Department of Chemistry
Cumulative Examinations

January 10, 2015

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 2-4
3) Inorganic Cumulative Examination, Pages 5-6
4) Organic Cumulative Examination, Pages 7-8
5) Physical Cumulative Examination, Pages 9-11

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 Cumulative Examination

January 10, 2015

Analytical chemistry is a quantitative science in which phenomena, measurements and instrumentation are best understood if they can be expressed in the form of an equation. This exam asks (i) that you write equations which apply to and/or describe the topics indicated below, including definitions of all terms in the equations, and (ii) that you then comment in the space of a page or less, on the significance and implications of each equation in analytical chemistry.

Half credit is for the equation and half for the comment. Give units wherever possible.

(Please write your answer clearly. If your answer can not be read, it won't get graded.)

YOU SHOULD ANSWER ONLY 10 OF THE 12 QUESTIONS

1. Mass analysis equation for a time-of-flight mass spectrometer
2. Number of theoretical plates in a thin layer chromatogram
3. Height equivalent of a theoretical plate
4. Nernst equation
5. Electron binding energy in XPS (ESCA)
6. Diffusion equation
7. Relationship between wavelength and wavenumber
8. Vibrational energy spacing in molecules
9. Relationship of half-life to rate constant for unimolecular reaction
10. Time constant for pure RC circuit
11. Beer's Law expressed in terms of detected intensities
12. Faraday's laws of electrolysis
1. The two fragments shown below become connected through phosphodiester bond formation. Please draw the final product. (15 points)

```
\[ \text{ssDNA} \]
```

```
\[ \text{Base} \]
```

```
\[ \text{OH} \]
```

```
\[ \text{O} \]
```

```
\[ \text{P} \]
```

```
\[ \text{O} \]
```

```
\[ \text{OH} \]
```

```
\[ \text{Base} \]
```

```
\[ \text{O} \]
```

```
\[ \text{P} \]
```

```
\[ \text{O} \]
```

2. The cDNA sequence of the protein ubiquitin C-terminal hydrolase L1 (UCHL1) reads (only one strand is shown):

```
5' ATGCAGCTCAAGCCGATGGAGATCAACCCCGAGATGCTGAACAAAGTGCTGTC
CCGCTGGGGGTCCGCGCGGAGTGCCCTGACGCTGGGGCTGGGAAGAG
GAGTCTCTGGCTGGTGCAGCGGCTCGCCTGCCGCTGCTGCTGCTGCTGCT
TCACGGCCAGCTAGAAGACTTCAGGGAAAGCGAGATGAGCTGAGGAG
AGATTTAGTCCCTAAAGTGTACATCTCATGAAGCAGCACCATTGGGAATTCCTGTCGC
ACAATCGGAATTTATGCAGCGATGGGCCAATAATCAAGACAAACTGGGATTTGAGG
ATGGATCAGTCTGAAACAGTTTTCTTCTGAAACAGAGAATGTCCTGAGAAG
CAGAGCAAAATGCTTTGAAAGATGAGGCCATACAGGCAGCCCATGATGCGCCTG
GCACAGGAAGGCGCAATCTGGTCTAGATGAACGGATTTATCTTCTTCATTTTCATCT
TTAACACGCTGGATGGCCACCTCTATGAACCTTGTGGAGCAATGGCCTTTCCGCT
GAACCATGGCCGCTACAGGAGCAACCCTGTGCAGGAGCAAGCTGCGCAAGTTCTGC
AGAGATTTACCGAGGCTGACAGGAGGAGATGTCCCTCTCTGGCCGCTCTCT
GCAAGCGAGCCTAA-3'
```

Based on this information, design a forward and reverse primer for the PCR reaction to amplify this DNA. Design your primers such that subsequent treatment of the PCR product with the restriction endonucleases BamHI and Xhol produces "sticky ends" so that the cDNA can be inserted into the pGEX-6P-1 vector to create a fusion construct with the glutathione S-transferase affinity tag (Figure 1). The nucleotide sequence of the restriction sites as part of the polylinker sequence is shown in the figure above the vector map. (25 Points)
Figure 1: Schematic drawing of the pGEX-6P-1 vector. The sequence of the polylinker region where your gene of interest can be inserted to generate a fusion construct with the glutathione S-transferase (GST) affinity tag is shown above the plasmid.

