Department of Chemistry
Cumulative Examinations
September 25, 2010

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 1-11
2) Biochemistry Cumulative Examination, Pages 12-13
3) Inorganic Cumulative Examination, Page 14
4) Organic Cumulative Examination, Pages 15-16
5) Physical Cumulative Examination, Page 17

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. Chemists take advantage of the phenomenon of absorbance for a variety of purposes. Discuss the characteristics of UV/visible absorbance versus IR absorbance with respect to analysis. How are they used? Are there particular advantages of one form of absorbance over the other for particular applications and why?

(10 points)

2. 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 points)

3. "Efficiency" is a commonly used term in column chromatography.
   a. What does the term ‘efficiency’ mean in column chromatography? (5 points)
   b. How is efficiency measured? (5 points)
   c. What theoretical model is most commonly used to describe the efficiency of a chromatographic column? Provide the relationship and describe the parameters to the extent that you are able. (10 points)

4. Every measurement is characterized by some degree of random error, as reflected by the standard deviation associated with the measurement method, $s_x$. The concentration or quantity of an analyte species is often not obtained directly from a measurement. Rather, some relationship is used to convert the measured property to analyte concentration.
   a. In general, how does uncertainty in a measurement of a property, $s_x$, such as voltage, current, absorbance, etc., propagate to uncertainty in concentration, $s_C$? (5 points)
   b. Depending upon the relationship between the measured quantity and concentration, the concentration error can be concentration dependent. Discuss and compare the concentration dependence of random error for a fluorescence measurement versus an absorbance measurement (remember that an absorbance measurement is really a transmittance measurement). Assume that the standard deviation associated with the measurement is constant with concentration (i.e., standard deviation of fluorescence signal, $s_F$=constant and standard deviation of transmittance measurement, $s_T$=constant). (15 points)
5. List at least 5 common ways to either identify or correct for systematic errors associated with a method for quantitative determination. (20 points)

6. Hypothesis testing is commonly used in quantitative chemical analysis. Name and describe the relevant statistical tests used to address the following questions:
   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?
(20 points)
Possibly (but mostly not) useful relationships for this exam:

\[ M(2) = \frac{M(1) \times V(1)}{V(2)} \]

\[ E = |x_i - x_t| \quad E_r = \frac{(x_i - x_t)}{x_t} \times 100 \]

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}} \]

\[ s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1}} \quad ; \quad s = \sqrt{\frac{\sum_{i=1}^{N} x_i^2 - \left( \frac{\sum_{i=1}^{N} x_i}{N} \right)^2}{N-1}} \]

\[ s^2 = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1} \]

\[ \%RSD = CV = \frac{s}{x} \times 100 \]

\[ s_{pooled} = \sqrt{\frac{s_1^2(N_1-1) + s_2^2(N_2-1) + s_3^2(N_3-1) + \ldots}{N_1 + N_2 + N_3 + \ldots - N_t}} \]

\[ S_m = \frac{s}{\sqrt{N}} \]
\[
\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}
\]

\[
z = \frac{x - \mu}{\sigma}, \quad z = \frac{x - \mu}{\sigma/\sqrt{N}}
\]

\[
t = \frac{x - \mu}{s/\sqrt{N}}
\]

\[
\mu = \bar{x} \pm \frac{z \cdot \sigma}{\sqrt{N}}
\]

\[
\mu = \bar{x} \pm \frac{t \cdot s}{\sqrt{N}}
\]

\[
t = \frac{\bar{x}_1 - \bar{x}_2}{s_{pooled} \sqrt{\frac{N_1 + N_2}{N_1 N_2}}}
\]

\[
F = \frac{s_1^2}{s_2^2}
\]

\[
Q = \frac{|x_q - x_n|}{w}
\]
\[ N = \frac{1 - p}{p \sigma_{\text{red,rel}}^2} \]

\[ S_{\text{overall}}^2 = S_{\text{sampling}}^2 + S_{\text{method}}^2 \]

**Linear regression relationships:**

\[ S_{xx} = \sum_{i=1}^{N} (x_i - \bar{x})^2 = \sum_{i=1}^{N} x_i^2 - \left( \frac{\sum_{i=1}^{N} x_i}{N} \right)^2 \]

\[ S_{yy} = \sum_{i=1}^{N} (y_i - \bar{y})^2 = \sum_{i=1}^{N} y_i^2 - \left( \frac{\sum_{i=1}^{N} y_i}{N} \right)^2 \]

\[ S_{xy} = \sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y}) = \sum_{i=1}^{N} x_i y_i - \frac{\sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i}{N} \]

