Department of Chemistry
Cumulative Examinations
March 4, 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.

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

2006 Analytical Cumulative Exam, Saturday March 4

Part I

a) Compute the average and unbiased variance for the three values, {13, 17, 12}. Write out both equations in symbolic form. Then use the equations to compute the parameters. Do all math by hand showing explicitly all terms in the equation. That is, do all the addition, subtraction, squaring and division by hand.

b) What are degrees of freedom, and how do they come into play with the answer to part (a)?

c) Further demonstrate your understanding of degrees of freedom by considering the variance of the fit for a quadratic least-squares. If there are N data points that were fit, how many degrees of freedom are used in the equation for the variance? Why?

Part II

d) Consider the equation, $z = ax + by$, where x and y are random variables and a and b are constants. Express the mean and variance of z in terms of the mean and variance of x and y.

e) Use the information in part (d) to derive the variance of the arithmetic average, $\overline{x}$, where x has the standard deviation σ.

f) Consider the equation, $z = x^2$, where x is a random variable. Use your knowledge of expectation value calculus to show that the mean of z is biased. What is the bias?

g) Use the results of (d-f) to determine the mean of the biased variance (uses the number of values instead of the degrees of freedom). The result should provide a factor that converts the biased variance into the unbiased variance.

Part III

h) Consider the equation used to compute the number of theoretical plates in chromatography,

$$n = 16\left(\frac{t_r}{w}\right)^2$$

where t_r is the retention time and w is the peak width. Assume that the width is computed by a difference between two times, $w = t_2 - t_1$, and that the error for all measured times is the same value, σ_t. Use a Taylor's series linearization to obtain a functional form for the variance in n. For $t_r = 100$ s, $w = 10$ s, and $\sigma_t = 0.1$ s what is σ_n? Which parameter, t_r or w, contributed most to the uncertainty in n. Hint: The math is easier if the value of σ_w is expressed as a function of σ_t and t_1 and t_2 are not substituted into the equation!

Cumulative Examination in Biochemistry

March 4, 2006

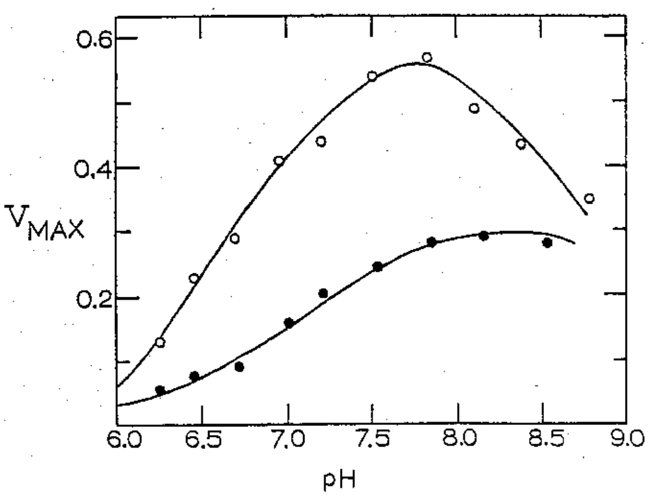
Instructions: There are five questions, worth 20 points each.

1. The enzyme urease catalyzes the hydrolysis of urea to CO_2 and ammonia. At 21°C the uncatalyzed reaction has a free energy of activation of 125 kJ mol^{-1}. In contrast, the enzyme-catalyzed reaction has a free energy of activation of 46 kJ mol^{-1}. By what factor does urease accelerate the reaction? (Show how you arrived at your answer.)

2. Undergraduate biochemistry texts often confuse general and specific acid-base catalysis. Using as an example the hydrolysis of N,N-dimethylacetamide in aqueous 1M acetic acid buffer at pH 4.5, present a pair of mechanisms that clearly differentiate the steps (including the likely rate-determining steps) in specific acid and general acid catalysis of this hydrolysis reaction.

