Department of Chemistry
Cumulative Examinations
December 9, 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, Page 1
2) Biochemistry Cumulative Examination, Page 2
3) Inorganic Cumulative Examination, Page 3
4) Organic Cumulative Examination, Pages 4-5
5) Physical Cumulative Examination, Page 6

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: 41
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 Cume Exam December 9, 2006

The equation $\sigma^2 = 2Dt$ describes the spread of a small zone of analyte in space.

1) Describe how this equation is of fundamental importance in predicting how to operate a capillary zone electrophoresis system.

2) This equation is of equal utility in gas chromatography. Which component of bandspreading depends on the phenomenon predicted by this equation?

3) It is possible in size exclusion chromatography of biopolymers in an aqueous mobile phase to interrupt the flow through the column for 24 hours without causing an increase in bandspreading. What does the above equation relate to this fact?

Cumulative exam questions in Biochemistry- December 2006

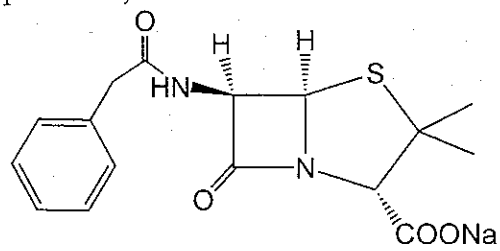
A. Describe the structure of an average mammalian cell plasma membrane. Include in your description:
1) the relative abundance of lipid, protein, carbohydrate, and nucleic acid in the total membrane structure,
2) the dimensions and compositional asymmetry of the major lipid components of the bilayer,
3) the major functions of proteins present in the membrane,
4) the major functions of lipids present in the membrane,
5) the major functions of the carbohydrates present in the membrane,
6) the components responsible for maintenance of membrane shape and stability.

B. Describe an efficient method to determine each of the following:
1) The amino acids of an integral membrane protein that likely span the membrane.
2) The rate of lateral diffusion of a protein in the membrane.
3) The distance from the lipid bilayer surface to the adrenaline binding site on the beta adrenergic receptor.
4) The rate of calcium influx into a cell following stimulation with thrombin.
5) The molecular weights of all peripheral proteins associated with the membrane.

Inorganic Chemistry Cumulative Exam
Purdue University
December 9, 2006

Question 1: (20 points)
When you wake up most mornings, you may find a gooey, slimy film covering your teeth. That film is an example of a bacterial biofilm. The bacterial cells gather together and produce amazingly large amounts of polysaccharides around themselves, thus creating the film. Bacterial biofilms can also be found in the lungs of cystic fibrosis patients (as an infection) and covering rocks in ponds. Describe a chemical approach to preventing the formation of biofilms. You may not use general antibiotics or non-stick surfaces such as Teflon (polytetrafluoroethylene).

Question 2: (20 points)
Speaking of bacteria… Many bacteria have now developed resistance to antibiotics. Briefly, what are antibiotics? Provide a detailed explanation for how bacteria can prevent the toxic effects of antibiotics. For simplicity, you may wish to center your discussion around a specific antibiotic compound such as penicillin, shown below.



Question 3: (20 points)
Hemes are very diverse functional groups in biology. Hemes are central to many processes such as electron transfer, oxygen transport, sensing of nitric oxide, and substrate oxidations.
A) Draw a heme. Your drawing need not be exactly correct to receive full credit. But your structure must show that you have some general idea of what a heme is.
B) How can one functional group be responsible for such a diverse array of reactions (electron transfer, substrate oxidations, etc.)?

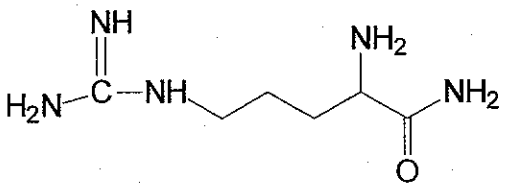
Question 4: (20 points)
What is chelation therapy? When might it be good to use? How does it work?

Question 5: (20 points)
What is the Marcus inverted region? What bearing does it have on photosynthesis?

ORGANIC CUMULATIVE EXAMINATION Dec. 9th, 2006

A recent JACS article ("*The Arginine Anomaly: Arginine Radicals Are Poor Hydrogen Atom Donors in Electron Transfer Induced Dissociations*", Xiaohong Chen and Frantisek Turecek; **128**, *38*, **2006**, 12520-12530) presents a study examining the mechanisms of a recently developed mass spectrometric activation method, electron transfer-induced dissociation (ETD), that is especially useful in peptide sequencing. This method involves electron transfer (for example from a filament) to polyprotonated peptides (ionized and evaporated into the mass spectrometer by electrospray ionization) to form an excited polyprotonated peptide radical that then undergoes structurally diagnostic fragmentation reactions.