\( N = \text{number of paired } (x_i, y_i) \text{ data used} \)

\[ \bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} \quad \text{and} \quad \bar{y} = \frac{\sum_{i=1}^{N} y_i}{N} \]
\[ s_c = \frac{s_r}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 S_{xx}}} \]

\[ y = a + b - c \quad s_y = \sqrt{s_a^2 + s_b^2 + s_c^2} \]

\[ y = \frac{a \cdot b}{c} \quad \frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2} \]

\[ y = a^x \quad \frac{s_y}{y} = x \left(\frac{s_a}{a}\right) \]

\[ y = \log_{10} a \quad s_y = 0.434 \frac{s_a}{a} \]

\[ y = \text{anti} \log_{10} a \quad \frac{s_y}{y} = 2.303 s_a \]

\[ \frac{d e^u}{dx} = e^u \frac{du}{dx} \quad \frac{d \ln u}{dx} = \frac{1}{u} \frac{du}{dx} \]

\[ \frac{P}{P_0} = 10^{-\varepsilon b C} \quad T = \frac{P}{P_0} \quad A = -\log T \quad T = 10^{-A} \]

\[ T = 10^{-\varepsilon b C} = e^{-2.3 \varepsilon b C} \]

\[ A = \varepsilon b C \]

\[ c = v \lambda \]

\[ \lambda = \hbar c/E \]

\[ F = k P_0 (1 - 10^{-\varepsilon b C}) \approx 2.3 \varepsilon b C (k P_0) \]
96,485 C = 1 faraday (F)
(charge of 1 mole of elementary charges)

\[ n_A = \frac{Q}{nF} \]

\[ I = \frac{Q}{t} \quad \text{where } I \text{ is constant current, } Q \text{ is charge, } t \text{ is time} \]

\[ Q = It \]

\[ K_D = \frac{(a_A)_{org}}{(a_A)_{aq}} = \frac{[A]_{org}}{[A]_{aq}} \]

\[ n_1 = \left( \frac{V_{aq}}{V_{aq} + V_{org} K_D} \right) n_0 \]

\[ n_i = \left( \frac{V_{aq}}{V_{aq} + V_{org} K_D} \right)^i n_0 \]

\[ [A]_{aq} = [A]_{org} \left( \frac{V_{aq}}{V_{aq} + V_{org} K_D} \right) \]

\[ \frac{n_{org}}{n_0} = \left( \frac{1 - n_1}{n_0} \right) = \left( 1 - \frac{V_{aq}}{V_{aq} + V_{org} K_D} \right) = \frac{K_D V_{org}}{V_{aq} + K_D V_{org}} \]
\[
\frac{[A]_{aq,i}}{[A]_{aq,0}} = \left(\frac{V_{aq}}{V_{aq} + V_{org} K_D}\right)^i
\]
\[
\frac{[A]_{org,i}}{[A]_{org,0}} = \left(\frac{K_D V_{org}}{V_{aq} + V_{org} K_D}\right)^i
\]
\[
D = \frac{C_{org}}{C_{aq}}
\]
\[
\frac{C_{A,aq,i}}{C_{A,aq,0}} = \left(\frac{V_{aq}}{V_{aq} + V_{org} D}\right)^i
\]
\[
\frac{C_{A,org,i}}{C_{A,org,0}} = \left(\frac{DV_{org}}{V_{aq} + V_{org} D}\right)^i
\]
\[
D = \frac{K_D}{1 + \frac{K_a}{[H^+]_{aq}} [H^+] + K_a} \cdot K_D
\text{ for organic acids}
\]
\[
D = \frac{K_D}{1 + K_f [I^-]} \quad \text{and} \quad K_f = \frac{[I^-]}{([I_2][I^-])} \text{ for } I_2 + I^- \rightleftharpoons I_3^-
\]
\[
K_C = \frac{(a_A)_S}{(a_A)_M} = \frac{[A]_S}{[A]_M}
\]
area = πr^2

\[ u = \frac{L}{t_M} \]
\[ v = \frac{L}{t_R} \]
\[ t_R = t_S + t_M \]