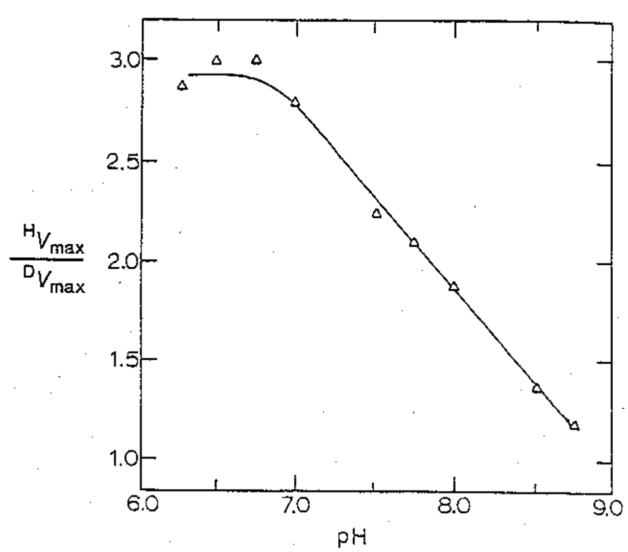
3. The enzyme enolase catalyzes the conversion of 2-phosphoglycerate to phosphoenolpyruvate in the glycolytic cycle. The following graphs show rate constant data as a function of pH for reaction of the normal (protio) substrate, and the 2-deuterio substrate (2-phospho[2-^{2}H]glyceric acid). The V_{max} values for the two substrates are plotted on the left graph, and the ratio of the rates at individual pH values are plotted in the right curve. Propose a reasonable chemical mechanism that is consistent with these data. Comment on the magnitude of the V_{max} ratio at neutral pH. Suggest a likely explanation for the decreased ratio of $\frac{^{H}V_{max}}{^{D}V_{max}}$ at high pH.

The parameter V_{max} for the enzymatic reaction was measured in the direction of dehydration, as a function of pH for the reactant containing protium and the reactant containing deuterium, respectively.[79]



Maximum velocities for protiated (○) and deuterated (●) reactants as a function of pH.

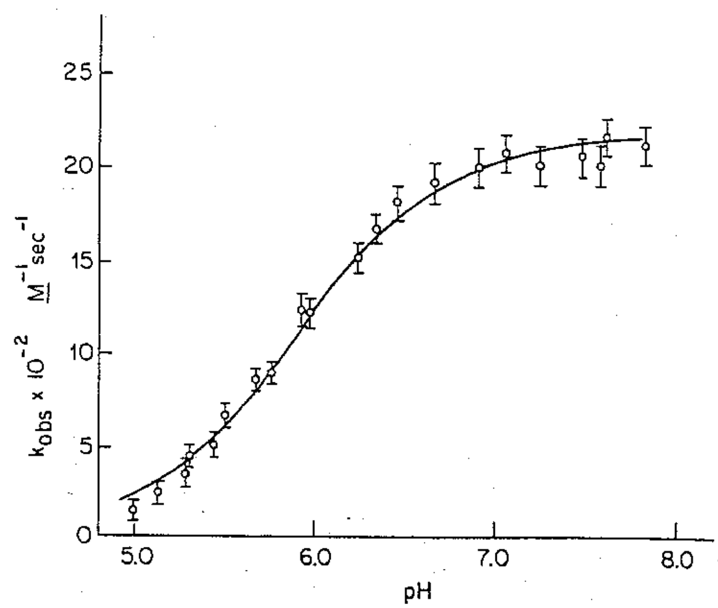
When the ratio of V_{max} for the two reactants is plotted as a function of pH, the following results were obtained



4. Describe in detail the biochemical role and also comment on the catalytic efficiency of carbonic anhydrase. Also comment on the mechanism of catalysis utilized by this enzyme. [Hints: The eukaryotic enzymes have three strictly conserved histidine residues. For a representative enzyme example, $K_m = 26$ mM and $k_{cat} = 4 \times 10^5 s^{-1}$ in the hydration direction].

5. Acetoacetate decarboxylase catalyzes the decarboxylation of acetoacetate to acetone and carbon dioxide. The following graph and figure legend describe experimental evidence that gave critical clues to the mechanism of the enzymatic reaction. What is the mechanism of the enzyme-catalyzed decarboxylation reaction? What is noteworthy about the pH dependence curve of the covalent modification curve?

