Department of Chemistry
Cumulative Examinations
February 3, 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 1-2
2) Biochemistry Cumulative Examination, Page 3
3) Inorganic Cumulative Examination, Page 4
4) Organic Cumulative Examination, Pages 5-6
5) Physical Cumulative Examination, Pages 7-9

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. The relationship between instrument response, R, and analyte concentration, C, for a particular method is:

$$R = e^{-(\alpha+\beta C)}$$

   a) Sketch the shape of the response versus concentration curve. **[5 pts]**

   b) What is the sensitivity of this method? **[10 pts]**

   c) What is the relationship between the error in R, ΔR, and the resulting error in C, ΔC? **[10 pts]**

   d) For a constant error in response (fixed ΔR), sketch the shape of the plot of the absolute value of error in concentration, |ΔC|, versus concentration. **[5 pts]**

   e) To minimize the relative random error (ΔC/C) associated with measuring concentration with this method, are measurements best taken at high concentration, intermediate concentration, low concentration, or is relative random error independent of concentration? Justify your answer. **[10 pts]**

   f) Indicate a quantitative analytical method for which the response versus concentration relationship is of the form indicated above. **[5 pts]**

2. Discuss the physical/chemical bases for the selectivities of the following approaches:

   a) Chemical ionization mass spectrometry **[5 pts]**

   b) Electrogravimetry **[5 pts]**

   c) Laser-induced fluorescence **[5 pts]**

   d) A Kjeldahl determination **[5 pts]**

3. Some analytical methods are based on the establishment of equilibrium (i.e., equilibrium methods) and some are based on the measurement of rates of reactions (i.e., kinetic methods).

   a) List two advantages of kinetic methods over equilibrium methods. **[5 pts]**

   b) List two disadvantages of kinetic methods relative to equilibrium methods. **[5 pts]**

   c) Glucose is the most widely determined biomarker in the world. Many of the approaches used for glucose determination are kinetic methods. Why is this so? **[5 pts]**

4. Species A reacts with species B with 1:1 stoichiometry, an equilibrium constant of 10^{40}, and a rate constant of $1.80 \times 10^{-2}\ M^{-1}s^{-1}$. After rapid mixing of solutions containing A and B, 50.0% of A was converted to products after 30.0 s. If the concentration of B was significantly higher than that of A such that the concentration of B was essentially constant over 30s, what was the concentration of B? **[10 pts]**

5. The concentration of a species of interest can be computed from the several measured values as follows:

$$C = 3.4x10^{-3}(\pm 2x10^{-4})M + \frac{2.6x10^{-3}(\pm 1x10^{-4})M \times 1.2x10^{-3}(\pm 3x10^{-4})M}{1.8x10^{-3}(\pm 2x10^{-4})M}$$

What is the uncertainty of the computed value of C? **[10 pts]**

Useful relationships:

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

Biochemistry Cumulative Exam

Title: Enzymology

Feb 3, 2007

1. (20 points). Define the following terms in two to three sentences:

   Abzymes

   Allosteric inhibitors

   Transition state analogs

   Ribozymes

2. (10 points) Suppose a mutant enzyme binds a substrate 100 fold more tightly than the native enzyme. What is the effect of this mutation on catalytic rate if the binding of the transition is unaffected?

3. (10 points). For an enzyme that follows simple Michaelis Menten kenetics, what is the value of V_{max} if V_0 is equal to 1 μM /minute at 1/10 K_M?

4. (20 points) Acetic acid has a pKa of 4.8. How many millilters of 0.1M acetic acid and 0.1 M sodium acetate are required to prepare 1 liter of 0.1M buffer solution having a pH of 5.8.

5. (10 points) What are the substrate specificities of trypsin and elastase?

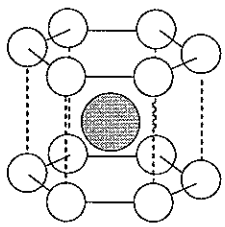
6. (10 points) Enzyme A has a K_{cat} of 360 sec^{-1} and a K_m of 10 μM. Enzyme B has a K_{cat} of 500 sec^{-1} and a K_m of 5 μM. Which enzyme is more efficient at 100 μM substrate concentration and why?

7. (10 points) Define a perfect enzyme.

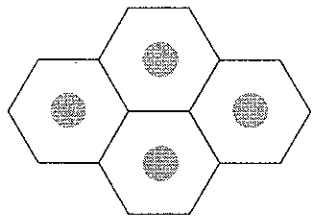
8. (a) (6 points) Name the three residues of the catalytic triad of Chymotrypsin.

