (15 points) Using a Maxwell relation, determine the quantitative value of $(\partial S/\partial a)_{p,T}$ from the relationship above.

(c) (15 points) Estimate the entropy change from ΔS from the results above if the area of the water/air interface increases by 4 Å^2 (about the size of a water molecule).

2. (28 points) Below are seven equations purporting to be equations for S(E,V,N) for various thermodynamic systems. However, four of them are not physically acceptable. Find the four impermissible equations and for each indicate why it cannot be correct. The quantities θ and v_o are in all case positive, intensive quantities with the dimensions of temperature and volume, respectively.

$$S = \left(\frac{k_B^2}{v_o\theta}\right)^{1/3} (EVN)^{1/3}$$

$$S = \left(\frac{k_B v_o^2}{\theta^2}\right)^{1/3} \left(\frac{EN}{V}\right)^{2/3}$$

$$S = \left(\frac{k_B v_o^2}{\theta^2}\right)^{1/3} \left(\frac{EN}{V}\right)$$

$$S = \left(\frac{k_B}{\theta}\right)^{1/2} \left(NE - \frac{k_B \theta V^2}{v_o^2}\right)^{1/2}$$

$$S = k_B N \ln\left(\frac{EV}{N^2 k_B \theta v_o}\right)$$

$$S = k_B N \exp\left(\frac{-EV}{N^2 k_B v_o}\right)$$

$$S = k_B N \exp\left(\frac{-EV^2}{N^2 k_B \theta v_o}\right)$$

3. (12 points) For a system with a fixed number of particles the reciprocal of the Kelvin temperature, T is given by which of the following derivatives? Explain your reasoning. (Clue: Dimensional analysis will work, but there's an even easier way)

$$\left.\frac{\partial p}{\partial V}\right)_S \quad \left.\frac{\partial p}{\partial S}\right)_V \quad \left.\frac{\partial S}{\partial p}\right)_E \quad \left.\frac{\partial V}{\partial p}\right)_E \quad \left.\frac{\partial S}{\partial E}\right)_V$$

4. Consider a region within a fluid described by the van der Waals equation

$$\beta p = \frac{\rho}{(1-b\rho)} - \beta a \rho^2$$

where $\rho = \langle N \rangle / V$. The volume of the region is L^3. Due to spontaneous fluctuations in the system, the instantaneous value of the density in that region can differ from its average by an amount $\delta\rho$.

(a) (10 points) A fluid is at its "critical point" when

$$\left(\frac{\partial \beta p}{\partial \rho}\right)_\beta = \left(\frac{\partial^2 \beta p}{\partial \rho^2}\right)_\beta = 0$$

Determine the critical point density and temperature for the fluid obeying the van der Waals equation. That is, compute β_c and ρ_c as a function of a and b.

(b) (10 points) Light that we can observe with our eyes has wavelengths of the order 500 nm. Fluctuations in density cause changes in the index of refraction, and those changes produce scattering of light. Therefore, if a region of fluid 500 nm across contains significant density fluctuations, we will visually observe these fluctuations. On the basis of the type of calculation performed in part (a), determine how close to the critical point a system must be before critical fluctuations become optically observable. The phenomenon of long wavelength density fluctuations in a fluid approaching the critical point is known as critical opalescence. (Note: You will need to estimate the size of b, and to do this you should note that the typical diameter of a small molecule is around 0.5 nm.)

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	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.)