Department of Chemistry
Cumulative Examinations

February 2, 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,                  Page 1
2) Biochemistry Cumulative Examination,                Pages 2-6
3) Inorganic Cumulative Examination,                   Pages 7-8
4) Organic Cumulative Examination,                     Page 9
5) Physical Cumulative Examination,                    Page 10

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.
Announced topic: The importance and future of analytical chemistry

1. [10] Define analytical chemistry in 50 words or less

2. [15] Summarize three singular major achievements of analytical chemistry in the past 30 years (5 lines each)

3. [10] For one of these, argue that the unique features of the subject of analytical chemistry were singularly responsible for the achievement.

4. [10] For the SAME case, argue that the credit for the achievement belongs in other discipline(s).

5. [20] Extremes in sensitivity, resolution, speed, detection limit, precision, molecular specificity are a hallmark of much current research in analytical chemistry. Give two experiments in which this is the case detailing the practical value of the ‘extreme’ information and how it is acquired.


7. [15] Based on your definition of analytical chemistry how do you think undergraduate education in analytical chemistry could be improved?
Instructions: Use the attached Information Sheet as well as your own diagrams and specific biochemical examples to answer the following questions.

1. Examine the following graph and answer the questions below. Where relevant include diagrams and biochemical examples to illustrate your answers. Also use the information on the provided Information Sheet to facilitate your answering of the questions.

![Graph showing oxygen consumption and lactate levels vs. running speed.]

- a) Suggest what goal and research questions were being addressed by the experiment which generated the plotted data in these graphs;
- b) What type of research subjects do you think were examined to collect the plotted data?
- c) Give details of the research methods that could have been used to collect the following data:
  i. Oxygen cost;
  ii. Blood lactate.
- d) What inferences can you make from the three data plots and how they relate to each other? How well do such inferences align with/address the research questions (your answer to part a) above).
- e) Based on your inferences provided in d), identify which metabolic pathways are represented by the data in the different parts of the three plots and explain what role these pathways are playing in the living system; include molecular details of the relevant pathways in your answer.
- f) Which membrane shuttle mechanism has a strong effect on the nature of some of the plotted data? Give molecular details of this mechanism and explain its metabolic role in the living system.
2. The function of brown adipose tissue is to transfer energy from food into heat. All mammals have brown adipose tissue. Use a specific metabolic example, as well as the First Law of Thermodynamics, to explain how this process works at the molecular level in mammals.

3. Explain how the Second Law of Thermodynamics can be used to predict whether a specific metabolic reaction will likely be controlled by:
   a) Changes in cellular concentrations of substrate, or by
   b) Enzyme inhibition or activation.

See next page for Information Sheet
Note: All enzymes can function physiologically in the reverse direction except those marked with an asterisk.
Summary of carbohydrate, fat, and amino acid metabolism

\[
V_0 = V_{\text{max}} \times \frac{[S]_{\text{in vivo}}}{K_m + [S]_{\text{in vivo}}}
\]
\[
\Delta G = \Delta G^\circ + RT \ln \frac{[B]/[A]}{K_{eq}}; \quad \Delta G^\circ = -RT \ln K_{eq}; \quad \Delta G = -RT \ln \frac{K_{eq}}{T}; \quad R = 8.314 \text{ J mol}^{-1}; \quad T = 310
\]
\[
E = E^\circ + \frac{(RT)}{(nF)} \ln \frac{([\text{oxidized form}]/[\text{reduced form}])}{F = 9.6487 \times 10^4 \text{ C/mol}; \quad T = 310}
\]
Summary of the regulation of carbohydrate and fat metabolism

Glycogen
- + AMP, Ca^{2+} (muscle)
- - ATP (muscle), glucose (liver), glucose 6-phosphate (muscle)

Insulin + (liver, muscle)
Glucagon + (liver)
Epinephrine + (liver, muscle)

Glyceraldehyde

Glucose
- + AMP, ADP, fructose 2,6-bisphosphate
- - ATP, citrate, alanine

Insulin + (liver, muscle)
Glucagon + (liver)
Epinephrine + (liver, muscle)

Pyruvate dehydrogenase complex
- + AMP, NAD^+, CoASH
- - ATP, NADH, acetyl-SCoA

CO_2

Acetyl-SCoA

(-) Malonyl-SCoA, acetyl-SCoA, NADH

(-) Palmitoyl-SCoA

Insulin + (liver)
Glucagon + (liver)
Epinephrine + (liver)

(-) Citrate

Citrate

Carbon cycle
- + ADP, Ca^{2+}
- - ATP, NADH, succinyl-SCoA

Fatty acids biosynthesis
Inorganic Cume Exam

This cume is based on the following article, which was announced ahead of time:


**Information from the article required to answer questions:**

(18-c-6) is a crown ether used to encapsulate the potassium ion.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR</th>
<th>$^{31}$P NMR</th>
<th>Reduction Potentials</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_2$ symmetric set of resonances</td>
<td>singlet at $\delta$ 33.6</td>
<td>-460 mV</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>single acidic proton at $\delta$ 13.84</td>
<td>singlet at $\delta$ 32.0</td>
<td>195 mV</td>
<td>One equivalent of acid results in a neutral compound with no Ru-O bond</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>singlet at $\delta$ 30.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>singlet at $\delta$ 30.69</td>
<td>-660 mV</td>
<td>One equivalent of base to compound 1 results in disappearance of the $^1$H NMR OH resonance resulting in complex 4.</td>
</tr>
</tbody>
</table>

**Exam Questions:**

1. Four structures from the article are depicted below, and have arbitrarily been assigned letters A-D.
   a. (5 points) In looking at the structures, how are these structures related?
   b. (15 points) Draw an appropriate chemical reaction that generates each compound from another starting with compound A.