A technique called neutralization-reionization mass spectrometry was used in this study to generate neutral arginine amide radicals (as models of polyprotonated peptide radicals) and examine their decomposition pathways. The experiment involves the generation of singly-protonated arginine amide in an electrospray ion source, isolation of the ion by using a mass analyzer, and neutralization by collisions with dimethyl disulfide to generate the neutral arginine amide radical. This radical has about 7 μs time to undergo unimolecular rearrangement and dissociation reactions before reionization of the radical and its products takes place upon collisions with oxygen gas, which is followed by mass spectrometric detection.



Arginine amide

Please answer the following questions about the above research:

1) What is the thermodynamically most favored protonation site in arginine amide and why? (ignore internal hydrogen bonding)

2) The most stable conformer of protonated arginine amide is stabilized by an internal hydrogen bonding interaction. Show the most likely structure for the hydrogen-bond stabilized protonated arginine amide.

3) In the neutralization/reionization experiment, accelerated protonated arginine amide molecules are very rapidly neutralized (within femtoseconds) by electron transfer from dimethyl disulfide. Is this a vertical or adiabatic process? Explain the difference between vertical and adiabatic processes.

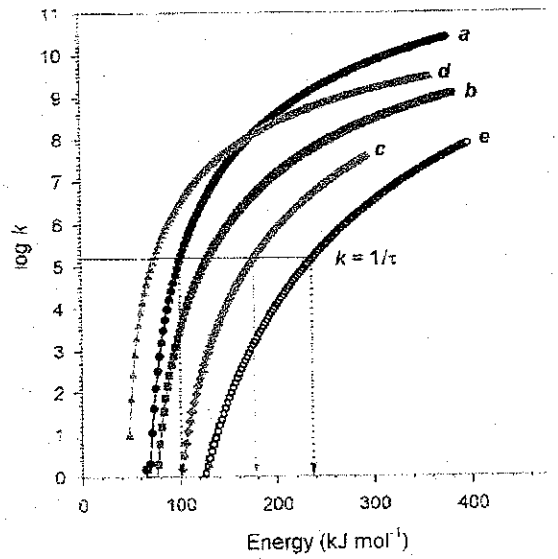
4) Draw the structure of the resulting radical, paying attention to your choice of either vertical or adiabatic process.

5) Why did the authors use dimethyl disulfide to neutralize and oxygen to ionize protonated arginine amide? Why not the other way, *i.e.*, use dimethyl disulfide to ionize and oxygen to neutralize?

6) The arginine amide radical undergoes two interesting fragmentations, loss of guanidine ($(NH_2)_2CNH_2$) and loss of both guanidine and ethyl radical. Draw likely mechanisms for these reactions.

7) The authors used quasi-equilibrium theory to understand better their results. Explain what is calculated by using this theory, and what sort of information the calculations provide for fragmentation processes.

8) The figure below shows the results of the QET calculations for five reactions of the excited arginine amide radical. We will only consider three here. Curve **a** corresponds to the guanidine loss, curve **c** to loss of a hydrogen atom from a guanidine N-H bond, and curve **d** to Cα-hydrogen atom migration from the amido moiety to the guanidyl radical moiety. Which one of these three reactions has the lowest activation energy? Justify your answer – why this particular reaction? Which reaction has the lowest frequency factor (*i.e.*, TS is entropically the least favorable one)? Again, justify. Which reaction will dominate at very low energies? Which will dominate at high energies?



9) What do you see as weaknesses of this study when trying to delineate possible mechanisms for polyprotonated peptides' fragmentation during ETD?

Physical Chemistry Cumulative Exam

December 9, 2006

(25 points)
(1) Discuss the Lindemann mechanism for unimolecular decomposition. Give the mechanism, derive the rate expression, and discuss the high pressure and low pressure limits. What other theories deal with unimolecular decomposition rates?

(25 points)
(2) The mechanism proposed for the decomposition of N_2O_5 is:

Reaction	Rate Constant
$N_2O_5 \rightarrow NO_2 + NO_3$	k_1
$NO_2 + NO_3 \rightarrow N_2O_5$	k_{-1}
$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	k_2
$NO + NO_3 \rightarrow 2\,NO_2$	k_3

Derive the expression for the disappearance of N_2O_5. State any assumptions made and indicate the conditions under which the assumptions are valid.

(33 points)
(3) Define or briefly describe the following the following:

(a) catalyst
(b) order of a rate law
(c) activation energy
(d) stop flow method
(e) activated complex
(f) cross section for a chemical reaction
(g) entropy of activation
(h) intramolecular vibrational energy redistribution
(i) Michaelis-Menten mechanism ant rate law
(j) diffusion controlled solution reaction
(k) microscopic reversibility

(17 points)
(4) Discuss how collision theory treats bimolecular reaction rates. What assumptions are made? What are the shortcomings of collision theory and how are they corrected within the framework of collision theory?

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.)