Department of Chemistry
Cumulative Examinations
April 28, 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 ***five*** examinations.

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

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 **April 28, 2007**

Analytical chemistry is a quantitative science in which phenomena, measurements and instrumentation are best understood if they can be expressed in the form of an equation. This exam asks (i) that you write equations which apply to and/or describe the topics indicated below, including definitions of all terms in the equations, and (ii) that you then comment in the space of a page or less, on the significance and implications of each equation in analytical chemistry.

Half credit is for the equation and half for the comment. Note (i) partially complete equations (knowing the parameters involved) will get partial credit (ii) wherever possible give units.

YOU SHOULD ANSWER ONLY 10 OF THE 17 QUESTIONS

1. Mass analysis equation for an ion trap mass spectrometer
2. Mass analysis equation for a time-of-flight mass spectrometer
3. Mass analysis equation for a sector mass spectrometer
4. Number of theoretical plates in a thin layer chromatogram
5. Height equivalent of a theoretical plate
6. Capacity factor
7. Unimolecular rate constant for dissociation of isolated gas phase ions
8. Nernst equation
9. Electron binding energy in XPS (ESCA)
10. Center of mass kinetic energy in terms of experimental parameters
11. Arrhenius equation
12. Vibrational energy spacing in molecules
13. Relationship of half-life to rate constant for unimolecular reaction rate constant
14. Gyromagnetic ratio
15. Time constant for pure RC circuit
16. Time-frequency Fourier transform
17. Beer's Law expressed in terms of detected intensities.

Biochemistry Cumulative Examination

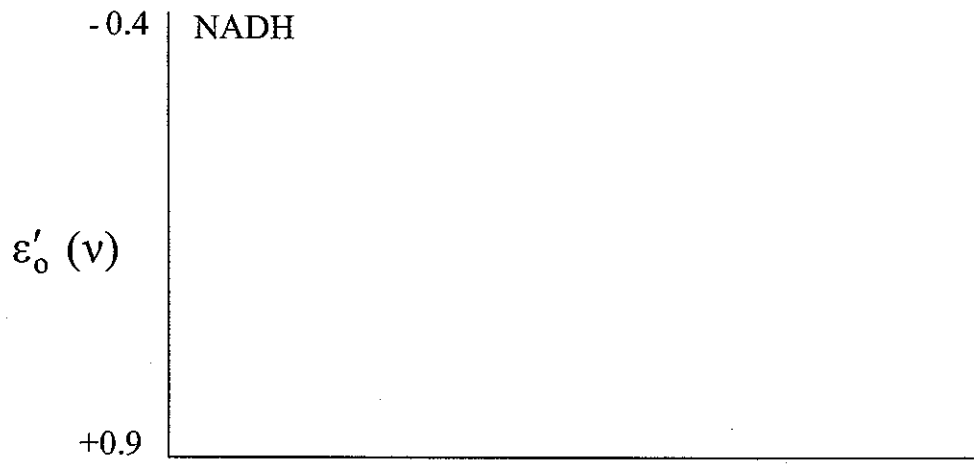
April 28, 2007

Instructions: There are six questions, and the point totals are given by each question.

1. (20) In metabolism, what are anaplerotic reactions? Give one example, including enzyme name(s), any required coenzymes, and structures of reactants and products. Explain the specific role played by this reaction.

2. (25) Mammalian pyruvate dehydrogenase is a massive structure, similar in size to the ribosome. Describe the location, general structure and role of pyruvate dehydrogenase. Give the net (overall) reaction. Then, break up the reaction process into individual, intermediate reaction steps, showing coenzyme involvement and reaction mechanisms at each step.

3. (15) Using commonly accepted symbols or acronyms, sketch the sequence of components of the respiratory electron carriers in the eukarytic electron transport system starting with NADH. (Copy the following framework onto a page of your blue book, and complete it there.) Include as many as you can, and place them in their approximate positions with respect to the standard ε'_o reduction potential.



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4. (15) In the context of aerobic catabolism, what is a P/O ratio? Suppose that gently prepared mitochondria are incubated with sodium malonate, and then the P/O ratio is measured for the oxidation of α-ketoglutarate. What value would you expect? Explain the basis for your answer.

5. (10) 2,4-Dinitrophenol (DNP) is extensively employed as a tool in investigations of the electron transport sequence. What does DNP do? Where and how does it act? What are the consequences?

6. (15) In the context of mitochondrial electron transport and oxidative phosphorylation, what is "proton motive force" (Δp)? What are the two major components of Δp? In terms of energetics, what is the approximate magnitude of Δp? (Explain the basis for your estimate.) How is the energy employed?

