

Department of Chemistry
Cumulative Examinations
March 1, 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.

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

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

U N I V E R S I T Y

Analytical Chemistry Cume

Topic: Nonlinear Optical Microscopy

1. (5 pts) List three merits of multiphoton microscopy in biological imaging.
2. (5 pts) Explain why nonlinear optical microscopy has inherent 3D sub-micron spatial resolution.
3. (5 pts) Spontaneous Raman scattering is very weak, making it time consuming to take a Raman image. Coherent anti-Stokes Raman scattering (CARS) microscopy allows high-speed vibrational imaging because the CARS signal from an objective is much larger than Raman signal. Explain why the CARS signal can be much larger than Raman signal.
4. (5 pts) The fluorescence signal goes forward and backward equally. Why does the SHG signal predominantly go forward?
5. (5 ps) List three ways to increase the tissue penetration depth in multiphoton microscopy.
6. (5 ps) In third-harmonic generation (THG) microscopy, the THG signal from a bulk solvent is canceled. Explain the reason.
7. (10 pts) In multiphoton fluorescence and other nonlinear optical microscopy, why is it desired to put the detector close to the tissue sample?
8. (10 pts) List the three mechanism for epi-detected CARS contrast.
9. (10 pts) A Ti:sapphire femtosecond laser with a repetition rate of 80 MHz is used for multiphoton fluorescence imaging. If the average excitation power is 5 mW. The pulse width is 100 fs. What is the peak power?
10. (10 pts) Two laser beams, one at 900.0 nm and the other at 1100.0 nm, are used to generate new wavelengths via nonlinear optical processes. What is the wavelength of the sum frequency generation signal?
11. (10 pts) Two beams at frequencies ω_1 and ω_2 ($\omega_1 > \omega_2$) are focused into a medium. Write down all the new frequencies generated through second order wave mixing.
12. (20 pts) The CARS field is generated by the interaction of the pump and Stokes field with a sample. The CARS intensity can be written as $I_{\text{CARS}} = \chi^{(3)} I_p^2 I_s$, where I_p and I_s are the pump and Stokes beam intensities, respectively. Suppose the total excitation intensity, $I_p + I_s$, is a constant, calculate the optimal ratio between I_p and I_s to generate the largest CARS signal.

Cumulative Examination in Biochemistry
March 1, 2008

00056

Instructions. There are five questions, and each question is worth 20 pts.

1. The X-ray crystallographic determination of a new protein structure is typically accompanied by a Ramachandran plot. What is a Ramachandran plot? With the help of appropriate structural diagrams, explain what is being plotted. Sketch a typical Ramachandran plot, indicating important points of interpretation. What is the role of the Ramachandran plot in the context of the structure description? There is an added complication in the use of a Ramachandran plot for the analysis of protein structures determined by NMR spectroscopy. What is that?

2. (A) When comparing regions of protein sequence, writers and speakers often confuse “homology”, “identity”, and “similarity”. Provide clear definitions that distinguish between these terms.
(B) Distinguish between orthologs and paralogs.
(C) What are isozymes? What is their origin? Name two important examples from mammalian biochemistry.

3. The Bohr effect plays an important role in human physiology and the biochemistry of oxygen transport. In qualitative terms, what is the Bohr effect? Draw a commonly used graph that represents oxygen transport in the absence and presence of the Bohr effect. Now describe in some detail the specific structural interactions that are responsible for the Bohr effect.

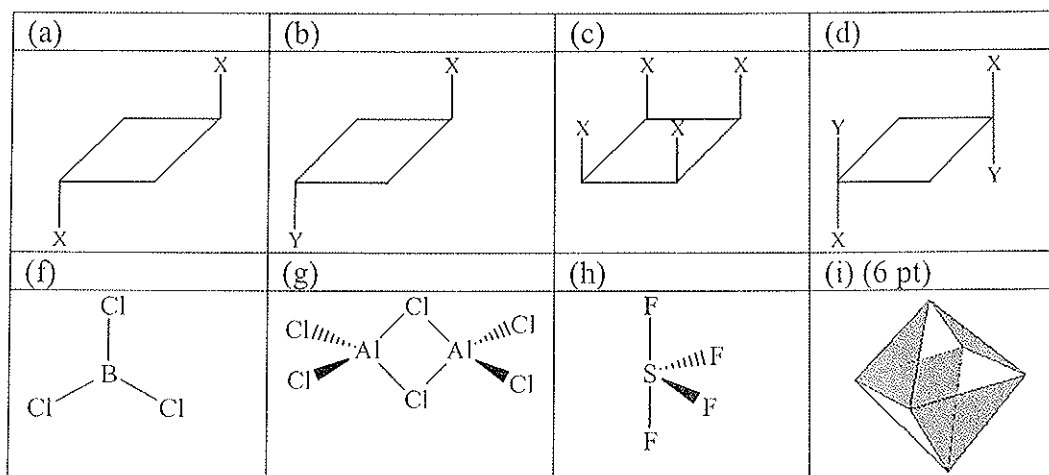
4. Typical cytoplasmic, globular proteins are characterized by the presence of a “hydrophobic core”. Briefly explain what is meant by this. Then, using specific biophysical and thermodynamic arguments, explain the actual basis for the formation of such a hydrophobic core.

