Department of Chemistry
Cumulative Examinations
January 11, 2003

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

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.
1. Virtually every branch of science is governed by **one** key quantitative relationship. Write this relationship for SIX distinct parts of analytical chemistry (e.g. separation science is one such part). Define each term and give units. Write a paragraph-long sketch of each topic based on a consideration of the relationship.

*Note: good answers to this question will contain original ideas, and these will be clearly argued. You are urged to spend time thinking carefully about your answer before proceeding.*

2. Consider two classical areas (branches) of analytical chemistry and suggest unexpected or little explored commonalities between them, **using a single pointed example to illustrate your argument**. Suggest how the recognition of the similarities that you have exposed might be useful in the continued development or utilization of one of the two classical areas.

*Note: good answers to this question will contain original ideas, and these will be clearly argued. You are urged to spend time thinking carefully about your answer before proceeding.*

*Illustration: you might, for example, decide that there are unexpected relationships between fluorescence and mass spectrometry. This could be supported by considered of detection limits in the two experiments and the influence of chemical noise. Other arguments could then be used to develop this connection. The usefulness of these ideas might be suggested by using tandem mass spectrometry to improve detection limits in mass spectrometry.*

[Obviously, this particular example must not be used]
Proteomics is the effort to characterize and identify large numbers of proteins simultaneously. A problem is that there can be multiple forms (variants) of the same protein. Some of these variations are from post-translational modifications while others are not.

1. What are some of the variant forms of a protein that might be encountered in cell lysates? List five. [It is thought that there are more than a hundred different ways that protein variants can be created.]

2. Can a protein vary at more than one site? If so, describe how this might happen and what type of variations might be expected.

3. How would you go about recognizing large numbers of protein variants of the same type of post-translational modification?

4. How would you identify the proteins in the case above and the sites at which they vary.

5. Why are mass spectrometers so important in proteomics?

6. It is frequently the case that mRNA expression and protein expression do not correlate. How would it be possible that the concentration of mRNA for a protein could increase more in a cell than the concentration of the protein itself?

7. It is frequently very difficult to trypsin digest proteins. Why?

8. Most post-translational modifications are based on an enzymatic reaction. Some are not. Describe a post-translational modification that occurs independent of enzyme catalysis.

9. Which would tend to give larger tryptic peptides, acidic or basic proteins? Why?

10. Methods are now being developed to identify protein:protein interactions between large numbers of proteins. Describe at least one way by which this is done.
Inorganic Cumulative Exam
January 11, 2003

1. (40 points) Answer the following utilizing Lewis structures, VSEPR rules, simple bonding theory, etc.

A. Which of the following molecules or ions have (has) a truly tetrahedral geometry? Which one is paramagnetic? Which have (has) a dipole moment? Briefly indicate your reasoning.
   a. \( \text{MnO}_4^- \)
   b. \( \text{XeF}_4 \)
   c. \( \text{SF}_4 \)
   d. \( \text{Ti(C}_5\text{H}_5)_2 \) (\( \text{C}_5\text{H}_5^- \) is the cyclopentadienide ion.)
   e. \( \text{NiCl}_4^{2-} \)

B. For the following, identify a transition metal \( M \) that could logically form the compound. Briefly explain your reasoning.
   a. \( [(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3]_2 \)
   b. \( M(\eta^6\text{-C}_6\text{H}_6)_2 \)
   c. \( M(\text{Co})(\text{CO})_9 \)

C. Predict structures for the following ring systems. Sketch answers, too.
   a. \( \text{B}_3\text{N}_3\text{H}_6 \)
   b. \( [\text{Rh(C}_5\text{H}_5)(\text{CO})]_3 \)
   c. \( \text{P}_3\text{S}_9^{1-} \)
2. (30 points) A red-violet chloride of chromium can be obtained from the combination of chromium and chloride. After exposing this compound to THF under mild conditions in the presence of a catalyst, one obtains a mixed-ligand complex that analyzes (in part) to contain 38.5%C, 13.9%Cr and 28.4%Cl. (At.wts. H 1.008, C 12.01, O 16.00, Cl 35.45, Cr 52.00)

\[
\text{THF} = \begin{array}{c}
\text{CH}_2-\text{CH}_2 \\
\downarrow \\
\text{O:} \\
\downarrow \\
\text{CH}_2-\text{CH}_2
\end{array}
\]

A. Deduce the likely molecular formula. Draw the structure and indicate any geometric isomers.

B. The product contains chloride, but it is a non-electrolyte. Why? How many unpaired electrons does the compound have?

3. (30 points) The figure that follows is the $^{19}$F-NMR spectrum of a solution of the planar, pentagonal XeF$_5^-$ anion in an acetonitrile solution. [I($^{129}$Xe) = ½, 26%; I($^{131}$Xe) = 3/2, 21.2%; I($^{19}$F) = ½, 100%]

A. Account for all peaks and the relative intensities. Why don’t we see splitting from both magnetically active Xe isotopes?

