Department of Chemistry
Cumulative Examinations

December 6, 2014

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, Page 5
4) Organic Cumulative Examination, Pages 6-8
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.
Analytical Cume

Potentiometry is an electroanalytical method in which the electrochemical cell potential is measured under the conditions of no current flow. The measured potential is then used to determine the analytical quantity (e.g., concentration) of the target molecule in solutions.

A group of undergrad students are instructed to use a setup shown in Figure 1 to determine H₂O₂ concentration in aqueous solutions. The setup consists of a high impedance voltmeter for voltage measurement, an indicator electrode (Pt), and a saturate calomel electrode (SCE) as the reference electrode. The reading of the voltage, \( E_{\text{cell}} \), represents the potential difference of the indicator electrode \( E_{\text{ind}} \) and the reference electrode \( E_{\text{ref}} \):

\[
E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}}
\]

The experimental procedures include a reaction step and a measurement step:

1. **Reaction step**: a certain volume of H₂O₂ solution (either standard solutions or the unknown solution) is mixed with 50.00 ml of a composite reagent stock solution and further diluted to 100.00 ml with deionized water. The composite stock solution consists of a catalyst, 0.404 M KI (in large excess) as the reducing reagent, and buffers to keep the solution *slightly* acidic. The reaction converts all H₂O₂ into H₂O and produces I₃⁻ in about 5 minutes.

2. **Measurement step**: After the reaction is done, a certain amount of the reaction solution is transferred to a clean beaker for potentiometric measurements using a setup shown in Figure 1 at 25 °C.

Data Processing:

A series standard solutions consisting of known concentrations of H₂O₂ is prepared and subjected to the reaction and potentiometric measurements as described above. A calibration plot is made based on \( E_{\text{cell}} \) vs. \( \ln C_{\text{H₂O₂}} \) as shown in Figure 2.

This calibration plot is later used for unknown concentration determination.

The following information is provided to help you to answer questions related to the potentiometric experiments:

\[
y = 0.0118x + 0.3581 \\
R^2 = 0.9899
\]
• The electrode potential of the saturated calomel electrode stays constant at room temperature: \( E_{\text{ref}} = 0.244 \) V
• Standard electrode potential, \( E^0(\text{I}_3^- / \text{I}) = 0.536 \) V
• Standard electrode potential, \( E^0(\text{H}_2\text{O}_2 / \text{H}_2\text{O}) = 1.776 \) V
• Nernst Equation: For a reduction half reaction: \( \text{aA} + \text{bB} + \text{..} + \text{n} \text{e}^- \rightarrow \text{cC} + \text{dD} + \text{..} \)

\[
E = E^* - \frac{RT}{nF} \ln \left( \frac{[C]^d[B]^b}{[A]^a[B]^b} \right) \quad \text{and} \quad E = E^* - \frac{0.0592}{n} \log \left( \frac{[C]^d[B]^b}{[A]^a[B]^b} \right) \quad \text{at} \ 25 \ ^\circ\text{C}
\]

• At \( 25 \ ^\circ\text{C}, \ 2.3RT/F = 0.0592 \) V, \( F = 96,485 \) C mol\(^{-1}\)
• Concentration error = measurement error/sensitivity
• Sensitivity \( \Phi = \frac{|d(\text{measurement})|}{d(\text{determination},c)} = \frac{s_y}{s_c} \)

Based on the above information, answer questions 1-8:

1. a) Write and balance the reaction when \( \text{H}_2\text{O}_2 \) is mixed with the composite reagent.  
   b) What is the total charge of electrons (in Coulombs) transferred in reducing 1 mmol \( \text{H}_2\text{O}_2 \)?  
   (10 points)

2. In one experiment, \( 10.00 \) ml of \( 2.65 \times 10^{-3} \) M \( \text{H}_2\text{O}_2 \) standard solution is mixed with \( 50.00 \) ml of the composite reagent stock solution and diluted by deionized water to \( 100.00 \) ml. (20 pts)
   a) Predict the theoretical \( E_{\text{cell}} \) value of this solution if a setup in Figure 1 is used. 
   b) Use the data in Figure 2 to predict \( E_{\text{cell}} \) value.

3. What is the sensitivity of the quantitation method based on the calibration curve in Figure 2?  
   Show derivation steps to receive full points. (10 points)

4. Draw relationships of following (10 pts):
   1) \( E_{\text{cell}} \) as a function of \( \text{C}_{\text{H}_2\text{O}_2} \)
   2) Sensitivity, \( \Phi_{E,C} \) as a function of \( \text{C}_{\text{H}_2\text{O}_2} \).

