Department of Chemistry
Cumulative Examinations
December 8, 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.

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
UNIVERSITY

Analytical Cumulative Examination December 8, 2007

Reversed phase chromatography (RPC) is ubiquitous in analytical chemistry.

1. What is the mechanism by which substances are separated in RPC?

2. It would be common with a series of hexapeptides of identical amino acid composition that RPC could resolve the mixture into multiple groups. How would this occur in light of your answer above?

3. There is currently great interest in capillary RPC columns. Why is this? What are the advantages of capillary chromatography columns?

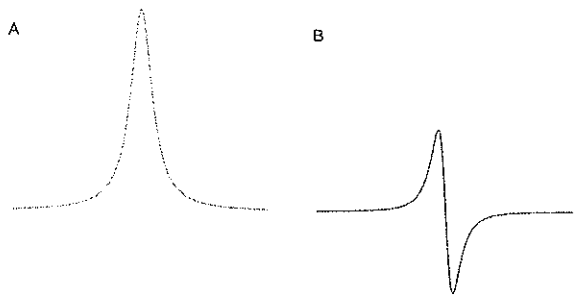
4. How is mass spectrometry being used to identify peptides eluting from RPC columns?

CUMULATIVE EXAMINATION IN BIOCHEMISTRY

Dec 8, 2007

It is expected that the answer should contain 1-4 succinct straight-to-the-point sentences. If you feel like elaborating, please stay within an 8 sentence limit anyway. All questions carry the same weight.

1. Shown below is the typical representation of the NMR (A) and ESR (B) spectral lines. Given that NMR and ESR are fundamentally similar techniques (both originate from resonance absorption of energy by a spin system), why do the spectral lines look different?



2. Amyloid plaques are the signature of neuropathological diseases, such as Alzheimer and Parkinson disease. The plaques are built of peptide (protein) material. What is the arrangement of peptide chains in the plaques (i.e. the principal secondary-structure motif)?

3. A standard DNA sequencing procedure relies on a polymerase chain reaction conducted in the presence of deoxynucleotides and dideoxynucleotides. What is the critical role of *dideoxynucleotides* in this process?

4. Controlled trypsinolysis is often used as a probe of change in conformational state of proteins. What is the conceptual basis of this approach?

5. An aqueous solution of a protein is prepared for *in vitro* studies. In order to improve the solubility of the protein it is recommendable to adjust the pH of a solution such that the pH is substantially higher or substantially lower than the protein isoelectric point, pI. What is the reason for this recommendation?

Footnotes: (*i*) the buffer should be selected accordingly

(*ii*) extreme pH values should be avoided to prevent protein unfolding

6. The so-called 'Levinthal paradox' illustrates an important idea in the theory of protein folding. What is the essence of this paradox?

7. Burial of hydrophobic surface upon formation of a protein complex is entropically favorable. Conversely, dissociation of a complex incurs an entropic penalty. Explain the origin of this entropic penalty.

8. Disulphide bridges are rare in cytosolic proteins, but common in secretory proteins. Why?

9. When studying enzymatic catalysis *in vitro*, it is often found that the catalytic turnover rate for deuterated substrates is lower than that for their protonated analogues. What is the main reason for this observation?

10. Biotin forms an unusually tight complex with avidin, $K_D \sim 10^{-15}$ M, which forms a basis for a variety of laboratory techniques including affinity chromatography applications. Suppose that in a certain purification protocol an avidin column is loaded with the biotinylated protein, and then the protein is eluted with an excess free biotin. Estimate the time required for such an elution step.

11. When applied to large biomolecules, the process of electrospray ionization (ESI) leads to formation of multiply charged ion fragments. A technique developed in the laboratory of Scott McLuckey, called 'ion parking', allows to bring (nearly) all product ions to a single charge state. How this technique can be useful for mass spectrometry analysis of proteins?

