Department of Chemistry
Cumulative Examinations
February 4, 2006

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 1-2
2) Biochemistry Cumulative Examination, Pages 3-4
3) Inorganic Cumulative Examination, Page 5
4) Organic Cumulative Examination, Page 6
5) Physical Cumulative Examination, Pages 7-9

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
UNIVERSITY

Analytical Chemistry Cumulative Exam February 2005

1. (15) Many surface analysis methods can be classified in terms of the input probe and the output signal. Classify THREE of the following surface analysis techniques in this way:
   X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, Rutherford backscattering, electron energy loss spectroscopy (EELS or HREELS).

2. (15) Show that you understand the basic process occurring in THREE of the following surface analysis methods using an annotated diagram or a very short paragraph:
   Low energy electron diffraction (LEED), temperature programmed desorption (TPD), electron stimulated desorption ion angular distribution (ESDIAD), Ion scattering spectroscopy (ISS)

3. (10) Consider the seven techniques of questions 1 and 2 : which of them is particularly useful for
   - i) quantitative analysis
   - ii) surface structural (geometrical) analysis
   - iii) depth distribution of implanted atoms
   - iv) molecular characterization of adsorbate
   - v) geometry of adsorption

4. (5) Name and give the standard acrynom for a generally applicable surface analysis technique not listed in questions 1 or 2 that has a particularly low detection limit. Give a typical detection limit for a particular class of analyte.

5. (5) What is the typical analysis depth of XPS and what factor controls it?

6. (10) Illustrate using electronic state diagrams showing electron occupancy in the course of EITHER the Auger process OR the process occurring in ESCA (XPS).

7. (10) Kinetic energy analysis is involved in several forms of surface spectroscopy; illustrate and label one device that is used for such analysis.

8. (16) List one example each for a method of surface microscopy which uses photons, electrons, ions and atomic probes. In each case give the resolution achieved and a major advantage of the method.

9. (13) Given the table of binding energies shown, illustrate the ESCA spectrum expected for poly(ethyleneterephthalate), $[-CH_2-CH_2-O(O)C-C_6H_4C(O)O-]_n$ Label the axes and indicate the elements and atomic states responsible for the signals.

Table of Binding Energies

Element	Binding energies (eV)						
	$1S_{1/2}$	$2S_{1/2}$	$2P_{1/2}$	$2P_{3/2}$	$3S_{1/2}$	$3P_{1/2}$	$3P_{3/2}$
H	14						
He	25						
Li	55						
Be	111						
B	188			5			
C	284			7			
N	399			9			
O	532	24		7			
F	686	31		9			
Ne	867	45		18			
Na	1072	63		31			
Mg	1305	89		52			
Al		118	74	73			
Si		149	100	99	8		3
P		189	136	135	16		10
S		229	165	164	16		8
Cl		270	202	200	18		7
A		320	247	245	25		12
K		377	297	294	34		18
Ca		438	350	347	44		26
Sc		500	407	402	54		32
Ti		564	461	455	59		34
V		628	520	513	66		38
Cr		695	584	575	74		43
Mn		769	652	641	84		49
Fe		846	723	710	95		56
Co		926	794	779	101		60
Ni		1008	872	855	112		68
Cu		1096	951	931	120		74
Zn		1194	1044	1021	137		87

Typical C_{1s} binding energies for organic samples*

Functional group		Binding energy (eV)
hydrocarbon	C–H,<u>C</u>–C	285.0
amine	C–N	286.0
alcohol, ether	<u>C</u>–O–H, <u>C</u>–O–C	286.5
Cl bound to carbon	<u>C</u>–Cl	286.5
F bound to carbon	<u>C</u>–F	287.8
carbonyl	<u>C</u>=O	288.0
amide	N–<u>C</u>=O	288.2
acid, ester	O–<u>C</u>=O	289.0
urea	$N-\underline{C}(=O)-N$	289.0
carbamate	$O-\underline{C}(=O)-N$	289.6
carbonate	$O-\underline{C}(=O)-O$	290.3
2F bound to carbon	$-CH_2CF_2-$	290.6
carbon in PTFE	$-CF_2CF_2-$	292.0
3F bound to carbon	$-CF_3$	293–294

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV, but some (e.g., fluorocarbon samples) can be larger

CUMULATIVE EXAMINATION IN BIOCHEMISTRY
Feb 4, 2006

It is expected that the answer should contain 1-4 succinct straight-to-the-point sentences. If you feel like elaborating, please, stay within an 8 sentence limit anyway. All questions carry the same weight.

1. Over 90% of biological crystallographers currently collect their data at around 100K. Why? Please comment on the physical chemistry that makes low temperatures preferable.

2. What is CASP? Comment on the usefulness of the methods employed by CASP participants as compared to x-ray crystallography and NMR spectroscopy.

3. Maltose-binding protein (MBP) undergoes a conformational change upon binding to a membrane-associated transporter. Briefly describe a possible design of an ESR experiment that would allow you to monitor these conformational changes.

4. What are inteins and how they are useful in preparing samples for spectroscopic studies?

5. Analytical ultracentrifugation is the standard technique for studying self-association of proteins. Please, explain the principle of these experiments.