   Clearly label x- and y- axis. Use equations to explain why such relationships exist.

5. If the standard deviation of \( E_{\text{cell}} \) measurements, \( s(E_{\text{cell}}) \), can be regarded as a fixed value, derivate the relationship of concentration error, \( s(\text{C}_{\text{H}_2\text{O}_2}) \), as a function of \( \text{C}_{\text{H}_2\text{O}_2} \) and draw the relationship. Clearly label the x- and y- axis. (10 pts)
6. For the unknown solution measurement, 10.00 ml solution is taken from the unknown sample, mixed with 50.00 ml of the composite reagent stock solution for reaction, and finally diluted to 100.00 ml for potentiometric measurement. A reading of 250 mV is obtained. Calculate the concentration of $\text{H}_2\text{O}_2$ in the original unknown solution (not the 100 ml diluted solution). (10 pts)

7. During the measurement of another unknown solution, one student made a mistake by only taking 20.00 ml of composite reagent stock solution instead of 50.00 ml for reaction while all the other procedures were same as in question 6. This student did not realize this mistake and used the calibration curve in Figure 2 to calculate the unknown concentration. Would this lead to a higher or lower estimation of $\text{H}_2\text{O}_2$ concentration? Support your prediction with graphs or equations. (20 pts)

8. a) Why iodide is used to detect $\text{H}_2\text{O}_2$? (5 pts)
   b) Why is detection of $\text{H}_2\text{O}_2$ useful? Name at least one application. (5 pts)
Biochemistry Exam Questions for December 2014

1. The interconversion of glucose and fructose 1, 6-bisphosphate occurs during both glycolysis and gluconeogenesis (i.e. glucoso catabolism and anabolism).
   a. Summarize the distinguishing features, including the net reactions and enzymes involved, between the catabolic and anabolic pathways connecting these intermediates. (20 points)
   b. What primarily assures the directionality of the catabolism of glucose, i.e., what prevents the catabolism of glucose from running backwards when the concentration of fructose 1, 6-bisphosphate is high? (7 points)
   c. How does [ATP] help regulate the direction of substrate flow between glucose and fructose 1, 6-bisphosphate? (10 points)
   d. What major hormones control the direction of these two pathways and how? (8 points)

2. Daily ATP Utilization by Human Adults
   a. A total of 7.3 kcal of free energy is needed to synthesize ATP from ADP and inorganic phosphate (P) when the reactants and products are both at 1 M concentration (standard state). Since the actual physiological concentrations of ADP, P, and ATP in the cells are not 1 M, the free energy required to synthesize ATP under physiological conditions is different from $\Delta \text{G}^0$. Calculate the free energy required to synthesize ATP in the human liver cell when the physiological concentrations of ATP, ADP, and P are 3.5, 1.50, and 5.0 mM, respectively. (15 points)
   b. A normal 68-kg (150-lb) adult requires a caloric intake of 2000 free kcal of food per 24-h period. This food is metabolized and the free energy used to synthesize ATP, which is then utilized to do the body's daily chemical and mechanical work. Assuming that the efficiency of converting food energy into ATP is 50 percent, calculate the weight of ATP (M$_r$~507) utilized by a human adult in a 24-h period. What percent of the body weight does this represent? (15 points)

3. The pentose phosphate pathway.
   a. Describe the two major functions of the pentose phosphate pathway. (10 points)
   b. Suggest a reason why patients that are deficient in glucose-6-phosphate dehydrogenase experience a hemolytic anemia when they eat foods containing oxidants such as fava beans? Justify your answer with a cogent biochemical explanation (7 points)
   c. Why do cancer cells consume more glucose in the pentose phosphate pathway relative to the amount consumed in glycolysis than normal cells? (8 points)
Inorganic Cumulative Exam

December 6, 2014

1. (30 points) Complete the syntheses below showing the structures of the products and specifying the preferred isomer if different isomers are possible.

\[
\begin{align*}
K_2PtCl_4 & \xrightarrow{4NH_3, \text{heat}} A & \xrightarrow{2HCl} & B \\
\text{excess} & & \text{excess} \\
C & \xrightarrow{2NH_3} D & \xrightarrow{Ag_2SO_4, H_2O} E & \xrightarrow{KCl} F
\end{align*}
\]

2. (20 points) The complex cis-platin exhibits anti-cancer activity. Describe briefly its mechanism of action (few sentences).

\[
\text{Cl}_{n-} \text{Pt} \text{Cl}_{\text{NH}_3} \text{NH}_3
\]

Cis-platin

3. (25 points) In cases where cis-platin resistance develops, oxaliplatin has been used. Show a synthetic route to oxaliplatin provided you have access to any ligands, reagents you may need.

