Department of Chemistry
Cumulative Examinations
November 16, 2013

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, Pages 5-7
5) Physical Cumulative Examination, Page 8

On your examination booklet:

1) Print your student ID number.
2) Print the 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.
Analytical Chemistry Cumulative Exam
November, 2013

1. A potential can be generated across a cell membrane when there are differences in ionic concentrations on the inside versus the outside of the cell. Provide a quantitative relationship to indicate the contribution to the cell membrane potential from the sodium ion concentrations inside and outside the cell. (10 pts)

2. a) What is meant by the term ‘efficiency’ in chromatography? (5 pts)
   b) What factors play a role in determining chromatographic efficiency in liquid chromatography? (5 pts)
   b) How is the efficiency of a chromatographic column for a particular analyte determined experimentally? (5 pts)
   c) Provide the theoretical model that is widely used to describe chromatographic efficiency. (5 pts)

3. How are UV/visible absorbance measurements different from IR absorbance measurements:
   a) From the standpoint of implementation. (10 pts.)
   b) From the standpoint of application. (10 pts)

4. a) What phenomena form the basis for chemical ionization in mass spectrometry? (5 pts)
   b) List and describe three significant differences between conventional chemical ionization conducted at 1 torr versus atmospheric pressure chemical ionization. (15 pts)

5. Explain the relationships between random measurement error, sensitivity, and concentration, and how they impact error in the determination of the concentration of unknown on the basis of a calibration curve, derived from UV/vis absorbance measurements. (20 pts)

6. Some analytical methods are based on the establishment of equilibrium (i.e., equilibrium methods) and some are based on the measurement of rates of reactions (i.e., kinetic methods).
   a) List two advantages of kinetic methods over equilibrium methods. (5 pts)
   b) List two disadvantages of kinetic methods relative to equilibrium methods. (5 pts)
Biochemistry Cumulative Exam for November 2013

1. Describe the features of the fatty acid shown below that are not likely to be found in normal eukaryotic organisms. (16 points)

[Chemical structure of a fatty acid]

2. Describe mechanistically how a hexagonal II phase lipid structure is thought to participate in membrane fusion. Please use a sketch of the hexagonal II phase and any intermediate structures to explain your answer. (18 points)

3. Describe how one might most efficiently prepare small unilamellar vesicles using a lyophilized preparation of phosphatidylcholine as the starting material. (14 points)

4. Explain the mechanism by which benzyl alcohol might alter each of the surface potential of a PS/PC membrane (8 points)

5. Summarize the general rules governing the passive permeability of molecules across phospholipid bilayers. (20 points)

6. Describe the basic phospholipid asymmetry that exists in a mammalian plasma membrane. Then list the enzymes involved in establishing this asymmetry and their properties. Finally, describe the enzyme involved in collapsing this asymmetry and its properties. (24 points)
1. Magnetic moment $\mu_S$ can be calculated via the equation below (n: number of unpaired electrons)

$$
\mu_S = \sqrt{n(n + 2)}
$$

Predict the magnetic moments (spin only) for the following species (20 points)

a. $[\text{Cr(H}_2\text{O)}_6]^{2+}$

b. $[\text{Fe(CO)}_6]^{2+}$

2. The aqueous solution of $[\text{Mn(H}_2\text{O)}_6]^{2+}$ is almost colorless; the extinction coefficients for all the peaks in its UV-vis spectrum are very small as shown in the figure on the right. Using the Tanabe-sugano diagram given below to explain why? (15 points)

![Tanabe-sugano diagram](image)

3. The complexes $[\text{Ce(NH}_3)_3X]^{2+}$ ($X = \text{Cl}^-, \text{Br}^-, \Gamma$) have charge transfer to metal bands. Which of these compounds would you expect to have the lowest-energy charge-transfer band? Why? (15 points)
(4) The Co(III) complexes are reduced by $[\text{Cr(H}_2\text{O)}_6]^{2+}$ with the reaction rates listed in the following table. Pick up a Co(III) complex which conducts the reaction via a sole out-sphere mechanism and a Co(III) complex which could proceed via an inner-sphere mechanism. For the inner-sphere reaction, please suggest the possible structure of the bridging intermediate. (10 points)

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>$k \ (M^{-1} \ s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{F})]^{2+}$</td>
<td>$1.8 \times 10^3$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{OH})]^{2+}$</td>
<td>$9.3 \times 10^4$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{NH}_3)]^{3+}$</td>
<td>$8 \times 10^{4a}$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{NCS})]^{2+}$</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{N}_3)]^{2+}$</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_5(\text{Cl})]^{2+}$</td>
<td>$\sim 5 \times 10^7$</td>
</tr>
</tbody>
</table>

(5) a. Based on the 18-electron rule, determine the expected charge on the following complex $[(\eta^5-C_5H_5)\text{Fe(CO)}_3]^+$ (10 points)

b. Identify the first-row transition metal for the following species which obeys the 18-electron rule.

