Department of Chemistry
Cumulative Examinations
November 11, 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, Page 3
3) Inorganic Cumulative Examination, Pages 4-5
4) Organic Cumulative Examination, Page 6
5) Physical Cumulative Examination, Page 7

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 Cume Based on the Announced Publication:

"Giant Magnetoresistive Sensors and Superparamagnetic Nanoparticles: A Chip-Scale Detection Strategy for Immunosorbent Assays" by R. L. Mcmillen, T. Kawaguchi, M. C. Granger, M. Tondra, and M. D. Porter, *Anal. Chem.* **2005**, *77*, 6581-6587.

1. What is an immunosorbent assay, and how is it performed in the present study?

2. Draw a detailed schematic of a single giant magnetoresistive (GMR) element and describe how the elements in your drawing affect magnetoresistivity (such a schematic and description were not included in the paper).

3. Consider the following figure, reproduced from the paper. Why do the two curves not overlay at low external magnetic fields? What implications might this have within the context of the most common commercial application of GMRs?

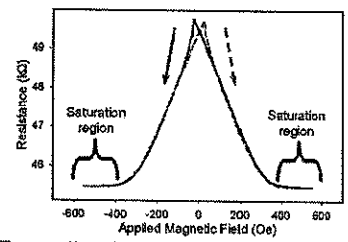


Figure 1. Change in resistance of a single GMR as a function of applied magnetic field. The applied magnetic field is aligned with the plane of the multilayer structure and is scanned from 560 to −560 Oe and back to 560 Oe (see Experimental Section for further details).

4. The authors developed a really clever approach for the construction of a localized Wheatstone bridge using reference and interdigitated sensing GMR elements, shown below. Describe the relationship between the Wheatstone bridge shown in the figure and the measurements shown in Figure 8. Specifically,

a) What is the nature of the raw signal that is measured?

b) How is that raw signal converted to a change in resistance as plotted in Figure 8?

c) Will the voltage difference (E1 - E2) be positive, negative, or zero if $R_{S1} = R_{S2} > R_{R1} = R_{R2}$? Explain (the explanation is worth considerably more than the correct answer).

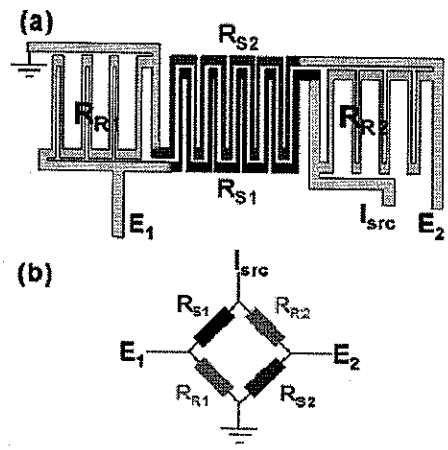


Figure 3. GMR sensor schematic, with an abbreviated GMR path length for clarity. (a) The two interdigitated sensing resistors, R_{S1} and R_{S2}, are shown in blue and red. The two reference resistors, R_{R1} and R_{R2}, are shown in green and are positioned on either side of the sense pad; the yellow lines represent the wire interconnects. (b) All measurements are made in a Wheatstone bridge circuit by sourcing a 5-mA current at I_{src}. The observed change in resistance is measured across E_1 and E_2.

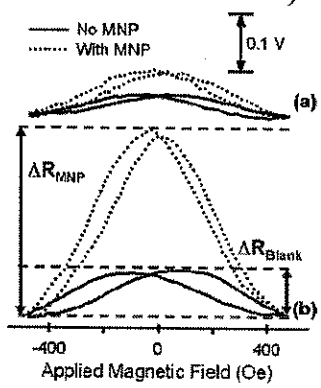


Figure 8. GMR response of sense pad versus magnetic field. Plot of the changing voltage difference ($E_1 - E_2$) of a GMR bridge versus the applied magnetic field. ΔR_{blank} was recorded after Au deposition but before immobilization of (a) 2.4 and (b) 13.3 pM of conjugated MNP. ΔR_{MNP} was recorded after MNP immobilization. The dotted lines in (b) illustrate the magnitude of ΔR_{MNP} and ΔR_{blank}. The dashed green line denotes the baseline response, which corresponds to the signal at saturation. The dashed red and dashed blue lines represent the blank response and the response upon capture of labeled MNPs. The responses in (a) and (b) are for separate GMRs. GMR response is equal to $(\Delta R_{MNP} / \Delta R_{blank}) \times 100$: (a) 206%; (b) 567%.

d) On which of the four GMRs shown in Figure 3 will MNPs bind during an assay?

