

**Department of Chemistry
Cumulative Examinations
November 10, 2007**

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 *four* examinations.

- 1) Analytical Cumulative Examination, Pages 1-2
- 2) Biochemistry Cumulative Examination, Pages 3-4
- 3) Inorganic Cumulative Examination, Pages 5-6
- 4) Organic Cumulative Examination, Pages 7-8
- 5) Physical Cumulative Examination, Page 9

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
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Analytical Cume November 2007

Correlations and NMR Spectroscopy

Correlation among data is well known and is currently of interest in NMR spectroscopy to achieve a number of improvements in time and resolution. We will explore some of these ideas in the following questions.

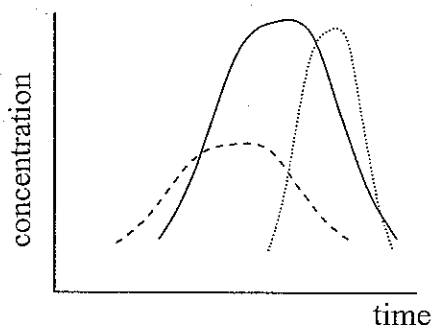
1. Draw a x-y scatter plot of data points (20-30 points, or alternatively a cloud of points) illustrating the following correlations:
 - a) 1.0 (highly correlated x- and y-data)
 - b) -1.0 (negatively highly correlated data)
 - c) 0.3
 - d) 0.0
2. In Correlation Spectroscopy, commonly called COSY, a two-pulse sequence is used to identify connections among the J-coupled protons in the molecule. The pulse sequence is as follows:



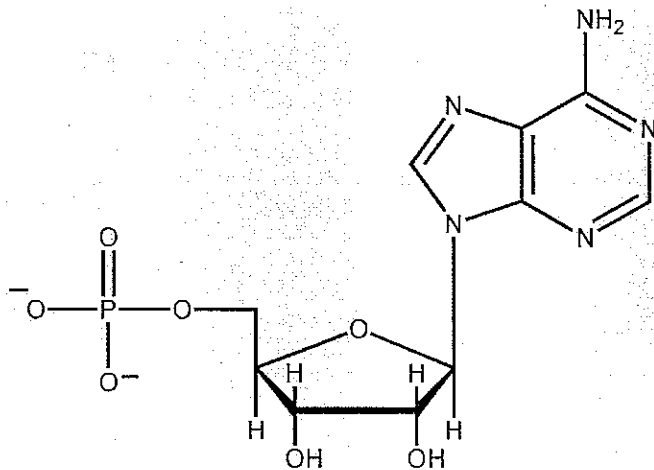
Essentially, the pulse sequence is repeated for a number of different t_1 delay values and the signal (free induction decay, or FID) is collected. Fourier transformation (FT) is then performed twice, first as a function of the acquisition time t_2 , and then along the so-called indirect or t_1 dimension. This leads to a 2D spectrum that chemists are very accustomed to seeing since 1976. (The combination of Fourier transform and 2D NMR led to a Nobel prize). Typically, 64 or 128 t_1 values are used, while there are often 16k points taken during a 2-second acquisition time.

- a) Briefly, explain Fourier transformation. If you can write down a formula please do.
- b) What is the Fourier transformation of a decaying exponential function?
- c) What determines the spectral resolution in FT NMR?
- d) In the example above, what would the spectral resolution (in each dimension) be for a 10 ppm spectrum taken at 500 MHz? (you can give your answer either in Hz or ppm).

