Department of Chemistry
Cumulative Examinations
September 24, 2011

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, Pages 6-7
5) Physical Cumulative Examination, Page 8

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
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Analytical Cume Examination September 24, 2011. Fred Regnier

There are 10 questions, each of 10 points value.

A. Electroomosis and electroosmotic flow (EOF) plays an important role in capillary electrophoresis (CE).

1) What is the origin of EOF?
2) Why is EOF important in capillary zone electrophoresis?
3) How can you alter EOF?

B. Mass spectrometry is an important mode of detection in capillary electrophoresis (CE).

4) What are the issues and how would you interface a CE system with a mass spectrometer (MS)?
5) Based on the fact that peaks are a second or less wide in CE and samples can have thousands of components, what type of MS would be best suited for identification and quantification in this case?
6) Describe the issues involved and some options for quantify analytes in CE-MS.

C. There are multiple forms of capillary electrophoresis.

7) What is isoelectric focusing (IEF) and how are analytes resolved by IEF?
8) How are molecules resolved according to the hydrodynamic radius in CE?

D. Sample introduction and band spreading are major issues in CE.

9) How are samples introduced into CE systems; what are the issues?
10) What are the origins of band spreading in CE?

Biochemistry cume (2 pages)

Overview: A group of enzymes selectively methylate CpG dinucleotides in the human genome. The enzymes methylate CpG at the carbon-5 position of cytosine, producing 5-meCpG. Cancerous cells often contain abnormal patterns of CpG methylation. Therefore, researchers have developed several methods to detect and localize 5-meCpG in normal and cancerous cells (reviewed by Kristensen and Hansen, 2009).

The cume focuses on a method known as "Methylation-sensitive melting-curve analysis". That method involves several steps:

- Genomic DNA is isolated and treated with sodium bisulfite under denaturing conditions: low pH and high temperatures (Kristensen and Hansen, 2009).
    - Under optimized conditions, cytosine is converted to Uracil (Fig. 1).
    - Under those conditions, 5-meC is not converted to U.
- After sulfonation and desulfonation reactions, the DNA is purified and subjected to Polymerase Chain Reaction (PCR), using appropriate primers.
- The PCR products are purified and incubated with Ethidium Bromide (EthBr).
- Subsequently, DNA-melting experiments are performed on the complex of DNA with EthBr. The melting profiles are determined by fluorescence (F).
- Differential melting curves are obtained by plotting the change of fluorescence (dF/dT) as the function of Temperature (Fig. 2).

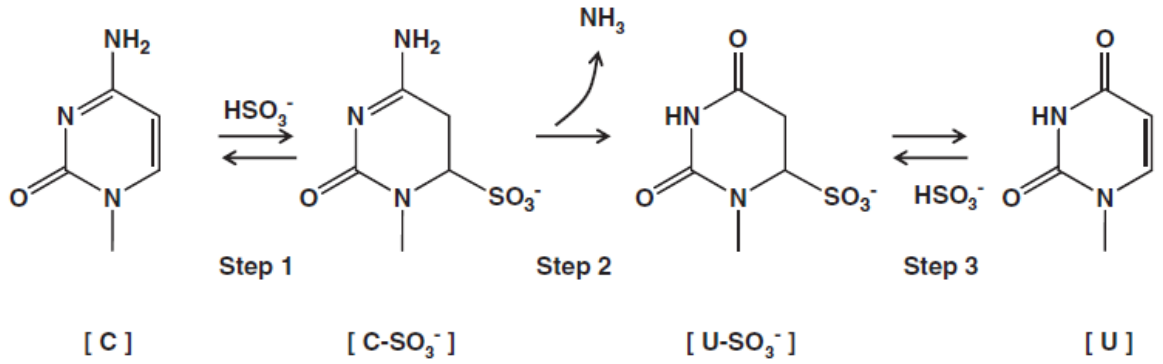


Figure 1

Kristensen LS and Hansen LL. PCR-based methods for detecting single-locus DNA methylation biomarkers in cancer diagnostics, prognostics, and response to treatment. Clin Chem. **55** :1471-83 (2009)