2. (20 points) For the four compounds given above, use the data presented in the table and assign the structures with their appropriate observations systematically. Each row is one compound.

3. (15 points) Please provide a paragraph rationale for each assignment from question 2.
4. (10 points) Analysis of the series of the compounds using X-ray crystallography was accomplished. In examining compounds B and C, what structural differences would you expect to see using X-ray crystallography?

![Structures B and C](image)

5. (10 points) Give the oxidation state, d electron count, and valence electron count for the series A-D. If you would like partial credit, please show your work.

Use the mechanism for the catalytic hydroboration of nitriles given in the paper to answer the following questions:

![Mechanism](image)

6. a. (15 points) In this study, it was found that precatalyst D was highly active for the catalytic hydroboration of nitriles, whereas precatalyst A showed no conversion to product. Provide a reasonable explanation as to why this is the case.

b. (10 points) Explain the importance of the boryl groups in the observed catalysis.
Organic Cumulative Exam
February 2, 2019

1. In the Journal of the American Chemical Society 2019, 141, 25-28 communication, Professor John Wood described the total synthesis of Herquiline B and C.

a) Please provide a mechanism to account for the formation of product 10 from starting material 6 using phenyl iodide diacetate (PIDA) and methanol.

\[
\begin{align*}
\text{6} & \xrightarrow{\text{PIDA, MeOH, 0 °C, 15 min}} \text{10} \\
\end{align*}
\]

b) Please provide a mechanism to account for the formation of product 14 from starting material 13 below using diethylaminosulfur trifluoride (DAST)

\[
\begin{align*}
\text{13} & \xrightarrow{\text{DAST, CH}_2Cl_2, -78 °C \text{ to } 26 °C} \text{14} \\
\end{align*}
\]

2. In the Journal of the American Chemical Society 2019, 141, 148-153 publication, Professor John Porco employed a chiral phosphoric acid catalyst (CPA G) to perform the following transformation. Please provide a mechanism to account for the formation of product 6 from starting material 2.

\[
\begin{align*}
\text{2} & \xrightarrow{\text{CPA G (5 mol%), CH}_2Cl_2 (50 mM), 40 °C, 16 h.}} \text{6 (23% yield, 42% ee)} \\
\end{align*}
\]

3. In the Journal of the American Chemical Society 2019, 141, 154-158 publication, Professors Robert Grubbs and Brian Stoltz carried out the following transformations. Please provide a mechanism to account for the formation of products 20 and 21 from starting material 19.

\[
\begin{align*}
\text{18: } \text{R} = \text{H} & \xrightarrow{\text{MeI, CaCO}_3, \text{MeCN/H}_2\text{O}, (04%)}} \text{20} \\
\text{19: } \text{R} = \text{TBS} & \xrightarrow{\text{cis-3-hexene, THF, Ru-4 (4 mol%)}} \text{21} \\
\end{align*}
\]
Physical - February 2, 2019

For a particle of mass \( M \) in a one-dimensional box of length \( L \), the energy levels and wave functions are given by:

\[
E_n = \frac{\hbar^2 n^2}{8ML^2} \quad n = 1, 2, 3, \ldots
\]
\( \hbar = \text{Planck's constant} \)

\[
\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad 0 \leq x \leq L
\]

This simple model has been applied to the \( \pi - \) electrons in linear conjugated hydrocarbons. Consider 1,3 -Butadiene \( \text{C}_4\text{H}_6 \) (Assume the length 4 \( a_0 \), where \( a_0 \) is Bohr radius. In atomic units \( \hbar = M_{\text{electron}} = a_0 = 1 \))

(1) Estimate the ionization energy and electron affinity of \( \text{C}_4\text{H}_6^+ \) (non-interacting electrons), explain your results. What happens if the electrons are interacting?

(2) What happens if you add a constant perturbation over half the molecule?

(3) Explain why the quantum number \( n \) does not start from zero \( (n=0) \) or negative \( n=-1,-2,\ldots \)

(4) Calculate the probability of each \( \pi - \) electron to be in the right half of the molecule.

(5) What are the missing terms in this simple model? Explain how you would improve this model to get better results? What ab initio methods you will use to get an exact energy levels.

(6) Why the wave function is \( \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \) and not \( \sqrt{\frac{2}{L}} \cos \left( \frac{n\pi x}{L} \right) \). Explain how you choose a good variational wave function for a given problem, give an example.

(7) Estimate the average momentum of the electrons in this molecule. Explain how you calculate the kinetic and potential energy of the electrons.

(8) Explain how do you obtain the vibrational normal modes of this molecule?

(9) Can this model be used to describe the rotational motion of the different chemical bonds? Explain your results.

(10) In your previous calculation of ionization, electron affinity, and the average velocity, of the \( \pi - \) electrons which one will not change if you raise the temperature from \( T = 0^\circ \text{k} \) to \( T=1000 \text{ k} \). Explain why.