   $[\text{M(CO)}_4(\text{PPh}_3)]^-$ (10 points)

(6) In aqueous solution, the redox potential for the Co$^{3+}$/Co$^{2+}$ pair is found to be as high as $+1.808 \text{ V}$. The potential is changed to $+0.108 \text{ V}$ in the presence of NH$_3$, and to $-0.83 \text{ V}$ in the presence of CN$^-$, as shown in the table below. Please offer an explanation for the listed potential changes. (20 points).

<table>
<thead>
<tr>
<th>Co(III)-Co(II) Reactions</th>
<th>$\varphi^o \ (V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$</td>
<td>$+1.808$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3]_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Co(NH}_3]_6]^{2+}$</td>
<td>$+0.108$</td>
</tr>
<tr>
<td>$[\text{Co(CN)}_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Co(CN)}_6]^{4-}$</td>
<td>$-0.83$</td>
</tr>
</tbody>
</table>
1. (60 pts) Crich and coworkers recently reported the design of a reaction clock that helped them distinguish between coupling mechanisms in glycosylation reactions [JACS 2012 134, 14746]. In the absence of an external nucleophile, two products were observed as shown below.

Cyclization clock:

When a competing nucleophile (2-propanol) was added to the reaction as a simple glycosyl mimic, two additional products were formed. Variation of the nucleophile concentration in the reaction produced a data set that is summarized in Table 1. The same data is plotted in the graph of product ratio vs. nucleophile concentration. (N.B.: 1-Octene is added as a scavenger of reaction byproducts to simplify the analysis.)

Table 1. O-Glycosylation in Competition with Cyclization

<table>
<thead>
<tr>
<th>entry</th>
<th>i-PrOH [mol/L]</th>
<th>9/(5 + 6)</th>
<th>10/(5 + 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8 (0.014)</td>
<td>2.17</td>
<td>0.15</td>
</tr>
<tr>
<td>2</td>
<td>1.2 (0.020)</td>
<td>3.66</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>1.5 (0.026)</td>
<td>5.36</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>2.5 (0.043)</td>
<td>10.99</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>3 (0.051)</td>
<td>13.09</td>
<td>1.28</td>
</tr>
<tr>
<td>6</td>
<td>4 (0.068)</td>
<td>15.75</td>
<td>1.14</td>
</tr>
<tr>
<td>7</td>
<td>5 (0.085)</td>
<td>19.38</td>
<td>1.53</td>
</tr>
<tr>
<td>8</td>
<td>6 (0.130)</td>
<td>24.34</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Experimental conditions: TTBP (4 equiv), 1-octene (10 equiv), 4 Å molecular sieves, and TFE (1.2 equiv) at -72 °C. *Number of equivalents (concentration is mol/L). *Molar ratios were determined by UHPLC/UV/MS.

Using $^{13}$C NMR analysis of the product distribution, the kinetic isotope effect values observed for the β-anomer were ~1.03, whereas those measured for the α-anomer were ~1.005.
Analogous experiments trapping experiments using trimethyl(methallyl) silane as an external nucleophile produced the data set shown in Table 2.

**Table 2. C-Glycosylation in Competition with Cyclization**

<table>
<thead>
<tr>
<th>entry</th>
<th>TMSCH₂C(Me)=CH₂</th>
<th>11/(5 + 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 (0.034)</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>4 (0.068)</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>8 (0.136)</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>12 (0.204)</td>
<td>0.55</td>
</tr>
<tr>
<td>5</td>
<td>15 (0.255)</td>
<td>0.69</td>
</tr>
<tr>
<td>6</td>
<td>20 (0.34)</td>
<td>0.87</td>
</tr>
<tr>
<td>7</td>
<td>30 (0.51)</td>
<td>1.40</td>
</tr>
</tbody>
</table>

*Experimental conditions: TTBP (4 equiv), 4 Å molecular sieves, and Tİ₂O (1.2 equiv) at −72 °C. b Number of equivalents (concentration in mol/L). c Molar ratios were determined by UHPLC/UV/MS.*

a. Write a plausible mechanism to account for the observed cyclization products.
b. Rationalize the observed kinetic behavior reported in Table 1 that is consistent with the observed kinetic isotope effects.
c. Explain the relative kinetic behavior reported for O- vs. C-glycosylation.

