Department of Chemistry
Cumulative Examinations
November 15, 2008

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.

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.

PURDUE
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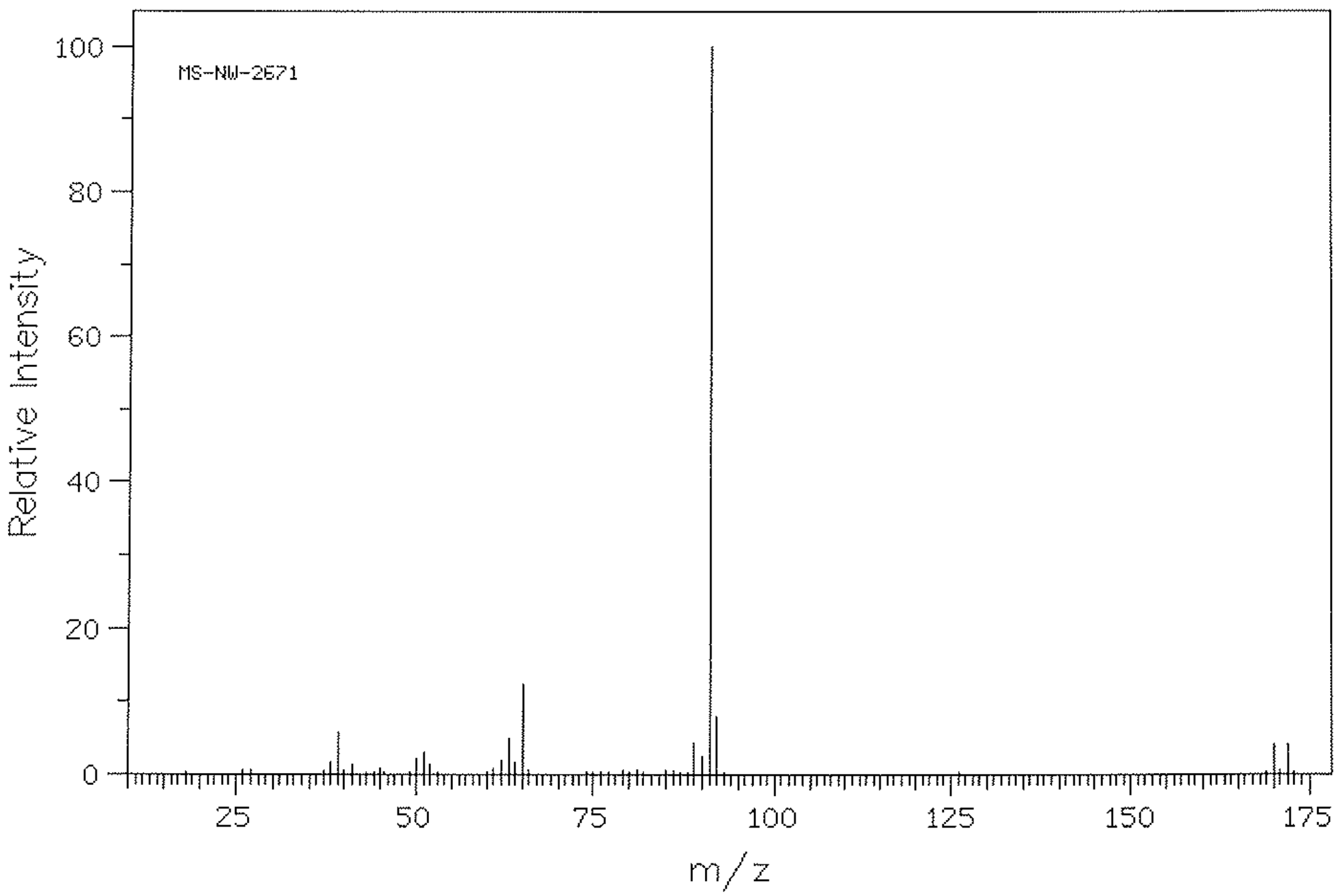
Analytical cumulative examination **November 15, 2008**

1. What compound produced the 70 eV electron ionization (EI) mass spectrum shown below? Justify.



2. Explain why collision-activated dissociation (CAD) mass spectra of molecular ions often look very different from the 70 eV EI mass spectra of the same compound.

