Department of Chemistry
Cumulative Examinations
October 22, 2005

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 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 Cumulative Examination
October 22, 2005

Analytical Chemistry Cume Based on the Announced Publications:

1. Single Silver Nanoparticles as Real-Time Optical Sensors with Zeptomole Sensitivity" A. D. McFarland, R. P. Van Duyne; *Nano Lett.* **2003**, 1057.
2. "Biomolecular Recognition Based on Single Gold Nanoparticle Light Scattering" G. Raschke, S. Kowarik, T. Franzl, C. Sönnichsen, T. A. Klar, J. Feldmann, A. Nichtl, K. Kürzinger; *Nano Lett.* **2003**, *3*, 935.

1. What is a surface plasmon? What is the primary difference between SPR and LSPR?

2. What was the transduction mechanism in each experiment (i.e., what was the experimental observable and how was it correlated to surface binding)? How was it measured experimentally?

3. The investigations by Rick Van Duyne's group (and presumably the Raschke work as well) utilized a single CCD camera for imaging AND localized optical spectroscopy. Describe how a single monochrometer/CCD camera system can be used for either spatially resolved imaging or localized optical spectroscopy by adjusting only one setting in the monochrometer. Can it do both simultaneously?

4. Describe the fundamental principles and practical implementation of dark-field microscopy. Draw a <u>detailed</u> schematic of a dark field microscope coupled to a CCD camera for detection.

5. Describe the principles and applications of nanosphere lithography. Describe the structures that result. What aspects of NSL are adjusted to control the height and length of the resulting nanostructures so precisely? Why could these structures not be generated using standard photolithography techniques?

6. In principle, the $\sim 10^8$ enhancement factors associated with LSPR could increase the efficiency of many optically driven processes, including fluorescence. In practice, the enhancements in fluorescence are often several orders of magnitude less than the enhancements in Raman when using a sufficiently intense excitation source, often saturating at $\sim 10^7$ - 10^8 fluorescence photons / second (compared to $\sim 10^6$ photons/second in the absence of enhancement). Why is the enhancement so much less than the theoretical maximum in fluorescence? Why does this same issue not affect the enhancements observed in Raman spectroscopic measurements?

7. What is the difference between extinction and absorption? Which one is measured by uv-vis spectrometry?

8. Let's take a step back to consider an established competing technology. Traditional SPR measurements can either be performed using a narrow-band fixed wavelength source or a white-light source. Draw a schematic for each instrument and describe the similarities and differences in their fundamental mechanisms of operation. In each case, what physical observable is measured and how is it affected by surface binding?

9. One of the key claims of each of the articles was the possible extension of this sensing approach to massively parallel assays. With infinite development time and resources, propose an experiment and instrument to accomplish this objective. What are some practical complications you may encounter? What are some practical advantages and disadvantages of single nanoparticle assays compared to traditional surface assays (e.g., in traditional SPR or from nanoparticle arrays)?

Biochemistry cume (2 pages)