12. In an electron transfer reaction, donor (D) and acceptor (A) are separated by an intervening short α-helix. As it turns out, the rate of the electron transfer depends on orientation of the helix. When do you expect to observe a faster rate: (*i*) long axis of the helix is oriented along the D-A axis, or (*ii*) long axis of the helix is perpendicular to D-A axis? Why?

Inorganic Chemistry Cume Exam

December 8, 2007

A. (70 points) Cyclopentadienyl (Cp) complexes of the transition metals constitute an extensive class of compounds that can display a variety of bonding modes for the Cp ligands. The structures and reactivities of these Cp complexes are often dependent upon the substituents that are present on the Cp rings and upon the transition metal and its oxidation state. The following questions relate to the synthesis, electronic and molecular structures, and reactivities of transition metal cyclopentadienyl complexes.

1.) Compounds of the types $(C_5R_5)MCl_3$ and $(C_5R_5)_2MCl_2$(R = H or Me; M = Ti or Zr) are important complexes for the synthesis of the other Cp derivatives. Draw the structures <u>and</u> give the electron counts for the metals in complexes of these two types when M = Ti or Zr.

Draw the structures of the metal complexes that are the products of the following reactions <u>and</u> in each case give the electron count for the metal.

(i) $(C_5H_5)_2TiCl_2$ + excess $Na^+C_5H_5^-$
(ii) $(C_5H_5)_2TiCl_2$ + excess PMe_3 in the presence of Mg metal
(iii) $(C_5Me_5)_2TiCl_2$ + C_7H_8 (cyclopheptatriene) in the presence of Mg metal.

2.) Draw the structures of the compounds of composition $M(C_5H_5)_2$ in the cases where M = V, Nb, Os, and Re. If more than one structure is known for any of these molecules, make sure you draw all known structures. Explain as best you can why structural differences exist within this set of compounds.

3.) Provide the details for the synthesis of $(C_5H_5)_2Ta(CH_3)_3$ and $(C_5H_5)_2Ta(CH_3)(CH_2)$ from $TaCl_5$. Draw very clearly the structures of both complexes and describe why $(C_5H_5)_2Ta(CH_3)(CH_2)$ is of special significance.

4.) What is Tebbe's reagent? Give its synthesis, draw its structure, and explain what it is used for.

5.) Although the η^1- and η^5-bonding modes of C_5R_5 ligands are the ones most commonly encountered, examples of η^3-bonding are known. Give <u>one</u> such example for a cyclopentadienyl complex whose crystal structure has been determined, draw its structure, and rationalize why a η^3-bound cyclopentadienyl ligand is present.

B. (30 points) Give an authentic example of each of the following that involves a transition metal from Groups IV-VII. For each example you have given, 1) provide a reaction to show how you would prepare the compound, 2) sketch its molecular structure, and 3) give a brief description of the electronic structure of the metal core that is present in the compound.

(i) A mononuclear transition metal tetrachloride MCl_4.

(ii) A transition metal pentachloride MCl_5 that is stable in the solid state

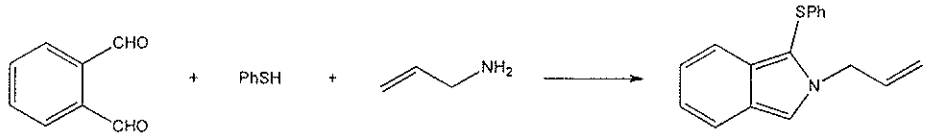
(iii) The metal-containing product from a reaction between a metal halide and an alcohol (specify the alcohol).

(iv) An acetylacetonate complex of the type $MCl_2(acac)_2$.