2. (10 pts) Berger & Montchamp have recently reported a method for the synthesis of P-stereogenic compounds [*Angew. Chem. Int. Ed.* **2013** *52*, 11377] that avoids the pseudorotation problems that often accompany attempts to prepare chiral phosphorus species. Allylation of \((S_p)-3\), followed by treatment with two equiv. of s-Buli in THF at −78 °C, gave \((S_p)-13\) in excellent diasteromeric excess.

Write a plausible reaction mechanism for the conversion of the allylated intermediate of \((S_p)-3\) to \((S_p)-13\).

\[(S_p)-3 \quad \rightarrow \quad \text{MenO}^\circ\quad \begin{array}{c} \text{Ph} \quad \text{R} \quad \text{R}_1 \quad \text{R}_2 \quad \text{OH} \\ (S_p)-13 \end{array} \]

13a R = Me (64%, > 99% de)
13b R = H (55%, 94% de)
3. (20 pts) Synthesis of 1,4-disubstituted poly(aryltriazole) produces a foldamer that self-assembles such that each aryl unit is in van der Waal's contact with two triazole units, one above and one below the ring. When the aryl units are substituted with the oligo(ethylene oxide) unit shown, the UV and CD behavior shown below was obtained as water was gradually titrated into a DMF solution of the material. Cryo-TEM images of the final state are shown. Rationalize these findings from the work of Rowan & Klumperman [Angew. Chem. Int. Ed. 2013 52, 11040].

4. (10 pts) Haberkorn and coworkers [Angew. Chem. Int. Ed. 2013 52, 11760] recently described the use of ribosome display to develop a library of miniproteins. Iterative rounds of panning enabled the discovery of an anti-angiogenic agent with low nanomolar binding affinity for delta-like ligand 4. Briefly describe the ribosome display method and contrast it with phage display and yeast two-hybrid display approaches.
1. (70 pts) Consider the molecule BO.
   a. (10) Build orbital diagram for this molecule.
   b. (10) What electron configurations of the molecule are likely to be low in energy? Consider all reasonable orderings of the molecular orbitals. Name the states corresponding to these configurations.
   c. (5) What are the bond orders in each of these states?
   d. (10) The true ground state of BO is $^2\Sigma$. Specify the $\pi/\sigma$ and u/g symmetries for this state.
   e. (5) Does ionization of the molecule to form a cation lead to a stronger, weaker, or equivalent bond strength?
   f. (20) Assuming that the energies of the molecular orbitals do not change upon ionization, what are the ground state, the first excited state, and the second excited state of the positive ion?
   g. (10) Considering only those states, predict the structure of the photoelectron spectrum you would obtain for ionization of BO.

2. (30 pts) Consider a system with three states, namely ground state 0, electronic excited state 1, and electronic excited state 2, such that state 2 is higher in energy than state 1. Consider a pump-probe experiment with the pump beam exciting the system from state 0 to state 1. After the system is allowed some time for relaxation within state 1, the probe beam is applied (the photon energy of the probe beam is tunable). There are three possible outcomes of the pump-probe experiment: (i) increase in the probe beam intensity due to photobleaching of state 0 by the pump beam; (ii) increase in the probe beam intensity due to a stimulated emission from state 1 to state 0; and (iii) decrease in the probe beam intensity due to state 1 to state 2 absorption of the probe beam (see Figure).

   a. (5) What should be the energy of the probe beam photons compared to the energy of the pump beam photons for a stimulated emission to be a possible outcome of the experiment?
   b. (15) Is it possible to distinguish between three possible outcomes if energy structure is unknown? Rationalize your answer.
   c. (10) What should be known about the energy spacing between levels 0, 1, and 2 for an unambiguous characterization of the pump-probe experiment?
Periodic Classification of the Elements

*Lanthanides

†Actinides

(Numbers in parentheses are the mass numbers of the most stable isotopes.)