Department of Chemistry
Cumulative Examinations

September 14, 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 2-5
3) Inorganic Cumulative Examination, Page 6
4) Organic Cumulative Examination, Page 7
5) Physical Cumulative Examination, Pages 8-9

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 division cume:

Structural elucidation of organic compounds by gas-phase ion-molecule reactions in tandem mass spectrometry

Please demonstrate your understanding on above research area by answering 6 of the below questions.

1) What are gas-phase ion-molecule reactions?
2) How are they studied using tandem mass spectrometry? (Give a description of one such mass spectrometry experiment)
3) What sort of mass spectrometers can be used to carry out tandem mass spectrometry experiments on gas-phase ion-molecule reactions? Give two examples and justify your answer.
4) Collision-activated dissociation experiments require acceleration of the selected gas-phase ions. Why? Is this also true for gas-phase ion-molecule reactions? Justify your answer.
5) Why can gas-phase ion-molecule reactions provide more structural information on unknown ionized analytes than collision-activated dissociation?
6) Are most analytical applications of gas-phase ion-molecule reactions based on ionic reagents reacting with neutral analytes or neutral reagents reacting with ionized analytes? Justify your answer.
7) Can gas-phase ion-molecule reactions be used to identify functionalities in unknown protonated analytes? If yes give an example.
8) Can gas-phase ion-molecule reactions be used in HPLC/tandem mass spectrometry experiments? Give two critical requirements for these experiments.
9) What controls the rates of gas-phase ion-molecule reactions?
10) What controls the collision rates of gas-phase ions with molecules?
Cumulative Examination in Biochemistry

Biochemistry: Metabolism and Systems Thinking

Instructions:
Use the attached Information Sheet and provide your own diagrams and specific biochemical examples of structures and processes to answer the following questions.

1. Metabolic pathways do not occur in isolation. Use ANY SPECIFIC physiological state or disease to explain how metabolic pathways are integrated (linked) via common intermediates to influence and regulate each other.

2. Describe any ONE method used in research to study the functioning of a metabolic pathway, process or individual metabolic reaction. Include details of structures, how function is monitored and how data is processed and analyzed to address a specific research question.

3. Use selected examples of specific biochemical processes to illustrate the crucial roles played by biomembranes in the regulation of metabolism. Include in your answer terms like hormone, transport and permeability.

See next page for Information Sheet
Information Sheet Biochemistry CUME (14Sept 2019)

Glucose
ATP → ADP
ADP → hexokinase
Glucose-6-phosphate
ATP → ADP → glucose phosphate isomerase
Fructose-6-phosphate
ATP → ADP → 6-phosphofructokinase
Fructose-1,6-bisphosphate
ATP → aldolase

3-Phosphoglycerate
ATP → ADP → phosphoglycerate kinase
3-Phosphoglycerate
ATP → ADP → phosphoglycerate mutase
2-Phosphoglycerate
ATP → ADP → phosphoglycerate
Phosphoenolpyruvate
ADP → NADH → pyruvate kinase
Pyruvate → lactate dehydrogenase

Note: All enzymes can function physiologically in the reverse direction except those marked with an asterisk.

Diagram:

From glycolysis → Pyruvate → Pyruvate dehydrogenase → Acetyl-CoA → Citrate synthase → Fumarase → Oxaloacetate → Malate → Malate dehydrogenase → NADH → Citrate → Isocitrate dehydrogenase → NADH → α-Ketoglutarate → α-Ketoglutarate dehydrogenase → NADH → ATP → GTP → Acetyl-CoA synthesis → Succinyl-CoA → Succinyl-CoA synthetase → Succinate → Succinate dehydrogenase → FAD → NADH → ATP → NADH → H+ → O2 → H2O → CO2 → H2O
Summary of carbohydrate, fat, and amino acid metabolism
Summary of the regulation of carbohydrate and fat metabolism

Fats (triacylglycerols)
- Insulin ↑ (liver, muscle)
- Glucagon ↑ (liver)
- Epinephrine ↑ (liver)
- Fatty acids
  - Insulin ↑ (liver)
  - Glucagon ↑ (liver)
  - Epinephrine ↑ (liver)
- Fatty acid biosynthesis
  - (+) Citrate(?)
  - (-) Palmitoyl-SCoA
- (-) Malonyl-SCoA, acetyl-SCoA, NADH
- Oxidation

Glycerol +

Fat biosynthesis

Fatty acids

Glycogen
- Insulin ↑ (liver, muscle)
- Glucagon ↑ (liver)
- Epinephrine ↑ (liver)

Glycolysis
- Insulin ↑ (liver)
- Glucagon ↑ (liver)
- Epinephrine ↑ (liver)
- Glucose
  - (+) AMP, ATP, fructose 2,6-bisphosphate
  - (-) ATP, citrate, alanine
- Pyruvate dehydrogenase complex
  - (+) AMP, NAD⁺, CoASH
  - (-) ATP, NADH, acetyl-SCoA

Acetyl-SCoA

Citric acid cycle
- (+) ADP, Ca²⁺
- (-) ATP, NADH, succinyl-SCoA

CO₂
1 (20) \( \text{H}_3\text{PO}_4, \text{H}_3\text{PO}_3 \) and \( \text{H}_2\text{PO}_2 \) all have a pK\text{a} value around 2, but the pK\text{a} values of HOCI, HClO\text{2} and HClO\text{3} are 7.5, 2 and -3, respectively. Explain the observed trends.