5. Describe the basic fundamental principles behind x-ray photoelectron spectroscopy (XPS), used to generate Figure 7. What issues do these measurements help resolve in the present study?

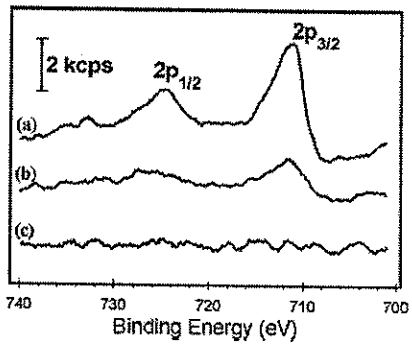


Figure 7. XPS characterization in the Fe(2p) binding energy region for GMR analogues exposed to solutions containing (a) 33 and (b) 11 pM conjugated MNPs. (c) is the capture antibody-modified surface only (i.e., no contact with conjugated MNPs).

6. Describe the fundamental principles behind superparamagnetism (or, as I like to call it, superparamagnatisticexpialadocism – if you say if loud enough, it's really quite atrocious). How does it differ from regular magnetism in bulk materials like iron?

7. Based on your critical review of this manuscript, what do you see as the greatest strengths and limitations of this GMR-based sensing approach relative to more traditional (e.g., fluorescence-based) immunosorbent assay detection methods?

1. Draw the structure of the dipeptide tryptophanylmethionine. Circle the atoms of the peptide bond that are coplanar. Explain why these atoms lie in the same plane and how this feature of the peptide bond allows one to describe the tertiary structure of a protein by defining each phi and psi angle along the polypeptide backbone.

2. Assume an enzyme has an active site that contains a glutamate residue that you hypothesize to be important in the enzyme's structure or catalytic activity. You decide to carry out mutagenesis to change the glutamate to another amino acid to assess the effect.

   A. Name two amino acids that you might use in place of glutamate, and describe how you might expect each replacement to reveal something about the function of glutamate in the original structure. Make sure to draw glutamate and the other two amino acids.

   B. Now assume that you have an isoleucine that you want to mutate because you think it might be important. Again, name two amino acid substitutions, draw the amino acids, and describe what you might learn about the role of isoleucine by making these mutations.

3. Globins.

   A. Compare and contrast the structures and functions of hemoglobin and myoglobin. Include in your discussion changes in the position of the Fe group resulting from oxygen-binding and the effect, if any, on protein structure.

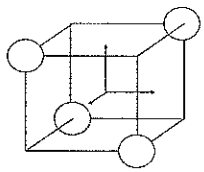
   B. Draw the curves describing O_2-binding to hemoglobin and myoglobin. How are these curves affected by the addition of bisphosphoglycerate? By the addition of carbon dioxide? By the addition carbon monoxide? Why is CO so poisonous?

4. Derive an equation to describe the binding of O_2 to myoglobin.

5. Describe the yeast two-hydrid screen, which is used to look for protein-protein interaction. This method can generate both false positives and false negatives in the search for real protein-protein interactions. List several reasons why these errors might occur. Describe another often-used method for detecting protein-protein interaction and contrast its strengths and weaknesses with those of the two hybrid system.

1. (40 points.) The frontier orbitals of a molecule are tremendously important for understanding reactivity and the electronic spectrum. For each of the molecules or ions below, sketch a contour of the specified frontier orbital. Be sure to specify the axes you have adopted, and name the atomic orbitals involved. If the level is degenerate, you only need to draw one contour, but characterize the degeneracy and indicate all atomic orbitals involved. For ease of drawing, in the metal complexes, assume that the orbital in question is entirely ligand- or metal-based, whichever is more appropriate. HOMO, LUMO, and SOMO respectively denote highest occupied, lowest unoccupied, and singly occupied molecular orbitals. Molecules with unpaired electrons have SOMO's.

In each case justify your answer using simple crystal-field theory, valence-bond theory, or simple MO concepts.



