

Department of Chemistry
Cumulative Examinations
February 5, 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, Pages 1-4
- 2) Biochemistry Cumulative Examination, Pages 5-6
- 3) Inorganic Cumulative Examination, Pages 7-8
Organic Cumulative Examination, Pages 9-10
- 5) Physical Cumulative Examination, Page 11

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

U N I V E R S I T Y

1. Assume that you will be measuring the concentration of a compound in the gas phase via its proton transfer reactions with a reagent ion. You begin with a fixed number of reagent ions in the presence of a constant concentration of analyte species. You are able to measure the abundances of the remaining reagent ion at two fixed times (which you know). Assuming you also know the rate constant for the reaction and that there are no other loss mechanisms for the reagent ion, answer the following questions:

a) Write the relationship you would use to determine the analyte concentration.

(5 pts.)

b) Draw a plot of the measured quantity versus concentration to show the qualitative shape of the relationship.

(5 pts.)

c) Assuming a fixed indeterminate error in the measurement discussed in b), how will the resulting absolute error in concentration depend upon concentration? Don't worry about the sign of the error, just its magnitude. Write the appropriate relationship and draw the shape of the absolute error versus concentration curve.

(10 pts.)

d) If the analyte were present at concentrations that exceeded the dynamic range of your procedure (i.e., the concentration is too high), provide and discuss two approaches to modify the procedure (other than sample dilution) that would allow for a measurement in the linear range of the procedure.

(10 pts.)

2. A method was used to determine H_2O_2 by reacting it quantitatively with excess iodide ion to produce I_3^- , followed by the determination of the concentration of this species potentiometrically. The relationship between electrochemical response and $[\text{I}_3^-]$ was:

$$E_{\text{cell}} = \alpha + \beta \ln[\text{I}_3^-]$$

Answer the following questions:

a) Draw the qualitative shape of the response as a function of concentration.

(5 pts.)

b) What is the relationship between concentration and sensitivity for this method? Write the appropriate relationship and draw the shape of the sensitivity versus concentration curve.

(5 pts.)

c) Provide the relationship between indeterminate error and the resulting concentration error (i.e., indicate how the measurement error propagates to concentration error). Draw the shape of the curve expected for concentration error versus concentration when the measurement error is constant with concentration.

(10 pts.)

d) How does the relative concentration error depend upon concentration for this method? Draw the shape of the curve expected for relative concentration error versus concentration when the measurement error is constant with concentration.

(10 pts.)

3. You are asked to determine the concentration of a particular species that you know fluoresces with a relatively high quantum efficiency. Assuming there are no significant matrix effects and that you can work under conditions in which the product of pathlength, molar absorptivity, and concentration is < 0.05 , answer the following questions:

a) Assuming a constant incident radiative power, how will the fluorescence signal vary with analyte concentration?

(5 pts.)

b) How will sensitivity depend upon concentration?

(5 pts.)

c) For a fixed indeterminate measurement error, how will concentration error vary with concentration?

(5 pts.)

d) For a fixed indeterminate measurement error, how will relative concentration error vary with concentration?

(5 pts.)

4. You are determining the concentration of the substrate of a particular enzyme via an approach based on Michaelis-Menten kinetics. That is, you are measuring a reaction rate or velocity, v , between the enzyme and substrate that obeys the relation:

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

where K_M is the Michaelis constant.

a) Of the three approaches discussed in questions 1-3, which will show qualitatively the most similar dependence of relative concentration error on concentration as the kinetic approach in this question? Again, assume a constant indeterminate error in the measurement of v .

(5 pts.)

b) Provide justification for your answer.

(10 pts.)

5. Estimate the absolute standard deviation for y , as determined from three values according to the following relationship:

$$y = \frac{251(\pm 1) \times 860(\pm 2)}{1.673(\pm 0.006)}$$

where the number in parentheses are the absolute standard deviations associated with each value.

(5 pts.)