3. A scientist is interested in understanding the physiological basis of alcoholism. She hypothesizes that the levels of the enzyme alcohol dehydrogenase, which is involved in the degradation of ethanol, are increased in individuals who routinely consumed alcohol. She develops a rat model system to test this hypothesis. What steps should she take to determine if the transcription of the gene for alcohol dehydrogenase is increased in the livers of rats who are chronically fed alcohol compared to control, abstinent population? (20 points)
4. Use the following hypothetical mRNA and the codon table below to predict the **longest possible** translation product from the provided sequence. List the sequence of the obtained peptide and indicate N and C termini. (15 points)

5'UAUGUAAUAAUAAUGCCCGAGCAACACGCAUGGCGUGAGAAAAGUUGAAU3'

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<td>Val</td>
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5. The enzyme Tsp451 recognizes the 5-base-pair site 5'-G-T-(either C or G)-A-C-3'. This site appears in exon 4 of the human gene for α-synuclein, where, in a rare form of Parkinson's disease (PD), it is altered by a single G-to-A mutation. Suppose you have primers that can be used in PCR to amplify a 200 base-pair segment of exon 4 containing the Tsp451 site, and that the Tsp451 site is 80 base pair from the right primer (forward primer). Describe the steps you would take to determine if a PD patient has this α-synuclein mutation. (25 points)
1. (40 points) The Figure below depicts a partial MO scheme for a diatomic molecule comprised of oxygen and an early transition metal atom. (Electrons not shown.) For simplicity the scheme only takes account of the 4s and 3d atomic orbitals of the metal and the 2p atomic orbitals of oxygen. The energy level with mostly 2s(O) character falls at much lower energy. Neither it NOR the 2s(O) valence electrons pertain to this question. Assume the internuclear axis defines the z direction.

![Diagram](image)

A. The MO’s in the scheme provided have σ, π, or δ symmetry. Identify a π* molecular orbital in the scheme, and sketch a contour. Assume that the x-axis is vertical and that the z-axis points to the right of the page. Label the two nuclei, and identify participating atomic orbitals.

B. Identify the δ orbital(s) and explain your reasoning.

C. ScO and VO are both paramagnetic molecules, but one has more unpaired electrons than the other. Explain.

D. Predict whether VO has a dipole moment and, if so, which end is positive?

5
2. (30 points) Each of the following contours is a qualitative representation of an unoccupied MO of either N₂, CO, or HF. Assume that the internuclear axis is the z-axis in each case and that the page is the xz plane. Assign each contour to a molecule, and indicate the nature of the MO (e.g., σ* antibonding). Show your reasoning by assigning specific atoms to the drawings, and identifying all participating atomic orbitals.

   I

   II

   III

3. (30 points) The following figure shows three molecules of increasing complexity. Predict how many distinct types of atoms in each. In other words, how many different \(^1\text{H}, \(^{13}\text{C}\) and \(^{15}\text{N}\) chemical shifts would you expect from an isotopically enriched form?
Department of Chemistry, Purdue University
January 10, 2015

Topic: Mechanistic Aspects of Controlled Chain-growth Polymerizations in Synthesis of Conjugated Polymers (JACS from 2012-2014)

(25 pts) Condensation polymerization typically proceeds in a step-growth manner, in which the resulting polymers presents a broad molecular weight distribution, and control over molecular weight and chain end fidelity is difficult. However, the mechanism of condensation polymerization of some monomers has been converted from step-growth to chain-growth by means of activation of the polymer end group, either due to the difference in substituent effects between the monomer and the polymer, or due to successive intramolecular transfer of catalyst to the polymer end. Please 1) list the characteristics associated with step-growth mechanism and chain-growth mechanism (20 pts), and 2) explain how to ensure a chain-growth polymerization to proceed in a controlled (living) manner (5 pts).

(50 pts) Write plausible mechanisms for any two of the following three controlled chain-growth polymerization reactions.


