

**Department of Chemistry
Cumulative Examinations
August 25, 2007**

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
- 4) Organic Cumulative Examination, Page 6-8
- 5) Physical Cumulative Examination, Page 9

On your examination booklet:

- 1) Print your student ID number.
- 2) Print this 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.

PURDUE

U N I V E R S I T Y

ANALYTICAL CUMULATIVE EXAM
August 25, 2007

ANSWER 2 of the following 3 questions

- A.
1. Give the definition (not the value) of the Faraday.
 2. Explain why this unit is fundamentally important.
 3. What is coulometry? [~3 lines]
 4. Illustrate the output of such an expt [Label the figure]
 5. What is a coulometric titration?
 6. Illustrate the output of an example coulometric titration [Label the figure; show the redox equation; state the analyte]
 7. Illustrate the output of a cyclic voltametry experiment [label the figure axes, show the redox equation]
- B.
1. Write the van Deemter equation, explain all the terms.
 2. Illustrate how plate height varies with mobile phase velocity in a typical LC experiment [label the figure, show realistic numerical values]
 3. It is relatively easy to minimize plate height. How could you achieve this and what other important factor(s) would be compromised?
 4. What is the capacity factor, explain the terms involved and its influence on the chromatogram.
- C.
1. Write an equation for fluorescence intensity. Explain all the terms.
 2. Illustrate by means of an energy diagram (Jablonski diagram) the origin of fluorescence and the competing processes. Label carefully and add explanation, up to 10 lines.
 3. There are two types of fluorescence spectra – emission and excitation spectra. Differentiate these using an energy diagram.
 4. Illustrate excitation and emission types of fluorescence spectra in the case of a simple polyatomic analyte [label the figure, show the redox equation]

**Cumulative Exam
Biochemistry
August 25, 2007**

Acids, Bases, Buffers and Biological Building Blocks

Show work for partial credit. Use the attached tables for reference.

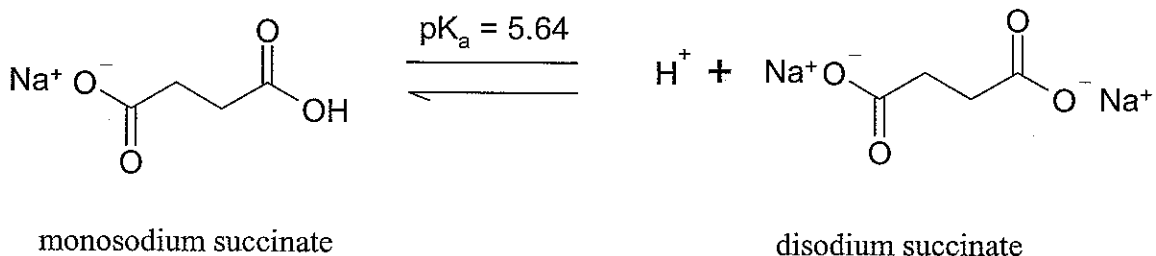
1. (15 points)

The amino acid **lysine** has multiple ionizable functional groups.

- a. Write the equilibrium equations with structures for the ionizations of **lysine**. Include the proper pKa's for each ionization.
- b. Calculate the pI of **lysine**.
- c. Sketch a rough titration curve representing the complete ionization of **lysine**. Be sure to label the axes appropriately.
- d. Indicate the point(s) on the graph where pH = pKa.

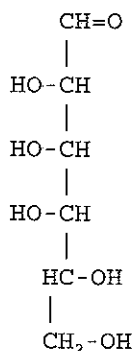
2. (15 points)

How many grams of sodium succinate (MW = 140 g/mol) and disodium succinate (MW = 162 g/mol) must be added to 1 L of water to produce a solution with pH = 6.0 and a total solute concentration of 50 mM?



3. (10 points)

- a. Draw the 5- and 6-member ring cyclized forms as Haworth projections of the sugar represented by the following Fischer projection. Circle the anomeric carbon in the structure that you drew.



4. (20 points)

- a. If 70 mL of 0.01 M HCl is added to 150 mL of 0.1M acetic acid, pH 5.0, what is the resulting pH?
- b. How many *moles* of a carbonic acid species (HA) and its conjugate base (A^-) do you need to add to 3.0 L of water to make a 0.60 M carbonate buffer at pH 10.00? For carbonic acid (H_2CO_3) $pK_{a1} = 6.37$ and $pK_{a2} = 10.26$. ONLY give the number of moles of HA in the answer.
- c. What is the pH of a 1.0 L solution that contains 47.1g of the weak acid phenol (C_6H_5OH) (molecular weight = 94.11 g/mol). $K_a = 1.0 \times 10^{-10}$?