Useful relationships:

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

Biochemistry Cumulative Examination

February 5, 2005

Instructions: There are four questions, each worth 25 points.

1. The major components of common (natural) honey are free glucose and fructose. ^{13}C NMR spectroscopy reveals five significant resonances in the spectral region corresponding to anomeric carbons. Write Haworth projection formulas for the most likely structures that are present.
2. A recently published study of the proteome of human serum described the construction and use of a multi-lectin column to isolate a fraction for study. (The lectins were Concanavalin A, Wheat Germ and Jacalin.) What do you think this study described? Describe a likely experimental approach, explaining in as much detail as possible why such a column might be constructed, how it might be constructed, and how it could be utilized.
3. A carbohydrate derivative was isolated from a mixture of products in a bioreactor. It exhibited the following characteristics:
 - 1) Negative-ion FAB-MS showed a peak at m/z 1295
 - 2) Exhaustive methylation with dimethyl sulfate followed by acid hydrolysis gave one equivalent each of 3,6-di-O-methyl-D-glucopyranoside, 2,3,4-tri-O-methyl-D-galactopyranoside and 2,3,4,6-tetra-O-methyl-D-galactopyranoside, together with five equivalents of 2,3,6-tri-O-methyl-D-glucopyranoside.

Use these data to elucidate the structure of the carbohydrate derivative. Draw a clear structural formula using Haworth projections. Indicate any structural ambiguities that may exist.

4. (A) Bovine ribonuclease B differs from bovine pancreatic ribonuclease A in that the B form contains an N-linked carbohydrate chain. Given the following sequence of bovine RNAase B, circle any residue(s) that would reasonably be expected to bear such an N-linked chain in a bovine protein.

KETAAAKFERQHMDSSSTAASSSNYCNQMMKSRNLTKDRCKPVNTFVHESLADVQAVCSQKN
VACKNGQTNCYQSYSTMSITDCRETGSSKYPNCAYKTTQANKHIIVACEGNPYVPVHFDASV

- (B) Draw a clear structural formula to show how the chain is joined to the protein.
- (C) Consider the following diagram showing silver-stained bands on an SDS gel. The lower two sets of bands were found to be immunoreactive to antibodies against denatured ribonuclease protein. (The upper bands correspond to the endoglycosidases Endo A, Endo H, Png I and Png F). What does this experiment tell you about the differing specificities of Png I and Png F? Suggest a potential role for Png I in the cell.

