Department of Chemistry
Cumulative Examinations
November 12, 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.

1) Analytical Cumulative Examination, Page 1
2) Biochemistry Cumulative Examination, Page 2
3) Inorganic Cumulative Examination, Page 3
4) Organic Cumulative Examination, Page 4
5) Physical Cumulative Examination, Page 5

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: 113
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 Cumulative Examination

November 12, 2005

Two dimensional gas chromatography coupled with time-of-flight (TOF) mass spectrometry is theoretically capable of seeing 60,000 compounds in 30 minutes. This new technique is becoming popular in the analysis of petroleum samples, metabolite analysis, and environmental monitoring where it is an advantage to examine and identify huge numbers of volatile organic compounds within a short time.

1. How is two dimensional gas chromatography (2-D GC) achieved in this instrument?

2. Discuss the stationary phases generally used in 2-D GC and the order in which they are coupled that contain them.

3. What are typical separation times in the first and second dimensions of GC?

4. Why is TOF preferred over other types of mass spectrometry?

5. What advantage does GC/GC-MS have over multidimensional MS as seen in the analysis of petroleum samples?

Cumulative Exam Questions for Biochemistry (November 12,2005)

1. The ΔG of denaturation of an average globular protein is ~15 Kcal/mole. Explain why this value is so low. Then explain which weak bonds contribute most to the stability of globular proteins and why. (20 points)
2. Calculate the diameter of a perfectly spherical globular protein of molecular weight 40,000. Show your work and state your assumptions. (20 points)
3. Describe the common structural features of all protein alpha helices and all beta pleated sheets. (30 points)
4. Draw the linear structure of the following peptide: ASPRTGEN (20 points)
5. Calculate the isoelectric point of the protein with the following composition: (10 points)
   Asp-5
   Ala- 4
   Gly-3
   Trp- 4
   Lys-6
   His-5
   Val-6
   Leu-4
   Tyr-2
   Phe-1
   Thr-7
   Ser-4
   Glu-4
   Arg-5
   Ile-6
   Cys-2
   Pro-1

Inorganic Cumulative Exam

Date: November 12, 2005

1. (32 points) Dipole moments

   a. (8 pts) The dipole moment of ammonia is 1.47D. Is the dipole moment of NF_3 greater or smaller? Explain.

   b. (8 pts) Is the dipole moment of phosphine, PH_3, greater or smaller than that for ammonia (NH_3)? Explain.

   c. (8 pts) The dipole moment of trimethylphosphine oxide, Me_3PO, is 4.37D. Is the dipole moment of trimethylamine oxide, Me_3NO, greater of smaller? Explain.

   d. (8 pts) The dipole moment of carbon monoxide is small (0.112D) and it has been determined recently that the oxygen atom is the <u>positive</u> end of the dipole, despite its greater electronegativity. Provide a plausible explanation for both, the small magnitude of the dipole moment and its direction using simple valence bond terms.

2. (24 points) In ligand field theory, the splitting 10Dq is given by the separation of the t_{2g} and e_g* orbitals.

   a. (6 pts) What is the occupancy of the t_{2g} and e_g* orbitals in a weak field complex like $[CrI_6^{3-}]$?

   b. (6 pts) What is the occupancy of the t_{2g} and e_g* orbitals in a strong field complex like $Cr(CO)_6$?

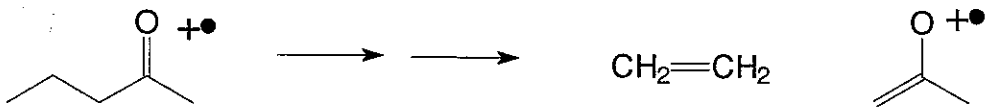
   c. (12 pts) Using a simplified energy level diagram showing t_{2g} and e_g* orbitals, explain why I^- is a weaker field ligand compared to NH_3 in the spectrochemical series.

3. (14 points) Explain the following observations: $[MnO_4]^-$ absorbs in the visible ($\lambda_{max} \approx 520$ nm), $[ReO_4]^-$ absorbs in the UV ($\lambda_{max} \approx 240$ nm), but $[ReS_4]^-$ absorbs in the visible again ($\lambda_{max} \approx 480$ nm). Hint: All three compounds are d^0.

4. (10 points) Derive the ground-state term symbols for the free ions in d^5 and d^7 configurations.

5. (20 points) This year's Nobel Prize in chemistry was awarded to Chauvin, Schrock, and Grubbs for the development of olefin metathesis. Provide a concise description of this reaction and its accepted mechanism. What was the contribution of each of the three winners?

Consider the only named unimolecular dissociation reaction in gas-phase ion chemistry and mass spectrometry, the McLafferty rearrangement, shown below for the radical cation of 2-pentanone:



1) Show two likely mechanisms (include arrows) for this reaction, a stepwise one and a concerted one (remember to indicate the formal charge and radical sites). Explain why you think that these mechanisms are thermodynamically and kinetically feasible. Compare them, and point out which one (if either) is likely to be more favorable thermodynamically and which one kinetically.

2) Sketch a potential energy surface for each mechanism, and explain where the mechanisms differ. Point out what structure corresponds to each energy minimum and transition state, and draw these structures.

3) Devise an experiment that might allow you to distinguish the above two mechanisms either in the gas phase or in solution. Explain what sort of data you expect, and how this data could allow you to distinguish the mechanisms.

4) Give a guess as to which mechanism is most likely, and justify your answer.

5) Show the products that McLafferty rearrangement should yield (if any) for the radical cations of acetone, ethyl acetate, ethyl propionate, and 1-pentene.

I. (50 points) Consider a system composed of *one mole* of a monatomic ideal gas. In answering each of the following questions, report your answer as a *number* with *units* (and with the *correct sign*).
Useful information: $P=\rho kT$, $U=(3/2)NkT$, $R = 8.3$ J/(K mol) = (6×10^{23} molec/mol) k (J/K)

1) What is the total kinetic energy of the gas?
2) How does the entropy of the gas depend on its volume (at constant temperature)?
3) How does the entropy of the gas depend on its temperature (at constant volume)?
4) How much would the chemical potential of the gas change if its volume doubled at a temperature of 300K?
5) How much would the Helmholtz free energy of the gas change if its volume doubled at a temperature of 300K?

II. (50 points) Consider a system composed of an arbitrary mixture of chemical components that is in a high density (liquid and/or solid) state. In answering each of the following questions report your number as a symbol or equation (and show your work).

1) What thermodynamic function must decrease in any spontaneous processes carried out at constant S, T and N_i (where N_i represents the number of molecules of component i in the mixture)?
2) Construct a thermodynamic function which must decrease in any spontaneous processes carried out at constant T, P, μ_1 and N_i (where i>1).
3) If the sample is composed of a liquid mixture containing a single-component solid precipitate (and the system is presumed to be at equilibrium) what is the relationship between the chemical potentials the compound in the precipitate and in the liquid phase?
4) If the sample is composed of a compound, A, which can react to form a dimer compound, B, what is the relationship between the chemical potentials of A and B at equilibrium?
5) How is the derivative, $(\partial P/\partial T)_{V,N_i}$ related to the isobaric thermal expansion coefficient, α_P, and isothermal compressibility, κ_T, of the system?

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.)