Department of Chemistry
Cumulative Examinations
March 3, 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, Pages 1-2
2) Biochemistry Cumulative Examination, Page 3
3) Inorganic Cumulative Examination, Pages 4-5
4) Organic Cumulative Examination, Pages 6-7
5) Physical Cumulative Examination, Pages 8-10

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.

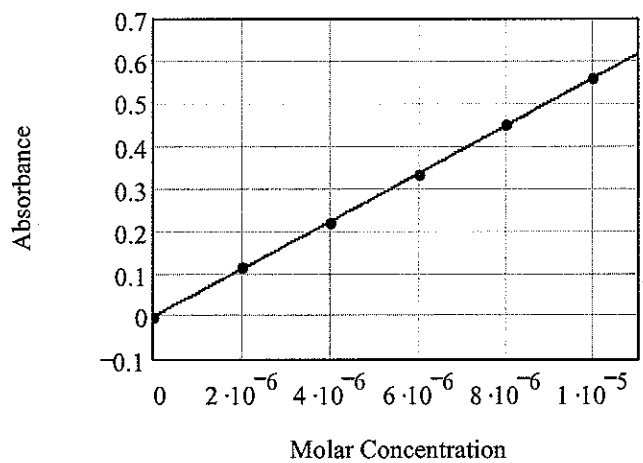
PURDUE
UNIVERSITY

Analytical Cumulative Exam Question
March 3, 2007

A spectrophotometric calibration curve for anthracene was constructed using a 1-cm cell. Six concentrations were used, resulting in six measured values of absorbance (molarity, absorbance).

$(0.0, -0.002)(2.0\times10^{-6}, 0.114)(4.0\times10^{-6}, 0.219)$
$(6.0\times10^{-6}, 0.332)(8.0\times10^{-6}, 0.450)(1.0\times10^{-5}, 0.558)$

The least squares coefficients for a straight line were: intercept, $a_0 = -1.571\times10^{-3}$; and slope, $a_1 = 5.601\times10^{4}$. The raw data and regression line are shown in the graph below.



a) What is the sensitivity of the method?
b) What is the limit of detection at a signal-to-noise ratio of 3?

For an un-weighted least-squares fit to a straight line, the variance of the intercept is given by the following equation.

$$\sigma_{a_0}^2 = \frac{\sigma^2}{\Delta}\sum_i C_i^2 \qquad \Delta = \begin{vmatrix} N & \sum_i x_i \\ \sum_i x_i & \sum_i x_i^2 \end{vmatrix}$$

c) Use the experimental data to compute the value of σ_{a0}^2.

d) Do the 95% t-limits about a_0 include zero? Given:

degrees of freedom	1	2	3	4	5	6
t	12.706	4.303	3.182	2.776	2.571	2.447

e) According to the manufacturer of the spectrophotometer, the standard deviation of the measured absorbance should be 0.001. Do the data support this conclusion at the 95% level of confidence given the following F-table (top row, numerator; left column, denominator)?

degrees of freedom	1	2	3	4	5	6	∞
1	161	200	216	225	230	234	254
2	18.5	19.0	19.16	19.25	19.30	19.33	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	3.67
∞	3.84	3.00	2.60	2.37	2.21	2.10	1.00

1. Cataloging the proteins expressed by an organism is greatly facilitated by knowing the sequence of the genome, i.e. all the genes in the system have been sequenced. Why would this be true? Put another way, what are the basic ideas on which proteomics is based.

2. Mass spectrometry is of major importance in proteomics. Why are the measurements made with a mass spectrometer inherently more important in determining the primary structure of a protein than those made with any other analytical instrument?

3. But mass spectral data generally only implies the structure of a polypeptide. It doesn't actually tell you the structure of the protein parent. Why, or how could this be true? How could errors be made in predicting the structure of a protein from mass spectral data? What kind of errors could be made in assigning protein structure?

4. Quantification has been a problem in proteomics. Why is that and what are some of the ways that quantification has been achieved? What are the relative merits of the methods you have listed?

5. Describe some global ideas or methods for recognizing post-translational modifications in proteins.

Inorganic Chemistry Cume Exam

March 3, 2007

A. This part of the exam deals with the assignment of formal oxidation states and electron counts for compounds of the transition metals.

(a) (20 points). Give the formal oxidation state and d^n configuration for the transition metal atom in each of the following ten neutral mononuclear compounds or ionic species.