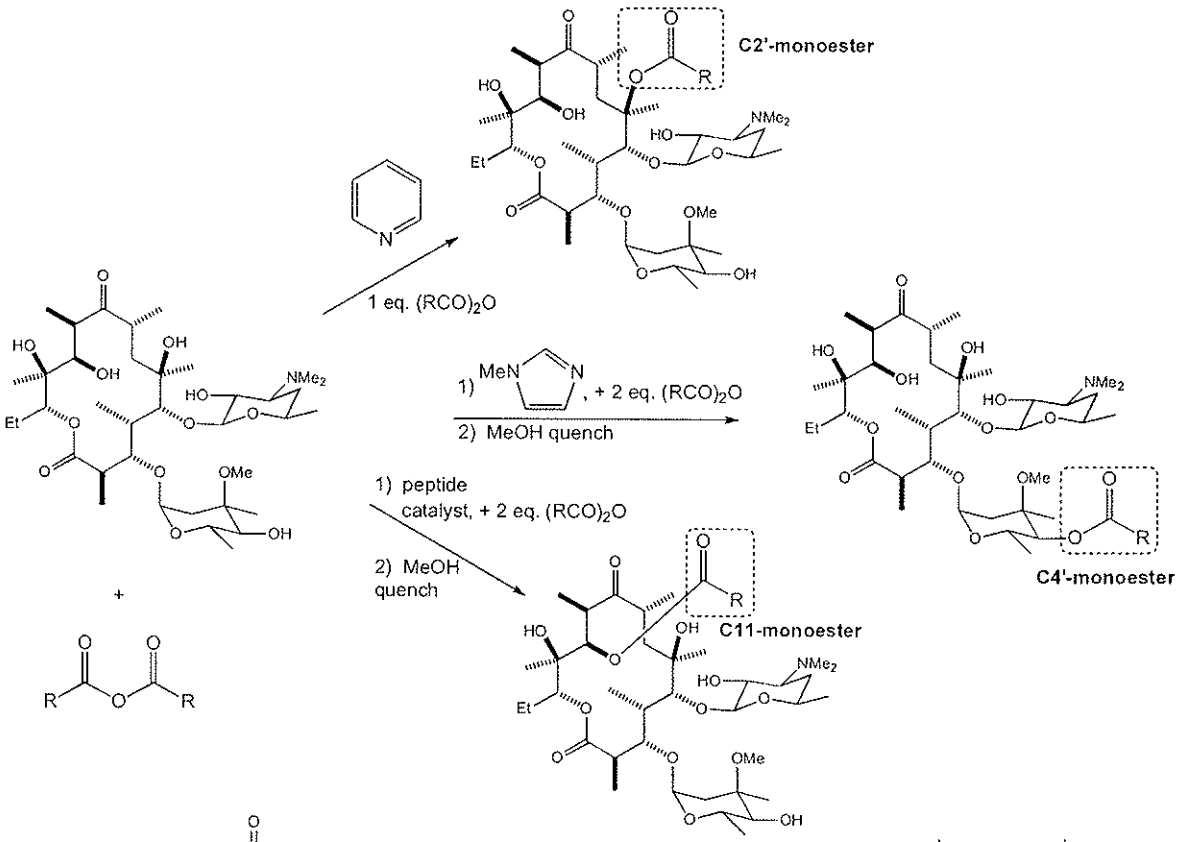
(v) A neutral paramagnetic carbonyl of the type $M(CO)_6$

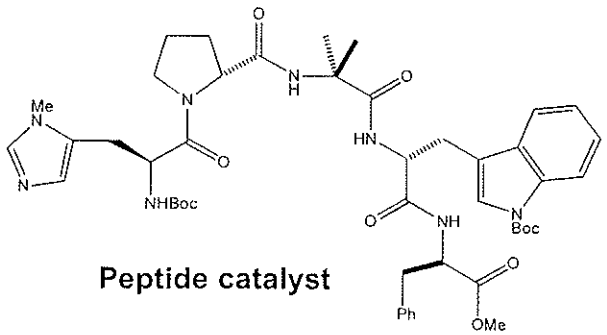
(vi) A complex that contains a carbonyl dianion of the type $[M(CO)_6]^{2-}$.