B. Predict in detail the $^{129}$Xe-NMR spectrum. Give any peak separations in units of Hz.

![NMR Spectrum Image]
1. (50 points) Provide a step-by-step mechanistic description for the reaction shown below (Fayol and Zhu, *Angew. Chem. Int. Ed.* 2002, 41, 3633-3635) which is believed to proceed through the intermediacy of oxazole A. Your mechanism should employ the curved-arrow formalism to describe electron movement and should include all likely intermediates. Describe what reaction must occur during workup.

![Reaction Scheme](image)

2. (50 points) Earlier this year, MacMillan and coworkers (Northrup and MacMillan, *J. Am. Chem. Soc.* 2002, 124, 6798-6799) described the first direct, enantioselective cross-aldol reaction, catalyzed by L-proline (1). Provide a catalytic cycle that explains how proline catalyzes this process and also includes a transition state model that accounts for the observed enantio- and diastereoselectivities of this process. EXTRA CREDIT: explain why isobutyraldehyde doesn’t act as the aldol donor in this reaction.

![Reaction Scheme](image)
1. The particle-on-a-ring is a model one-dimensional quantum mechanical system. The motion of the particle of mass \( m \) is considered free (i.e., \( V(\phi)=0 \)) if the particle remains on the ring (with radius \( r=r_0 \)). The time-independent Schrodinger equation for this system is:

\[
-\frac{\hbar^2}{2Mr_0^2} \frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi)
\]

If we divide both sides of the equation by \( \hbar \), then the constants \( E \) and \( F \) have units of wavenumbers (\( \text{cm}^{-1} \)), and the differential equation can be written:

\[
\frac{d^2\psi(\phi)}{d\phi^2} = -\frac{E}{B} \psi(\phi) \quad \text{where} \quad B = \frac{\hbar}{8\pi^2 cMr_0^2}
\]

(1)

(a) Show that eigenfunctions \( \psi(\phi) \) in equation (2) satisfy the differential equation (1). In so doing, define the quantum number \( 'm' \) in terms of \( E \) and \( B \).

\[
\psi(\phi) = \alpha \cdot \sin(m\phi) + \beta \cdot \cos(m\phi)
\]

(2)

(b) What are the boundary conditions on \( \psi(\phi) \) in order that the wave function is single-valued?

(c) Apply this boundary condition to determine that the allowed values of \( 'm' \) are:

\( m = 0, \pm 1, \pm 2, \ldots \)

(d) Draw an energy level diagram for the particle-on-a-ring, assuming that \( F=5.3 \text{ cm}^{-1} \). Label the energy levels in terms of the quantum number \( 'm' \).

(e) Identify the energy levels that are doubly degenerate.

(f) Normalize the wave function for \( m=0 \) and give its final functional form \( \psi_{m=0}(\phi) \).

(g) What freedom do we have in expressing the form of the wave functions for the doubly-degenerate pairs of states?

(h) Choose appropriate linear combinations of the doubly-degenerate eigenfunctions, and normalize the resulting eigenfunctions, to show that

\[
\psi^+_m(\phi) = \left( \frac{1}{\pi} \right)^{1/2} \cos(m\phi) \quad \text{and} \quad \psi^-_m(\phi) = \left( \frac{1}{\pi} \right)^{1/2} \sin(m\phi)
\]

where now \( m=0,1,2,\ldots \)
2. The particle-on-a-ring from problem 1 is the starting point for describing hindered internal rotation in molecules. We will consider the hindered internal rotation of the methyl group relative to the phenyl ring in ortho-fluorotoluene:

\[
V_{6\phi}(\phi) = \frac{1}{2} V_3^{6\phi}(1-\cos(3\phi)).
\] (3)

(a) Graph the potential over the range from \(\phi = 0\) to \(2\pi\).

(b) First consider the limiting case that \(V_3^{6\phi}\) is very large; i.e., that the barrier to internal rotation is very high. In this limit, the internal rotation becomes a torsional vibration with negligible tunneling between the wells. Using the harmonic oscillator as a model, draw the first several vibrational energy levels on an energy level diagram, taking the harmonic frequency to be \(200\) \(\text{cm}^{-1}\). What is the degeneracy of each of the vibrational levels in this limit?

