I wrote a minor correction on question 2a) of the Biochemistry exam

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Cumulative Examinations
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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 2-3
3) Inorganic Cumulative Examination, Page 4
4) Organic Cumulative Examination, Page 5
5) Physical Cumulative Examination, Pages 6-7

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: 68
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 Chemistry Cumulative Exam

October 19, 2002

EDTA is widely used for the determination of metal ions. Answer the following questions about its use.

(a) Give the structural formulas of EDTA (show all atoms and charges) and its Cu(II) complex.

(b) What are the properties of EDTA that make it so useful for metal ions titrations? Sketch a pCu vs EDTA titration plot.

(c) Chromel is an alloy composed of nickel, iron, and chromium. A 0.6472-g sample was dissolved and diluted to 250.0 mL. When a 50.00-mL aliquot of 0.05182 M EDTA was mixed with an equal volume of the diluted sample, all three ions were chelated, and a 5.11-mL back titration with 0.06241 M copper(II) was required. The chromium in a second 50.0-mL aliquot was masked through the addition of hexamethylenetetramine; titration of the Fe and Ni required 36.28 mL of 0.05182 M EDTA. Iron and chromium were masked with pyrophosphate in a third 50.0-mL aliquot, and the nickel was titrated with 25.91 mL of the EDTA solution. **Calculate the percentages (by mass) of nickel, chromium, and iron in the alloy.** The atomic masses are Ni = 58.69, Fe = 55.85, Cr = 52.00.

(d) Answer the following questions about the procedure in (c):

(1) Outline a method to dissolve the chromel alloy.

(2) Explain why a back titration **must** be used for this sample.

(3) What is meant by masking agents? Why are they used in the above procedure?

(4) Suggest an effective means for determining the equivalence point in EDTA titrations.

BIOCHEMISTRY
CUMULATIVE EXAM
Proteins
October 19, 2002

1. Proline and glycine differ from the other 18 coded amino acids in significant ways. This affects their analytical chemistry, their contribution to folded proteins and their behavior in unfolded protein chains. Please describe all of these differences in some detail.

2. a) Proteins that carry out closely similar functions may be homologous. If they are not, they are called analogous. Provide an example of ~~such a pair.~~ an analogous pair. Have the members of your pair evolved by divergent or by convergent evolution?

   b) By analyzing a genenome of a single species you found several genes that code for proteins that are homologous to each other. What word describes more precisely their relation to one another?

   c) Provide an example of a protein or of a region in a protein that evolves very rapidly. Also provide an example of a protein that evolves very slowly.

3. a) The Edman method of protein sequencing involves a succession of coupling and cleavage steps. Describe these steps in more detail. The steps are carried out under dramatically different conditions. This is a great advantage for sequencing. Why?

   b) In the periplasm of E. coli protein, especially proteins containing disulfide bridges, fold much more rapidly than in E. coli cytoplasm. This is due to the high concentration of three different kinds of protein or protein assemblies that aid the folding. Name them and describe the detailed function of each?

4. Describe the molecular structures of

a) nucleosomes

b) ribosomes

c) proteosomes

d) chaperonins

Please base your discussions on the most recent structural determinations that you know and as much as possible indicate the investigators and the time when the structures were done.

Items a) and b) differ from items c) and d). What is the difference?

Inorganic Cumulative Exam

October 19, 2002
Theme: Nanotechnology
100 points total

Important note: Please do not go over the specified number of sentences to answer the question, or else only the specified number will be graded.

1. 15 points. In 5 sentences or less, define nanotechnology and indicate why nanotechnology has become an intense field of research only over the past decade or so (why not in the 1960's, for instance?).

2. 30 points. Describe precisely 3 projects that would be funded by NSF or other federal funding agencies in the field of nanotechnology, not including the one described in question 3. Please use 4 sentences or less to describe each project.

3. (45 points total) One area of research that is the subject of intense research efforts is light emission from quantum dots (nanoparticles). Photoluminescence from nanoparticles may have several different origins.

Please answer each of the following questions in 4 sentences or less.

a) (10 points) Give 2 possible explanations for light emission from a nanoparticle in 3 sentences or less.

b) (10 points) How is the electronic structure of a quantum dot different and yet similar to that of a molecule? 3 sentences or less.

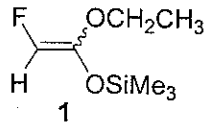
c) (10 points) What happens to the light emission when you incrementally change the size of a cadmium sulfide (or any photoemissive nanoparticle) quantum dot from ~1 nm through to ~20 nm in diameter? 3 sentences or less.

d) (15 points) Using simple band structure diagrams, explain the answer to 3 c. Please no more than 5 total written sentences.

4. (10 points) The Nobel Prizes were announced last week. Write down the names of at least 2 different people who have shared a Nobel Prize (for 2 different prizes *in any area*) over the past 5 years (from 1997-2002) and in 3 sentences, describe the research for which they merited the biggest prize in the history of chemistry.