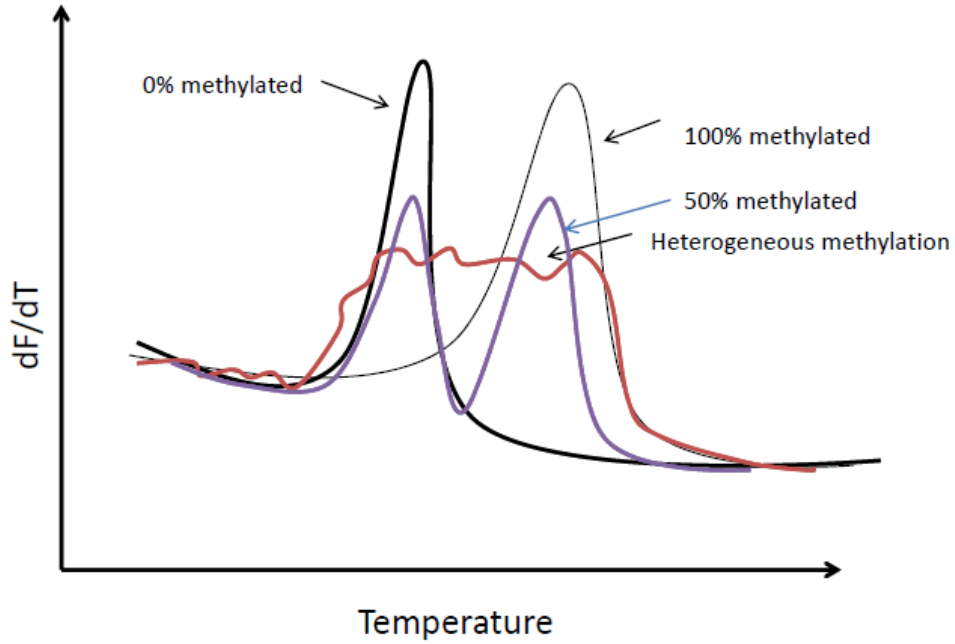


Figure 2

Cume questions:

1. What is a DNA melting curve?
2. How is dF/dT determined to construct a differential melting curve?
3. Explain how EthBr works in the DNA melting experiments.
4. In the sequence shown below, a * marks the position of methylated C residues in a short DNA fragments:

   ----------AT*CGGTCCCT*CGTTTAAA----------

Provide the sequence obtained after sulfonation and desulfonation reactions.

5. Provide the sequence after several rounds of PCR amplification.
6. In an experiment, the starting genomic DNA fragment did not contain any methylated cytosine. Subsequent to experimental steps, described in previous page, researchers obtained the differential melting curve (labeled 0%) shown in Figure 2.

   In another experiments, 100% of the CpGs in the starting genomic DNA fragment were methylated. Subsequent to experimental steps, researchers obtained the differential melting curve (labeled 100%) shown in Figure 2.

Explain the reason for the differences in the observed curves.

Inorganic Chemistry Cumulative Exam
Saturday, September 24, 2011

Question 1 (21 points)
During the recent BP oil spill in the Gulf of Mexico, many people were saying that Nature has organisms that can eat and degrade the oil. For the most part, these organisms are bacteria. Although there may be many oil eating bacteria and enzymes within, only two have been characterized in appreciable detail. Both enzymes use inorganic chemistry to catalyze the breakdown of oil.

A) What are these bioinorganic, oil eating enzymes called?

B) What metals are used by the enzymes? Answer for both enzymes.

C) Draw a very rough picture of each enzyme active site. You need only show the relative orientation of the metals and a general idea of how they are bound by the protein.

Question 2 (18 points)
The infrared stretching frequency of CO gas is 2143 cm^{-1}. The CO stretching frequency is provided for each of the following compounds.

$[Mn(CO)_6]^+ = 2090\ cm^{-1}$
$Cr(CO)_6 = 2000\ cm^{-1}$
$[V(CO)_6]^- = 1866\ cm^{-1}$
$[Ti(CO)_6]^{2-} = 1750\ cm^{-1}$

A) Why do these stretching frequencies differ from that of CO gas?

B) Explain the trend.

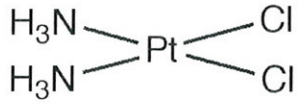
Question 3 (21 points)
Think about gold mining.

A) What is the classic method used to extract gold from the ore dug out of the ground?

B) Why is it bad?

C) Propose an alternative.

Question 4 (20 points)



A) What is the claim to fame of this molecule? What is it called most often?

B) Give a brief explanation of the mechanism by which this compound does what it is famous for. One paragraph maximum for your explanation.

