Department of Chemistry
Cumulative Examinations
January 13, 2007

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, Pages 1-3
2) Biochemistry Cumulative Examination, Page 4
3) Inorganic Cumulative Examination, Pages 5-6
4) Organic Cumulative Examination, Pages 7-8
5) Physical Cumulative Examination, Page 9

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: 42
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 cumulative examination **January 13, 2007**

1) Demonstrate your general knowledge about mass spectrometry and related topics by answering the following questions:

a) Why do mass spectrometers usually operate on gas-phase ions (*e.g.*, require the analyte to be charged and under collision-free conditions)?

b) Give a definition for mass resolution, and explain its importance in mass spectrometric analyses.

c) Give a specific example where high resolution is absolutely necessary.

d) Explain the difference between precision and accuracy.

e) Define dynamic range.

2) Demonstrate your general knowledge about mass spectrometers by answering the following questions:

a) Give an example of a mass spectrometer with high resolution and another one with low resolution. Explain why this is so.

b) Why are time-of-flight mass spectrometers commonly used to analyze very large biomolecules?

c) Why is electrospray ionization (ESI) the commonly used ionization method in these experiments?

3) In order to demonstrate your general knowledge on what the local mass spectrometrists are excited about and why, please answer these three questions:

a) What is the new invention that Professor Graham Cooks made recently on sample introduction into mass spectrometers, and why is everybody excited about this invention?

b) Why is Professor Hilkka Kenttämaa receiving funding from Pharmaceutical industry to develop gas-phase ion/molecule reactions for structural characterization of compounds?

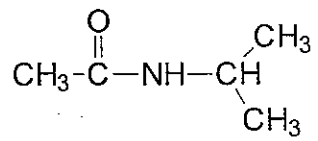
c) Why is Professor Scott McLuckey so famous for his studies on reactions that reduce the charge states of ESI-generated multiply charged peptide ions?

4) Demonstrate your general knowledge about the chemistry and energetics related to mass spectrometry experiments by answering the following questions:

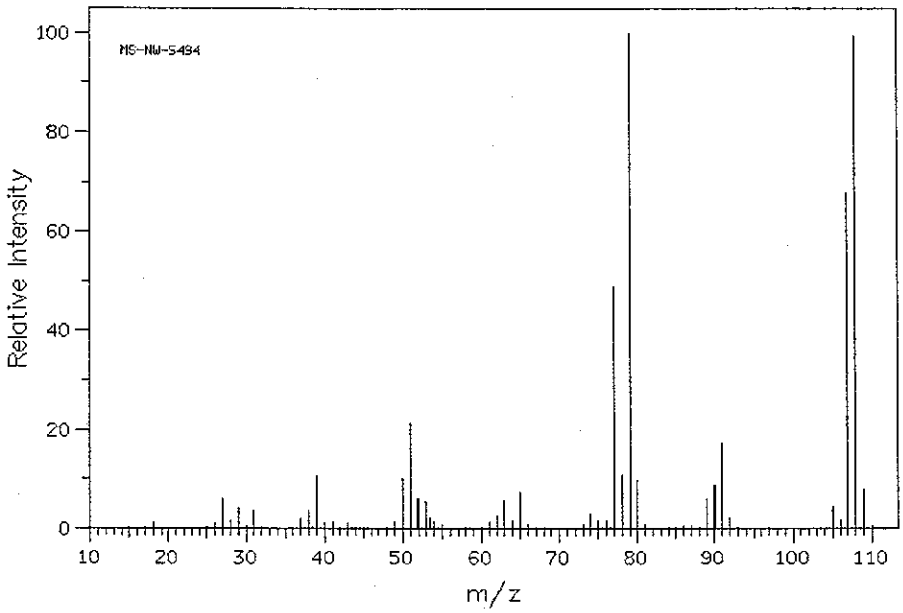
a) Give a rough estimate for the energy typically required to cause dissociation of an ionized organic molecule, and for the average energy that gas-phase ions gain in collision-activated dissociation (CAD).