(25 pts) **Write a plausible mechanism for cyclopolymerization polymerization and explain the role of additive**

(1) In the case of a chemical reaction, the temperature-dependent change in Gibbs free energy is linked to the enthalpy change via the Gibbs-Helmholtz equation

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p = -\frac{\Delta H}{T^2}$$  \hspace{1cm} (1)

(a) Derive equation 1 from the Gibbs free energy.

(b) By starting from the temperature dependence of the Gibbs free energy under standard conditions, derive the following equation ($K$ is the equilibrium constant, $R$ is the gas constant):

$$\left[ \frac{\partial (\ln K)}{\partial \left( \frac{1}{T} \right)} \right]_p = -\frac{\Delta H^0}{R}$$  \hspace{1cm} (2)

(c) Assume that $\Delta H^0$ remains constant between $T_1$ and $T_2$ characterized by $K_1$ and $K_2$, respectively. On the basis of equation 2 (known as van’t Hoff equation), provide a relationship, which links changes in temperatures and equilibrium constants!

(2) Consider $N$ molecules of an ideal gas.

(a) Show that the change in entropy of this gas is described by:

$$dS = N \left( \frac{c_p}{T} dT + k \frac{dV}{V} \right)$$  \hspace{1cm} (3)

(b) The ideal gas occupies an initial volume $V_1$, and is separated from another volume $V_2$, which is evacuated. Derive an expression for the entropy change $\Delta S$ as a function of $V_1$ and $V_{tot} = V_1 + V_2$ after the barrier between $V_1$ and $V_2$ has been removed. Indicate whether $\Delta S < 0$, $\Delta S > 0$, $\Delta S = 0$. Justify your answer!

(c) One liquid of mass $m_1$, specific heat $c_1$, and temperature $t_1$, is mixed with another liquid of mass $m_2$, specific heat $c_2$, and temperature $t_2$. After some time, the mixed system will reach thermal equilibrium at a temperature $T_{eq}$. Derive an expression for $T_{eq} = T_{eq}(m_1, c_1, T_1, m_2, c_2, T_2)$. In addition, calculate the entropy change, $\Delta S = \Delta S(T_1, T_2, T_{eq})$, of the system due to the mixing process.
The motion of solutes is well described by Fick’s laws of diffusion which are (for the one dimensional case)

\[ J = -D \frac{dc}{dx} \]  

(4)

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]  

(5)

The thermodynamic driving force \( F_d \) and the frictional force \( F_f \) for the molecular motion are then given by

\[ F_d = -\frac{RT}{c} \left( \frac{dc}{dx} \right) \]  

(6)

\[ F_f = f \nu \]  

(7)

\( f \)…frictional coefficient  
\( \nu \)…velocity  
\( D \)…diffusion coefficient

(a) Show that

\[ c = \frac{\alpha}{t^{1/2}} e^{-x^2 / 4Dt} \]  

(8)

is a solution of equation 5.

(b) Show that \( D \) and \( f \) are related via the Einstein equation

\[ D = \frac{kT}{f} \]  

(9)

c) Confocal fluorescence correlation spectroscopy is a modern imaging technique that relies on the measurement of average diffusion times of fluorescent probes during their movement through the confocal spot (confocal spot size corresponds to size of *E.coli* bacterium). On the basis of equation 9, several fascinating experiments are possible, such as the study of receptor-ligand interactions in cellular systems or the observation of the aggregation behavior of photoluminescent semiconductor nanoparticles in blood serum to explore their potential for high-resolution in vivo imaging applications. Explain why equation 9 can provide the theoretical basis for such studies!
d) Wide-field single molecule fluorescence microscopy represents another fluorescence-based technique that allows for diffusion studies at the single molecule level. In this case, the square displacement $r^2$ of individual tracks of diffusing molecules is observed as observed over time. Which of the following two equations provide the proper relationship between $r^2$ and diffusion coefficient $D$, which is a macroscopic thermodynamic parameter? Justify your answer!

$$D = \frac{r^2}{4t_{\text{lag}}}$$

$$D = \frac{\langle r^2 \rangle}{4t_{\text{lag}}}$$

$\langle r^2 \rangle$.....average value of $r^2$

t_{\text{lag}}.... time lag between successive positional recordings
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<th><strong>IIA</strong></th>
<th><strong>IIIA</strong></th>
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**Note:** Numbers in parentheses are the mass numbers of the most stable isotopes.