5. (10 points)

- a. Draw the complete structure of ATP
- b. Describe briefly two distinct and specific uses for ATP in a cell.

6. (10 points)

- a. Alpha-linolenic acid is an essential omega-3 fatty acid designated by the formula, $18:3^{\Delta 9,12,15}$. Using this formula, draw the structure of this fatty acid and be sure to show the proper configuration of any double bonds.

7. (20 points)

Answer the following questions regarding the peptide **MCRIGEF**

- a. What is the sequence of amino acids written as the **THREE** letter code?
- b. Draw the structure of the peptide **MCRIGEF** as it would exist at pH 12.2.
- c. What is the approximate **pI** of **MCRIGEF**

Acid	HA	K_a	pK_a
Formic acid	HCOOH	1.78×10^{-4}	3.75
Acetic acid	CH ₃ COOH	1.76×10^{-5}	4.75
Pyruvic acid	CH ₃ COCOOH	3.16×10^{-3}	2.50
Lactic acid	CH ₃ CHOHCOOH	1.38×10^{-4}	3.85
Malic acid	HOOC—CH ₂ —CHOH—COOH	(1) 3.98×10^{-4}	3.40
		(2) 5.5×10^{-6}	5.26
Citric acid	$\begin{array}{c} \text{OH} \\ \\ \text{HOOC—CH}_2\text{—C—CH}_2\text{—COOH} \\ \\ \text{COOH} \end{array}$	(1) 8.14×10^{-4}	3.09
		(2) 1.78×10^{-5}	4.75
		(3) 3.9×10^{-6}	5.41
Carbonic acid	H ₂ CO ₃	(1) 4.3×10^{-7}	6.4
		(2) 5.6×10^{-11}	10.2
Phosphoric acid	H ₃ PO ₄	(1) 7.25×10^{-3}	2.14
		(2) 6.31×10^{-8}	7.20
		(3) 3.98×10^{-13}	12.4
Ammonium ion	NH ₄ ⁺	5.6×10^{-10}	9.25

TABLE 4.2

Table of pK values for the 20 amino acids found in proteins^a

Name	pK_1	pK_2	pK_R
Glycine	2.4	9.8	
Alanine	2.3	9.9	
Valine	2.3	9.6	
Leucine	2.4	9.6	
Isoleucine	2.4	9.7	
Methionine	2.3	9.2	
Phenylalanine	1.8	9.1	
Proline	2.0	10.0	
Serine	2.1	9.2	
Threonine	2.6	10.4	
Cysteine	1.8	10.8	8.3
Asparagine	2.0	9.8	
Glutamine	2.2	9.1	
Tyrosine	2.2	9.1	10.9
Tryptophan	2.4	9.4	
Aspartate	2.0	10.0	3.9
Glutamate	2.2	9.7	4.3
Histidine	1.8	9.2	6.0
Lysine	2.2	9.2	10.8
Arginine	1.8	9.0	12.5

^a pK_1 values are assigned to the α -carboxyl group, pK_2 values to the α -amino group, and pK_R to ionizable groups in the R group (side chain).

Briefly define the following terms using words and give an example of the application of each term to an inorganic system.

1. 18 electron rule
2. Antibonding molecular orbital
3. Bronstead-Lowry base
4. Chelate effect
5. CO insertion reaction
6. Delta bond
7. Disproportionation
8. Fluxional molecule / Stereochemically-nonrigid molecule
9. High spin configuration
10. Inert complex
11. Jahn-Teller effect
12. Outer-sphere mechanism
13. Oxidative addition
14. Pi-acid
15. Sigma bond
16. Spectrochemical series
17. Strong-field electron configuration
18. Trans effect
19. Unit cell
20. Ziegler-Natta catalyst

