Department of Chemistry
Cumulative Examinations
December 7, 2002

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

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.
Tandem mass spectrometry experiments, whether performed in quadrupole, sector or time-of-flight instruments, or a combination thereof, are most commonly based on ionization of the analyte, isolation of an analyte ion and examination of its unimolecular degradation products produced by collisional activation with some inert target gas. However, gas-phase ion-molecule reactions can provide some advantages compared to these collision-activated dissociation (CAD) experiments. Demonstrate your knowledge of this area of mass spectrometry by addressing the following questions.

1) Give three situations (chemical examples) wherein ion-molecule reactions may provide more useful analytical information than CAD.

2) Draw a sketch that illustrates the most important events of a process wherein a gas-phase collision of ethylamine radical cation with an argon atom results in activation and dissociation (show likely dissociation products), and another for an ion-molecule reaction between ethylamine radical cation and ethylamine (show likely reaction products).

3) Do the above CAD and ion-molecule reaction experiments typically employ similar kinetic energies for the analyte ion? Give typical values for each. Explain why they differ/don’t differ.

4) Draw sketches of the potential energy surfaces related to each reaction. Label the x- and y-axes, reactants, products, and transition states. Pay attention to the relative potential energy levels of the different chemical species. Show the total energy level of each system.

5) Give the energetic constraints for the two different types of reacting systems (what determines whether a reaction is observed or not)
Biochemistry Cumulative Examination
December 7, 2002

Please answer the following questions as briefly and succinctly as possible.

1. Discuss ONE mechanism by which solutes can be moved across a membrane against a concentration gradient? Provide an example. (6 points)

2A. A mutant gene (ras) is found in as many as one third of all human cancers including lung, colon, and pancreatic, and may be partly responsible for the altered metabolism in tumor cells. The Ras protein coded for by the ras gene is involved in cell signaling pathways that regulate cell growth and division. The Ras protein must be converted to an isoprene-anchored membrane protein in order to have cell signaling activity. The enzyme farnesyltransferase (FT) has been selected as a potential chemotherapy target for inhibition. Suggest why FT might be a reasonable target. (6 points)

2B. In addition to isoprenylation, name TWO other ways in which proteins may interact with membranes? (6 points)

3. Glucose enters some cells by simple diffusion through channels or pores, but glucose enters red blood cells by passive transport. Draw a plot below with two lines; one which represents diffusion through a channel or pore and another which represents passive transport. If the rates differ, explain why. Plot the rate of glucose transport (y-axis) versus glucose concentration (x-axis). Be sure to label both lines. (6 points)

4. Plasma membranes are asymmetric. What does this mean at the molecular level (i.e. what is asymmetric and how)? How is membrane asymmetry achieved? (6 points)

5. Fish is a food rich in polyunsaturated fatty acids. Assuming that fish did not evolve in order to lessen our risk of cardiovascular disease, present a teleological argument to explain this observation in the light of your knowledge of lipid aggregation. What would be another strategy to accomplish the same objective? (6 points)

6A. Briefly describe the fluid mosaic model for biological membranes. (8 points)

6B. Recent evidence points to the existence of microdomains (also known as detergent resistant domains or lipid rafts) in lipid bilayers. These domains are rich in cholesterol and sphingomyelin. What are the molecular features of cholesterol and of sphingomyelin that contribute to the formation of detergent resistant domains (DRMs)? Suggest a function for these microdomains? (7 points)

6C. In the laboratory, detergent resistant membrane (micro)domains (DRMs) are isolated by exposing membranes to detergents at low temperature. What are the molecular reasons for choosing these conditions and why might these conditions introduce artifacts into the characterization of DRMs? (5 points)
7A. Name the two major types of glycoprotein linkages. Which amino acids on proteins can be glycosylated? (8 points)

7B. Give three roles for the oligosaccharide chains on glycoproteins. (6 points)

