Department of Chemistry
Cumulative Examinations
December 13, 2003

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, Pages 5-6
5) Physical Cumulative Examination, Page 7

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: 1
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.

Analytical Cume **December 13, 2003**

Ion-molecule reactions are commonly used in mass spectrometry to ionize analytes (e.g., chemical ionization, sometimes in MALDI). Demonstrate your knowledge of this area of mass spectrometry by addressing the following questions.

1) Give an example for chemical ionization by electron transfer and another example for proton transfer. Show all the steps of each process. Use real molecules in your examples to make them as detailed as possible.

2) Define proton affinity and ionization energy by showing the relevant thermochemical equations. Give proton affinity and ionization energy values that are typical for organic compounds. Show how these thermochemical parameters (proton affinities, ionization energies) are related to the exothermicities of the two ionization reactions that you gave for part 1.

3) Which one of the following reagents would you use to create an intact protonated molecule from a fragile analyte of PA = 215 kcal/mol: H_2 (PA 101), CH_4 (PA 132), H_2O (PA 173), I-butane (PA of isobutene is 196 kcal/mol), NH_3 (PA 205) or $(CH_3CH_2)_3N$ (PA 231 kcal/mol). Justify your choice.

4) Draw a sketch that illustrates the difference between a vertical and adiabatic ionization process. Give an example of each.

5) Draw a schematic potential energy surface for interaction of one of the reagent ions you chose for part 1 with some suitable analyte (that is successfully ionized). Mark the axes and any energy minima and maxima on your surface.

Biochemistry Cumulative Exam Questions

December 13, 2003

1. Draw the structures of all intermediates of the Krebs Cycle. Then, account for all of the ATP that can be generated from the products of a complete turn of the cycle. (40 Points)

2. Explain the chemiosmotic hypothesis of mitochondrial ATP synthesis. Include in this explanation a description of the steps that lead to generation of potential energy in the mitochondrion and an accounting of the use of this potential energy to synthesize ATP. (35 Points)

3. Describe the regulation of glycolysis in detail; i.e. where does it occur and by what compounds? (25 Points)

Inorganic Cume Exam
December 13, 2003
Transition Metal Chemistry:
Metal-Metal Bonds, Halides and Carbonyls

1. (36 points)

A) Give an authentic example of each of the following:

(i) A compound that contains a metal-metal quadruple bond.

(ii) A compound that contains a metal-metal triple bond.

(iii) A neutral metal carbonyl that contains a trinuclear cluster of metal atoms.

B) For each example you give in part (A), sketch the molecular structure and give a detailed description of the electronic structure (including the ground state electronic configuration if appropriate).

2. (40 points)

$TiCl_4$ (a liquid under normal conditions) is an important starting material for the synthesis of many other titanium compounds.

A) Show how $TiCl_4$ is converted to the following compounds (make use of balanced equations in all cases).

(i) $TiCl_3$

(ii) $TiCl_2(acac)_2$ (acac is the acetylacetonate anion)

(iii) $(CH_3)_3TiCl$

(iv) $(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)_2$

B) Sketch the molecular structure of $TiCl_4$ and contrast it with the structures of $ZrCl_4$ (solid), VCl_4 (liquid) and $NbCl_4$ (solid).

C) What are the colors of $TiCl_4$ and VCl_4? Using Ligand Field Theory, explain the difference in terms of the electronic and molecular structures of the compounds.

3. (24 points)
Mononuclear carbonyl complexes of the transition elements constitute an extensive class of compounds whose preparation, structures and reactivities have attracted considerable attention.

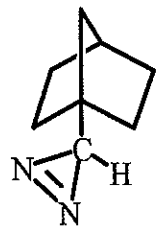
A) Give examples of known homoleptic neutral mononuclear carbonyls of Fe and Ni. (A homoleptic carbonyl is one of the type $M(CO)_n$ i.e. it contains only CO ligands). **Carefully** sketch their molecular structures.