Inorganic Cumulative Exam
April 28, 2007

1. (10 points) Draw the five d-orbitals and label them.

2. (15 points) Start with the splitting of d-orbitals in an octahedron field and show how the d-orbitals splitting would change as the O_h molecule distorts (Jahn-Teller) to lower symmetry (D_{4h}).

3. (20 points) Construct a molecular orbital (MO) diagram for molecular oxygen. According to the Pauli exclusion-principle, show the electron occupancy in your MO diagram. What is the spin for ground state oxygen? Show the different binding modes O_2 could adopt as a ligand on a transition metal.

4. (15 points) What is the point group for B_2H_6? Discuss briefly the bonding in this molecule.

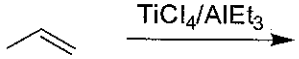
5. (20 points) Give the products for the following reactions:

(a) $Xe + PtF_6 \rightarrow$

(b) $Pt(py)Cl_3^- + py \rightarrow$

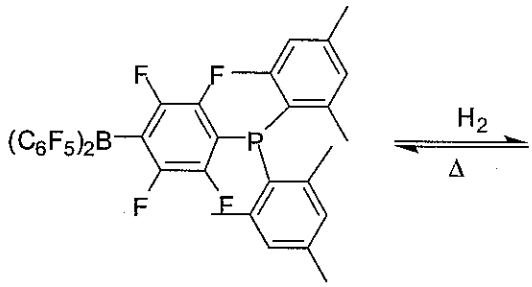
(c) $(C_5H_5)MgBr + FeCl_3 \rightarrow$

(d) $Re_2O_7 + xs\ CO \rightarrow$

(e) 

(f) $C + steam\ (H_2O) \xrightarrow{Cat./\ high\ temp.}$

6. (20 points) Construct an MO diagram for dihydrogen and discuss how transition metals affect dihydrogen splitting more successfully than main group compounds. A recent paper in *Science* reported (*Science* **2006**, *314*, 1124) reversible binding of H_2 to the main group compound shown below. Suggest what the product is.

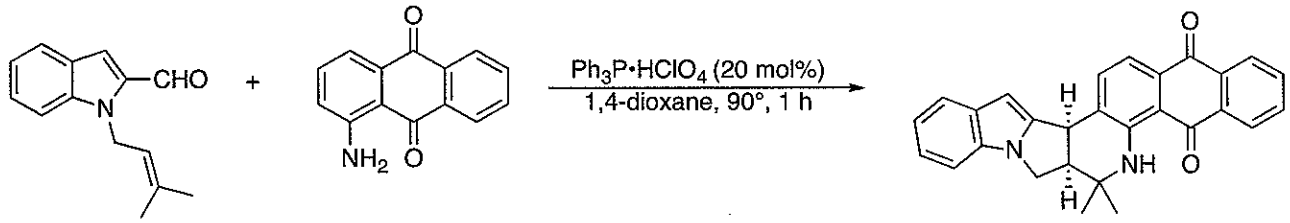

F
F
(C6F5)2B
P
F
F
H2
Δ

Organic Cumulative Examination

April 28, 2007

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

1.



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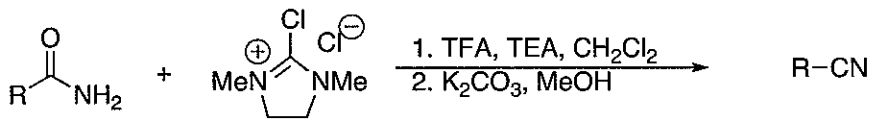

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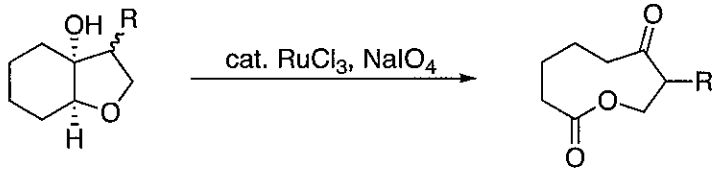

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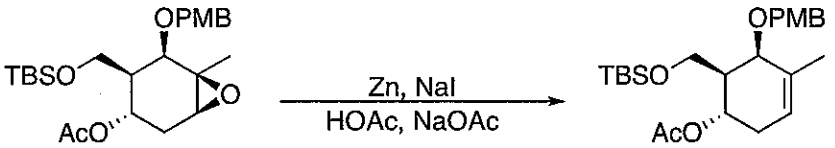