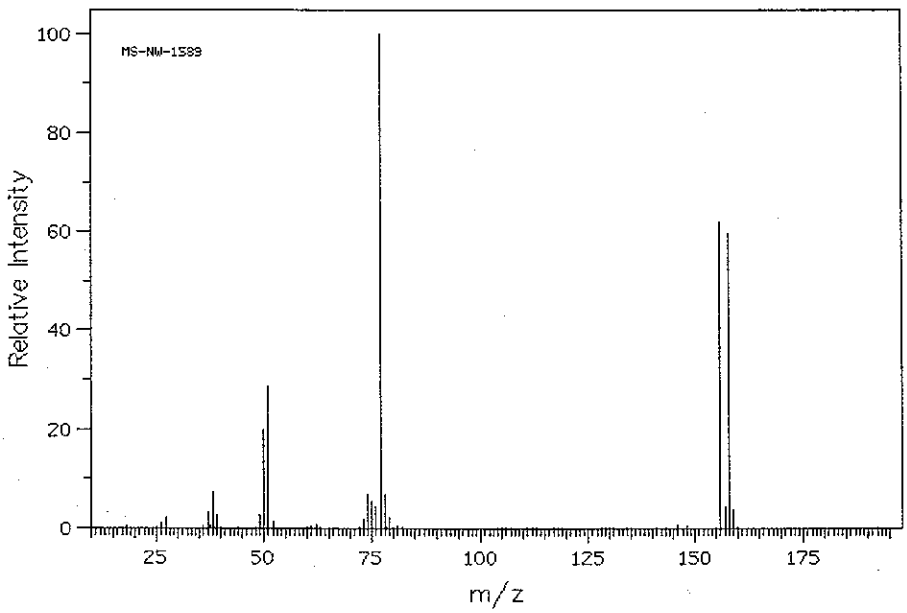
b) Explain what factors control the dissociation products obtained in CAD experiments. What theories could you use to predict (calculate) a mass spectrum, and what information do you need to do that?

c) A new method to fragment protonated analytes in mass spectrometry is called electron transfer-induced dissociation. This method involves bombarding protonated analytes with electrons to generate the corresponding radicals by electron capture. These radicals then undergo structurally characteristic fragmentations. Show that you understand the process by writing the chemical equations for every step of the experiment (starting with ionization) for the molecule shown on right.



10) Consider the positive ion EI mass spectra given below. What sort of structural information can you extract from them?





Biochemistry Cumulative Examination
January 2007

1. A recent article on "glycosylation engineering" included a section on the importance of introducing galactosyltransferase and sialyltransferase enzymatic activities into cultured insect cells, where such activities are normally absent. What role (if any) do such enzymes have in human biochemistry? Explain in detail. What is the point of introducing them into cultured insect cells?

2. When pure D-mannose is crystallized from methanol, crystals with mp 133° and (initial) specific rotation $[\alpha]_D^{20} = +29.3°$ (water) are obtained. When it is crystallized from acetic acid, crystals with mp 132° and (initial) specific rotation = −17.0° (water) are obtained. If each of the two aqueous solutions are allowed to stand, an identical $[\alpha]_D^{20} = +14.2°$ is reached. What is happening here? Use appropriate detailed structural formulas to explain your answer.

3. Cellulose is the primary structural component of plant cells. It provides major load-bearing strength and makes it possible for plant cells to deal with enormous (multi-atm) differences in osmotic pressure. Describe in detail the structure of cellulose, including clear structural formulas with portions of individual chains, and sketches and/or descriptions of chain-chain interactions.

4. Both in nature and in biotechnology applications, the enzyme lysozyme is used to lyse the cell walls of Gram-positive bacteria. How are Gram-positive and –negative bacteria distinguished? Briefly describe the operational classification procedure developed by Gram, and describe in detail the major structural differences between the respective cells. Then explain what lysozyme does, using structural formulas where possible. Briefly comment on how lysozyme catalyzes the reaction.

Inorganic Chemistry Cumulative Exam

Purdue University

January 13, 2007

There are 100 possible points in this exam.

1. (54 points) Consider metal spheres that are packed to form a primitive, a body-centered, and a face-centered cubic structure. Fill in the blanks assuming that the edge of each cube is 4.0 Å long.

	Primitive Cubic	Body-Centered Cubic	Face-Centered Cubic
Distance to a nearest neighbor (nm)	(a)	(g)	(m)
Number of first nearest neighbors	(b)	(h)	(n)
Distance to a second nearest neighbor (nm)	(c)	(i)	(o)
Number of second nearest neighbors	(d)	(j)	(p)
Distance to a third nearest neighbor (nm)	(e)	(k)	(q)
Number of third nearest neighbors	(f)	(l)	(r)

2. Consider a metal atom of radius r (so the volume of the atom is $4/3\pi r^3$). Assume that these atoms are packed to form a primitive cubic structure with each atom touching adjacent atoms. The packing efficiency of a lattice is defined as the volume occupied by metal atoms per unit cell divided by the volume of the unit cell.

a) (5 points) Express the edge of the cube in r.

b) (5 points) Calculate the packing efficiency for a primitive cubic structure.

c) (5 points) Consider the same metal spheres packed to form a face-centered cube. Express the edge of the cube in r.

d) (5 points) Calculate the packing efficiency for a face-centered cubic structure.

