Department of Chemistry  
Cumulative Examinations  
September 23, 2000

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

On your examination booklet:

1) Print your student ID number.  
2) Print this Exam Booklet number: 100  
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.
In his Amy-Mellon Lecture, Prof. Bard presented applications of faradaic electrochemical responses at an ultramicroelectrode, involving a “scanning electrochemical microscope” (SECM) arrangement.

1) What are ultramicroelectrodes (UME’s)? Outline some key reasons, stressing basic electrochemical principles, why such electrodes are now widely utilized in electroanalytical chemistry. Summarize specifically at least one type of application of UME’s other than SECM.

2) Explain the basic principles behind SECM, involving the concept of “positive” and “negative” current feedback when the tip is placed near conducting and insulating regions, respectively, of the surface of interest.

Answer also one of the two following questions:

3) Distinguish between the physical phenomena responsible for surface imaging with the SECM and with scanning tunneling microscopy (STM). Suggest reasons why STM is capable of achieving spatial surface resolution down to atomic dimensions, whereas the resolution limit of SECM is no better than ca. 10 nm.

4) Prof. Bard claimed to have achieved “single-molecule electrochemical detection” by using the SECM. Outline the experiment involved, the nature of the results, and the basis by which single-molecule detection is apparently feasible with this approach.
1. (30 pts) The enzyme glycogen phosphorylase occupies a central role in human metabolism. (A) Write out the reaction catalyzed by this enzyme, including appropriate structural formulas of reactants and products. (B) Describe the important regulatory interactions that affect this enzyme. Include in your description the names of any other important proteins that participate directly in the regulation, and illustrate their action with equations and/or structures where possible.

2. (20 pts) The first step of DNA base excision repair pathways involves the removal of the damaged base by hydrolytic cleavage of an N-glycosidic bond by a DNA glycosylase. Based on this description, write out the reaction (including structural formulas) for the reaction catalyzed by the enzyme uracil DNA glycosylase.

3. (25 pts) A recently characterized NAD-dependent aminoaide dehydrogenase from plants catalyzes the conversion of 4-aminobutyraldehyde to 4-aminobutyric acid. The enzyme is irreversibly inhibited by treatment with small amounts of p-chloromercuribenzoate ion or N-ethylmaleimide. (A) Write out the overall reaction catalyzed by this enzyme. (B) What is a likely (molecular) interpretation of the inhibition data? (C) Propose a mechanism for the reaction, consistent with the information provided and your knowledge of related enzymatic reactions. [Hint: could glyceraldehyde phosphate dehydrogenase provide a possible analogy?]

4. (25 pts) A fermentation broth supernatant from Aspergillus oryzae was observed to contain an aminopeptidase activity that released a wide variety of amino acids from natural peptides. A homogeneous enzyme was isolated, partially sequenced, cloned and expressed. The resulting homogeneous enzyme aminopeptidase II was recently characterized, and its catalytic activity towards a variety of amino acid p-nitroanilides (pNAs) was measured (Table 1). Incubation of the enzyme for 30 min with 1 mM phenylmethanesulfonyl fluoride (PMSF), EDTA and orthophenanthroline resulted in enzyme samples that retained 95, 90 and 9% residual activity, respectively. (A) Select one of the substrates from Table 1. Write out the reaction, including structures of substrates and products. (B) What is the general significance of \( k_{cat}/K_m \) in an experiment such as that described in Table 1? Suggest two specific conclusions that you could reach in the case of aminopeptidase II, based on the data presented in Table 1.