(i) $TiO(acac)_2$ (acac = acetylacetonate anion)

(ii) $Ti(acac)_3$

(iii) $[VCl_2(H_2O)_4]^+$

(iv) $[MnCl_4]^{2-}$

(v) $Cr[N(SiMe_3)_2]_3$

(vi) $[Fe(CN)_6]^{4-}$

(vii) $Ni(CO)_4$

(viii) $(\eta^5\text{-}C_5H_5)_2Fe$

(ix) $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$

(x) $[V(CO)_6]^-$

(b) (20 points). For each of the following organometallic compounds and ions, give the <u>electron count</u> for the transition metal atom and conclude whether or not the '18-electron rule' is obeyed. <u>Show all working</u>. **NOTE**: you will need to know the structure of these compounds.

(i) $(\eta^5\text{-}C_5H_5)_2V$

(ii) $(\eta^5\text{-}C_5H_5)_2Fe$

(iii) $(\eta^6\text{-}C_6H_6)_2Cr$

(iv) $(\eta^5\text{-}C_5H_5)_2TiCl_2$

(v) $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$

(vi) $[Ti(CO)_6]^{2-}$

(vii) $V(CO)_6$

(viii) $[Fe(CO)_6]^{2+}$

(ix) $Ru_3(CO)_{12}$

(x) $Ir_4(CO)_{12}$

B. The chemistry of the Group IV transition metals Ti, Zr and Hf is representative of much of the chemistry of the early transition series elements.

(a) (12 points). The tetrahalides TiF_4(solid), $TiCl_4$(liquid) and $ZrCl_4$(solid) have different structures. Draw very clearly the structure of each of them.

(b) (15 points). Give balanced equations to show how $TiCl_4$ is converted to $TiCl_3$ and $TiCl_2$. Draw clearly the structure of the three compounds that are formed upon reacting $TiCl_3$ separately with CH_3CN, NMe_3 and $Li^+[N(SiMe_3)_2]^-$.

(c) (10 points). Give a balanced equation to show how $TiCl_4$ is converted into $TiOCl_2$. What is the product of the reaction of $TiOCl_2$ with acetylacetone (Hacac)? Draw its structure and compare it with that of its vanadium analog.

(d) (15 points). Starting from $ZrCl_4$, show how the organometallic species $[Zr(CO)_6]^{2-}$, $[Zr(CH_3)_6]^{2-}$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ are prepared. In the case of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, use balanced equations to show how it is converted to (i) $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ and (ii) $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$.

(e) (8 points). Which infra-red active CO stretching frequency (i.e. ν(CO)), goes with which carbonyl species?

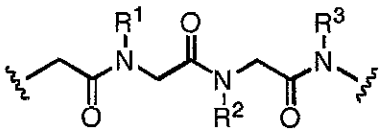
ν(CO): 2004, 2198, 1757 cm^{-1}

carbonyl species: $[Zr(CO)_6]^{2-}$, $Mo(CO)_6$, $[Ru(CO)_6]^{2+}$

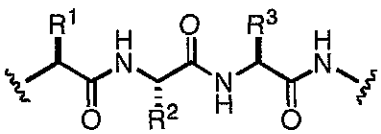
Explain your reasoning very clearly.

Organic Cumulative Exam: 03/03/07

I) (40 pts) Peptoids (**A**) are a class of peptidomimetics that have their side chains appended to nitrogen atoms along the polyamide backbone, rather than to the α-carbons, as in peptides (**B**). Answer any four out of five following questions about peptoids:



A



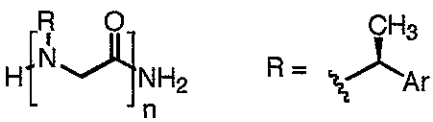
B

1) Kwon and Kodadek have developed a transcriptional assay to monitor cell permeability of peptides and isomeric peptoids (*JACS* **2007**, *129*, 1508). The authors have discovered that peptoides were generally more than 20 times more cell-permeable than peptides. *Briefly*, rationalize these findings, considering that cell permeation has been found to correlate with **desolvation energy** necessary on entering the lipid region of the membrane.

2) In addition to the cell permeation, list one more principle advantage of peptoids over peptides as drugs or biological probes.

3) List at least two coded amino acids not amenable to direct representation by peptoid peptidomimetics. Explain your choices.