B) Which mononuclear homoleptic carbonyl-containing species of Hf, Ta and Re are isostructural and isoelectronic with $W(CO)_6$?

C) Rank clearly these species (in (B)) in order of increasing values of the ν(CO) modes (use > or < signs) and explain fully the trend in ν(CO) values.

ORGANIC CUMULATIVE EXAM
December 2003

1) (60 points) In a recently reported study, Roach and Warmuth (*Angew. Chem., Int. Ed. Eng* **2003**, *42*, 3039) reported the photolysis of 1-bicyclo[2.2.1]heptyldiazirine, **1**, encapsulated within a hemicarcerand. By carrying out the reaction within the hemicarcerand, it is possible to inhibit the reactivity to allow for the investigation of unstable intermediates.

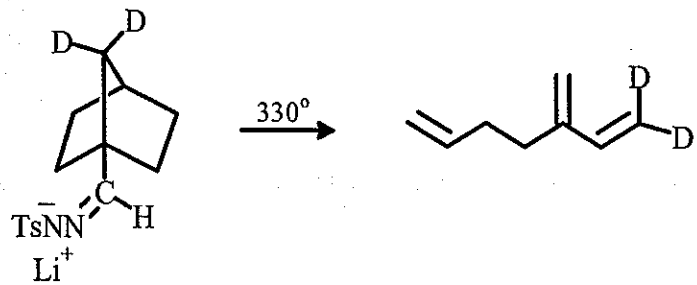


1

Two different products were observed, depending on the photolysis wavelength. The key features in the NMR spectra are signals at 4.55 ppm and 4.41 ppm, which are doublet of doublets, and each correspond to one proton.

a) On the basis of these data, propose structures for the two products.

b) In a related experiment, many years ago, Wolf and Jones reported the solution thermolysis of a deuterium labeled compound **2** and observed formation of **3**. Show why this product is consistent with only one of the intermediates from part (a).



2 **3**

R = 8.3 J/(K mol)

1. Consider a system containing a non-reactive mixture at a temperature of 300 K.

a) (10 points) How is the chemical potential of a each species related to the total Gibbs free energy of the mixture.

b) (10 points) If the system were entirely composed of ideal gases and the volume of the system were doubled (at constant temperature), much would the chemical potential of each component in the mixture change ?

2. Consider a chemical reaction of the form, $A \rightarrow B$, taking place in a system at constant T and P. Your answer to each of the following three questions should consist of a number and an brief explanation.

a) (10 point) If you assume that all species in the above reaction may be treated as ideal gases and if you furthermore assume that there is no change in the electronic, vibrational or rotational partition functions associated with this reaction, what does that imply about the Gibbs free energy associated with converting the pure reactant entirely to the pure product, each at the same T and P (your answer should be a number with an explanation.

b) (15 points) Calculate the equilibrium constant for the above reaction at 300 K, if the electronic energy of the product were 10 kJ/mol below that of the reactant, and other conditions remained as described above.

c) (15 point) Calculate the Gibbs free energy for the above reaction if the ratio of the total molecular partition of the product molecule were exactly twice that of the reactant molecule (both of which are in the low density ideal gas state) ?

3. Consider a chemical reaction of the form, $A + B \rightarrow C$, taking place in a system at constant T and P.

a) (10 points) What is the relationship between the chemical potentials of the reactant and product species of the above reaction at equilibrium (explain) ?

b) (10 points) What would the relationship between the chemical potentials of the reactant and product species be if the reaction were equilibrated in an adiabatic container of constant V ?

c) (10 points) Would you expect the equilibrium constant of the above reaction to increase, decrease or stay the same if the size of the chamber were increased, while holding the temperature of the system constant, assuming that all species may be treated as ideal gases (explain) ?

d) (10 points) Would you expect the equilibrium concentration of the product to increase, decrease or stay the same if the size of the chamber were increased, while holding the temperature of the system constant, assuming that all species may be treated as ideal gases (explain)?

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.)