Department of Chemistry
Cumulative Examinations

August 24, 2019

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 1-3
2) Biochemistry Cumulative Examination, Page 4
3) Inorganic Cumulative Examination, Pages 5-6
4) Organic Cumulative Examination, Pages 7-8
5) Physical Cumulative Examination, Page 9

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.
1. The behavior of an enzyme catalyzed reaction is often consistent with the generalized mechanism

\[
E + S \xrightarrow{k_1} ES \xrightarrow{k_2} P + E \xleftarrow{k_{-1}}
\]

where E is the enzyme, S is the substrate, ES is an enzyme-substrate complex, and P is the product.

a) Two scientists are associated with proposing this mechanism. What are their last names? (5 pts)

b) The relationship that gives the rate of product formation, \( v \), (sometimes referred to as the velocity of the reaction) is given below:

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

In terms of rate constants and concentrations, what is the relationship for the maximum rate, \( v_{\text{max}} \)? (5 pts)

c) What conditions will make the measured rate pseudo-first order in initial enzyme concentration? (5 pts)

2. Any measurement that seeks to determine the concentration of an unknown via an instrumental technique relies upon a relationship between the measured quantity (e.g., a voltage, a current, absorbance/transmittance) and concentration. The following questions relate to the random error associated with the measured quantity and its relationship to the resulting random error in concentration. (Assume no systematic error.)

a) A common means for determining the concentration of an analyte species in solution is to compare the radiant power of light transmitted through the analyte
solution, P, with radiant power, P₀, transmitted through a solution with negligible analyte present (i.e., a blank solution) under otherwise identical conditions. What is the relationship between concentration, C, in the limit of low concentration, and P/P₀? Define all symbols that you provide. (5 pts)

b) Provide a mathematical relationship for the sensitivity associated with this measurement? (10 pts) (note: sensitivity ≠ detection limit)

c) For a fixed error in the measurement of P/P₀ (i.e., $s_{P/P₀} = \text{constant}$) what is the relationship between the error in concentration, sC, that arises from the error in P/P₀? (10 pts)

d) For $s_{P/P₀} = \text{constant}$ with concentration, draw the shape of a plot of sC/C versus C (i.e., a plot of the relative concentration error versus concentration). (10 pts)

3. What is a coulometric titration? Describe the principle behind the measurement and a typical way to conduct such a measurement. Compare and contrast a coulometric titration with the more traditional volumetric titration. What are the relative advantages/disadvantages of a coulometric versus volumetric titration? (10 pts)

4. 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)

c) Glucose is the most widely determined biomarker in the world. Many of the approaches used for glucose determination are kinetic methods. Why is this so? (5 pts)

d) Species A reacts with species B in an essentially irreversible reaction with 1:1 stoichiometry and with a rate constant of $1.80 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}$. After rapid mixing of solutions containing A and B, 50.0% of A was converted to products after 30.0 s. If the concentration of B was significantly higher than that of A such that the concentration of B was essentially constant over 30s, what was the concentration of B? (10 pts)

5. Hypothesis testing is commonly used in quantitative chemical analysis. Name and describe the relevant statistical tests used to address the following questions: (15 pts)

a) Is there bias in my method?
b) Are the precisions of two different methods the same?

c) Am I justified in considering a data-point to be an outlier?

d) Are the quantities of active ingredients in these two tablets the same?

e) How well does the model I have chosen fit the data?
Biochemistry Cumulative Exam

Title: Signal Transduction

August 24\textsuperscript{th}, 2019

1. (10 points) Outline the structural features of GPCRs. Provide the mechanism by which they activate downstream signaling pathway.

2. (10 points) What are heterotrimeric G proteins? How are they activated? Name three specific consequences of their activation?

3. (10 points) How is insulin receptor signaling propagated?

4. (10 points) Which enzymes degrade cAMP? Name one enzyme which is activated by cAMP.

5. (20 points) Define the specificities of the following protein modules in signal transduction.
   (a) SH3 domain; (b) WW domain; (c) PH domain; (d) PTB domain.