Figure 4–12: pH–Rate profile for the reaction of 2,4-dinitrophenyl propionate with acetoacetate decarboxylase. Solutions of 2,4-dinitrophenyl propionate were prepared at various values of pH buffered with lutidine sulfate, *N,N,N′N′*-tetramethylethylenediammonium sulfate, or 4-[(2-dimethylamino)ethyl]morpholinium sulfate at 30 °C. The spontaneous rate of hydrolysis was recorded, and then a sample of acetoacetate decarboxylase was added. This caused a burst of 2,4-dinitrophenol production. The rate of the spontaneous release of the 2,4-dinitrophenol in the absence of enzyme was subtracted from the rate of this burst, and a pseudo-first-order rate constant was calculated from the rate at which the enzyme reacted with the 2,4-dinitrophenyl propionate for each sample. This pseudo-first-order rate constant was divided by the concentration of 2,4-dinitrophenyl propionate to obtain the apparent second-order rate constant, k_{obs} (molar^{-1} second^{-1}), for the reaction of acetoacetate decarboxylase with the 2,4-dinitrophenyl propionate, and this parameter is plotted as a function of pH. In separate experiments it was shown that the amplitude of the entire burst of 2,4-dinitrophenol was equal to the molar concentration of active sites, that after the burst was complete, the enzyme had lost greater than 98% of its activity, that the loss of activity was coincident with the burst, that enzyme acetylated at the lysine within its active site showed no burst, and that occupation of the active site with acetopyruvate also eliminated the burst.



Inorganic Chemistry Cumulative Exam

Purdue University

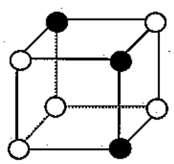
March 4, 2006

Subject: Symmetry, Point Group, Character Table

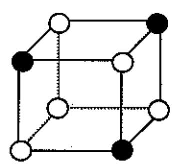
There are 100 possible points in this exam.

1. (30 points) Determine the point groups of the following cubes.

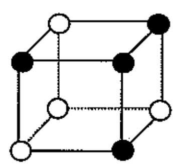
(a)



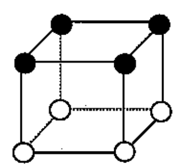
(b)



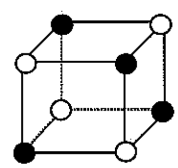
(c)



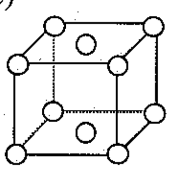
(d)



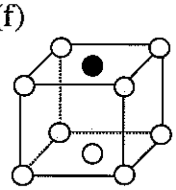
(e)



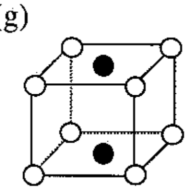
(e)



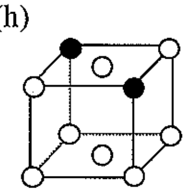
(f)



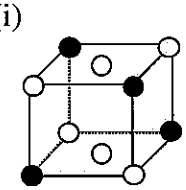
(g)



(h)



(i)



2. (20 points) A C_{2v} character table is given below. To which irreducible representations do x, y, z, and xy functions belong?

C_{2v}	E	C_2	σ(xz)	σ (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

3. (10 points) Explain the meaning of "group" in the term, "point group".

4. (10 points) Identify subgroups of D_{4h}.

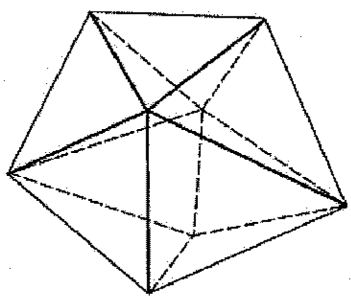
5. (10 points) Determine whether each of the following point groups is centrosymmetric or noncentrosymmetric.

(a) C_{2h} (b) C_{3h} (c) C_{4v} (d) T_d

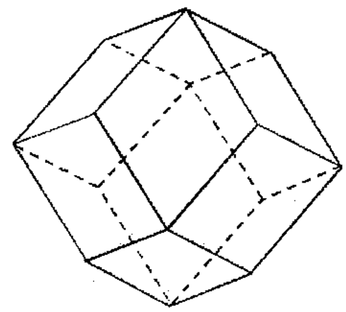
6. (10 points) What group is obtained by adding a center of inversion, *i*, to C_3?

7. (10 points) To what point group does each of these dodecahedra belong?