3. The perovskite structure shown below is adopted by many oxides that have the chemical formula, ABO_3. The general crystal structure is cubic, with the A-cation in the middle of the cube, the B-cation in the corner, and the anion, commonly oxygen, in the centre of the edges. Assuming that the edge of the cube is 4 Å, answer the following questions.

a) (6 points) What is the lattice type of this structure (e.g. primitive cubic, body-centered cubic, face-centered cubic)?

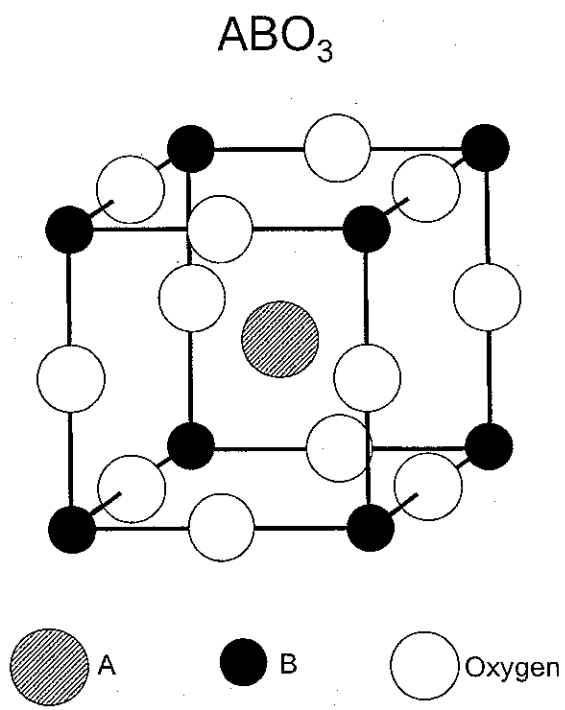
b) (4 points) How many oxygen atoms (nearest neighbors) are coordinated to B?

c) (4 points) How many oxygen atoms (nearest neighbors) are coordinated to A?

d) (4 points) What is the shortest A-O distance?

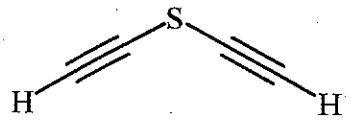
e) (4 points) What is the shortest A-A distance?

f) (4 points) $BaTiO_3$ has a perovskite structure and is a technologically important material due to its interesting ferroelectric and piezoelectric properties. Is this compound paramagnetic? Explain.



Organic Division Exam
January 2007

1) In a recent article (*JOC*, **2006**, *71*, 9602-9608), McMahon and co-workers described a matrix isolation photolysis study of diethynyl sulfide (**DES**)



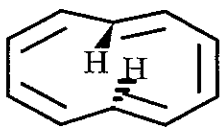
DES

Upon irradiation at 254 nm, the characteristic IR bands of **DES** in a nitrogen matrix at 3318 cm^{-1} disappear, and new bands are formed at 3326 and 1762 cm^{-1}, with the latter band being very intense.

a) Propose a structure for the newly formed product
b) The same product is formed upon irradiation of 2,5-diiodothiophene, suggesting that they are formed via a common reactive intermediate. Propose a structure for the intermediate.
c) Propose a mechanism for the reaction of **DES** to form the product (although the answers for parts (a) and (b) are suggestive, McMahon and co-workers provide three different possibilities, only one of which depend explicitly on those answers)

2) In an earlier issue of JOC, Warner described calculations of aromaticity in [11]annulenium cations ($C_{11}H_{11}^{+}$) (*JOC*, **2006**, *71*, 9271-9282)

a) The benefits of aromaticity in large rings are more difficult to come-by, because angle and steric strain can destabilize planar structures. Thus, the most stable isomer of [10]annulene, **1**, is expected to be only weakly aromatic because it is non-planar.



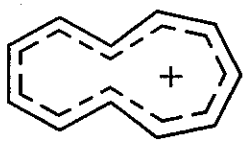
1

In fact, it was originally believed on the basis of DFT calculations carried out by Schaefer in the mid-90s that **1** was not the lowest energy isomer of $C_{10}H_{10}$, and that the actual lowest energy structure was planar, such that it could benefit from aromaticity.

i) What is that isomer?
ii) What does DFT stand for?