- e) Normally, “zero-filling” is done along the indirect dimension to extend the data with zeros and double or even quadruple the number of t_1 increments. What does this accomplish?
3. A recently reported alternative approach for some 2D NMR experiments is called “Covariance NMR.” In this approach, the data are collected as before, but instead of the Fourier transformation in the indirect direction, a cross-covariance calculation *between different frequencies* is performed to identify the couplings between the protons in the molecule.
- a) (Hard) The correlation between x and y data is given by the following expression:
- $$r_{xy} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{(n - 1)s_x s_y},$$
- where \bar{x} is the mean of the x data, s_x is the standard deviation, and similarly for the y data. The covariance is the same expression without the normalization by the standard deviations. Given the NMR data or signal is of the form $S(\text{freq}, t_1)$, explain in words what is being correlated and what is being summed over.
- b) The big advantage of this approach is that the resolution is improved. Along what dimension does the improvement occur? Can you explain how?
- c) If $n=16$ for the covariance experiment, what would this represent compared to the Fourier transform approach? What is the advantage?
- d) There is of course, no free lunch, and so this approach has a down side. The computation is a bit slower, but more importantly, if there are more peaks than n , one can get artifacts such as extra peaks. How would this be a problem for say biofluid samples?
4. A newly reported application of covariance processing is to de-convolve overlapped peaks in complex spectra such as in LC/NMR. Given 3 different compounds, each with its own NMR spectrum, and slightly different elution profile such that spectra are overlapped, how could you use covariance or correlation to figure out what the 3 different molecules are?



1. Which of the following hormones is NOT a polypeptide?
(A) Insulin
(B) Oxytocin
(C) Cortisol
(D) Somatostatin
(E) Glucagon
2. Which of the following amino acids undergoes NADPH-dependent oxidation to yield nitric oxide.
(A) L-Lysine
(B) D-Lysine
(C) L-Arginine
(D) L-Glutamine
(E) D-Arginine
3. The structure of Adenosine Monophosphate (AMP) is given below.



Draw the structure of cyclic AMP.

What is the name of the group of enzymes that catalyze the formation of cyclic AMP from ATP?

What is the name of the group of enzymes that catalyze the hydrolysis of cyclic AMP to produce AMP?

4. What is a G Protein-Coupled Receptor (GPCR)?
5. Describe briefly the mechanism of receptor-mediated activation of adenylate cyclase.
6. What is a protein kinase?

Depending on the amino acid sequence of their substrates, kinases can be divided into two types. What are the types?

Provide a rationale as to why there are so many protein kinases (estimated number is approximately 2000) in the human genome.

What are phosphatases?

7. Describe briefly the general mechanism of signal transduction by a receptor tyrosine kinase.
8. Briefly describe a mechanism by which the intracellular production of cyclic AMP can be linked to the recognition of a hormone present on the outside of a cell.
9. Describe briefly, in the context of phosphoinositide signaling, how an external stimulus (for example, binding of a ligand to its receptor) can lead to the increase of Ca^{2+} concentration in the cytosol.
10. What are heterotrimeric G proteins? Discuss briefly their function.

Inorganic Chemistry Cumulative Exam

Purdue University

November 10, 2007

There are 100 possible points in this exam.

1. (30 points) The unit cell of MgO is shown below. The size of Mg^{2+} and O^{2-} ions are 0.086 nm and 0.126 nm, respectively. Estimate the volume (in cm^3) and density (in g/cm^3) of MgO. (No partial points will be given to incorrect or incomplete answers.)

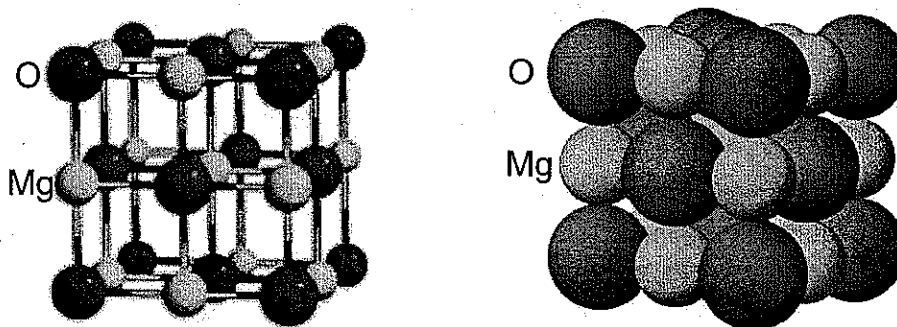


Figure 1. Two different representations of the MgO unit cell.