\[ v = \frac{L}{t_R} = \frac{L}{t_M} \cdot \frac{t_M}{t_R} = u \cdot \frac{t_M}{t_R} \]

\[ v = u \left( \frac{V_M}{V_M + V_S K_C} \right) \]

\[ k_A = \left( \frac{t_R - t_M}{t_M} \right) = \frac{t_S}{t_M} \]

\[ \alpha = \frac{k_B}{k_A} = \frac{(t_{R,B} - t_M)}{t_{R,A} - t_M} = \frac{(t_{R,B} - t_M)}{(t_{R,A} - t_M)} = \frac{K_B}{K_A} \]

\[ N = \frac{L}{H} \]

\[ H = \frac{\sigma^2}{L} \]
\[ N = \frac{L^2}{\sigma^2} \]
\[ \tau = \frac{\sigma}{L} \frac{1}{t_r} \]
\[ \sigma = \frac{LW}{4t_r} \]
\[ N = 16 \left( \frac{t_r}{W} \right)^2 \]
\[ H = \frac{\sigma^2}{L} = \frac{LW^2}{16t_r^2} \]
\[ H = A + \frac{B}{u} + (C_s + C_M)u \]
\[ R_s = \frac{2|t_{r,B} - t_{r,A}|}{W_A + W_B} \]
\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k_B}{1 + k_B} \right) \]
\[ \frac{V_sK_B}{V_M} = \left( \frac{t_r - t_M}{t_M} \right) = \frac{t_s}{t_M} = k_B \]
\[ \alpha = \frac{k_B}{k_A} = \frac{K_B}{K_A} \]
\[ N = 16R_s^2 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{1 + k_B}{k_B} \right)^2 \]

\[ t_{R,B} = \frac{16R_s^2 H}{u} \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{1 + k_B}{k_B} \right)^3 \]
1. (10 points) Which of the following pentapeptides is (are) likely to have a net positive charge in an aqueous buffer of pH 7.5? Justify your answer.
   (a) Gly-Ser-His-Arg-Asp
   (b) Gly-Gln-Glu-Arg-Asp
   (c) Gly-Pro-Arg-Glu-Lys
   (d) Gly-Ser-His-Glu-Arg
   (e) None of the above

2. (10 points) Which of the amino acids has (have) a side group that can function both as a proton donor and acceptor under physiological conditions (pH 7.4)? Justify your answer.
   (a) Ser
   (b) Cys
   (c) Lys
   (d) His
   (e) Ala

3. (i) (4 Points) Which of the following amino acids has (have) two chiral centers?
   (a) Leu
   (b) Ile
   (c) Thr
   (d) Lys
   (e) Gly

   (ii) (6 points) Calculate the pH of a 0.025 N solution of an ideal, strong acid at 25 °C.

4. (10 points) Which of the following solutions is (are) expected to exhibit optical activity? Justify your answer.
   (a) A 0.01 M solution of the tetrapeptide Gly-Gly-Gly-Gly
   (b) A 0.01 M solution of Gly-Ala-D-Ala-Gly
   (c) An equal volume mixture of 0.01 M Gly-Ala and 0.01 M Gly-D-Ala
   (d) An equal volume mixture of 0.01 M Gly-D-Ala and D-Ala-Gly
   (e) A 0.01 M solution of Ala-D-Ala

   (D-Ala is D-Alanine)

5. (10 points) Draw the structure of the following oligopeptide with its cysteine residue cross-linked by a disulfide bond.

   Ser-Ala-Cys-Pro
6. (10 points) Calculate the pH of a 0.01 N solution of the very weak acid HY (K_a of HY is 3.2 x 10^{-7}). State any assumption that you are going to use for this calculation.

7. (20 points) Calculate the change in pH caused by dissolving 1.025 g of anhydrous sodium acetate in 100 ml of 0.25 M acetic acid (molecular weight of anhydrous sodium acetate = 82; assume the apparent pK_a of acetic acid to be 4.74).

8. (10 points) Explain why peptide bonds are planar.

9. (10 points) Two complementary strands of DNA readily form a double helix at pH 7.0. However, if the pH is raised above 9.5 the double helix dissociates into two separate strands. Why do the strands dissociate?
Inorganic Cumulative Exam  
September 25, 2010 (All things about boron)

1. (20 pt) Boron hydride compound $B_3H_9$ was tested as a rocket fuel during the Cold War. Please (a, 5 pt) draw its structure; (b, 5 pt) determine its point symmetry group; (c, 10 pt) describe the types of covalent bonds in this molecule.