Question 5 (20 points)
The color for each titanium halide is provided.

TiF_4 colorless/white

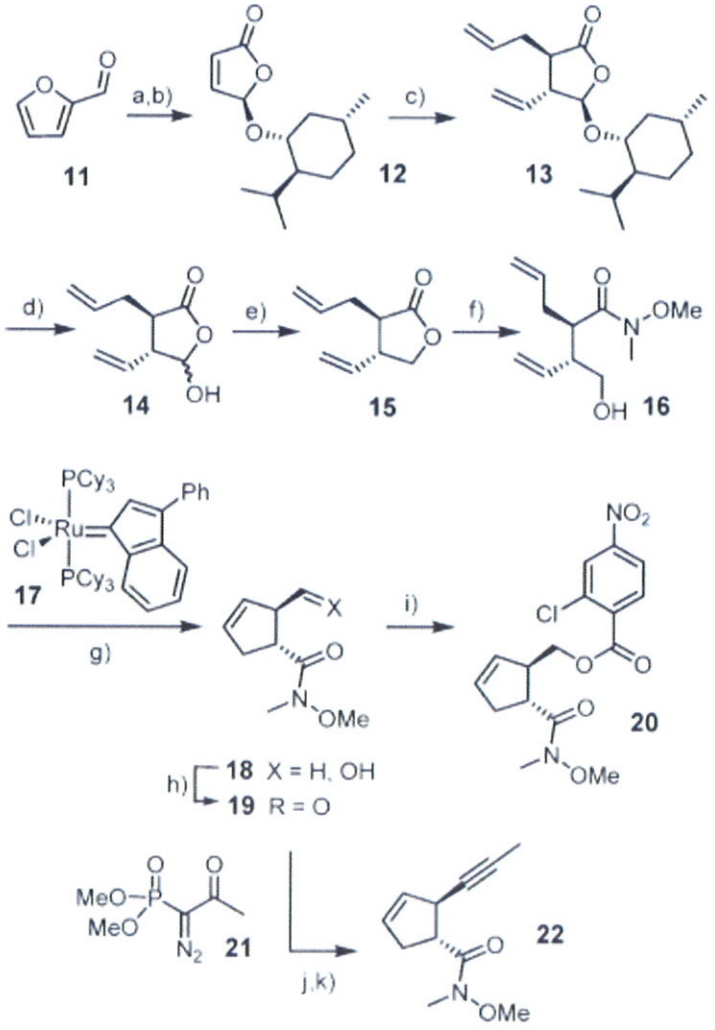
$TiCl_4$	pale yellow
$TiBr_4$	orange
TiI_4	black

Explain the lack of color with TiF_4 but the presence of color with the other compounds. What is the origin of these colors?

Organic Cumulative Exam – September 2011

JACS, Vol. 133, No. 34, 2011

1. (pg 13471). In Furstner's protecting-group-free total synthesis of hybridalactone, intermediate 22 below was a fragment used. Please provide a reasonable mechanism to account for the formation of product in steps **C**, **F**, **G**, and **J/K** below (do not show any of the other steps).



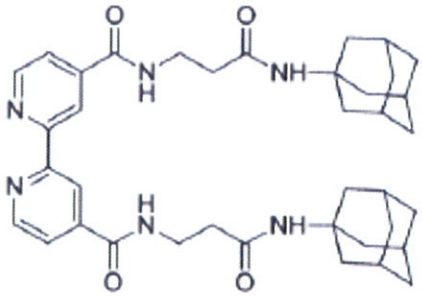
[a] Reagents and conditions: a) O_2, rose Bengal, hν, MeOH, 79%; b) L-menthol, CSA cat., toluene, reflux, then recrystallization from hexanes, cf. ref 33; c) $H_2C{=}CHMgBr$, CuI, THF, −78 °C, then allyl iodide, −60 °C, 2 h, 86%; d) aq. TFA, 16 h, 95%; e) $NaBH_4$, MeOH, 2 h, then HCl in Et_2O, reflux, 1 h, 75%; f) Me(MeO)NH·HCl, Me_3Al, CH_2Cl_2, 4 h; g) **17** (4 mol %), CH_2Cl_2, 16 h, 74% (over both steps); h) Dess-Martin periodinane, $NaHCO_3$, CH_2Cl_2, 1.5 h, 73%; i) 2-chloro-4-nitrobenzoyl chloride, Et_3N, DMAP cat., CH_2Cl_2, 16 h, 65%; j) **21**, K_2CO_3, MeOH, 16 h, 75%; k) LiHMDS, MeOTf, THF, −78 °C, 2.5 h, 80%.