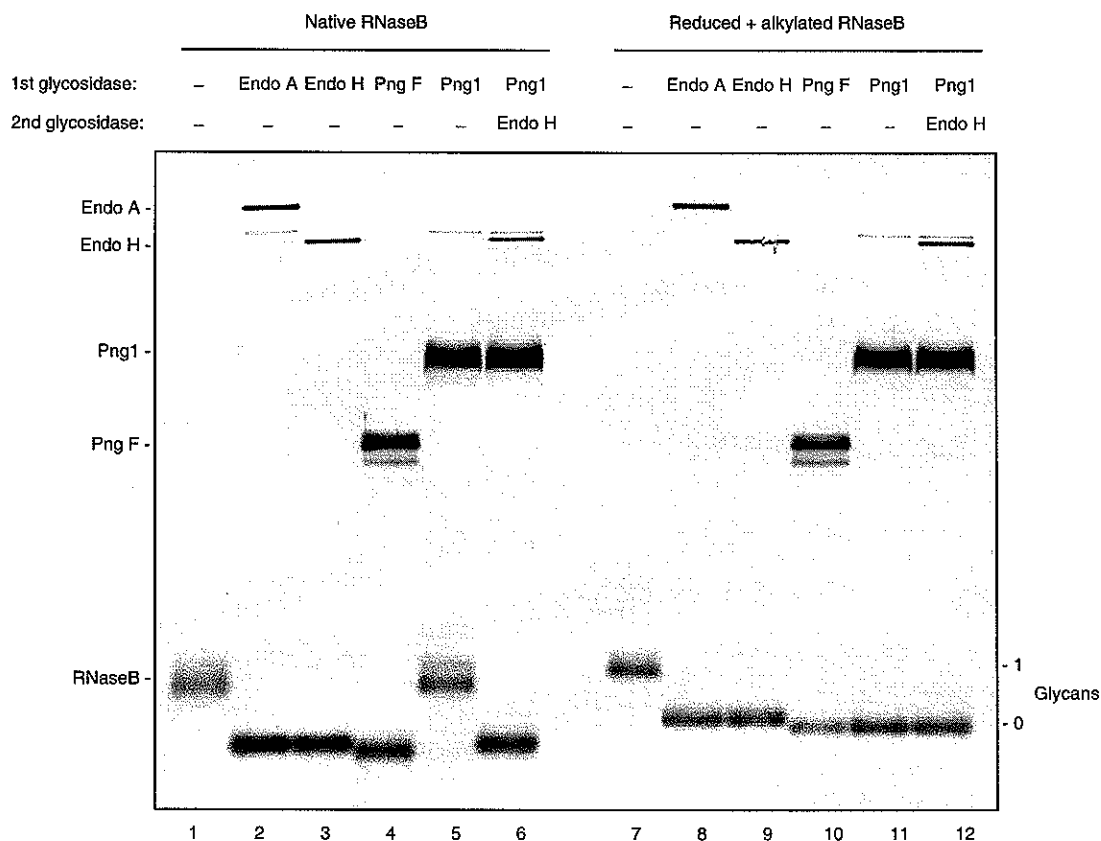
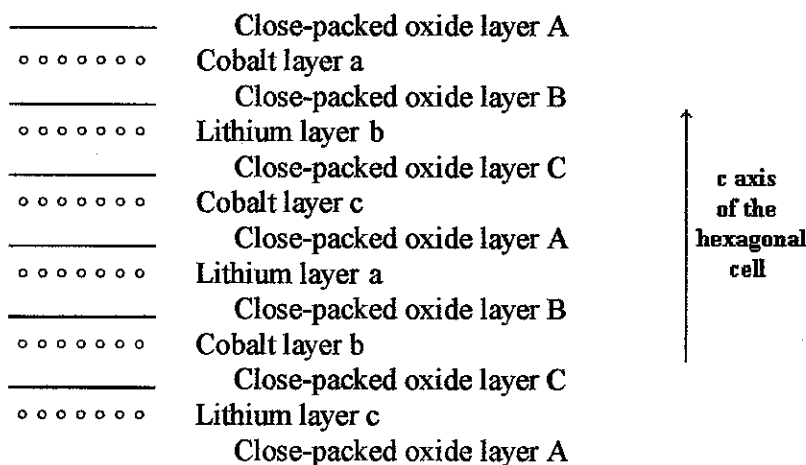


Fig 21 (Lanes 1-6) Digestion of native RNaseB (lane 1) with the indicated glycosidases (lanes 2-6). (Lanes 7-12) Digestion of reduced and alkylated RNaseB (lane 7) with the indicated glycosidases. After enzymatic digestion, samples were analysed by SDS-PAGE followed by silver staining. The number of glycans is indicated on the right. The following amounts of enzyme were used: Endo A: 1,440 U; Endo H: 100 U; Png F: 5,000 U; Png1: 420 U. The total amount of substrate (RNaseB) for each reaction volume was 0.4 μ g in 50 μ l. Samples were incubated at 20-23 $^{\circ}$ C for 16 h.

Part I. Stoichiometric lithium cobalt oxide is a compound with a layered rock-salt-like (NaCl-like) structure in which the lithium and cobalt ions are situated in octahedral holes in alternate (111) planes of the rock-salt structure. However, the ordering of cobalt and lithium ions produces a slight distortion and reduces the cubic NaCl space group to hexagonal ($a = b = 2.81 \text{ \AA}$, $c = 14.04 \text{ \AA}$). Viewed from the side, and perpendicular to the hexagonal c axis, we have:



(Each part A-E is worth 10 points.)