2. (20 pt) Ammonia-borane ($NBH_6$) has attracted significant interest in recent years as a promising hydrogen storage material. Please (a, 5 pt) calculate the mass percentage of H; (b, 5 pt) draw its Lewis dot structure. (c, 10 pt) Borazine is one of the most stable products formed from the dehydrogenation of ammonia-borane. Draw its structure and determine the mass percentage of H released from ammonia-borane upon the formation of borazine.

3. (15 pt) Sketch the structure of $B_3H_6$ and construct the SALCs of $\sigma$($B$-$H$) using a proper character table chosen from below.

4. (45 pt) The first metal oxoboryl complex trans-[$(Cy_3P)_2BrPt(BO)$] (Cy being cyclohexyl) was reported in Science this year. Please determine the followings based on your knowledge of basic inorganic chemistry: (a, 10 pt) the charge and Lewis dot structure of the “BO” ligand; (b, 25) a MO diagram that contains all valence orbitals around the Pt center and comment on the role of “BO”; and (c, 10 pt) the “BO” stretch frequency ($v_{BO}$) assuming its force constant comparable to that of CO ($v_{CO} \sim 2050$ cm$^{-1}$).

Character tables potentially useful for Q3

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14
Three reaction schemes from a recent literature article (J. Org. Chem. 2010, 75, 5048-5064) entitled, An Enantioselective Convergent Route to Pamamycin 621A are copied below.

I. Using curved arrows, provide a mechanism for the conversions of

(i) 11 to 12, (ii) 14 to 15, (iii) 18 to 19, (iv) 23 to 24, (v) and (vi) 26 to 27 (both steps), and (vii) 27 to 9.

(Seven mechanisms in all for 70 points, variable credits). The workup of each of these reactions has to be assumed and shown in the complete mechanism.

**SCHEME 2**

**SCHEME 3**
II. (30 points, variable credits)

(i) Provide the oxidation number of I in NaIO₄.

(ii) Define oxidation number?

(iii) Give a complete balanced equation (show the half-reactions) for the oxidation of ethanol to acetic acid by chromate ion.

(iv) How many moles of permanganate are required to oxidize one mole of toluene to benzoic acid. Explain your answer.

III. Extra-credit (10 points)

(i) Name the first reaction in Scheme 2. (ii) Name the chemist(s) who discovered the reaction involving the conversion of aldehydes to acetylenes (the last two reactions in scheme 5). (iii) Provide the structures for DDQ, TMEDA, TBAF, MOMCl, Dess-Martin Periodinane.
The following questions pertain to the oxygen molecules (O₂) in this room, which have a mass of \(\sim 32\) g/mol, a bond length of 0.12 nm, and a vibrational frequency of \(\sim 1510\) cm\(^{-1}\).

Fundamental constants:
- \(R \approx 8.3\) J/(K mol)
- \(k_B \approx 1.4 \times 10^{-23}\) J/K
- \(\hbar \approx 6.6 \times 10^{-34}\) J s
- \(N_A \approx 6 \times 10^{23}\) molecules/mol

a. (10 points) Predict the average translational kinetic energy of oxygen (in kJ/mol units).

b. (10 points) Predict the root-mean-squared translational velocity of oxygen (in m/s units).

c. (10 points) Do you expect the translational root-mean-squared velocity of oxygen to be larger or smaller than its most probably translational velocity (explain very briefly, in words)?

d. (10 points) Predict the average rotational energy of oxygen (in kJ/mol units)?

e. (10 points) What would the average translational kinetic energy of oxygen molecules be if they were confined to a two dimensional (rather than three dimensional) space?

f. (10 points) What is the rotational moment of inertia of oxygen (including units)?

g. (10 points) What is the vibrational force constant of oxygen (including units)?

h. (10 points) Predict the vibrational zero-point energy of each oxygen molecule (expressed in J/molecule units)?

i. (10 points) If oxygen's vibrational degree of freedom behaved classically, what would the average vibrational kinetic energy of each oxygen molecule be (in J/molecule units)?

j. (10 points) If oxygen's vibrational degree of freedom behaved classically, what would the average vibrational potential energy of each oxygen molecule be (in J/molecule units)?
## Periodic Classification of the Elements

### Periodic Table

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