   (b) (4 points) How diisopropyl fluorophosphate (DFP) acts as an inhibitor of chymotrypsin.

(*Chem. Mater.* **2006**, *18*, 5088-5096 and references therein.) Figure I represents a slice of a solid that contains hafnium (dark sphere) and boron (light spheres). Within the HfB_2 lattice, hafnium ions intercalate between layers of boron bonded together in two-dimensional hexagonal networks that resemble the layers of graphite. Figure II provides a top view of the structure in which the dark spheres represent hafnium ions positioned under a layer of borons. Borons (not shown) occupy all vertices in the hexagonal network.



I



II

1. (65 points). Crystal structure.

A. The structure shown in Figure I is not a proper unit cell, but it does translate in three dimensions to generate the lattice. Show that the hexagonal prism (I) correctly embodies HfB_2 stoichiometry.

B. Calculate the interplanar spacing if the B-B bond distance is 1.828 Å within a layer, and the density of $HfB_2(s)$ is 11.2 g/cm^3. (1 Å = 1 x 10^{-8} cm, AW: Hf, 178.49; B, 10.81)

C. Find the coordination number of boron in the lattice.

D. The four Hf centers in Figure II define the base of a proper unit cell. Determine the angles and the length of the sides of the parallelogram in question.

E. Draw the complete unit cell and show that it, too, is consistent with the stoichiometry.

2. (35 points). Some chemistry.

A. What is the oxidation number of Hf if the boron centers are isoelectronic with the carbon atoms of graphite? One can layer the material onto a chip by a chemical vapor deposition method because of the thermal decomposition reaction given below. Balance the reaction and identify all atoms that undergo formal oxidation or reduction in the process.

$$Hf(BH_4)_4(g) \rightarrow HfB_2(s) + B_2H_6(g) + H_2(g)$$

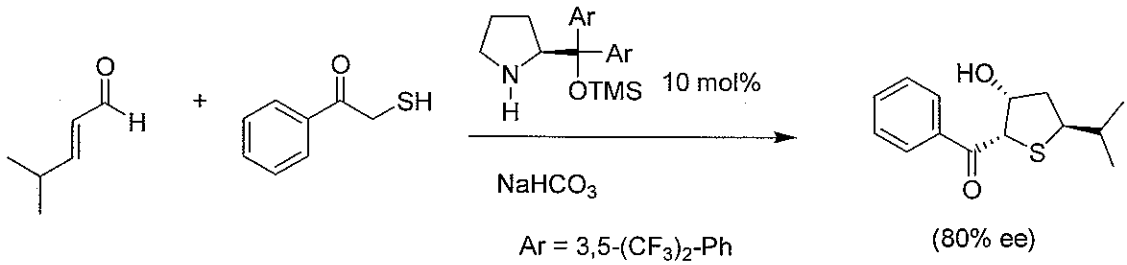
B. If the z-axis is perpendicular to the boron layers, adopt the perspective of crystal field theory and identify which d-orbital(s) of hafnium, if any, is (are) occupied. Explain your reasoning.

C. HfB_2 is a conductor. Do you expect the material to be an electronic conductor or an ionic conductor? Explain.

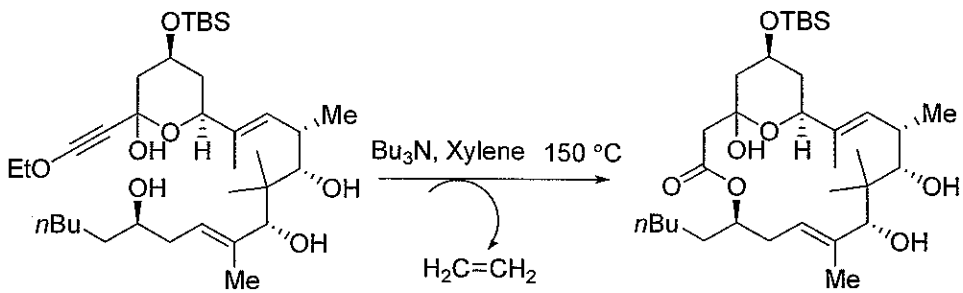
Organic Division Exam
February 2007

1. *JACS*, (**2006**) *128*, 14986.