JACS, Vol. 133, No. 35, 2011

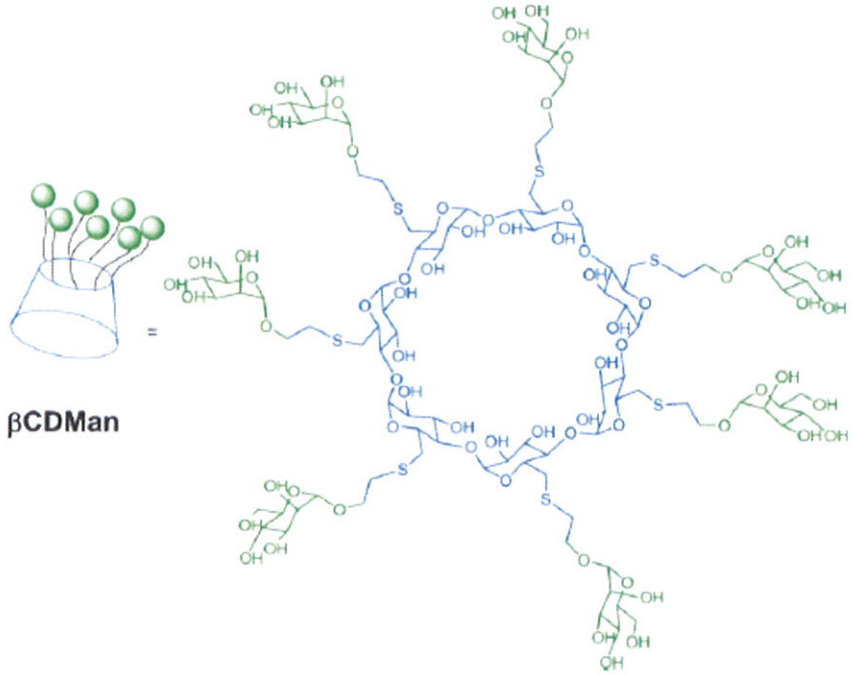
2. (pg 13957) In the publication from Seeberger and coworkers, the following 3 components were used to generate a supramolecular sensor for bacteria. Draw the final supramolecular structure that would result from these components. The authors used SPR to measure the binding of the supramolecular structure to ConA – what does SPR stand for? What is ConA and what part of the supramolecular structure is it binding to? When the supramolecular structure was added to bacteria the authors could detect binding because the bacteria associated with the supramolecule were red – why would this be the case?

1. $RuCl_3$

2.



3.



1. [10 points] Write down the Hamiltonian for the hydrogen molecular ion H_2^+ in atomic units. Place nucleus *A* at $-R/2$ and nucleus *B* at $+R/2$. Use r_A and r_B to indicate the distance of the electron from nuclei *A* and *B* respectively.

2. [40 points] The ground-state energy of an isolated hydrogen atom is -0.5 a.u. Let $|A\rangle$ and $|B\rangle$ stand for the normalized ground states of hydrogen atoms *A* and *B* when isolated.

   Use $|\psi\rangle = |A\rangle + |B\rangle$ as a trial function to estimate the ground-state energy of H_2^+ when the separation between nuclei *A* and *B* is $R = 2.5$ a.u.

   Feel free to use:

$$\langle A|B\rangle = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

$$\left\langle A\left|\frac{1}{r_A}\right|B\right\rangle = e^{-R}(1 + R)$$

$$\left\langle A\left|\frac{1}{r_B}\right|A\right\rangle = \frac{1}{R}\left(1 - e^{-2R}(1 + R)\right)$$

3. [40 points] **(a)** Estimate the magnitude of the vertical bonding – antibonding excitation energy in H_2^+ when $R = 2.5$ a.u. **(b)** Which process requires a higher energy photon: ground-state dissociation of H_2^+ into H and H^+, or vertical electronic excitation of H_2^+ from ground (bonding) to excited (anti-bonding) state.

4. [10 points] Discuss briefly how you would calculate more accurate values for the ground and excited-state energies of H_2^+.

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.)