(c) Now look at the energy level diagram for the actual case, shown to the right: Use the limiting cases of free internal rotation (problem 1) and high barrier (problem 2a) to explain the energy level structure observed in the actual molecule where \(V_3^{6\phi}=230\) \(\text{cm}^{-1}\). [NOTE: The numbers labeling the internal rotation states \((0a_1, 1e, 2e, 3a_2, 3a_1, 4e, 5e, 6a_2, 6a_1)\) refer to the ‘\(m\)’ quantum number from the free internal rotation description, while the \(a_1, e, a_2\) labels are symmetry designations in the 3-fold molecular symmetry group (equivalent to \(C_{3v}\)).]

(d) One could calculate the energy levels using time-independent perturbation theory using the free internal rotor functions as zeroth-order wave functions and the perturbation as the \(V_3\) potential in equation (3).

i. Consider the \(m=0\) zeroth-order wave function. Which states will be coupled to this state by the perturbation? Why?

ii. Which state will be most strongly coupled and why?

iii. Answer the same questions for the two \(m=1\) states \(\psi_{m=1}^+\) and \(\psi_{m=1}^-\).
(e) The alternative way to proceed would be to carry out a variational calculation using the free internal rotor wave functions as basis functions.

(i) Set up the Hamiltonian matrix for such a calculation using free rotor wave functions up through \( m=6 \). Use symmetry to block-diagonalize the matrix. Explain your choice of ordering of the basis functions.

(ii) Show the non-zero off-diagonal matrix elements. [No need to do the integrals ... just show which ones are non-zero.]

(f) So far, this problem has dealt exclusively with internal rotation in the ground electronic state. However, each electronic state of the molecule will have its own set of internal rotor levels, and these can vary from one state to the next due to the changes in the barrier height and position upon electronic excitation. The spectrum shown below is a fluorescence excitation spectrum of ortho-fluorotoluene cooled in a supersonic expansion. This spectrum is recorded by tuning the laser through the \( S_0-S_1 \) electronic transition, and the transition labeled \( 0a_1 \) is a transition from the \( 0a_1^\prime \) ground state level to the \( 0a_1^\prime \) excited state level. It turns out that under supersonic expansion cooling, all of the population in the ground electronic state is initially in the \( 0a_1^\prime \) and \( 1e^\prime \) levels (where the “ denotes the ground electronic state).

(i) Looking at the transition frequencies, is the internal rotor barrier smaller, about the same, or greater in the \( S_1 \) state than in the ground state (\( S_0 \))?  

(ii) Draw a quantitatively correct energy level diagram for the internal rotor levels in the \( S_1 \) state.

(iii) The intensities of the various internal rotor transitions are determined by the Franck-Condon factors, which are given by:

\[
I = |\langle \psi_{\text{exc}}(\phi) | \psi_{\text{gd}}(\phi) \rangle|^2.
\]

Transitions to which states will be allowed when \( \psi_{\text{gd}} = 0a_1^\prime \)?  
Transitions to which states will be allowed when \( \psi_{\text{gd}} = 1e^\prime \)?

Draw in these transitions on your energy level diagram, by adding \( 0a_1^\prime \) and \( 1e^\prime \) lower states below your diagram and connecting the allowed transitions by arrows on the diagram.

Some useful trig identities and integrals:

\[
\int \sin^2 x = \frac{1}{2} x - \frac{1}{4} \sin 2x \quad \text{and} \quad \int \cos^2 x = \frac{1}{2} x + \frac{1}{4} \sin 2x
\]

\[
\sin (A+B) = \sin A \cdot \cos B + \cos A \cdot \sin B
\]

\[
\cos (A+B) = \cos A \cdot \cos B - \sin A \cdot \sin B
\]

\[
\sin A \cdot \cos B = \frac{1}{2} [\cos (A-B)-\cos(A+B)]
\]

\[
\cos A \cdot \cos B = \frac{1}{2} [\cos(A-B) + \cos(A+B)]
\]

\[
\sin A \cdot \sin B = \frac{1}{2} [\sin (A-B) + \sin (A+B)]
\]

\[
E_n(1) = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = H_{nn}^{(1)}
\]

\[
\sum_{m=n}^{(1)} \frac{H_{mm}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}
\]

\[
\text{Wavenumber in } \text{cm}^{-1}
\]

\[
37561.5 \text{ cm}^{-1}
\]

\[
0_0^0
\]

\[
F \quad \text{CH}_3
\]