4) Absence of intrinsic secondary structure is considered to be the principle limitation of peptoids. Goske and Blackwel (*JACS* **2006**, *128*, 14378) have successfully induced helicity within a peptoid backbone through the incorporation of substituents of the following type (Ar = aryl):

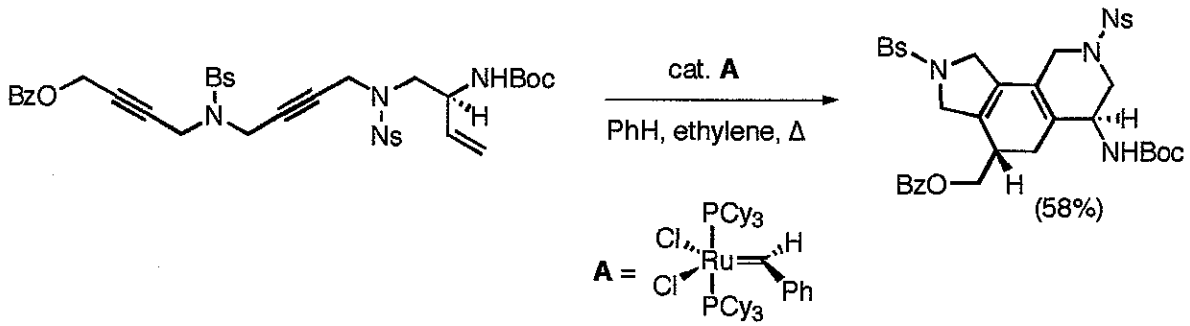


The authors have concluded that π-stacking plays only a limited role in the helicity induction by testing peptoids containing alternating phenyl and pentafluorophenyl aromatic groups (Ar = C_6H_5 and C_6F_5). *Briefly*, explain their choice of controls for detection of the π-stacking influence.

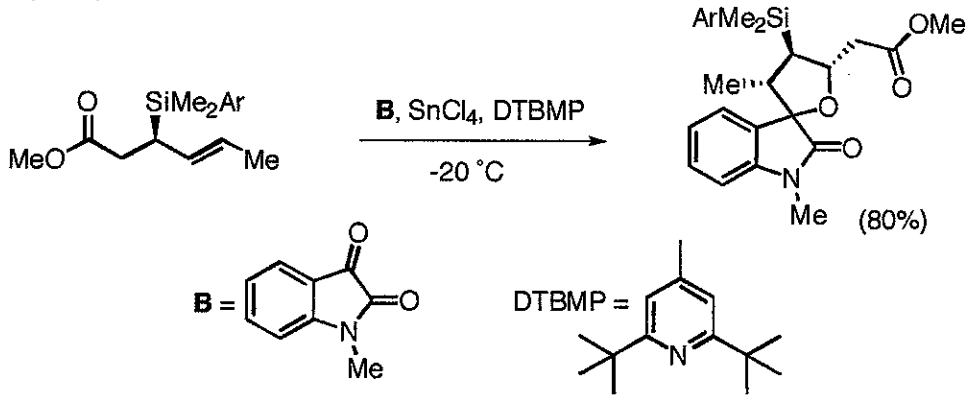
5) Propose an iterative solution phase synthesis of a tripeptoid (choose an optimal synthesis direction, monomer unit, coupling strategy, etc.).

II) (40 pts) Provide reasonable mechanistic explanations for two out of three transformations below (account for any relevant stereochemistry in the products):

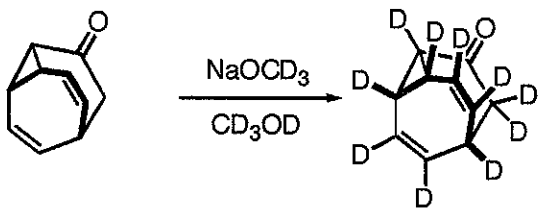
1) *JACS* **2006**, *128*, 14766:



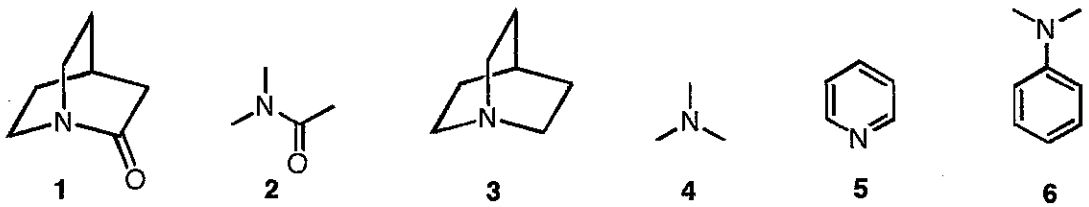
2) *JACS* **2007**, *129*, 1020:



3) *JACS* **2006**, *128*, 14738:



III) (20 pts) Ly and co-workers have recently measured proton affinity of 2-quinuclidone (**1**) and have determined that the site of protonation in this molecules differs from other tertiary amides, such as dimethylacetamide (**2**), in that a protonation at the nitrogen atom is favored by ≈ 90 kJ/mol over a protonation at the oxygen center (*JACS* **2007**, *129*, 1864). Provide an explanation for this finding and rank the compounds below in terms of their basicity.