2. (10 points) NaCl and MgO have the same crystal structure. Which compound do you predict to have a higher melting point? Explain. (Answers without explanation will not receive any points.)

3. (10 points) Explain what is wrong with the following statement, and correct it.

“Molecular weight of NaCl is 58.44 amu.”

4. (10 points) NaCl is an ionic compound while H_2O is a covalent compound. The melting point of NaCl (804°C) is much higher than that of H_2O (0°C). Can you use these data to make a conclusion that in general ionic bonds are much stronger than covalent bonds? Explain.

5. (10 points) Fill in the blanks (a-b) in the following statement.

“The effective ionic radius of Co^{2+} ions in a crystal structure is affected by (a) and (b) of Co^{2+} ions.”

6. (10 points) The crystal structures of NaCl and CsCl are shown below. Why would CsCl not adopt the same crystal structure as NaCl?

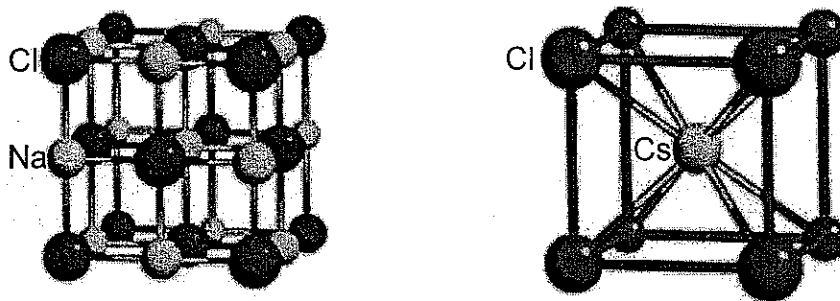


Figure 2. Crystal Structures of NaCl (left) and CsCl (right).

7. (20 points) A unit cell of calcium fluoride is shown below.

- (a) What is the coordination number of fluoride ions?
- (b) What is the local environment of fluoride ions (e.g. octahedral, tetrahedral, square planar, trigonal pyramid, trigonal prism, etc.)?
- (c) How many fluoride ions are present per unit cell?
- (d) How many calcium ions are present per unit cell?

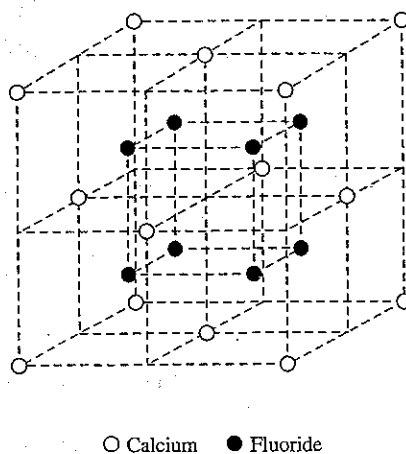
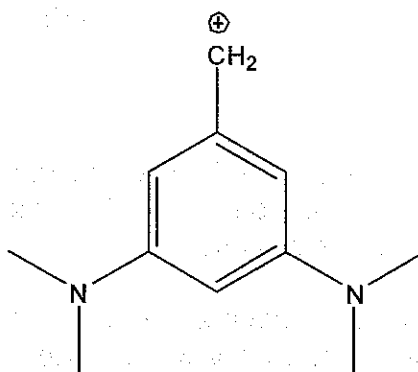


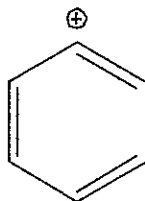
Figure 3. A unit cell of calcium fluoride.