2 (30) (a) Derived the rate law and \( k_{\text{obs}} \) (hint: it contains two rate constants) for nucleophilic substitution in a square planar complex shown below:

\[
\begin{align*}
\text{T} & \quad \text{M} & \quad \text{X} & \quad + & \quad \text{Y} & \quad \rightarrow & \quad \text{T} & \quad \text{M} & \quad \text{Y} & \quad + & \quad \text{X} \\
& & & & & & & & & & & & \text{L} & \quad \text{L}
\end{align*}
\]

(b) Discuss briefly the mechanistic implication based on the magnitude of rate constants;
(c) Elaborate why kinetic measurement in nucleophilic solvents is needed in some cases.

3 (10) \( [\text{Mo}_6\text{O}_{19}]^{2-} \), one of the simplest polyoxometallates, can be readily prepared from \( \text{MoO}_4^{2-} \) in aqueous solution. Provide a balanced equation that includes necessary reagents / byproducts, and sketch the skeletal structure of \( [\text{Mo}_6\text{O}_{19}]^{2-} \).

4 (20) A neutral macrocyclic ligand with four donor atoms produces a red diamagnetic low spin complex of Ni(II) if the anion is the weakly coordinating \( \text{ClO}_4^- \). When the perchlorate is replaced by two thioyanate (SCN\(^-\)), the complex turns violet and is high spin with two unpaired electrons. Interpret the change in terms of structure and identify the highest occupied \( d \) orbital(s) in each case (must indicate XYZ).

5 (20) (a) Determine the point group of the PF\text{3} molecule. (b) What is the maximum degeneracy of its molecular orbitals? (c) Which of 3\text{p} orbitals of P center contribute to the degenerate MOs? (note: character table is not needed; must indicate XYZ).
1. For the following transformation (J. Am. Chem. Soc., 1977, 99, 7067), please provide a plausible mechanism.

2. Provide the product and mechanism for the key sequence shown below, utilized in the total synthesis of (-)-Histrionicotoxin (J. Am. Chem. Soc., 1990, 112, 5875).

3. The total synthesis of (+)-15-(S)-Prostaglandin A_2 (J. Am. Chem. Soc., 1976, 98, 1583) utilized the following substrate and reagent conditions. Provide the product and mechanism along with the name of the transformation.

4. In Stork's total synthesis of (+)-Digitoxigenin (J. Am. Chem. Soc., 1996, 118, 10660), the authors implemented a novel cycloaddition reaction to furnish the tetracyclic system. Provide a mechanism accounting for the observed stereochemistry.
Physical Chemistry Cume
Quantum Mechanics

September 14, 2019

**Problem 1 (70 pts).** A particle in 1D is described by the following wavefunction:

$$\Psi(x, t) = A\exp(-ax^2 - ibt)$$

Answer the following questions. Show your work and/or write one sentence of justification for your answers. All questions are 5 points.

a) Normalize the wavefunction.

b) Sketch probability density corresponding to this wavefunction.

c) To which potential $V(x)$ does this wavefunction correspond?

d) What is the expectation value of the position $\langle x \rangle$?

e) What is the expectation value of the momentum $\langle p \rangle$?

f) Compute the uncertainty in the position of this particle $\sigma_x$.

g) Compute the uncertainty in the momentum of the particle $\sigma_p$.

You perform a measurement of the position of this particle and find it at $x = x_0$. What are the values of the following quantities right after this measurement?

h) What is $\langle x \rangle$?

i) What is $\langle p \rangle$?

j) What is $\sigma_x$?

k) What is $\sigma_p$?

Instead of measuring the position of the particle, you measured its momentum and found it to be $p = p_0$. What are the values of the following quantities right after this measurement?

l) What is $\langle x \rangle$?

m) What is $\langle p \rangle$?

n) What is $\sigma_x$?

o) What is $\sigma_p$?

**Problem 2 (25 pts).** Suppose two electrons in He are in a spatial state

$$\psi(\vec{r}, \vec{r}') = \frac{1}{\sqrt{2}} [\psi_{100}(\vec{r})\psi_{200}(\vec{r}') - \psi_{100}(\vec{r})\psi_{200}(\vec{r}')]$$

All questions are 5 points.

a) What is the spin state of electrons in He (singlet, doublet, triplet,...)? Write one sentence of explanation.

b) Assuming that **electrons in He do not interact**, compute the energy of this electronic state of He (express the answer in multiples of the hydrogen atom values).

c) Compute the excitation energy from the ground state to this state of He (express the answer in multiples of the hydrogen atom values).

d) Compared to the Hartree-Fock model, which term(s) is/are ignored in the calculations you just did?

e) If these (ignored) terms are included, how the energy of He atom would change? (Increase, decrease, stay same). Write one sentence of explanation.
You might need the following integrals:

\[ \int_0^\infty e^{-ax^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \]

\[ \int_0^\infty x e^{-ax^2} \, dx = \frac{1}{2a} \]

\[ \int_0^\infty x^2 e^{-ax^2} \, dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \]

Hydrogen atom:

\[ E_n = -\left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi \varepsilon_0} \right) \right]^2 \frac{1}{n^2}, \quad n = 1, 2, 3, \ldots \]

\[ E_1 = -13.6 \, \text{eV} \]