6. A two-dimensional NMR spectrum of a 1 mM protein sample is recorded in 4 hrs yielding an average signal-to-noise ratio S/N=100. The measurement is then repeated under the same conditions except the concentration of the sample is reduced to 0.7 mM. What should be the duration of the second measurement in order to achieve the same S/N ratio as before?

7. Why do small proteins run faster than large proteins in SDS-PAGE gel, but slower than large proteins in a gel filtration column?

8. IPTG is used in recombinant expression of the proteins. What is, in general terms, its mechanism of action?

9. The enzyme-substrate binding rate predicted by a simple diffusion model assuming two uniformly reactive spherical molecules is 10^9-10^{10} $s^{-1}M^{-1}$. In reality the rates are typically in the range 10^6-10^8 $s^{-1}M^{-1}$. Briefly describe possible reasons for this discrepancy.

10. Describe typical geometries of backbone hydrogen bonds in proteins

11. Consider a two-dimensional Fourier-transformed IR spectrum of a peptide. What is the meaning of a cross-peak (i.e. off-diagonal peak) in the spectral map? What defines the linewidths of the peaks in such a spectrum?

12. Two proteins have a sequence identity of 30%. For one of them a (very-)high-resolution x-ray structure is available. This structure is used to model the other protein. What kind of accuracy can we generally expect from such a model? Please, give a best-guess estimate in terms of backbone coordinate rmsd.

Inorganic Chemistry Cumulative Exam
Purdue University
February 4, 2006

Question 1: (20 points)

Your pet lobster looks to be anemic (e.g., not getting enough oxygen). Why will giving him iron supplements not help? Hint: Giving iron supplements might help anemic people or whales.

Question 2: (20 points)

Why does EDTA make for a good food preservative?

Question 3: (20 points)

Many Gd^{3+} complexes are used to enhance the contrast of MRI images, once the complex locates in a particular region of the body.

A) What is the mechanism by which Gd^{3+} complexes work to enhance MRI images? Hint: Think about how MRI works.

B) Why is Gd^{3+} the most commonly used metal ion for MRI?

Question 4: (20 points)

A) What are zinc fingers? Drawing a general picture might help your answer. Provide as much detail as possible.

B) Why might zinc fingers use zinc rather than other metals such as iron?

Question 5: (20 points)

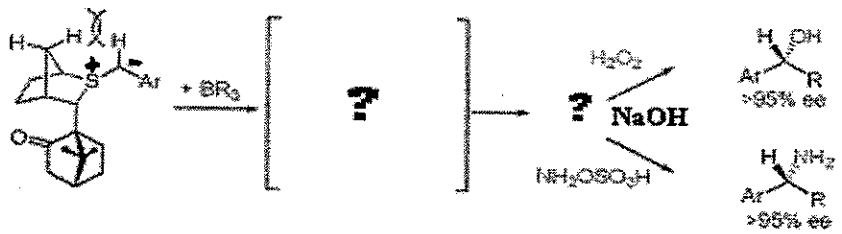
Biology uses hemes for many different functions such as electron transfer, oxygen transport, and substrate oxidations. Just considering electron transfer of hemes (i.e., $Fe^{2+} \Leftrightarrow Fe^{3+}$), the reduction potential of hemes vary tremendously. One common way protein-bound heme reduction potentials are varied is by burying the heme in the protein interior or allowing exposure to the environment. What influence does such heme environments have on reduction potential? In other words, how is the $Fe^{3+} \rightarrow Fe^{2+}$ reduction potential influenced by being buried in the protein or more exposed at the protein surface?

I. Expand the following acronyms and provide their structures
(i) HMPA (ii) THF (iii) DCC (iv) DMAP (v) DEAD (vi) DDQ (Vii) NMO (viii) DMF (ix) 9-BBN (x) AIBN

(25 points)

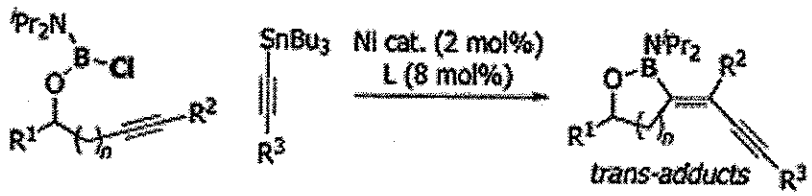
II-V. Provide a mechanism (curved arrow and/or catalytic cycle) for the following reactions (rationale for enantiomer stereochemistry is not needed).