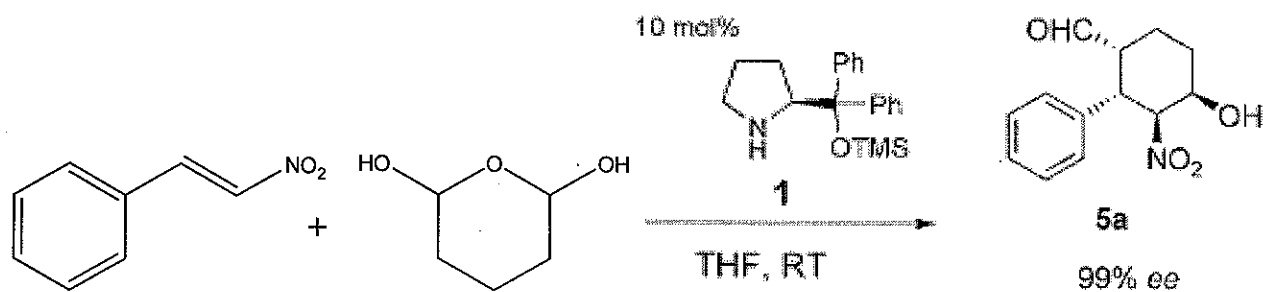
ORGANIC CUME (Aug 2007)
(3 pages)

1. (24 pts) Provide the following information. An order of magnitude estimate will receive half credit.

- (a) The diameter of a benzene ring.
- (b) The bond dissociation energy of the weakest bond in propene.
- (c) The boiling point of diethyl ether.
- (d) The ^{13}C NMR spectrum of CD_2Cl_2
- (e) The most stable conformation of cis 1,4-dimethylcyclohexane.
- (f) The structure of R-cyclohexenol
- (g) The activation energy for the chair to chair inversion of cyclohexane and its rate at 25°C .
- (h) The pK_a values and isoelectric point of phenylalanine.

2. (25 pts) Hayashi and coworkers (*Angew Chem* 46, 4922-4925, 2007) reported

Diphenylprolinol Silyl Ether as a Catalyst in an Enantioselective, Catalytic, Tandem Michael/Henry Reaction for the Control of Four Stereocenters**



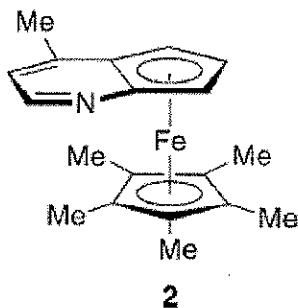
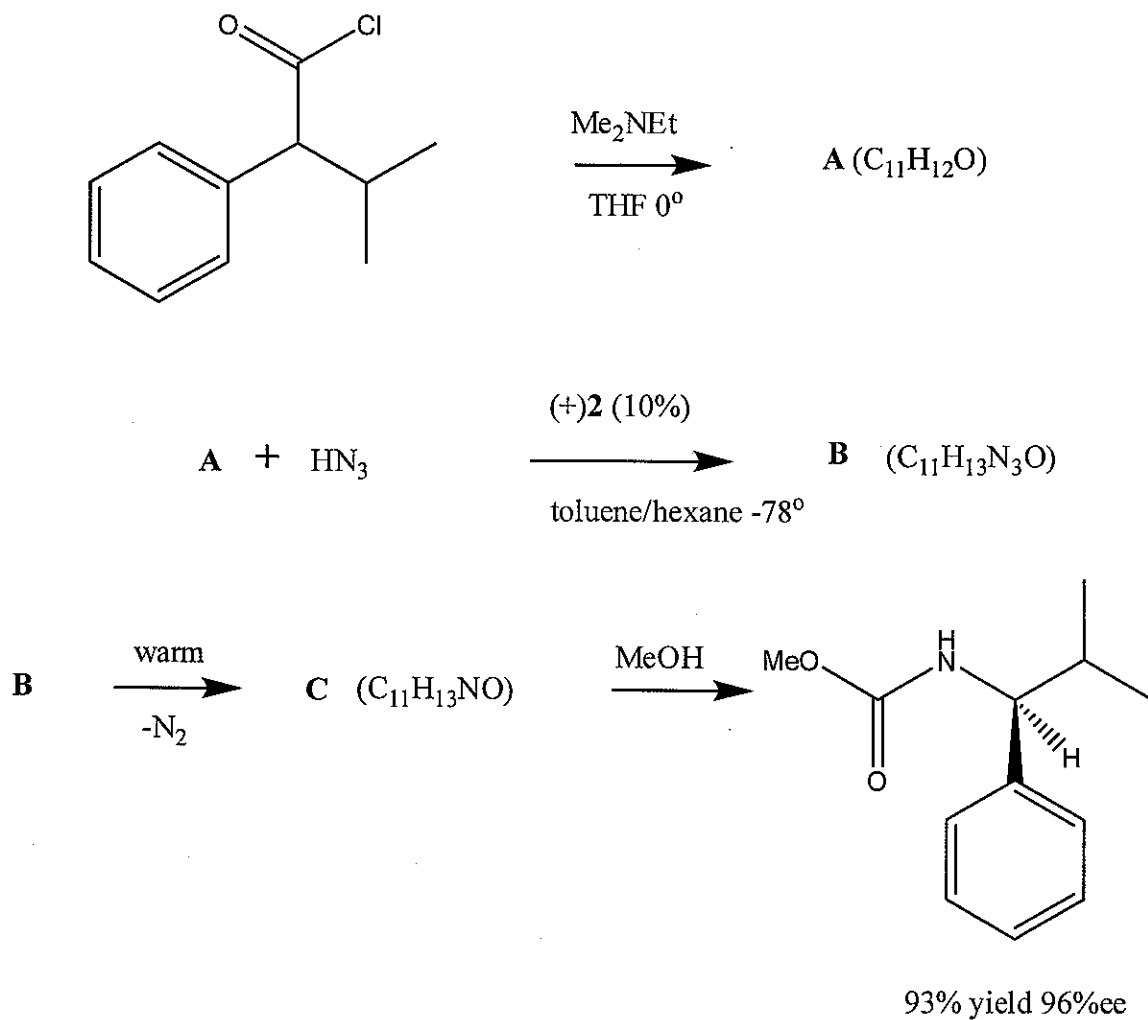
(a) The first step involves the condensation between the catalyst and the product of the dehydration of the starting diol. Give the structure of this intermediate.