3. What type of compounds are likely to produce similar high- (keV) and low-energy (eV) CAD mass spectra? Justify.

4. How much internal energy in average does an activated ion gain upon 70 eV EI, 10 eV CAD, and 3 keV CAD?

5. Give a typical bond dissociation energy of an organic molecule.

6. Are the bonds in ions likely to be stronger or weaker? Justify.

7. Give at least three problems that may be associated with using multiple activating collisions in CAD experiments.

8. Explain what is electron capture dissociation (ECT) and how is the experiment performed.

9. Why is this new activation method creating a lot of enthusiasm among mass spectrometrists?

10. Show the main fragmentation reaction of the molecular ion of ethyl amine.

Biochemistry Cumulative Exam Questions

November 15, 2008

1. Describe the phospholipid asymmetry that exists in an average mammalian cell plasma membrane. Then, describe the enzymes that are involved in both maintenance and loss of this asymmetry. Finally, describe the physiological functions of the induced loss of phospholipid asymmetry that can occur when a cell is triggered to scramble its asymmetry.

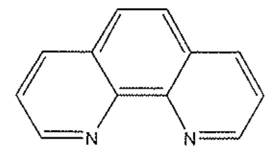
2. Draw the structure of stearoylsphingomyelin and explain why it might tend to segregate into sphingolipid-rich domains (e.g., lipid rafts).

3. Explain how a transmembrane electrical potential is established across a mammalian cell plasma membrane and then describe how this transmembrane potential is used to perform at least two distinct cell functions.

4. Membrane-spanning proteins are commonly comprised of either α-helical or β-pleated sheet segments. Explain why other protein structures are not commonly found in membrane-spanning domains. Then describe how a hydropathy plot is constructed and explain why a hydropathy plot can be used to identify membrane-spanning α-helical but not membrane-spanning β-pleated sheets.

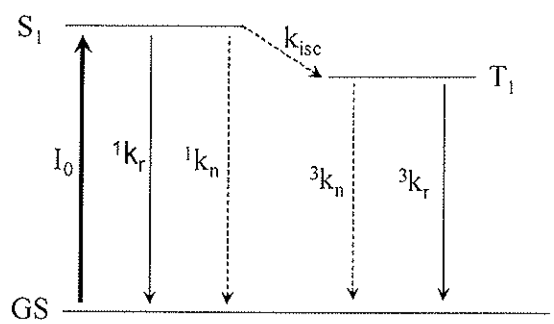
Inorganic Cume

1. (15 pts) The lowest energy absorption bands of the chromate CrO_4^{2-} and Cu(1,10-phenanthroline)$_2^+$ ions have comparable intensities but involve distinct types of charge-transfer excitation. Be as specific as possible and describe the nature of each transition.



1,10-phenanthroline

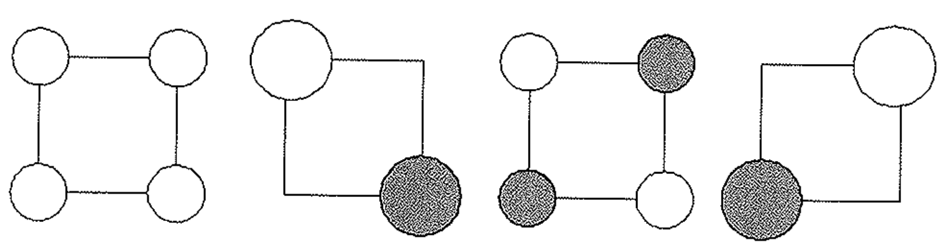
2. (20 pts) The Figure shows a typical Jablonski diagram for a closed shell molecule which has a singlet excited state (S_1) that can decay by intersystem crossing (k_{isc}) to the lower energy triplet state (T_1), emitting a photon (^1k_r process), or non-radiatively converting back to the ground state (^1k_n process) with release of heat energy. The radiative and non-radiative decay constants for the triplet state are ^3k_r and ^3k_n, respectively.



If a steady-state kinetics treatment yields the following expression for the quantum yield of phosphorescence, write the intersystem crossing yield ϕ_{isc} in terms of the relevant rate constants from the Jablonski diagram.