More recent, higher level calculations, however, indicate that **1** is indeed the lowest energy isomer, its lack of aromaticity notwithstanding.

b) The lowest energy isomer of [11]annulenium cation is similar to **1**



Like **1**, it is non-planar. However, calculations indicate that it is aromatic. What are the three general physical properties used to determine whether systems are aromatic or not?

c) Give a molecular orbital explanation as to why $C_{11}H_{11}^{+}$ is considered "aromatic" in the first place (a π orbital energy diagram for the all-*cis* isomer might be a useful illustration; just saying that it is 4n+2 is NOT sufficient)

d) The modern perspective of aromaticity is not quite as clear. For example, Sasson Sheik is a theoretician who is famous for his disagreement with the π MO explanation of aromatic stability. What does he claim is the actual reason that benzene is a stable structure?

e) π systems in aromatic structures are highly polarizable, and therefore can contribute to favorable intersystem interactions, such as π stacking. However, π stacking is still pretty weak (but if you have enough of those types of interactions, it can add up – see DNA). Stronger π-π interactions can be created by using substituents (see *JOC*, **2006**, *71*, 9260-9271). Thus, explain the following observations:

   i. Pure benzene and hexafluorobenzene are both liquids, but a carefully prepared mixture of the two is solid at room temperature

   ii. 1,3,5-trifluorobenzene is also a solid at room temperature

1. (35) Spectroscopy

   (a) (10) Different regions of the electromagnetic spectrum (Microwave, Far Infrared, Infrared, Visible and Ultraviolet) are used to investigate different molecular processes. Which regions of the electromagnetic spectrum correspond to (a) Rotation of small molecules (b) vibrations of flexible bonds (c) Rotation of polyatomic molecules and (d) Electronic transitions, explain.

   (b) (5) Explain what is the fundamental line and second overtone line in the observed vibrational spectra.

   (c) (5) What is the main difference between Frank-Condon Principle and Born Oppenheimer approximation for diatomic molecules.

   (d) (5) For a given diatomic molecule, the Frank-Condon factor is zero (or very small) for the transition $v = 0 \rightarrow v' = 0$, where $v = 0$ is the vibrational state on the ground state electronic potential energy and $v' = 0$ on the first excited electronic potential energy curve. What can you learn about the minimum position of the excited electronic potential energy curve. Explain.

   (e) (10) Because a symmetric top has a unique principle moment of inertia, there are two types of symmetric tops. When the unique moment of inertia is larger than the two equal ones, the molecule is called an *oblate symmetric top.* When the unique moment of inertia is smaller that the two equal ones, the molecule is called a *prolate symmetric top.* Classify BCl_3 (Planar molecule) and CH_3I (tetrahedal molecule) as either an oblate or a prolate symmetric top, explain.

2. (35) A particle in a box with its walls located at 0 and L: The quantized energies $E_n = \frac{h^2n^2}{8mL^2}$; $n = 1, 2, 3, ...$ result from the boundary conditions $\Psi(0) = \Psi(L) = 0$.

   (a) (10) $< x >= L/2$ and $< \frac{d}{dx} >= 0$, are these results physically reasonable

   (b) (5) What is the average potential $< V(x) >$ for a particle in this box? Explain your results

   (c) (5) What are the degeneracies of the first two energy levels for a particle in a three dimensional box, when all sides of the box are equal? Explain your results

   (d) (5) Why is the ground state energy E positive and not zero? Could the energy be zero in classical mechanics.

   (e) (10) Why is the wave function $\Psi(x) = e^{-x}$ not a solution for this problem?

3. (30) Consider the one-dimensional problem of a particle of mass m in a potential
   $V(x) = \infty \;\; for \;\; x < 0, \;\; V(x) = 0 \;\; for \;\; 0 \leq x \leq \alpha,$
   $V(x) = 10 \;\; \alpha < x \leq \beta, \;\; and \;\; V(x) = 0 \;\; for \;\; x > \beta$
   Without solving the Schrodinger equation:

   (a) (15) Sketch the wave function $\Psi(x)$ for $E << 10$ and explain the behavior of $\Psi(x)$ as a function of the variable x and the parameters α and β

   (b) (15) Sketch the wave function for $E >> 10$ and explain your results

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.)