1. This problem involves the calculation of equilibrium constants $K_{eq}(T)$ for the reaction

$$H_2(g) + I_2 \rightleftarrows 2HI(g) \qquad 1.$$

in a range $T \geq 298.15K$ and $T \leq 450$ K. You will require the two sheets at the end of the exam for data. Note from the first sheet I_2 is a solid until T = 386.85K and then forms a liquid until T = 457.4K. Also as indicated in (1) H_2 and HI are gases over the whole T range.

You will need the following additional information:

(i) For an <u>arbitrary</u> <u>molar</u> <u>state</u> <u>function</u> $X \equiv X_m$ and a <u>generic</u> <u>reaction</u>

$$\nu_A A + \nu_B B \rightleftarrows \nu_C C + \nu_D D \qquad 2.$$

ΔX for the reaction is defined as

$$\Delta X \equiv \nu_C X_C + \nu_D X_D - \nu_A X_A - \nu_B X_B \text{ -} \qquad 3.$$

(ii) For the reaction of (2)

$$\Delta G^0(T) = -RT\ln K_{eq}(T). \qquad 4.$$

where $0 \equiv P = 1$bar. (Recall $G = G_m \equiv \mu$).

(iii) For the reaction of (2)

$$\frac{d\ln K_{eq}(T)}{dT} = \frac{\Delta H^0(T)}{RT^2}. \qquad 5.$$

Solve the following three problems

(a) Compute K_{eq} (298.15K)
(b) Compute K_{eq} (380K)
(c) Compute K_{eq} (450K)

State all assumptions and show all your work. Make approximations required by the data available (that is do all calculations using <u>only</u> the data available).

1.

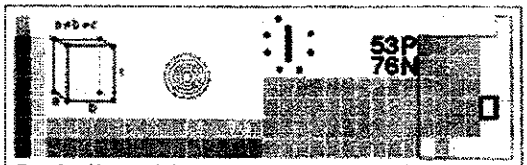
Iodine

Physical Cume Exam
March 3, 2007

From Wikipedia, the free encyclopedia

Iodine (IPA: /ˈʌɪə(ʊ)ˌdi□n/, Greek: *iodes*, meaning "violet"), is a chemical element in the periodic table that has the symbol **I** and atomic number 53. Chemically, iodine is the least reactive of the halogens, and the most electropositive halogen after astatine. Iodine is primarily used in medicine, photography and dyes. It is required in trace amounts by most living organisms.

As with all other halogens (members of Group VII in the Periodic Table), iodine forms diatomic molecules, and hence, has the molecular formula of $\mathbf{I_2}$.

53	tellurium ← iodine → xenon
Br ↑ **I** ↓ At	 Periodic Table - Extended Periodic Table

General	
Name, Symbol, Number	iodine, I, 53
Chemical series	halogens
Group, Period, Block	17, 5, p
Appearance	violet-dark gray, lustrous [redacted]
Atomic mass	126.90447(3) g/mol
Electron configuration	[Kr] $4d^{10}\ 5s^2\ 5p^5$
Electrons per shell	2, 8, 18, 18, 7
Physical properties	
Phase	solid
Density (near r.t.)	4.933 $g{\cdot}cm^{-3}$
Melting point	386.85 K (113.7 °C, 236.66 °F)
Boiling point	457.4 K (184.3 °C, 363.7 °F)
Critical point	819 K, 11.7 MPa
Heat of fusion	(I_2) 15.52 $kJ{\cdot}mol^{-1}$
Heat of vaporization	(I_2) 41.57 $kJ{\cdot}mol^{-1}$
Heat capacity	(25 °C) (I_2) 54.44 $J{\cdot}mol^{-1}{\cdot}K^{-1}$

Vapor pressure (rhombic)

P/Pa	1	10	1001	k	10 k	100 k
at *T*/K	260	282	309	342	381	457

Atomic properties	
Crystal structure	orthorhombic
Oxidation states	±1, 5, 7 (strongly acidic oxide)

Contents

Occurrence on earth

Iodine naturally occurs in the environment chiefly as dissolved iodide in seawater, although it is also found in some minerals and soils. The element may be prepared in an ultrapure form through the reaction of potassium iodide with copper(II) sulfate. There are also several other methods of isolating this element. Although the element is actually quite rare, kelp and

2.

Compound	H_m^0(298.15K), in kJ/mol)	μ^0(298.15K), in kJ/mol)	S_m^0(298.15K), in J/(mol-K)]
HI(g)	26.5	1.7	114.7
H_2(g)	0	0	130.68
I_2(s)	0	0	116.14

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.)