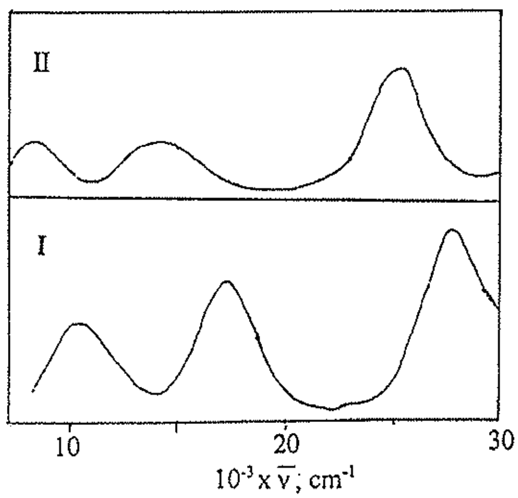
$$^3\phi_r = \phi_{isc}\frac{^3k_r}{^3k_r + {}^3k_n}$$

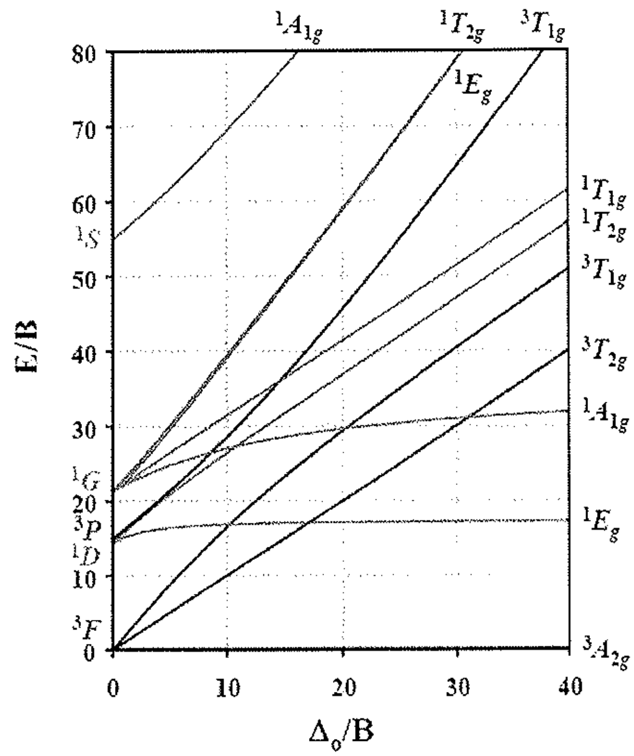
3. (20 pts) Consider the π molecular orbitals of the $C_4H_4^-$ anion, and assume it adopts a square planar structure. The Figure presents, in no particular order, top-down views of the π MO's. Arrange the orbitals in order of decreasing energy from top to bottom, and explain your reasoning. (Note that two of the MO's are degenate and have the symmetry label e with respect to the four-fold symmetry axis. The other two MO's have symmetry a and b.) Finally, attach a symmetry label to each energy level.



4. (15 pts) Find the ground term of the Cr^{3+}(g) ion, and show how many microstates the term entails. (Note you do not have to derive the entire term scheme.)

5. (30 pts) The aquo ion $Ni(OH_2)_6^{2+}$ is pale green in solution while the ammonia complex $Ni(NH_3)_6^{2+}$ is violet. The figure below presents crude representations of the d-d absorption spectra.