One long-standing interest of synthetic chemists has been in finding persistent high-spin organic molecules for use in ferromagnetic organic polymers. A recent JACS article ("*Benzylic Cations with Triplet Ground States: Computational Studies of Aryl Carbenium Ions, Silylenium Ions, Nitrenium Ions, and Oxenium Ions Substituted with Meta π Donors*", Arthur Winter, Daniel Falvey, Christopher Cramer and Benjamin Gherman, **2007**, 129, 10113-10119) presents computational results that suggest that a π, π^* -diradical state (triplet state) of benzyl cations is stabilized by π -donating *meta*-substituents. Notably, the 3,5-bis(*N,N*-dimethylamino)benzyl cation (shown below in its singlet state) is calculated to have a triplet ground state by 1.9 kcal/mol.



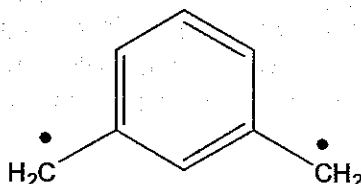
Please answer the following questions related to the above research:

- 1) The above singlet cation is resonance stabilized. Please draw all reasonable resonance structures for it.
- 2) As opposed to benzyl cations, the phenyl cation (below) is not resonance stabilized. Why not?



- 3) Define a π -donating substituent. Give an example of a π -acceptor, σ -donor and σ -acceptor substituent.

- 4) Illustrate the different electron distributions in the singlet and the π, π^* -diradical states of the 3,5-bis(N,N-dimethylamino)benzyl cation (for the triplet state, promote an electron from the lone pair of the substituent into the LUMO formally associated with the benzylium based p-orbital). The π, π^* -diradical state is analogous to the triplet ground state of *meta*-xylylene (below), a non-Kekule diradical conjugated with non-disjoint SOMOs.



- 5) Draw a three-dimensional picture to illustrate the relative orientations of the singly-occupied molecular orbitals in the triplet state of the 3,5-bis(N,N-dimethylamino)benzyl cation.
- 6) Why does the π, π^* -diradical state-stabilizing substituent have to be a π -donor instead of a π -donor, σ -acceptor or σ -donor?
- 7) Why does the substituent have to be in the *meta*-position? Show resonance structures for the *para*-isomer to illustrate your point.
- 8) Illustrate the electron distributions in the σ, π -triplet state of the phenyl cation.

PChem Cume – Nov 10, 2007.

1. Using the notation Ψ_{1s} , Ψ_{2px} , etc, give expressions for the normalized sp^2 hybrid orbitals.
2. What are the molecular orbitals that will be generated from the valence shell orbitals of the molecule BeH_2 ?
3. Using an LCAO-MO approach, draw the π molecular orbitals for benzene (six different ones) and indicate the nodal planes for each.
4. Calculate the probability that an electron described by a hydrogen atom 1s wave function will be found within one Bohr radius of the nucleus.

$$\begin{aligned}\Psi_{100} &= \frac{1}{\sqrt{4\pi}} R_{1s}(r) \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}\end{aligned}$$

$$\int_0^1 x^2 e^{-2x} dx = \frac{1}{4} - \frac{5}{4} e^{-2}$$

5. Draw the radial probability densities associated with the 3s, 3p and 3d orbitals.
6. Given:
 $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$ $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$ $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$
and that \hat{L}^2 commutes with each of \hat{L}_x , \hat{L}_y , and \hat{L}_z

Find:

$$[\hat{L}_z, \hat{L}_+] \text{ and } [\hat{L}^2, \hat{L}_+]$$

Periodic Classification of the Elements

I A

0

1 H 1.00797											2 He 4.0026	
IIA											10 Ne 20.183	
3 Li 6.939	4 Be 9.0122											
IIIB											18 Ar 39.948	
11 Na 22.9898	12 Mg 24.312											
IIIB											36 Kr 83.80	
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	35 Br 79.909
IIIB											54 Xe 131.30	
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	53 I 126.9044
IIIB											86 Rn (222)	
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	85 At (210)
IIIB											87 Fr (223)	
87 Fr (223)	88 Ra (226)	89 Act (227)										

VIII

I B

VIB

IIIB

IIIA IVA VA VIA VIIA

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
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.)