II. Synthesis and Applications of Chiral Organoboranes Generated from Sulfonium Ylides
Varinder K. Aggarwal, Guang Yu Fang, and Andreas T. Schmidt (J. Am. Chem. Soc., 2005, 127, pp 1642 – 1643)



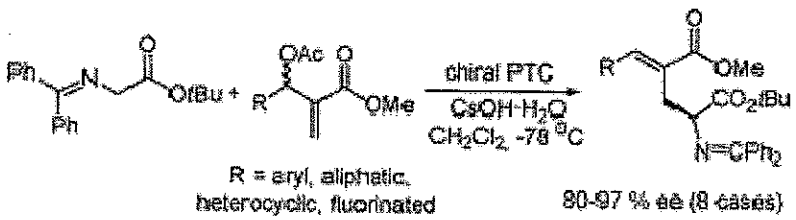
(30 points)

III. Nickel-Catalyzed *trans*-Alkynylboration of Alkynes
Akihiko Yamamoto and Michinori Suginome (J. Am. Chem. Soc., 2005, 127, pp 15706 – 15707)



(30 points)

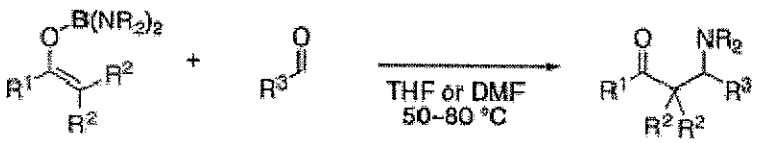
IV. Catalytic Enantioselective Synthesis of Glutamic Acid Derivatives via Tandem Conjugate Addition-Elimination of Activated Allylic Acetates under Chiral PTC Conditions
P. Veeraraghavan Ramachandran, Sateesh Madhi, Layla Bland-Berry, M. Venkat Ram Reddy, and Martin J. O'Donnell (J. Am. Chem. Soc., 2005, 127, pp 13450 – 13451)



(15 points)

Extra Credit

V. A New Look at Boron Enolate Chemistry: Aminative C-C Bond Formation Using Diaminoboron Enolate with Aldehyde
Michinori Suginome, Lars Uehlin, Akihiko Yamamoto, and Masahiro Murakami (Organic Letters, 2004, 6, pp 1167 – 1169)



(20 points)

(1) (a) Show that the entropy of an ideal gas at constant particle number as a function of T and V is

$$S(T,V) = S_0(T_0,V_0) + Nk \ \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\} \qquad (1)$$

(b) The inner energy of an ideal gas can be expressed via

$$U(S,V,N) = U_0\left(\frac{N}{N_0}\right)^{5/3}\left(\frac{V_0}{V}\right)^{2/3}\exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\} \qquad (2)$$

with: $U_o = \frac{3}{2}N_0kT_0$ and $S_o = \frac{3}{2}Nks_0$

By starting from equation (2), show that the free energy F(T,V,N) of the ideal gas can be written as

$$F(T,V,N) = NkT\left[\frac{3}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right] \qquad (3)$$

(c) Two separate bulbs contain ideal gases A and B, respectively. The density of gas B is half that of gas A. The molecular weight of gas B is twice that of gas A. Both gases are at the same temperature. Calculate the ratio of the pressure of gas A to that of gas B.

(2) The equation of state of the van der Waals gas is given by

$$\left(p + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT \qquad (4)$$

(a) Discuss the physical meaning of the parameters a and b in equation (4)!

(b) A container filled with compressed gas cools down when the gas escapes quickly (example: gas spray bottles). During such a rapid gas expansion, no external work needs to be applied and no heat is exchanged with the surroundings. By starting form the expression of the internal energy of a real gas

$$U(V,T) = U_0((V_0,T_0) + C_V(T - T_0) - N^2 a\left(\frac{1}{V} - \frac{1}{V_0}\right) \qquad (5)$$

determine expressions for the temperature change ΔT and the maximum temperature change ΔT_{max} of the real gas during expansion.

(c) What would be the corresponding expression for ΔT during rapid expansion of an ideal gas?

(d) The Joule-Thompson experiment allows the study of the irreversible expansion of a real gas in more detail. Describe the setup of the experiment and discuss its thermodynamic conditions, particularly, related to pressure p and enthalpy H.

(e) Show that the Joule-Thompson coefficient δ can be written as

$$\delta = \left.\frac{\partial T}{\partial p}\right|_H = \frac{1}{C_p}\left(T\left.\frac{\partial V}{\partial T}\right|_p - V\right) \qquad (6)$$

(3) Consider the one-dimensional motion of solute molecules between positions x and x+dx. Both positions are characterized by different concentrations of solute molecules c and c+dc.

(a) Derive an expression for the free-energy difference per molecule, dG, between c and c+dc. Consider diluted conditions and write the expression in the form dG=dG(c).

(b) Show that the thermodynamic driving force, F_d, for molecular motion of this ideal solution is

$$F_d = -\frac{RT}{c}\left(\frac{dc}{dx}\right) \qquad (7)$$

Consider that: (d/dx)lnc=(1/c)dc/dx

(c) The driving force in eq. 4 is counterbalanced by the frictional force

$$F_f = fv \qquad (8).$$

f.....frictional coefficient
v....velocity

In addition, Fick's first law

$$J = -D\frac{dc}{dx} \qquad (9)$$

provides a relationship between flux of solute molecules, J, diffusion coefficient, D, and concentration gradient, dc/dx. Provide a relationship between diffusion and frictional coefficents by showing that

$$D = \frac{kT}{f} \qquad (10).$$

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	O
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.903	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac† (227)															

*Lanthanides	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
†Actinides	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)