5. The past few years have seen dramatic advances in our understanding of intracellular protein turnover in eukaryotic organisms. What is the major pathway for eukaryotic, intracellular protein turnover? Describe in detail the process and the molecular structures involved.

Inorganic Cumulative Exam

March 1, 2008

- 1 (30) A recent inorganic literature seminar was titled “Unconventional mixed valency”. The following questions are about conventional mixed valency (stuff you may find in *Miessler and Tarr*).
- A Sketch the structure of the Creutz-Taube ion (be as precise as you can).
- B Write the so-called *comproportionation* equilibrium equation for the Creutz-Taube ion.
- C Provide a graphic sketch to explain the term “IVCT”.
- D The formal oxidation potentials related to a mixed valent monocation are: $E^{\circ}(+2/+1) = -0.40$ V and $E^{\circ}(+2/+1) = -0.76$ V at 25 °C. What is the *comproportionation* constant for this mixed valent species? ($2.3026 RT/F = 59.16$ mV at 25 °C)
- 2 (30) Assign symmetry point groups for the following molecules/objects (**mark symmetry elements clearly**).



3. (20) What are the SALCs made up of σ -orbitals on F atoms that can be employed in forming P-F bonds in PF_5 ?
- 4 (20) Provide a representative reaction equation for reactions catalyzed by each of the following catalysts
- Grubbs 2nd generation catalyst
 - Wilkinson's catalyst
 - $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}/\text{base}$ (Sonogashira)
 - $\text{CuSO}_4/\text{ascorbic acid}$ (*click* reaction)

Character tables -- choose one suitable for problem #3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1	-	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	-	-
E	2	-1	2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	-
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

C_{4v}	E	$2C_4(z)$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	-
B_1	1	-1	1	1	-1	-	x^2-y^2
B_2	1	-1	1	-1	1	-	xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

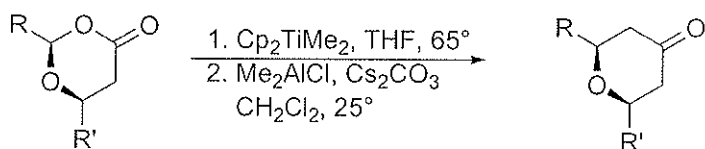
D_{4h}	E	$2C_4(z)$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	-	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	-
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	-	x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	-	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	-	-
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	-
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	-	-
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	-	-
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	-

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1	-	x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	-
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1	-	-
A_2''	1	1	-1	-1	-1	1	z	-
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

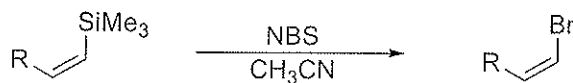
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Propose stepwise mechanisms to explain 4 of the 7 following transformations. Use curved arrow formalism to show electron movement and show all likely intermediates.

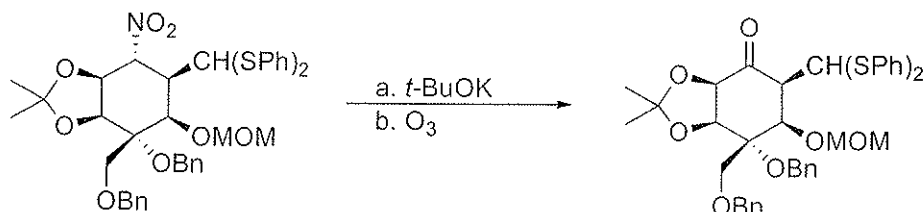
1.