ORGANIC CUME
October 19, 2002

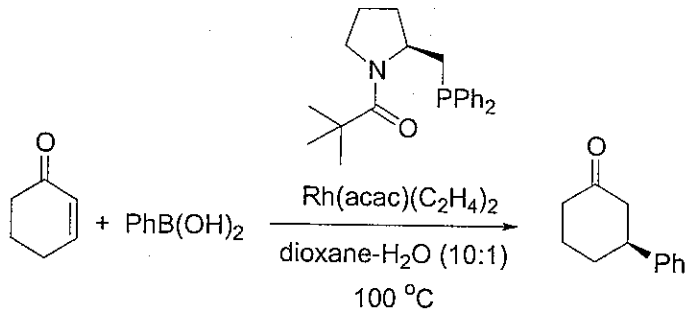
I. Recently (*J. Org. Chem.* **2002**, *67*, 3231), Huang and Chen reported the "Stereoselective Synthesis of α-Fluorosilyl Enol Ethers (eg: **1**) and Their Aldol Reaction."



1

(a) Write a mechanism for a typical aldol reaction. (10 pts)
(b) Write the *E*-isomer of **1**. (5 pts)
(c) Write the structure of a pair of diastereomers of the product from the aldol reaction of **1** with benzaldehyde and assign their configurations (*R*, *S* notation). (10 pts)

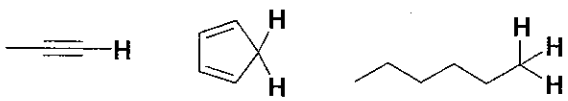
II. Tomioka and coworkers recently reported an asymmetric 1,4-addition reaction as shown below (*JACS*, **2002**, *124*, 8932).



Write the catalytic cycle for an <u>*achiral*</u> <u>*version*</u> of this reaction. For convenience, you may use Rh(OH)L as the Rhodium catalyst. (25 pts).

Extra credit (10 pts) if you discuss the catalytic cycle for the enantioselection.

III. Arrange the following molecules in their decreasing order of acidity and justify their pK_as (approximate values). (20 pts)

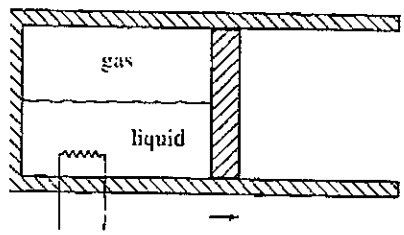


IV. Provide a typical example for the following reactions. (3x10 pts)

(a) Robinson annulation
(b) reductive amination
(c) malonic ester synthesis

Problem 1. (35 points)

In the following figure there is a liquid in equilibrium with its vapor and an electrical resistor. These are in a cylinder with a friction-free piston. The *system* is the interior of the cylinder, including the gas, liquid and resistor.



The initial state of the system is described by:

$$V_1 = 0.2200\ m^3,\ T_1 = 300.0\ K, \text{ and } p_1 = 2.50 \times 10^5\ Pa$$

A constant current is then passed through the resistor at I = 0.5000 A for 1600 s. The resistor has electrical resistance R_{el} = 50.00 Ω. The piston moves slowly to the right against a constant external pressure equal to the vapor pressure of the liquid, 2.50 x 10^5 Pa, and some of the liquid vaporizes. Assume that the process is adiabatic, and that T and p remain uniform and constant. The final state of the system is describe by:

$$V_2 = 0.2400\ m^3,\ T_2 = 300.0\ K, \text{ and } p_2 = 2.50 \times 10^5\ Pa$$

a. Calculate q, w, ΔU, and ΔH. Recall that electrical work is given by $dw_{el} = Vdq$, where q is electrical charge and V is the potential.

b. Is the process reversible or irreversible. Briefly explain.

Problem 2. (30 points)

The Maxwell distribution for the x-component of velocity is given by:

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}$$

Show that the probability that the x-component of velocity lies between $-v_{x1}$ and v_{x1} can be expressed in terms of the error function, defined as:

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} dz$$

Problem 3. (35 points)

The Joule-Thomson coefficient is defined by:

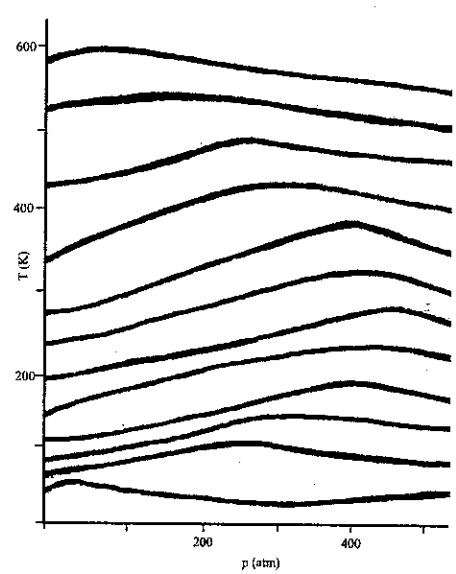
$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

a. Starting with the total differential of the enthalpy of a closed, one-phase sytstem in the form:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

derive an expression for the Joule-Thompson coefficient in terms of the heat capacity at constant pressure.

b. In the following figure, the lines are lines of constant enthalpy (isenthalps). Indicate on the figure the region of this graph in which cooling would occur upon expansion of a gas from a higher pressure to a lower pressure.



c. What is the Joule-Thomson coefficient for an ideal gas? Justify your answer with a calculation or derivation.