(b) Propose a mechanism to account for this transformation. The catalyst is recovered when the product is quenched with water.

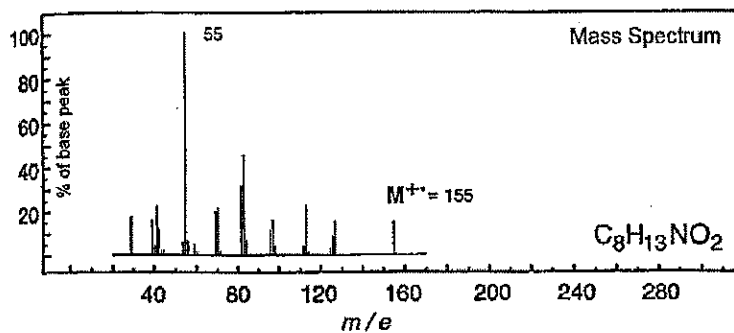
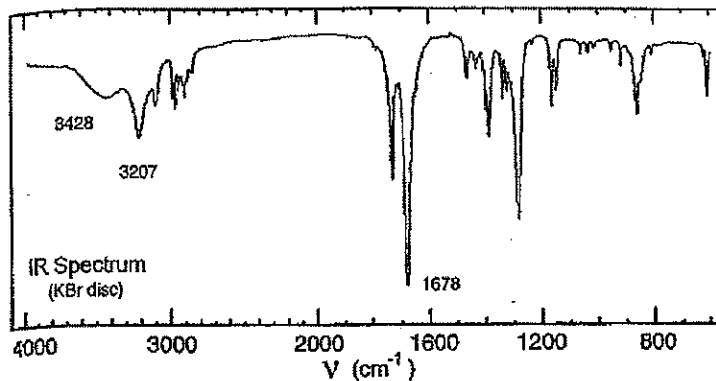
3. (25 pts) Fu and coworkers (*Angew Chem* **46**, 4367-4369, 2007) have reported the following sequence of reactions.

(a) Propose structures for the unknowns A–C.

(b) Propose plausible mechanisms for each transformation.



4. (26 pts) Determine the structure of the compound whose spectra are shown below. Briefly show your reasoning. Partial credit given for partial structures.