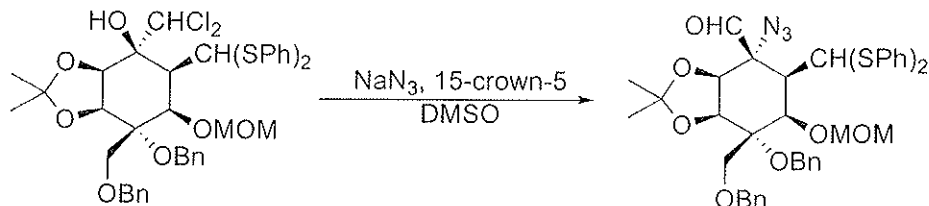
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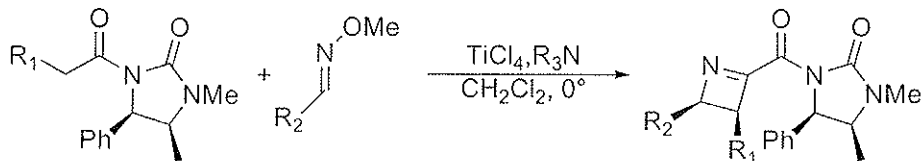
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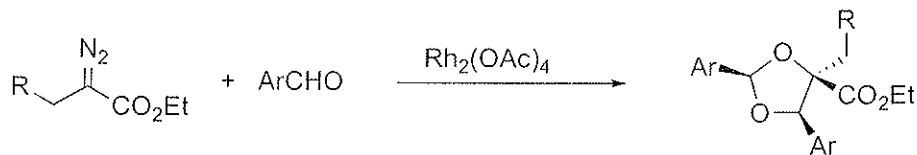
4.



5.



6.



7.



Physical Chemistry Cume

March 1, 2008

Spin operators and the Pauli spin matrices

The spin angular momentum, S , obeys the following commutation rules:

$$[S_x, S_y] = i\hbar S_z \quad [S_y, S_z] = i\hbar S_x \quad [S_z, S_x] = i\hbar S_y$$

$$\text{And } S_{\pm} = S_x \pm iS_y$$

1. The two eigen-operators for spin s are S^2 and S_z . These operators and their eigenvalues parallel similar ones for angular momentum L . What are the eigenvalues for these two operators when they act on state $|s, m_s\rangle$?

- a) In other words, what are $S^2 |s, m_s\rangle$ and $S_z |s, m_s\rangle$?
- b) What are the eigenvalues when $s = 1/2$ and $m_s = -1/2$?

2. For a spin- $1/2$ nucleus, the raising and lowering operators are given by:

$$S_+ |s, m_s\rangle = \hbar (s(s+1) - m_s(m_s+1))^{1/2} |s, m_s+1\rangle$$

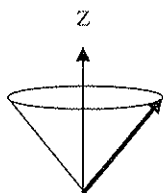
$$S_- |s, m_s\rangle = \hbar (s(s+1) - m_s(m_s-1))^{1/2} |s, m_s-1\rangle$$

When $s=1/2$ and $m_s = 1/2$, this state is called α .

When $s=1/2$ and $m_s=-1/2$ this state is called β .

- a) What are the eigenvalues for these two operators for state α ?
- b) What are the eigenvalues for these two operators for state β ?

3. In NMR, the sample is often described as an ensemble of isolated spin systems. As a simple example, for an isolated set of spin- $1/2$ nuclei such as the protons in a water sample, the spins at equilibrium start pointing along the z axis, and are thus in a state α . The spin rotates around the z axis at the Larmor (NMR) frequency. This is shown below for a single spin:



- a) What is the value of $\langle S_z \rangle$ at equilibrium?
- b) What is the value of $\langle S_x \rangle$ at equilibrium?

4. Spin operations in quantum mechanics is often represented by the Pauli spin matrices. The Pauli spin operator σ is related to the spin angular momentum S by the following: $\sigma = \frac{2}{\hbar} S$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = i \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- a) Show that at least one of the S-spin commutation rules is followed for the Pauli spin matrices.

5. Using this matrix representation, the states α and β are given by:

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- a) What is the eigenvalue when σ_z operates on state α ?
 b) What is the eigenvalue when σ_x operates on state β ?
6. In the NMR experiment from problem 3 above, after a 90-degree radio frequency pulse the magnetization points along the x-axis.
- a) What is the new eigenvalue when σ_z operates on the new state?
 b) What is the new eigenvalue when σ_x operates on the new state?
 c) Can you write the new state in terms of α and β ?
 (hint, you can use the answer to (b) to set up an equation to solve for the state)
 d) What is this new state called when it is made up of states such as α and β ?

Periodic Classification of the Elements

I A		II A		III A		IV A		V A		VI A		VII A		VIII		IX A		X A																																																																																				
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	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	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)	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)

*Lanthanides

†Actinides

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