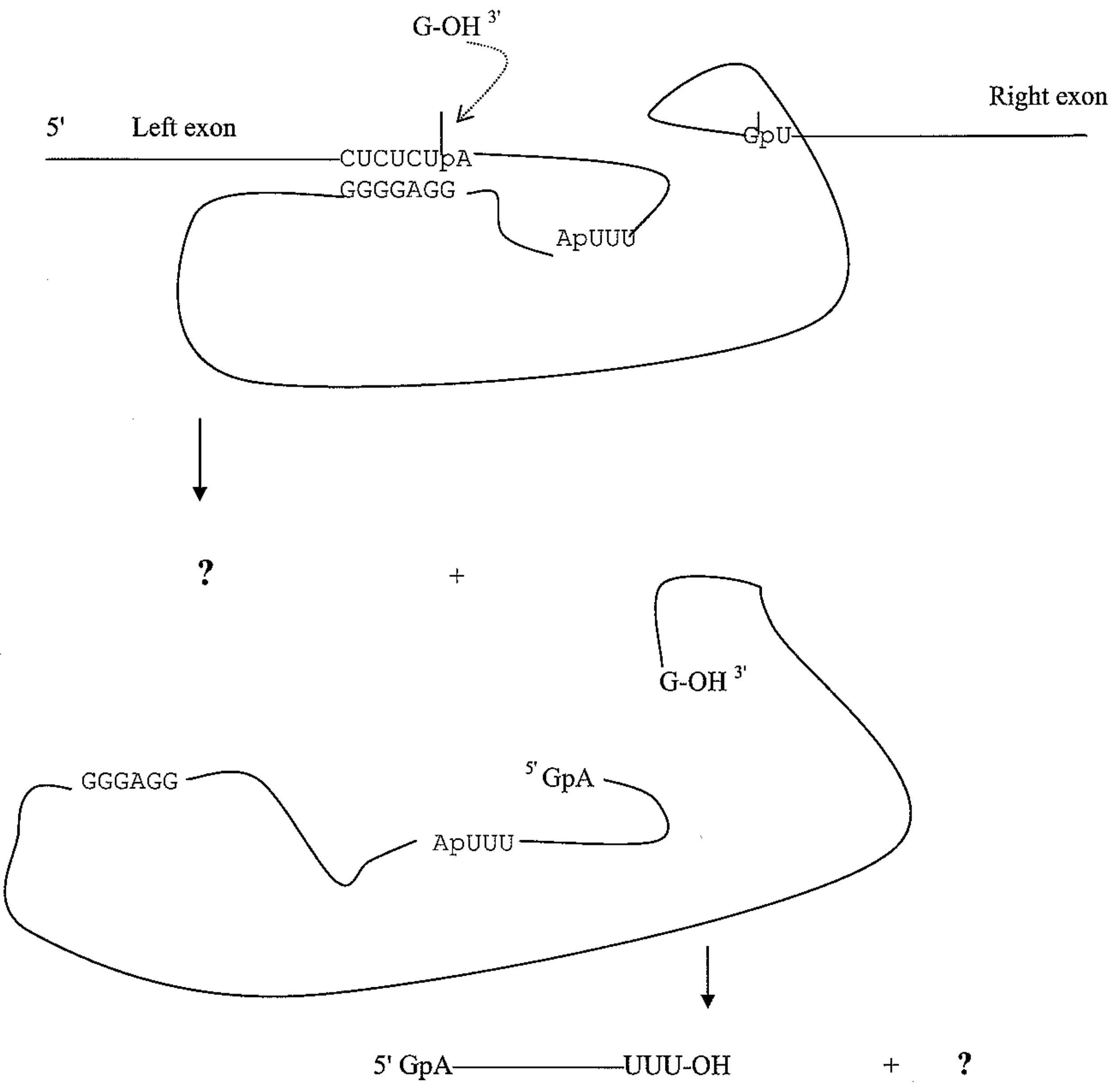
1. In 1989, Sidney Altman and Thomas check received the Nobel Prize in chemistry for their discovery of ribozymes.

(A) What is a ribozyme?

(B) Why the discovery of ribozymes was considered to be important?

(C) What did their discovery imply about the origin of life?

2. Shown below is a diagrammatic representation of a pre-rRNA that can undergo splicing. Provide a diagrammatic representation of the molecules marked by a question mark.



3. Shown below is the genomic organization of a gene that contains two introns.

(The broken arrow marks the position of the transcription initiation site).

To investigate whether the mature mRNA is produced via mRNA splicing, an investigator performed the following experiment.

She isolated and purified cytoplasmic mRNA molecules corresponding to the processed transcripts of the gene. The antisense cDNA to that mRNA was synthesized and subsequently hybridized to genomic DNA.

Draw a diagram to predict the expected micrograph if the mature mRNA was produced via the mechanism of mRNA splicing.

4. Previously investigators attempted to create therapeutic reagents using antisense RNA. However, emerging evidence indicates that small interfering RNA molecules (siRNAs) provide a more effective approach.

(A) Concisely describe how an antisense RNA could act as a therapeutic reagent (give an example).

(B) Concisely describe the mechanism through which siRNAs work and discuss why siRNAs could be more effective therapeutic agent than antisense RNA.

1. (60 points.) The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of a molecule often guide the reactivity. For example, in the case of a Lewis base, interaction/overlap with the HOMO is usually key to adduct formation.