In their asymmetric synthesis of tetrahydrothiophenes, Jorgensen and co-workers use an organocatalytic domino reaction. Provide a plausible mechanism for the following enantioselective reaction.

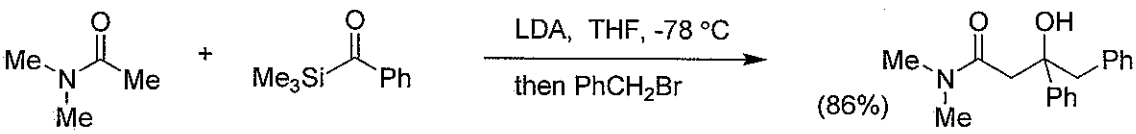


2. *JACS* (**2006**) *128*, 15106.
Jamison and co-workers recently reported an elegant total synthesis of (+)-Acutiphycin. The key macrocyclization reaction involved heating alkyne derivative in the presence of *n*-butylamine in xylene with loss of acetylene. Provide a detailed mechanism for the following transformation.



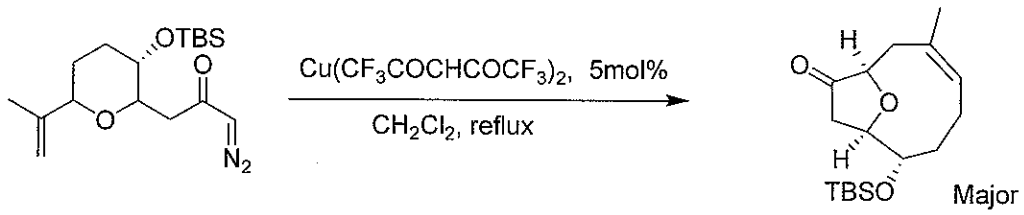
3. *JACS* (**2006**)*128*, 15566

Recently, a methodology for synthesis of tertiary β-hydroxy amides was published by the Scheidt group at Northwestern University. Propose a reaction mechanism for the following reaction.



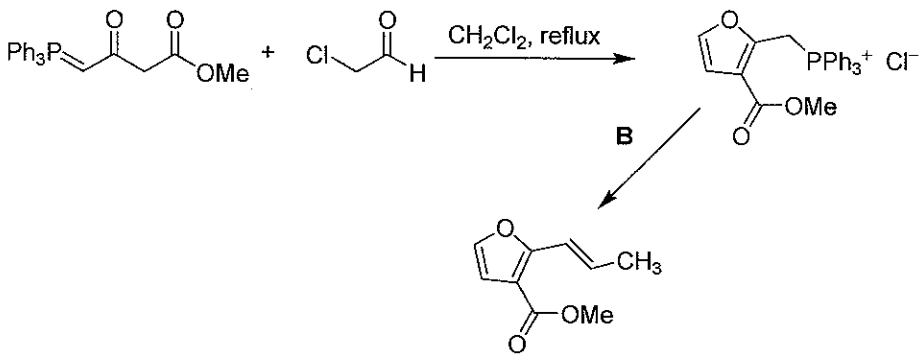
4. *Angew. Chem* (**2007**) *46*, 437.

In their total synthesis of (±)-Vigulariol, Clark and co-workers have exploited a carbenoid meditated ring expansion reaction. Please provide a plausible reaction mechanism for the following transformation.



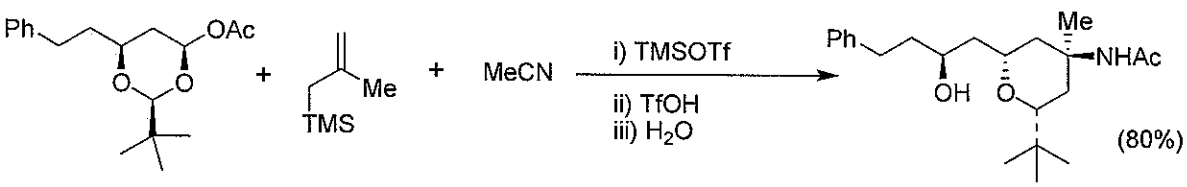
5. *JOC* (**2006**) *71*, 8045

A recent publication in JOC dealt with the synthesis of 2-Alkenyl-3(alkoxycarbonyl)furans. This work was published by Langer and co-workers and involved a cyclocondensation of (2,4-Dioxobutylidene)phosphoranes with α-chloroacetaldehyde as shown in the following reaction. Write a mechanism for the formation of phosphonium salt and identify the chemical **B.**



6. *JACS* (**2006**)*128*, 16480

Epstein and Rovis, recently reported a method for synthesis of 4-amino tetrahydropyrans. The method contains a Sakurai-Prins-Ritter sequence. Provide a plausible reaction mechanism for the transformation.