6. (20 points) Define autocrine, paracrine and endocrine signaling. Provide one example of autocrine and paracrine signaling.

7. (20 points) How is Ras protein activated in response to a ligand?
Inorganic Chemistry Cumulative Exam
Purdue University
Crystallography
August 24, 2019

Question 1. A cubic crystal has $a = 6.00 \text{ Å}$. (a) Calculate $d$ for the (211) planes and (b) draw the miller plane in a cubic unit cell. (5 points)

Question 2. Demonstrate how a 64 screw axis works using a stereogram. (5 points)
[Hint: Do this in a step-by-step mechanism on an arbitrary point.]

Question 3. A cubic unit cell has $a = 10 \text{ Å}$. What are the shape and size of its reciprocal unit cell? (4 points)

Question 4. Both Na and CsCl have body-centered cubic (BCC) structures with atoms at $(0,0,0)$ and $(1/2,1/2,1/2)$ positions within the unit cell. Provide a valid explanation for why their diffraction patterns are different even though they have the same structure. (5 points)

Question 5. Consider two space group symbols: P3121 and Pmna. What can you tell about the unit cell geometry, symmetry elements present in these space groups, and the orientation of the symmetry elements with respect to the crystal axes? (7 points)

Question 7. Display how a c-glide perpendicular to the projection plane works. (5 points)
[Hint: Do this in a step-by-step mechanism on an arbitrary point.]

Question 6. The oxidation state of iron and antimony in Na$_2$FeSbO$_5$ can be estimated from the bond valence sum (BVS). Using the table below and the BVS method, determine the empirical oxidation number of both iron and antimony in Na$_2$FeSbO$_5$. (9 points)
[Hint: Fe is in a tetrahedral coordination environment and both antimony atoms (Sb1 and Sb2) are in octahedral coordination environments.]

\[
B = 0.37 \text{ Å}; \ Sb-O = 1.912 \text{ Å}; \ Fe-O = 1.759 \text{ Å}
\]
Selected Bond Distances of (in Å) Na₂FeSbO₅

<table>
<thead>
<tr>
<th>Paired atoms</th>
<th>Bond distance (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb1-O4</td>
<td>2.014 x 2</td>
<td>Sb1 Oxidation # = ?</td>
</tr>
<tr>
<td>Sb1-O1</td>
<td>1.933 x 2</td>
<td></td>
</tr>
<tr>
<td>Sb1-O2</td>
<td>2.030 x 2</td>
<td></td>
</tr>
<tr>
<td>Sb2-O2</td>
<td>1.980 x 2</td>
<td>Sb2 Oxidation # = ?</td>
</tr>
<tr>
<td>Sb2-O3</td>
<td>1.982 x 2</td>
<td></td>
</tr>
<tr>
<td>Sb2-O4</td>
<td>1.999 x 2</td>
<td></td>
</tr>
<tr>
<td>Fe-O5</td>
<td>1.831</td>
<td>Fe Oxidation # = ?</td>
</tr>
<tr>
<td>Fe-O5</td>
<td>1.865</td>
<td></td>
</tr>
<tr>
<td>Fe-O1</td>
<td>1.901</td>
<td></td>
</tr>
<tr>
<td>Fe-O3</td>
<td>1.914</td>
<td></td>
</tr>
</tbody>
</table>
Propose stepwise mechanisms to explain 4 of the 7 following transformations. Use curved arrow formalism to show electron movement and show all likely intermediates.