8. Asymmetry is a feature of most plasma membranes. What is meant by this and how is it achieved? Provide an example of what the cell might be accomplished by maintaining an asymmetric membrane? What is an important consequence of loss of asymmetry? (6 points)

9. You are investigating the properties of a newly cloned plasma membrane-associated protein. You suspect that it may be glycosylated. Describe experimental approaches that you would use to identify the glycosylation site(s) on this protein. (10 points)

10A. The figure below shows something called an "inside-out" micelle; the polar head groups of the fatty acid molecules are indicated as balls and the hydrocarbon tails as wavy lines. Describe the circumstances under which such an "inside-out" micelle could exist. (7 points)

10B. How would the situation differ if phospholipids molecules were placed in an aqueous solution? What membrane structure(s) is favored under these conditions? Why? Feel free to use drawings if helpful. (7 points)
There are 3 questions and 100 points on this exam.

**Question 1: 35 points**

How does the Space Shuttle get off the ground? Consider only the solid rocket boosters, as shown in the figure below. The solid rocket booster fuel is composed of 70% ammonium perchlorate, 16% aluminum metal powder, and 14% of an organic binder to make the material pliable. The majority of the propulsion is derived only from the ammonium perchlorate, with out any reaction with the aluminum or organic binder. Most fuels work by combustion (i.e., redox) processes. Keep in mind that the shuttle launches into environments beyond most of the Earth's atmosphere. Thus, the shuttle cannot use external, atmospheric oxygen as an oxidant.

1A) **20 points:** Just consider the 70% ammonium perchlorate. Describe the chemical reaction (i.e., write an equation) by which the shuttle can use ammonium perchlorate as solid fuel. Note entropic and enthalpic changes. Your answer need not be the predominant reaction taking place, but should be a reasonable one.

1B) **10 points:** Now consider the ammonium perchlorate and the 16% powdered aluminum metal. This aluminum, while not necessary, adds extra propulsion to the mix by reacting with products of the above reaction. Describe one of the reactions employing aluminum to yield extra propulsion for the shuttle launch. Again, your answer need not be the predominant one, but should be a reasonable one from which propulsion can be derived.

1C) **5 points:** What are the two liquid fuels used in the external tank? They are each stored in two separate tanks within the external tanks and combined to generate thrust. Describe the chemical reaction by which these two fuels are combined to yield energy for launch.
Question 2: 40 points
If you wish to identify or quantify the metal content of a new sample, you will most likely turn to either atomic absorption spectroscopy (AA) or inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2A) 30 points: How do each of these two techniques work? (15 points each)

2B) 10 points: Why is ICP-AES more sensitive than AA?

Question 3: 25 points
Consider the effects of hydrogen bonding on reduction potentials. A model of the prototypical biological tetranuclear iron-sulfur center is shown below with benzenethiolate ligands.

When looking at the $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + e^- \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ reduction potential, it can be changed by adding hydrogen bonds to the benzenethiolate ligands. Below are shown three different benzenethiolate ligand derivatives along with average reduction potentials of the $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ complexes. Homoleptic $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters can be prepared in which all 4 terminal thiolates are one of the three ligands shown below.

Ligand: 

Complex: $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{2-}$ $\quad [\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4(\text{NHCOR}))_4]^{2-}$ $\quad [\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4(\text{NHCOR})_2)_4]^{2-}$

Reduction potential: -0.8 Volts -0.6 Volts -0.4 Volts

Explain this trend in reduction potentials. In other words, why does adding hydrogen bonds to the ligand increase the reduction potential of the iron-sulfur complexes?
In *J. Am. Chem. Soc.* **2002**, *124*, 6914 – 6920, Tokitoh and co-workers reported the synthesis and reactivity of a stable germabenzene, which will be the focus of this exam:

\[
\begin{array}{cc}
\text{Ge} & \text{Ge} \\
R & H \\
1 & 1H
\end{array}
\]

\[
R = 2,4,6\text{-tris[trimethylsilyl]methyl}phenyl
\]

1) (30 points) Use the appropriate character table on the attached page to determine the symmetry types of the π molecular orbitals in 1H, and derive the molecular orbitals. Use the 2p orbitals on C and the 4p orbital on Ge as your basis set.