\[
\text{Oxaliplatin}
\]

4. (25 points) The \(^1\text{H}\) NMR spectrum (200MHz) of the chemical warfare agent Sarin (phosphonofluoridic acid) is shown below. Assign and interpret the spectrum showing all appropriate coupling constants. What splitting patterns do you expect to see in the \(^{19}\text{F}\) and \(^{31}\text{P}\) NMR spectra? Explain your answer.
1. (50 pts) Living polymerization reactions have been developed over the last 30 years to provide precise control over the uniformity, predefined molecular weight, controlled topology, and precisely placed functional groups within a highly diverse family of polymeric architectures (e.g., stars, bottlebrushes, combs, etc). This family of reactions is a key tool in the development of nanomaterials with well-defined structures and properties. Write plausible mechanisms for any two of the following three living polymerization reactions.

a.

b.

c.
2. (25 pts) Höger, Sheiko & Matyjaszewski [JACS 2014 136, 12762-12770] recently reported the synthesis of molecular stars with spoked wheel cores and bottlebrush arms using an ATRP approach. Their GPC data indicated the formation of molecular stars with the predicted molecular weight (i.e., where \( R^2 \) in the figure below is a bottlebrush arm comprised of \((300-g-150)_n\) units); however, their AFM data on mica substrates suggests that the structure and uniformity of the sample is time-dependent. **Briefly rationalize their findings.**
3. (25 pts) Armes and coworkers have recently reported the synthesis of nanoparticles with relatively controlled diameters using 4,4'-azobis-4-cyanopentanoic acid (ACVA) as initiator, benzyl methacrylate as monomer, and two different macromolecular chain transfer reagents to generate diblock copolymers in a RAFT polymerization sequence in ethanol. The authors systematically varied the polymethacrylic acid chain transfer agent ratios while keeping the benzyl methacrylate feed constant. The resulting diblock copolymer product solutions where then deposited onto glow-discharged electron microscopy grids, stained with 0.75% UO₂(O₂CH)₂, and analyzed by transmission electron microscopy to produce the data set below. 

**Draw the products of the RAFT polymerization and briefly rationalize their observations.**

![Diagram of diblock copolymers](image)

**2 diblock copolymers:**
- PMMA₆₂-PBzMA₃⁵₀
- PMMA₁₇₁-PBzMA₃⁵₀

![Figure 1](image)

Figure 1. Representative TEM images and corresponding phase diagram determined for \([x \text{PMMA}_{62} + (1-x) \text{PMMA}_{171}] - \text{PBzMA}_{350}\) particles synthesized by RAFT dispersion polymerization of BzMA at 70 °C using a binary mixture of PMMA₆₂ and PMMA₁₇₁ macro-CTAs in ethanol at 20% w/w solids. Intensity-average diameters and polydispersities were determined by DLS in ethanol (0.10% w/w solids). S indicates spheres and V indicates vesicles.
For the hydrogen atom:

1. Indicate the value of (use your favorite units, but say what they are):
   a. The first ionization energy: $I = \underline{\hspace{2cm}}$ (4 points)
   b. The ground-state energy: $E = \underline{\hspace{2cm}}$ (4 points)
   c. The ground-state kinetic energy: $T = \underline{\hspace{2cm}}$ (4 points)
   d. The ground-state potential energy: $V = \underline{\hspace{2cm}}$ (4 points)

2. Write down the equation that you would need to solve in order to find the energy spectrum of the hydrogen atom. Define in detail every term in this equation. (12 points)

3. Provide a complete description of the energy spectrum. You can use plots and/or equations (it is more challenging to be accurate with just words, but you can try that too). (12 points)

4. What is the Bohr radius? What is its numerical value, and how would you determine it if you did not know its numerical value? (10 points)

5. Sketch the radial probability densities corresponding to $n=1$ through $n=3$, labeling the axes and indicating as many features of these densities as you can (note: these are 6 plots). (18 points)

6. Name three operators that commute with the Hamiltonian. (12 points)

7. How does the energy spectrum change when you apply:
   a. A static electric field (10 points)
   b. A static magnetic field (10 points)
### Periodic Classification of the Elements

<table>
<thead>
<tr>
<th>Group I A</th>
<th>1 H (1.00797)</th>
<th>Group II A</th>
<th>2 He (4.0026)</th>
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<td>1 Li (6.939)</td>
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<td>21 Sc</td>
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<td>24 Cr</td>
<td>40 Zr (91.22)</td>
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<td><strong>Period IV</strong></td>
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<td>48 Cd (112.40)</td>
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<td>33 As</td>
<td>49 In</td>
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