- A. Describe the cubic rock-salt structure using graphics and words, as needed.
- B. Describe the distribution of lithium and cobalt ions in the cubic NaCl unit cell using graphics and words, as needed.
- C. What is the empirical formula of stoichiometric lithium cobalt oxide. Explain your reasoning. Which ions are present in this compound?
- D. Above about 1000°C , stoichiometric lithium cobalt oxide decomposes to nonstoichiometric $\text{Li}_x\text{Co}_{1-x}\text{O}$ (with $x < 0.5$) by loss of Li_2O and O_2 . What ions are present in this nonstoichiometric compound? What is the mole ratio of lithium to total cobalt and the mole ratio of the two types of cobalt ions when $x = 0.45$?
- E. Write the equation for the reaction or reactions that occur when nonstoichiometric $\text{Li}_x\text{Co}_{1-x}\text{O}$ dissolves in an aqueous solution of HCl.

Part II. The +2 oxidation state of Ca is common, not because Ca^+ compounds are not stable, but because Ca^{2+} compounds are more stable than Ca^+ compounds.

- A. (25 points) Show that the formation of CaCl from calcium and chlorine is an exothermic process. Calculate ΔH_f for $\text{Ca(s)} + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{CaCl(s)}$ using Kaptunsky's equation (given below) to determine the lattice energy.
- B. (25 points) Show that the disproportionation of CaCl to give Ca(s) and CaCl_2 is even more exothermic.

Data (all units kJ/mole unless given):

for Ca $\Delta H_{\text{sub}} = 201$
 1st IE = 589
 2nd IE = 1143
 Electron affinity = -170
 Radius of Ca = 1.97 Å
 Assumed radius of Ca^+ = 1.20 Å
 Radius of Ca^{2+} = 1.14 Å

For Cl_2 $D_{\text{Cl-Cl}} = 121$
 1st IE = 1250
 Electron affinity = -349
 Covalent radius of Cl = 0.99 Å
 Radius of Cl^- = 1.81 Å

For CaCl_2 $\Delta H_f = -799$

Kaptunsky's equation $U = (nZ_+Z_-/d)K(1 - 0.345/d)$

U = approximate lattice energy
n = number of ions per formula unit
K = 1.21 MJ Å Mole⁻¹
Z = charge on ion
d = interionic distance

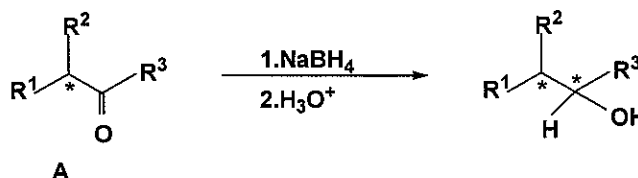
ORGANIC CUMULATIVE EXAMINATION

February, 2005

I (70 pts). Statistics plays important roles in chemistry. Answer **all** questions below.

1 (10 pts.). **Ketone A** bearing just one asymmetric center is optically pure and 100% *R*. If it undergoes a nonasymmetric reduction with a metal hydride, e.g., NaBH₄, to give a 50:50 mixture of two stereoisomeric secondary alcohols (i.e., no internal asymmetric induction), what would be the enantiomeric purity of each of the two products? Select the correct answer.

- (a) 0%
- (b) 50%
- (c) 100%



2. (40 pts.) If **Ketone A** is 90% *R* (and 10% *S*) and if it undergoes an asymmetric reduction to give a mixture of alcohols that are also 90% *R* and 10% *S* at the newly generated HO-bearing carbon, what would be the answers to the following questions?

2-i (10 pts.). How many stereoisomers are formed?