(a)

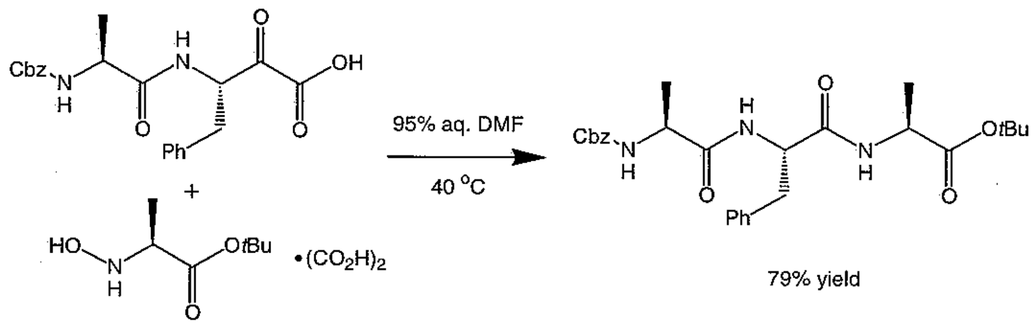


(b)



Organic Cumulative Exam March 4, 2006

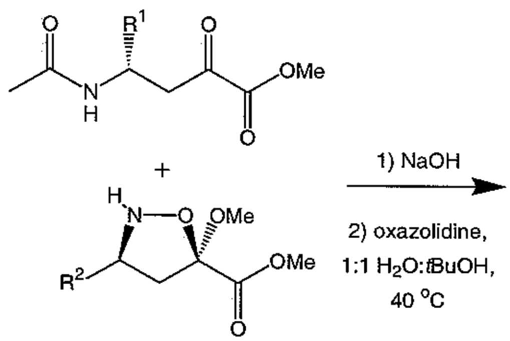
1. (25 pts.) Bode and co-workers have recently developed a novel way to form peptide linkages from *N*-alkylhydroxylamines and α-ketoacids (*Angew. Chem. Int. Ed.* **2006**, *45*, 1248-52). This coupling reaction is remarkable because it requires no activating agents.



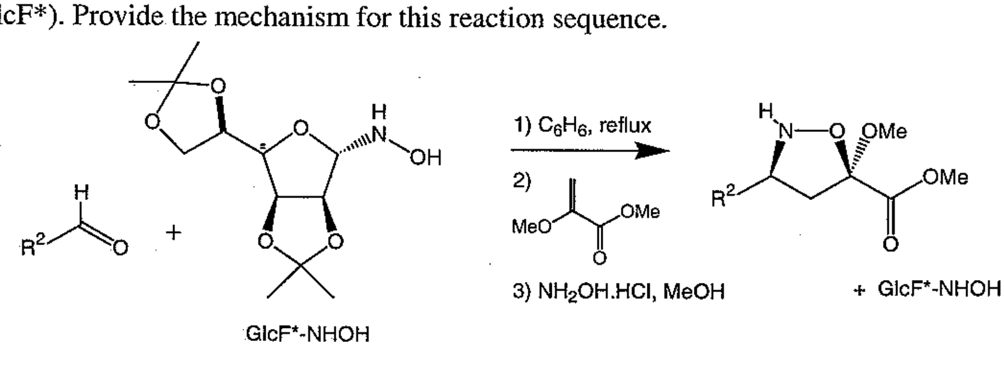
Provide a mechanistic explanation for the reaction above.

2. (25 pts.) Bode *et al.* apply their decarboxylative coupling reaction toward the reiterative synthesis of β-peptide oligomers, using isoxazolidine acetals as building blocks (*J. Am. Chem. Soc.* **2006**, *128*, 1452-53). The yields of these couplings are reported to be well over 90%.

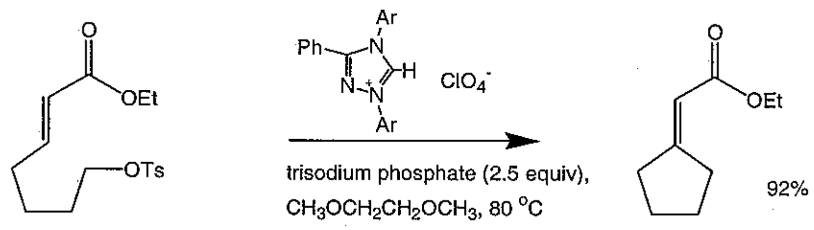
Draw the structure of the reaction product, supported by a detailed mechanism. (In this reaction, the α-ketoesters is treated with NaOH prior to addition of the isoxazolidine)



3. (25 pts.) The isoxazolidines are prepared *via* a chiral nitrone intermediate, which react with an enol pyruvate and are treated with NH_2OH under acidic conditions for recovery of the chiral auxiliary (GlcF*). Provide the mechanism for this reaction sequence.