d^8 Tanabe Sugano diagram

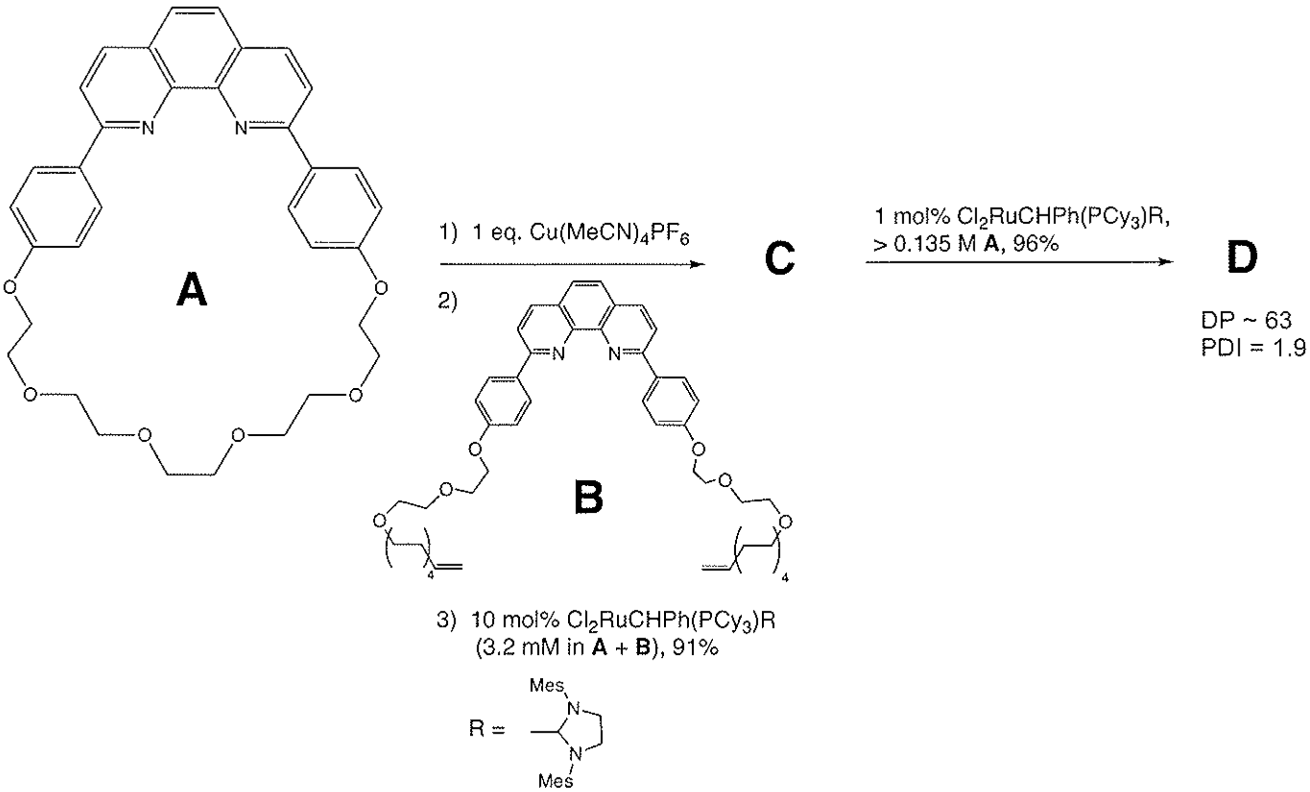
A. Use the Tanabe Sugano diagram to assign the three transitions in spectrum II (top). All three transitions are weak. The extinction coefficients are never more than about 10 $M^{-1}cm^{-1}$. Why?

B. If $\Delta/B = 12.2$ for spectrum I (bottom), use the Tanabe-Sugano diagram and estimate values for B and Δ. Clearly show your work. Define what Δ is.

C. For the Ni^{2+} free ion (no ligands), the Racah parameter B = 1080 cm^{-1}. Explain why B is smaller in the complex.

Organic Cumulative Examination
November 2008

1. (60 pts) In an effort directed toward the synthesis of network polymers with mobile slip-link crosslinks, Mayer and coworkers recently reported the following synthesis:



a. Draw products **C** and **D** that you would expect from this reaction sequence.

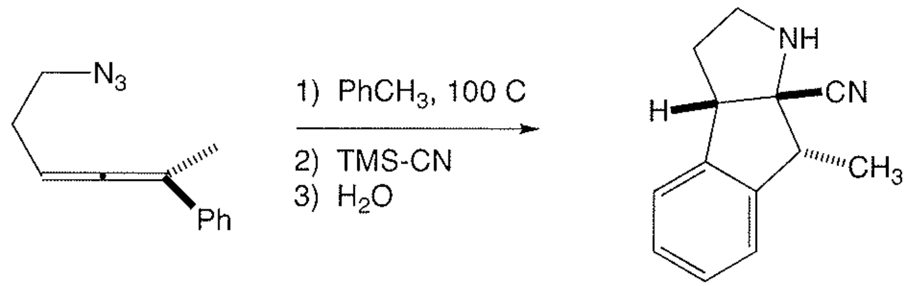
b. What is the role of Cu(I) in this pathway?

c. Consider the SEC data below, where the R_T for **C** is 17.5 minutes. What are the identities of the other peaks in the chromatogram and why do they elute in this order? (Note that the sample was extracted with aqueous KCN/CH_2Cl_2 before injection into the SEC instrument and elution with CH_2Cl_2.