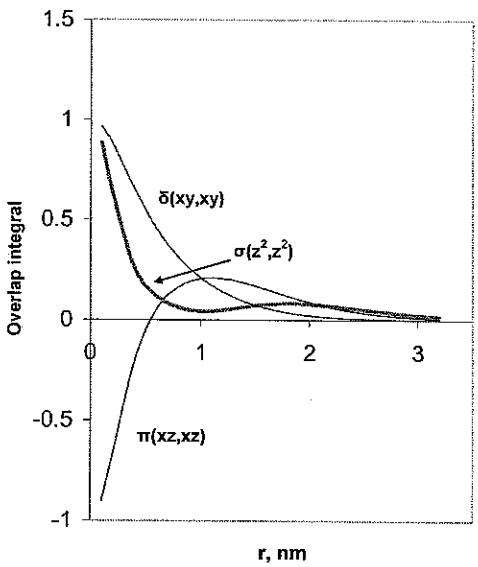
A. SOMO of MnO_4^{2-} (tetrahedral with one unpaired electron)

B. LUMO of $Co(NH_3)_6^{3+}$ (complex is diamagnetic)

C. HOMO of $CuCl_2^-$ (linear, diamagnetic ion)

D. HOMO of $Mo_2Cl_8^{4-}$ (quadruply bonded and diamagnetic)

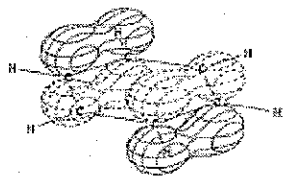
2. (10 points.) An article in *Chem Comm* **2006**, 2164 considers how the overlap integral varies with distance for d-orbitals on a pair of adjacent metal atoms. The plots below show how the overlap varies for sigma, pi and delta interactions when the metal-metal bond is the z-axis.

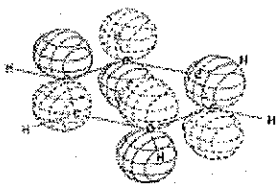


Draw juxtaposed atomic orbitals at a couple of distances and rationalize the detailed distance dependence of the overlap for each type of interaction, including the reason for the sign of the net overlap. If the bonds are between two molybdenum atoms, what is the principal quantum number associated with the atomic orbitals?

3. (50 points.) Each of the following pairs represent the HOMO and LUMO of a molecule, or a SOMO and a neighboring filled orbital. The energy ordering (left to right) within each pair is random. Identify the LUMO or the SOMO in each pair and briefly justify your answer. The molecules are benzene, water, nitric oxide, methyl isonitrile, and carbon dioxide. Some of the levels are degenerate, but we show only one orbital for each energy. Again use MO concepts, valence bond ideas, reactivity principles, nodal properties, etc. Figures from Jorgensen and Salem's book.