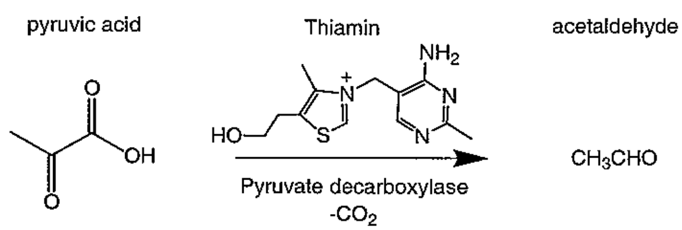
4. Fu and coworkers report a method for generating a nucleophilic carbene catalyst under basic conditions (*J. Am. Chem. Soc.* **2006**, *128*, 1472-73). They demonstrate its utility for organic synthesis in the "umpolung" (electrophile–nucleophile reversal) reaction below:



(a) (10 pts.) Draw two resonance structures of the <u>active</u> carbene species (*Note*: molecules similar to the triazolinium salt above are reported to have pK_a's between 14-18).

(b) (15 pts.) Provide a mechanistic description of the reaction sequence which regenerates the carbene catalyst. "Ar" = *p*-$MeOC_6H_4$.

5. <u>Extra credit</u> (15 pts.) The catalyst above bears some resemblance to thiamin (vitamin B_1), an enzyme cofactor. Thiamin is the active ingredient in pyruvate decarboxylase, which converts pyruvic acid into acetaldehyde (see below). Thiamin also has a remarkably low pK_a, and can be deprotonated in the environment of an enzyme active site.



Provide the mechanistic details of this classic transformation in enzyme chemistry. (The accepted mechanism was proposed 50 years ago by Ronald Breslow at Columbia University).

Physical Chemistry Cumulative Exam March 4, 2006

1. The use of quantum mechanics for angular momentum is crucial for a complete understanding of all types of magnetic resonance spectroscopy, for electron spin coupling in open shell states, for understanding the correlation of states in chemical reactions, and so on.

a. (30 points) For the set of the four spherical harmonic functions (Y_{JM}) for which J=3/2 and M=–3/2, –1/2, 1/2, and 3/2, find the 4-by-4 matrix representation of the operator J_X.

b. (20 points) For the same set of functions, use the operator identity $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ and other available information to find the matrix representation of $\hat{J}_y^2$

2. (30 points) Given a unitary matrix **U** and two real, symmetric matrices **A** and **B**, and given that $\mathbf{UAU}^{-1} = \mathbf{a}$ and $\mathbf{UBU}^{-1} = \mathbf{b}$ are both diagonal, prove that **AB** = **BA**. Explain the full significance of this theorem for having some operator, B, that commutes with the Hamiltonian operator, H, for the system of interest.

3. (20 points) An operator, A, is Hermitian in the space of a set of functions $\{\Psi_i\}$ if for all choices of functions from that set, $<\psi_i \mid \hat{A}\psi_j> = <\hat{A}\psi_i \mid \psi_j>$. Prove that Hermitian operators can only have real-valued (not complex) eigenergies.

Some possibly helpful angular momentum relations:

$$\hat{J}_\pm \mid JM> = \hbar\sqrt{J(J+1) - (M^2 \pm M)} \mid JM \pm 1>$$

$$\hat{J}^2 \mid JM> = \hbar^2 J(J+1) \mid JM>$$

$$\hat{J}_z \mid JM> = \hbar M \mid JM>$$

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \qquad \text{and} \qquad \hat{J}_- = \hat{J}_x - i\hat{J}_y$$

$$\vec{J}_1 \bullet \vec{J}_2 = J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z} = J_{1z}J_{2z} + \frac{1}{2}(J_{1+}J_{2-} + J_{1-}J_{2+})$$

$$\vec{J} = \vec{J}_1 + \vec{J}_2 \quad \Rightarrow \quad \hat{J}^2 = \hat{J}_1^2 + \hat{J}_2^2 + 2\vec{J}_1 \bullet \vec{J}_2$$

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	0
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.)