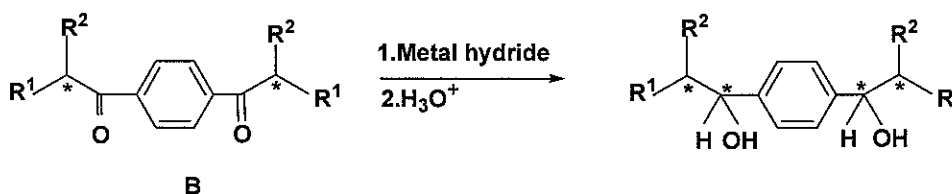
Label them using the *R,S* notation. Arbitrarily designate the HO-bearing carbon as 1 and the originally asymmetric carbon as 2.

2-ii. (10 pts.). What is the relative abundance (in percent of the total) of each isomer?

2-iii (10 pts.). What is the diastereomeric ratio (dr) of the product? All isomers must be considered, but do not consider enantiomeric ratio(s).

2-iv (10 pts.). What is the enantiomeric purity (in percent of the total) of the *R,R* isomer? If you express it in % ee, what is the figure in % ee?

3 (20pts.). Suppose that the starting chiral **Ketone B** has the structure shown below and further suppose that both of the preexisting chiral centers and the newly generated HO-bearing chiral centers are all 90% *R* and 10% *S*, what would be the enantiomeric purity of the *R,R,R,R* isomer?



Compare the two cases of reduction of **A** and **B**. What statistics-based conclusion or generalization would you come up with? Your answer must be very brief but to the point.

II (30 pts.). Give an example (or a generic equation) of the following name reactions. Show an equation each indicating the reactant(s), product(s), key reagent(s), and catalyst(s).

Choose 3 out of 4.

1. Heck reaction
2. Mitsunobu reaction
3. Suzuki coupling
4. Swern oxidation

Listed below are three very important approximations used in various ways to understand the quantum mechanical states of molecules, chemical reactions, bonding, molecular energetics, and so on. For each, explain concisely *what* is approximated. This means describe as precisely as possible quantum mechanical items that are replaced by approximate forms. (Not more than a paragraph is really needed to answer each. Use mathematical expressions where appropriate or helpful.)

- [20] 1. Born-Oppenheimer approximation
- [20] 2. Normal mode approximation for molecular vibrations
- [20] 3. Self-consistent field approximation for electronic wavefunctions
- [20] 4. Choose one of the approximations (from 1, 2 or 3) and give an example of how the approximation is useful in ways that might not be evident from having stated *what* is approximated. Then indicate two possible circumstances or conditions or problem types that differ significantly in the suitability of this approximation. In other words, give some idea of how the approximation works well in relation to how it doesn't.
- [20] 5. The harmonic oscillator problem is a standard model problem for introductory quantum chemistry. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

Consider a system of units in which Planck's constant is 1, and a specific problem with $k=1$ and $m=1$. The Hamiltonian then looks like,

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2$$

Consider how one would start from the solutions to this problem when a perturbing potential is applied. Below are three such perturbing potentials (A, B, C) and three types of treatment (1,2,3). Match the perturbing potentials to the treatments based on what would be the most effective in total (for all three). Look at a treatment and a perturbing potential and ask which 3 matches would give the most accurate results. You don't have to show any work. Write your answer as three sets of letters with numbers, using each letter and each number only once.

A. $H^{(1)} = 18x^2$

B. $H^{(1)} = 18x$

C. $H^{(1)} = e^{-x^2}$

- Finding the ground state energy using a variational treatment ($H + H^{(1)}$) with the first ten eigenfunctions of $H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2$ as a basis set.
- Finding the $n=20$ state energy using first order perturbation theory.
- Finding the $n=0$ to $n=1$ excitation energy by first order perturbation theory.

Periodic Classification of the Elements

I A

1 H 1.00797																	2 He 4.0026
IIA																	
3 Li 6.939	4 Be 9.0122															10 Ne 20.183	
11 Na 22.9898	12 Mg 24.312															18 Ar 39.948	
IIIA IVA VA VIA VIIA																	
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
IIIB IVB VB VIB VIIB VIII I B IIB																	
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 Act (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.)