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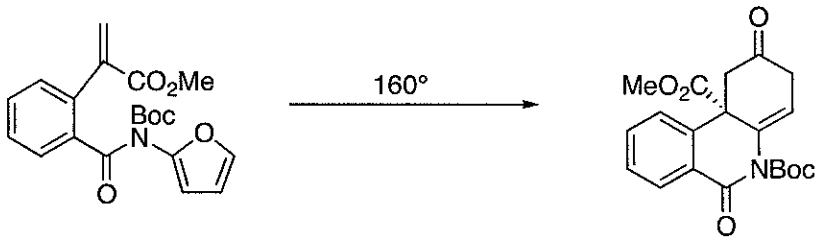

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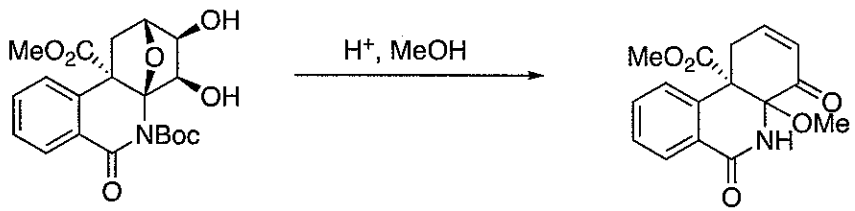

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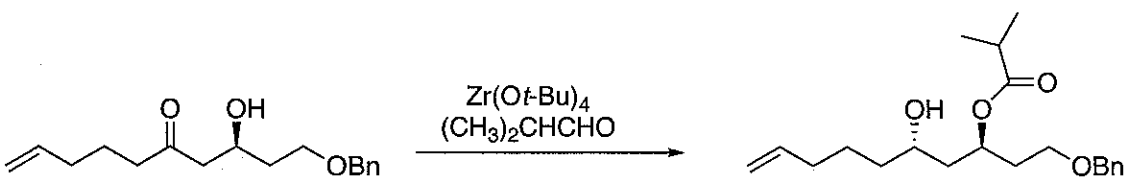

Physical Chemistry Cume

(April 2007)

1. Derive an expression for collision frequency with a surface, defined as the number of collisions per unit time per unit area. You may want to use the following information:

   velocity distribution: $f(v_x) = \sqrt{\frac{m}{2\pi kT}}\, e^{-mv_x^2/2kT}$

   general information: $\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$

2. Approximately what air pressure is necessary to keep a metal surface at least 90% clean for 30 minutes at 25°C, assuming a surface area of 1 cm^2 and sticking probability of 1? Describe any assumptions you make.

   $k = 1.381 \times 10^{-23}$ J/K

   1 atm = 101,325 Pa = 760 Torr Pa = kg m^{-1} s^{-2}

3. Surface adsorption processes are often described using adsorption isotherms. A simple example for an adsorption process that can be described as

   $$A\ (g) + S\ (s) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A\text{-}S\ (s)$$

   is the Langmuir isotherm, which has the form: $\theta = \frac{K_c[A]}{1 + K_c[A]}$

   where θ is the fraction of surface sites that are covered (i.e. the number of A-S versus the number of surface sites, S, available.) For the simple surface reaction shown, the rates of adsorption and desorption are given by:

   rate of adsorption $= k_a[A]N(1-\theta)$

   where N is the total number of sites, and N(1-θ) is the number of available sites

   rate of desorption $= k_d N\theta$

   Now consider a surface-catalyzed bimolecular reaction between molecules A and B that has a rate law of the form

   Rate = $k_3\theta_A\theta_B$

   Where θ_A is the fraction of surface sites occupied by reactant A and θ_B is the fraction of surface sites occupied by reactant B. A mechanism consistent with this reaction is as follows:

$$A\ (g) + S\ (s) \underset{k_d^A}{\overset{k_a^A}{\rightleftharpoons}} A\text{-}S\ (s) \qquad \text{(fast)}$$

$$B\ (g) + S\ (s) \underset{k_d^B}{\overset{k_a^B}{\rightleftharpoons}} B\text{-}S\ (s) \qquad \text{(fast)}$$

$$A\text{-}S\ (s) + B\text{-}S\ (s) \xrightarrow{k_3} \text{products}\ (g)$$

Take K_A and K_B to be the equilibrium constants for the first two steps, respectively. Derive expressions for θ_A and θ_B in terms of [A], [B], K_A, and K_B.

4. Diffusion in a perfect gas can be written as a simple function of mean free path and mean speed:

$$D = \tfrac{1}{3}\lambda\bar{c}$$

For each of the following effects, say whether it will increase, decrease or not affect the diffusion coefficient. For each one, give a justification for your answer.

a. increase in pressure of the gas
b. increase in temperature
c. increase in size of the gas molecules, without increasing the mass

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.)