1. \[
\text{Ar-}
\begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\text{O-}
\begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\text{Ar} \\
\xrightarrow{\text{NC-CN (4 eq)}}
\text{Ar}
\begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\text{CN} \quad \text{R}_3\text{N (10 mol%)} \quad 78\%
\]
\[
\text{(Ar = p-tolyl, R}_3\text{N = chiral tertiary amine)}
\]

2. \[
\text{R}
\begin{array}{c}
\text{O} \\
\text{Br}
\end{array}
\text{Ar} + (\text{bpy})\text{CuSCF}_3
\xrightarrow{\text{“Pd(PAr}_3\text{)}_2“}
\text{Et}_3\text{N, CH}_3\text{CN, 100°C}
\xrightarrow{42\text{-}86\%}
\]
\[
\text{(bpy = 2,2’-bipyridyl; Ar=p-tolyl)}
\]

3. \[
\begin{array}{c}
\text{R} \\
\text{Br}
\end{array}
\text{Br}
\begin{array}{c}
\text{N} \\
\text{OBn}
\end{array}
\xrightarrow{\text{DiPEA}}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\xrightarrow{\text{HFIP, 0°C}}
\text{Ph}
\begin{array}{c}
\text{Ph} \\
\text{Bn = benzyl, Ph = phenyl, DiPEA = N,N-diisopropylethylamine, HFIP = hexafluoroisopropanol}}
\end{array}
\]

4. \[
\text{OTBS}
\xrightarrow{\text{I}_2, \text{THF, 0°C}}
\text{OTBS}
\begin{array}{c}
\text{Ph} \\
\text{C=C}
\end{array}
\xrightarrow{86\%}
\text{TBS= tert-butyldimethylsilyl, TMS= trimethylsilyl)}
\]

5. \[
\text{Ph}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\text{Ph}
\xrightarrow{\text{PF(NMe}_2)_3}
\text{Ph}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\xrightarrow{62\%}
\text{Ph}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\text{Ph}
\text{Ph= phenyl, Ph= phenyl, PF(NMe}_2)_3= phosphorous tri-N,N-dimethylamide)
\]
6. \[
\text{NH}_2 \quad + \quad \text{Ph} \quad \text{H} \quad \xrightarrow{\text{Et}_3\text{N}, \text{NH}_4\text{I}} \quad \text{PhCl, 120°C, air} \quad 92\%
\]

(Ph=phenyl)

7. \[
\text{Ph} \quad \xrightarrow{[\text{Au}^+ \ (5 \text{ mol})]} \quad \text{dioxane, 60°C} \quad 68\%
\]

(Ph=phenyl)
The Hamiltonian operator for a particle of mass $m$ that moves in one dimension under the action of a harmonic potential is given by:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

where $\hat{x}$ and $\hat{p}$ are the position and momentum operators that satisfy the commutation relation $[\hat{x}, \hat{p}] = i\hbar$.

1. [5 points] What are the units and physical meaning of $\omega$?

2. [20 points] One can define the operator $\hat{a}$ and its adjoint $\hat{a}^\dagger$ as:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} + \frac{i}{m\omega} \hat{p}) \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} - \frac{i}{m\omega} \hat{p})$$

With these definitions, the position and momentum operators are given by:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}) \quad \hat{p} = i \sqrt{\frac{m\omega}{\hbar}} (\hat{a}^\dagger - \hat{a})$$

Prove that $[\hat{a}, \hat{a}^\dagger] = 1$

3. [20 points] Prove that $\hat{H} = \hbar \omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right)$

4. Using $|n\rangle$ to label the $n^{th}$ energy eigenstate ($n = 0, 1, 2, \ldots$), one can show that

$$\hat{H} |n\rangle = \hbar \omega \left( n + \frac{1}{2} \right) |n\rangle$$

(a) [5 points] Sketch the energy spectrum indicating clearly where “zero” is.

(b) [5 points] What is the physical meaning of the operator $\hat{a}^\dagger \hat{a}$?

(c) [5 points] Prove that $\hat{a} |n\rangle$ is proportional to $|n - 1\rangle$ (except for when $n = 0$).

(d) [5 points] Prove that $\hat{a}^\dagger |n\rangle$ is proportional to $|n + 1\rangle$

5. [20 points] One of the many applications of the quantum harmonic oscillator is to modeling molecular vibrations. Explain in as much detail as possible why light cannot induce vibrational transitions that change the vibrational quantum number by more than one unit. This is an important selection rule in IR vibrational spectroscopy.

6. [15 points] What are “coherent states” and why are they important? (Use the same notation introduced in the previous questions).