Table 1
Substrate specificity of recombinant aminopeptidase II expressed in F. venenatum toward amino acid pNAs at pH 7.5 (50 mM sodium phosphate buffer, 21°C)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( K_m ) (mM)</th>
<th>( k_{cat} ) (min⁻¹)</th>
<th>( k_{cat}/K_m ) (min⁻¹ mM⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leu-pNA</td>
<td>7</td>
<td>210</td>
<td>31</td>
</tr>
<tr>
<td>Lys-pNA</td>
<td>9</td>
<td>110</td>
<td>12</td>
</tr>
<tr>
<td>Ala-pNA</td>
<td>3.5</td>
<td>41</td>
<td>12</td>
</tr>
<tr>
<td>Glu-pNA</td>
<td>1.5</td>
<td>8</td>
<td>5.3</td>
</tr>
<tr>
<td>Val-pNA</td>
<td>13</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>Pro-pNA</td>
<td>15</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>Ile-pNA*</td>
<td>51</td>
<td>11</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Solubility of the substrate is not sufficient in order to have the concentrations comparable to \( K_m \).
Inorganic Chemistry Cumulative Exam

Purdue University

September 23, 2000

Question 1: (30 points)
Draw and label all the $d$ orbitals. Put each on its own set of $x,y,z$ axes.

Question 2: (30 points)
Draw the $d$ orbital ligand field splitting diagrams and label each orbital for the following general coordination environments about a metal. Note that for the square pyramids and trigonal bipyramids there are no unique diagrams, so a reasonable approximation will be given full credit.

A) Octahedral
B) Tetrahedral
C) Square planar
D) Square pyramid
E) Trigonal bipyramid
F) A Jahn-Teller distorted octahedron (of $D_{4h}$ symmetry).

Question 3: (15 points)
The complex $[\text{Fe}^{II}(\text{OH}_2)_6]^{2+}$ is attracted to a magnet and $[\text{Fe}^{II}(\text{CN})_6]^{4-}$ is not. Why? Figures may help your explanation.

Question 4: (25 points)
Dissolution of many metal salts in water causes the water to become acidic. Why? Explain in as much detail as you can.
Amos Smith and Zehong Wan have reported the total syntheses of the Ansamycin Antibiotic (+)-Thiazinotrienomycin E (J. Org. Chem. 2000, 65 (12), 3738; Cover page of June 16, 2000 issue).

I. During their synthesis, Smith and Wan carried out the following reactions. Write the structures of the products A, B, C and D.

(a) (10 pts)

(b) (10 pts)

(c) (10 pts) Provide reasoning for the formation of products in (a).
(d) (20 pts) Smith and Wan started their synthesis with (+)-8. Provide a scheme to prepare 8 (ignore the absolute stereochemistry) starting from 1,3-propane diol.

\[
\begin{align*}
\text{HO-} & \quad \text{OTBS} \\
(+) & \quad 8
\end{align*}
\]

II. During their synthesis, Smith and Wan utilized Horner-Emmons reaction, Julia olefination, Swern oxidation, and Stille cross-coupling reactions. Provide a representative example for each of these reactions with reagents and conditions (5x4 pts).

III. One of the techniques that organic chemists use during a synthesis is kinetic or thermodynamic product control. Show the reaction coordinate for any reactant providing kinetic and thermodynamic products. Briefly discuss the product stability, temperature dependence, and the reversibility of these pathways (20 pts).

IV. Provide a curved arrow mechanism for the following transformation (10 pts).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{1A} & \quad \text{1B}
\end{align*}
\]

\[
\text{CH}_3\text{Li, THF} \quad -78^\circ\text{C to 25}^\circ\text{C}
\]

V. (Extra credit 5 pts) Name the journal served by Prof. Amos Smith as the editor-in-chief.
For six of the following equations, principles, or laws associated with specific scientists, outline in detail the underlying physical concepts, validity, and applicability. Where appropriate, provide some historical background as regards their original development. Give mathematical relationships whenever appropriate, but be careful to define the terms involved and their underlying physical meaning.

1) Debye-Hückel theory
2) Franck-Condon principle
3) Born-Oppenheimer approximation
4) Maxwell-Boltzmann distribution law
5) London forces
6) RRKM (Rice-Ramsperger-Kassel-Marcus) theory
7) Hartree-Fock wave function
8) Raoult's Law
9) Gibbs-Duhem equation
10) Lennard-Jones Potential Function