Figure 1 is a qualitative MO diagram for the valence orbitals of the cyanide ion, which can act as a Lewis base. The three contours (I-III) are crude representations (with carbon to the left) of three different molecular orbitals implicit in the scheme. (Though we depict only one orbital per energy level, the level could be degenerate.) In Figure 1 assume that the internuclear axis defines the z-direction and that the plane of the page is the yz plane.

A. Assign each contour to an energy level in the MO scheme, and explain your reasoning. For convenience the energy levels of cyanide have letters for labels. Identify all participating atomic orbitals in each contour (I-III) in light of the axis system defined above.

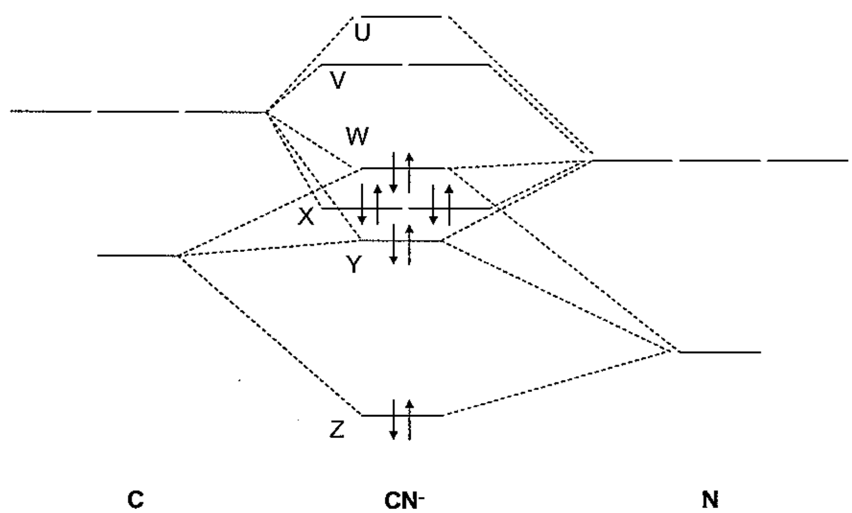
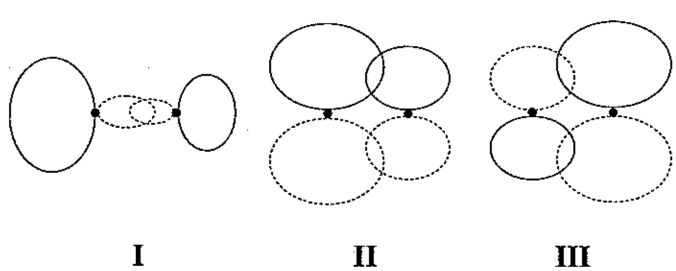


Figure 1



1. Continued.

B. Explain why sigma bonding logically favors formation of a linear HCN molecule with the proton attached to carbon.

C. In contrast, calculations by Bursten et al. suggest that cyanide prefers to bind via the nitrogen end in $UO_2(CN)_4^{2-}$ (see Figure 2). The authors attribute this to π bonding. Deduce the oxidation state of uranium, and explain whether the cyanide ligand will act as a π donor or π acceptor in the complex. Finally, show how this rationalizes the observed connectivity to nitrogen.

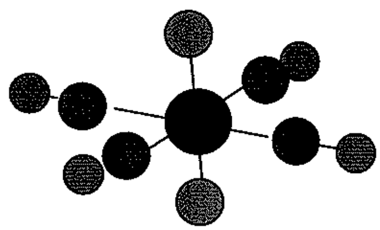


Figure 2

2. (40 points.) For any FOUR of the following, sketch a contour of the indicated orbital. Be sure to specify the axes adopted, give the signs of the lobes, and name the participating atomic orbitals. If the level is degenerate, you may draw only one contour, but you must describe the other orbital(s) 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. If you attempt all five, we grade the first four answers.