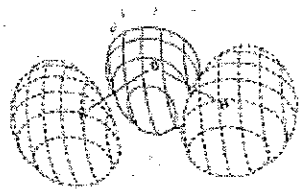
A1

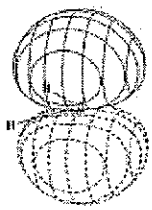




A2

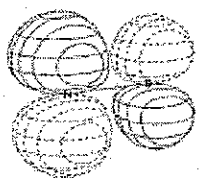
B1

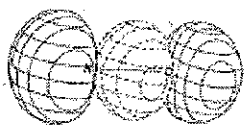




B2

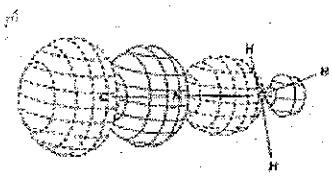
C1

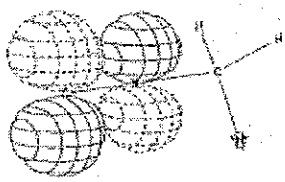




C2

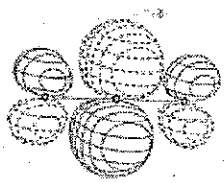
D1

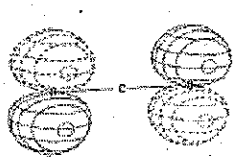




D2

E1



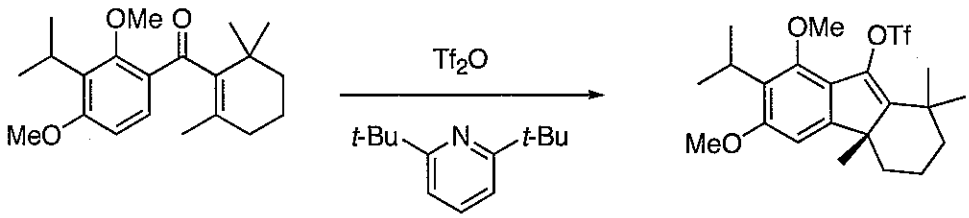


E2

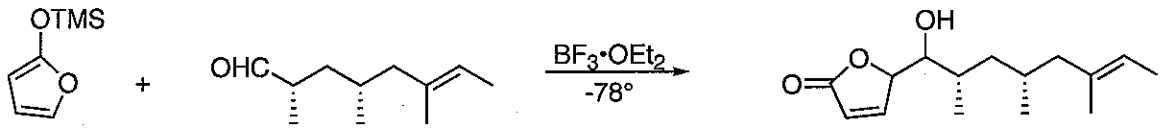
Organic Cumulative Exam – November 2006

Please provide a mechanism for the following five reactions.

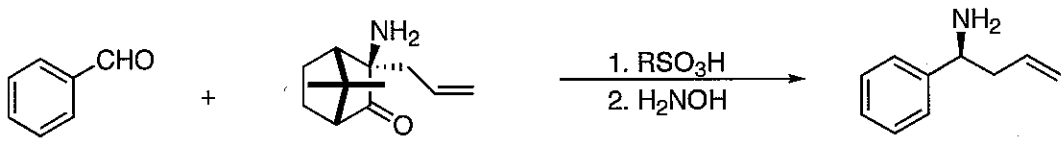
1. JACS, (2006) 128, 11022.



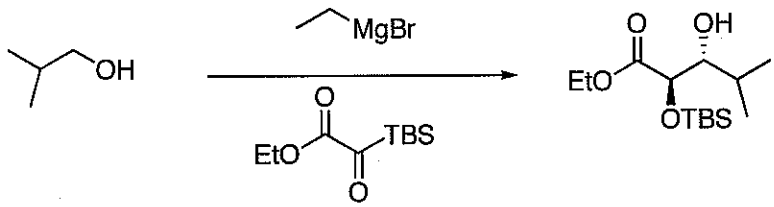
2. JACS, (2006) 128, 11032.



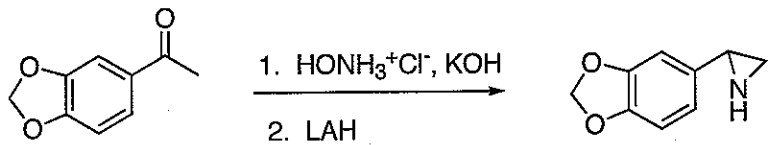
3. JACS, (2006) 128, 11038.



4. JACS, (2006) 128, 9302.



5. JACS, (2006) 128, 10370.



Physical Chemistry

November 11, 2006

The frequency $\bar{\nu}(cm^{-1})$ of a hydrogen-like (one-electron) atom are given by

$$\bar{\nu} = \mathrm{R}_N \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}} \right)$$

where $n_1 = 1$ (Lyman lines), $\mathrm{n}_1 = 2$ (Balmer lines,) . . . and where $\mathrm{n}_2 = \mathrm{n}_1 + 1, n_1 + 2, \ldots$
Note that

$$\mathrm{R_N} = \frac{\mu_N}{\mu_H}\mathrm{R_H} \quad \text{where } \mathrm{R_H} = 109677 cm^{-1}$$

where $\mu_N = \dfrac{m_N m_e}{m_N + m_e}$ and $\mu_{\mathrm{H}} = \dfrac{m_p m_e}{m_p + m_e}$

and where $\mathrm{m_N}$ is the mass of the atom's nucleus, m_e is the mass of an electron, and m_p is the mass of a proton. To evaluate μ_N and μ_H, you will need the values of m_e and m_p. These are

$$m_e = 9.10938 \text{ x } 10^{-31}\text{kg}$$
$$m_p = 1.67262 \text{ x } 10^{-27}\text{kg}.$$

Given the above information solve the following two problems.

a. Calculate the mass of a D nucleus (one proton and one neutron) m_D in kg given that the first Lyman absorption lines of H and D occur, respectively, at 82, 259.098 cm^{-1} and 82,281.476 cm^{-1}.

b. Positronium consists of an *electron* e^- and a *positron* p^+. A positron is a positively charged particle with the same mass m_e as the electron. Thus the reduced mass of positronium is

$$\mu_{pos} = \frac{m_e^{\,2}}{2m_e} = \frac{m_e}{2}.$$

Compute the binding energy of positronium in ev. Note that 1ev = 8065.5 cm^{-1}.

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.)