(1) Consider n moles of gas molecules of an ideal gas in a cubic box of volume, V. In this case the pressure, p, is given by:

$$p = \frac{1}{3}\frac{nM}{V} < v^2 > \qquad (1).$$

M.....molecular weight
$<v^2>$...mean square velocity

(a) Show that the total translational energy of N gas molecules is

$$E = \frac{3}{2}nRT \qquad (2).$$

(b) The velocity distribution (Maxwell distribution) of the gas molecules is given via:

$$N_v = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \qquad (3).$$

N_v.....number of molecules per unit velocity interval

Explain (verbally or graphically) how a temperature reduction will affect the (1) width of the Maxwell distribution; (2) the value of N_v at the most probable velocity; and (3) the value of the most probable velocity.

(c) The viscosity of ideal gas molecules is related to their average velocity by:

$$\eta \propto < v >$$

Determine how the viscosity is related to temperature.

(2) The one-dimensional diffusion of a solute is described by Fick's first and second laws of diffusion. Fick's first law of diffusion provides a relationship between the diffusive flux J and the concentration gradient of the solute $\partial c / \partial x$:

$$J = \frac{dn}{dt} = -DA\frac{\partial c}{\partial x} \qquad (3)$$

where D is the diffusion coefficient and dn represents the amount of solute crossing a specific area A during the time dt. Fick's second law of diffusion describes how the diffusion affects the rate of change of concentration:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (4).$$

(a) Consider the one-dimensional diffusion of a solute across an area A between positions x and x+dx characterized by concentrations c and c+dc, respectively. Derive Fick's second law of diffusion from Fick's first law of diffusion. Assume that D is independent of the position x.

Name

(b) Show that

$$c = \frac{\alpha}{t^{1/2}} e^{-x^2/4Dt} \qquad (5)$$

is a solution of equation 4.

(c) Consider the case of one-dimensional diffusion where all n_0 solute molecules are initially concentrated within a plane at x=0. The constant α in equation 5 is given by

$$\alpha = \frac{n_0}{2(\pi D)^{1/2}} \qquad (6)$$

Explain verbally or graphically how the concentration profile of solutes will change as a function of time after the solute molecules are allowed to spread out from the initial plane at x=0.

(d) The average squared net distance $\langle x^2 \rangle$ represents a useful parameter for the study of the movement of solute molecules in a diffusion process. Using equations (5) and (6), derive an expression for $\langle x^2 \rangle$ as a function of D and t for the case of one-dimensional diffusion. To solve the problem use the following integral solution:

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

(e) Does it make sense to consider the average net distance $\langle x \rangle$ to describe a diffusion process of solute molecules? Justify your answer!

3. A macromolecule in a centrifugation experiment is exposed to the following three forces

(i) Centrifugational force: $F_{cent} = m\omega^2 x$

(ii) Buoyant force: $F_B = m\overline{v_2}\rho\omega^2 x$

(iii) Frictional force: $F_{frict} = fu$

with m being the mass of the macromolecule, ω being the rotational speed, x being the the distance from the rotational axis, $\overline{v_2}$ being the specific volume of the macromolecule, ρ being the density of the medium, f being the frictional coefficient, and u being the velocity of the macromolecule.

(a) Show that the sedimentation coefficient $s = \frac{u}{\omega^2 x}$ at equilibrium, where F_{cent} is counterbalanced by F_B and F_{frict}, is given by the expression

$$s = \frac{m\left(1 - \overline{v_2}\rho\right)}{f}$$

(b) At 20°C the diffusion coefficient, D=kT/f, of a macromolecule is found to be $D=8.3*10^{-7}cm^2s^{-1}$ (k: Boltzmann constant, T: temperature). Its sedimentation constant is $s=3.2*10^{-13}sec$ in a solution of density $\rho=1.06gcm^{-3}$. The specific volume is $\overline{v_2}=0.656cm^3g^{-1}$. Calculate the molar mass of the macromolecule. The gas constant and the Avogadro constant are $R=8.314JK^{-1}mol^{-1}$ and $N_0=6.022*10^{23}mol^{-1}$.

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.)