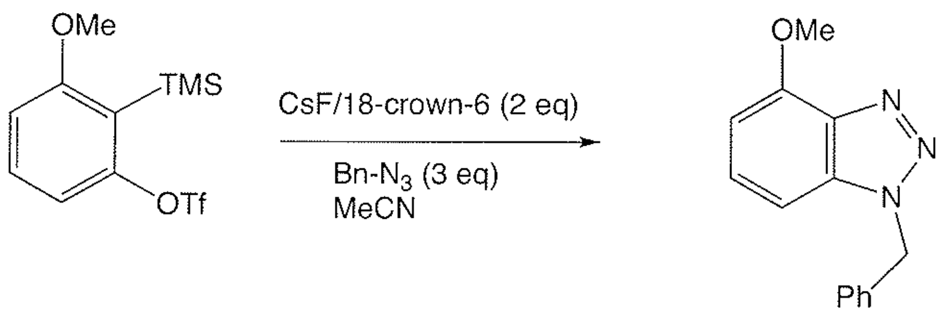
d. What are the next step(s) necessary for the researchers to reach their goal?

2. (40 pts) Propose plausible reaction mechanisms for the following transformations:

a.



b.



P. Chem. Cume Exam Topic: Quantum Chemistry

1. (60) The "double well" is a very primitive one-dimensional model for the potential experienced by an electron in a diatomic molecule (the two wells represent the attractive force of the nuclei). Consider the double square well potential shown in Fig. 1. Suppose the depth V_0 and the width *a* are fixed, and large enough so that several bound states occur.

a. (30) sketch the ground state wave function ψ_1 and the first excited state wave function ψ_2, (i) for the case b = 0 (i.e., there is no barrier), (ii) for b ≈ a, and (iii) for b » a.

b. (20) qualitatively, how do the corresponding energies (E_1 and E_2) vary, as b goes from 0 to infinity? Sketch $E_1(b)$ and $E_2(b)$.

c. (10) If the nuclei are free to move, they will adopt the configuration of minimum energy. In view of your considerations in (b), does the electron tend to draw the nuclei together, or push them apart?

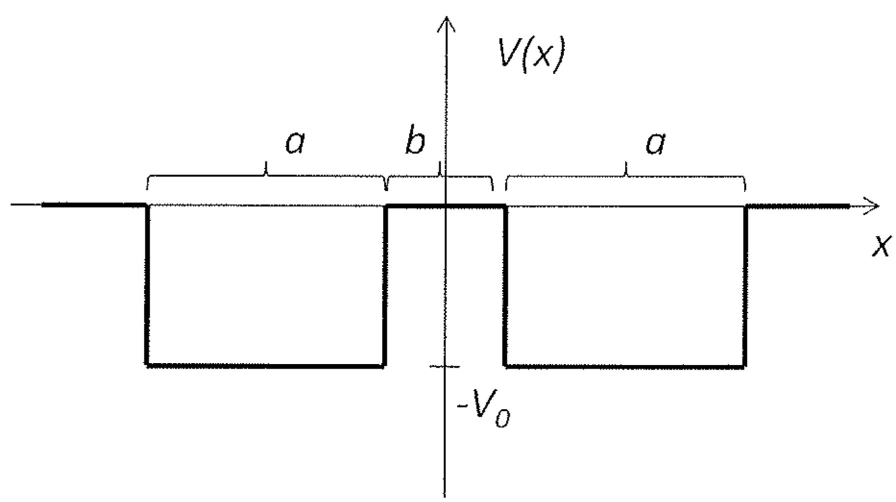


Figure 1. The double square well.

2. (40) A crude treatment of the π electrons of a conjugated molecule regards these electrons as moving in the particle-in-a-box potential, where the box length is somewhat more than the length of the conjugated chain. For a particle in a box of length L, the energy levels are given by $E = \frac{n^2h^2}{8mL^2}$, n =1,2,3...

a. (20) Estimate the wavelength of light absorbed when a π electron is excited from the highest occupied to the lowest-vacant box level in butadiene CH_2=CHCH=CH_2 (take the box length as 7.0 Å).

b. (10) Will the absorption wavelength increase or decrease when the size of the molecule increases?

c. (10) Consider conjugated polymer $(CH)_n$. Based on the conclusions you made in (b), do you expect this polymer to be an electric conductor, semiconductor, or isolator? Justify.

$m_e = 9.1 \times 10^{-31}$ kg (electron mass)
$h = 6.6 \times 10^{-34}$ J·s
1 Å = 0.1 nm = 10^{-10} m

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	0
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.)