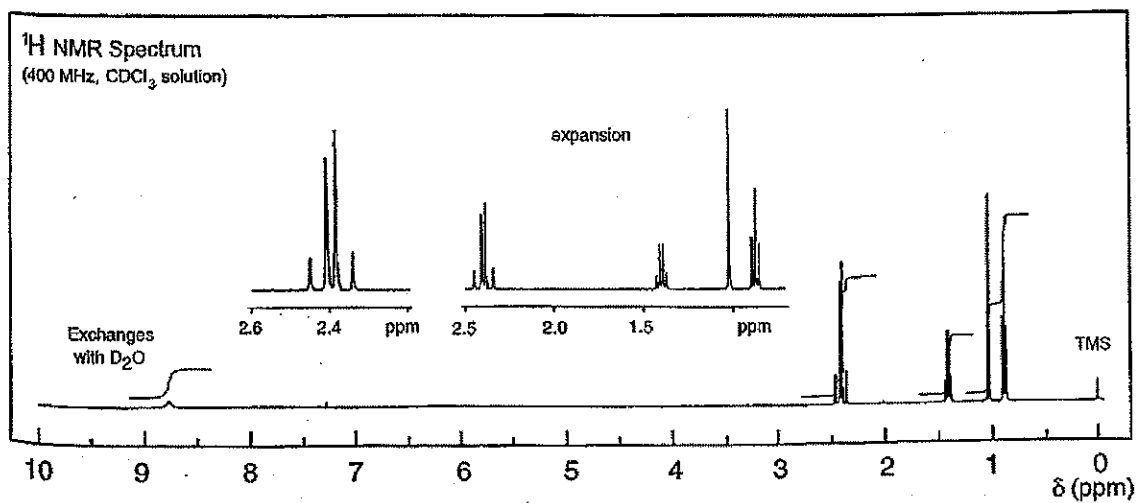
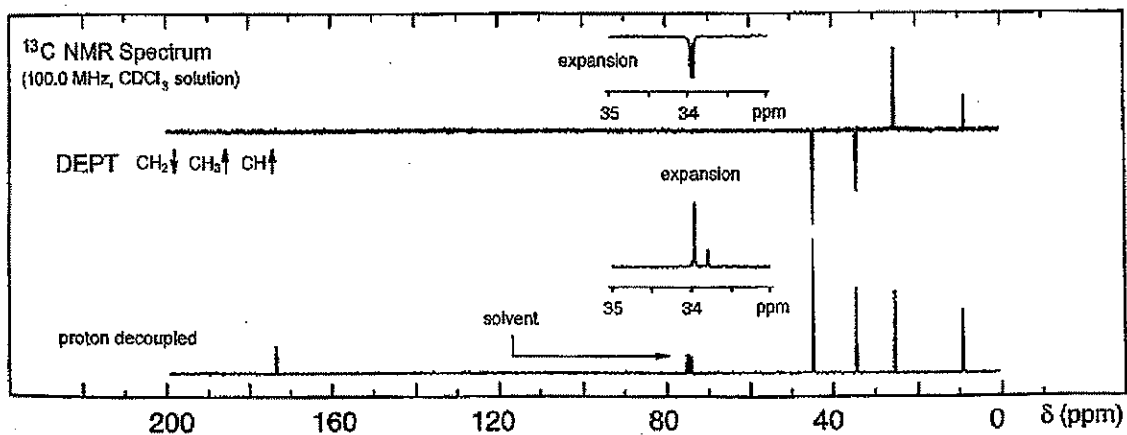


UV Spectrum

λ_{max} 230 nm ($\log_{10} \epsilon$ 3.6) pH 11

λ_{max} 230 nm ($\log_{10} \epsilon$ 4.4) pH 13

solvent: water



Consider a general system of fixed temperature T and volume V , which has quantum states of energy ε_i and degeneracy g_i .

- 1) (20 points) Write an expression for the partition function of the above system.
- 2) (10 points) What is the physical significance of the partition function?
- 3) (10 points) Write an expression for the probability of finding the above system in exactly one of the states of energy ε_i .
- 4) (10 points) Write an expression for the probability of finding the above system in any one of the states of energy ε_i .
- 5) (20 points) Consider a system consisting of a single N_2 molecule at 300K in a container of 1 m^3 volume. Estimate the values of the electronic, vibrational, rotational and translational contributions to the partition function. [These can all be rough estimates obtained without performing a detailed calculation – you can make reasonable assumptions regarding any missing information.]
- 6) (10 points) How is the partition function of a system composed of n identical molecules in a dilute gas related to that of a single molecule (of the same type at the same temperature and volume)?
- 7) (10 points) Write an expression for the Helmholtz free energy of the above n molecule system?
- 8) (10 points) Write an expression for the entropy of the above n molecule system?