2) (30 points) In principle, one might think that germabenzene is aromatic, in that it should have a \(4n + 2\) π electron system. One test for aromaticity is “unusual thermodynamic stability” with respect to some non-aromatic model, as reflected by the aromatic stabilization energies (ASEs). Propose three ways of calculating the ASE of 1H, and comment on the strengths and weaknesses of each approach. Assume that any thermochemical values you need are known.

3) (30 points) Provide a thorough description of at least three additional physical criteria that could be used to test for aromaticity. For full credit, provide examples of where these criteria work and where they don’t work, as the case may be.

4) What do the structure and reactivity of 1 indicate about its aromaticity?
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Conjugate variables in quantum mechanics can be recognized by the fact that their commutators have the value $i\hbar$.

1. Using this property, show that the operator conjugate to position, $\hat{x}$, is that for momentum, $\hat{p}_x$.

2. Consider the wavefunction for a free particle. What physical property of this wavefunction is determined by its momentum?

3. What can you say about the position, $x$, of a free-particle wavefunction with a well-defined momentum?

4. Consider now a wavefunction composed of a linear combination of free-particle wavefunctions:

$$\varphi(x) = \sum_i c_i \varphi_i(x)$$

with values of $c_i$ chosen such that the sum has finite amplitude within a very narrow region about a definite position $x'$. What can you say qualitatively about the momentum of $\varphi(x)$? What does this suggest to you about the measurement uncertainty of conjugate variables?

5. To be more precise, we can define variances:

$$(\Delta x)^2 = \left\langle \varphi \left| (x - \langle x \rangle)^2 \right| \varphi \right\rangle$$

$$(\Delta p_x)^2 = \left\langle \varphi \left| (p_x - \langle p_x \rangle)^2 \right| \varphi \right\rangle$$

where $\langle x \rangle$ and $\langle p_x \rangle$ represent expectation values. The Schwarz inequality requires:

$$(\Delta x)^2(\Delta p_x)^2 \geq \left| \left\langle \varphi (x - \langle x \rangle)(p_x - \langle p_x \rangle)\varphi \right\rangle \right|^2$$

The operator product on the right-hand side factors to yield the sum of two Hermitian operators: The covariance, $\langle xp_x \rangle - \langle x \rangle \langle p_x \rangle$, which is zero when position and momentum are uncorrelated, and a residue, $i\frac{1}{2} C$, with a real expectation value, $\frac{1}{2} C$.

For the position/momentum problem, the residual operator is $xp_x - p_x x$. What then is $C$, and what is the relation between the commutator for conjugate variables and the Uncertainty Principal relation for $\Delta x \Delta p_x$?
6. Let us turn now to problems in which time, $t$, becomes a variable. Like position, the operator for time is simply multiplication by $t$. Just as for position, there exists a variable conjugate to time, with an associated operator. This question asks you to find that operator, and from it, deduce the quantum mechanical variable that is conjugate to time.

From the commutation relation for conjugate variables,

$$\left[ \hat{A}, \hat{B} \right] = i\hbar$$

find $\hat{B}$ when $\hat{A}$ is the operator, $t$.

What is the quantity, conjugate to time, that is associated with this operator? Use the following as starting points:

The complete Schrödinger wave equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x)\Psi(x, t) = \hat{H}(x)\Psi(x, t)$$

together with the fact that, for a time-independent Hamiltonian, solutions are always separable into spatial and temporal parts,

$$\Psi(x, t) = \varphi(x)\phi(t).$$

7. What does the commutation relation between these conjugate variables tell you about the measurement uncertainty of this pair of quantities?