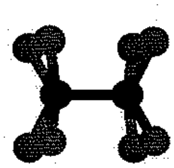
A. Highest occupied or half-occupied orbital of $NiCl_4^{2-}$ (tetrahedral complex with 2 unpaired electrons)

B. LUMO of $Fe(CN)_6^{4-}$ (octahedral and diamagnetic)

C. LUMO of CO

D. HOMO of NH_3

E. delta bonding orbital of $Re_2Cl_8^{2-}$



Organic Cumulative Exam

October 22, 2005

Define and/or give an example of the following twenty questions:

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a. Provide and example and a use for an atropisomer.

b. Double stereoselection.

c. Lightest Man-made radioactive element.

d. A chiral compound without a chiral center.

e. Structure of cholesterol.

f. Show a transition state drawing and indicate the resultamt steterchemistry of a Cope rerrangement.

g. Strength of the C-H bond of ethane (± 5 Kcal)?

h. What is the most important economic use for Helium?

i. Draw an example of a vinylogous carboxylic acid; estimate its pKa.

j. What is the energy difference between two materials in equilibrium (25°[C) if their ratio is 9:1?

k. What is the structure and a use of methyl triflate.

l. Give the mechanism of the Swern oxidation of an alcohol to a ketone.

m. Give the Lewis structure of the mono sodium salt of nitromethane, including all formal charges.

n. Provide the structure of a non-natural alpha aminocarboxylic acid which is not simply an enantiomer of a natural amino acid.

o. Representative structure and significance of PCB's.

p. Optimal catalyst for cyclopropanation of a diazo precursor.

q. Provide a mechanistic scheme showing the use of N-chlorosuccinimide.

r. Give 5 NMR active nucleii with I = 1/2.

s. Draw the expected parent ion region of the mass spectrum for chloroform.

t. Draw the fluorine and carbon-13 spectra of trifluoroethanol.

Physical Cumulative Examination
October 22, 2005

1. Consider a mixture of ideal gases A and B in a container of volume V. The number of A molecules is N_A while that of B is N_B. The system is in equilibrium with a thermostat at tempreature T.

   (a) For all the questions bellow, please express your answers in terms of T, V, N_A and N_B and recall that we are describing ideal gases.

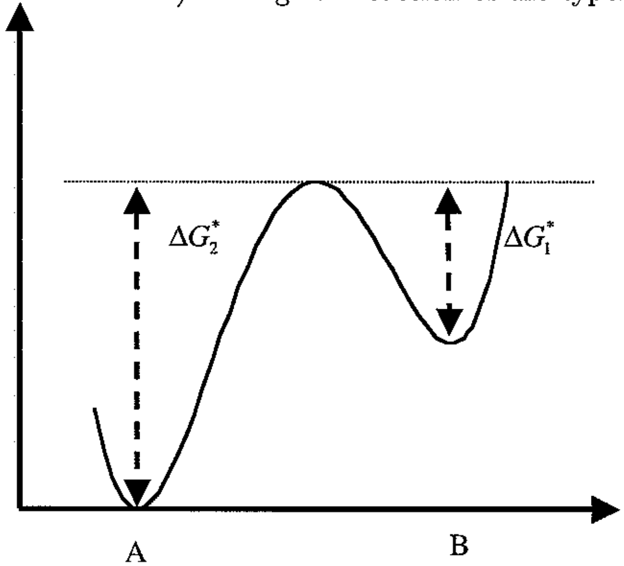
      i. What are the pressure and the isothermal compressibility of the gas? Hint: The isothermal compressibility is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

      ii. In Physical Chemistry textbooks the introduction of the minus sign in the definition of the isotehrmal compressibility is explained by stating that in this way the quantity is going to be positive since an increase in pressure always decreases the volume. Can you think of any thermodynamic condition for any system (including non-ideal ones!) for which the isothermal compressibility is negative? Is there any fundamental law that helps us in here? Explain your reasoning.

      iii. Imagine now that we partition the container into two boxes of equal volume $V/2$ each. What will be the total number of molecules and that of each species in each of the partitions? What is the order of magnitude of the fluctuation in the number of molecules in each partition?

2. The potential energy surface (free energy as a function of the proper reaction coordinate) for a given reaction of the type $A \rightleftarrows B$ is of the form



3. Write an expression for the thermodynamic equilibrium constant of the reaction in term of the relevant difference in free energy.

4. If we consider the kinetics to be of the form

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B]$$

what is the relationship between the kinetic constants k_1, k_2 and the free energy differences ΔG_1^*, ΔG_2^*. Is there any relationship between the equilibrium constant of the reaction and the kinetic constants? Explain.

5. Can you find the equilibrium constant for the above given chemical reactions from the knowledge of the A and B chemical potentials? Explain how you could do that.

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII	VIII	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.)