1. (30 pts) Propose a plausible reaction mechanism for the following transformation:



2. (35 pts) A proline-based chiral catalyst has recently been reported as a tool for remodeling natural product medicinal agents to enhance their pharmacologic profile (*Angew. Chem. Int. Ed.* **2006** *45*, 5616). The performance of one such catalyst (discovered from a search of a library of 137 peptide catalysts) on the site-selective modification of the natural product polyol, erythromycin A, relative to uncatalyzed and *N*-methylimidazole(NMI)-catalyzed reactions, is shown below.





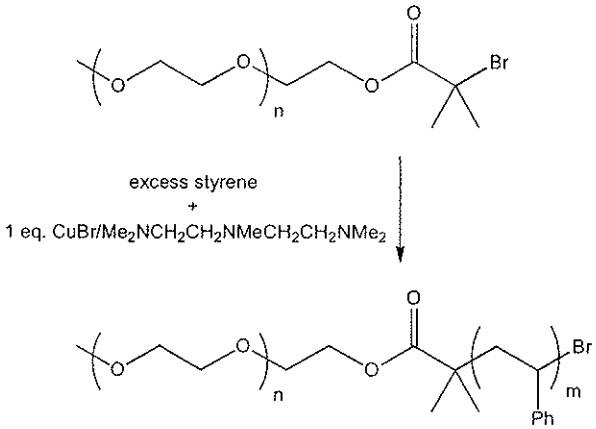
Peptide catalyst

Catalyst Ester prod ratio	NMI C4':C11	peptide C4':C11
R = Me	4:1	1:5
R = Et	2:1	1:3.5
R = $(CH_2)_7CH_3$	>10:1	1:9
R = $(CH_2)_2CH{=}CH_2$	2:1	1:5
R = $(CH_2)_2NHBoc$	5:1	1:>10

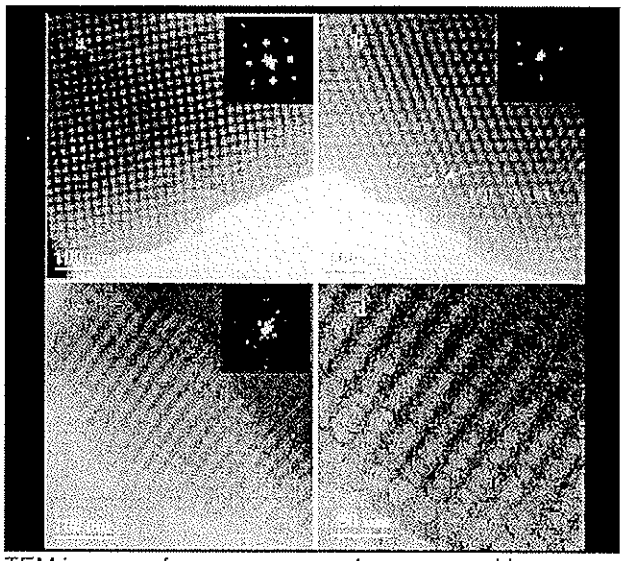
a. (10 pts) Propose a plausible mechanism for the catalyzed esterification reactions.
b. (15 pts) Briefly rationalize the observed differences in organocatalyst activity that account for the changed pattern of reactivity.

3. (35 pts) One of the major challenges in the synthesis of nanomaterials is the creation of materials whose shape and display of functional groups approaches the level of control that is currently achievable with small organic molecules. Two important tools in this endeavor are (1) living polymerization and (2) templated synthesis. A recent JACS paper (*JACS* **2007** *129*, 1690) combined these two techniques to prepare a nanoporous carbon material.

a. (10 pts) Propose a plausible mechanism for the living polymerization reaction shown.



b. (15 pts) Upon mixing the diblock copolymers prepared via living polymerization with a resol precursor solution (i.e., a 20 wt% phenol-formaldehyde mixture in THF), slowly evaporating the THF 24h at 100°C and then pyrolyzing the samples in a N_2 atmosphere for 3h at 800°C, the nanoporous materials of the type shown below were formed. It was further observed that the pore sizes and wall thicknesses were dependent on the ratio of poly(ethylene oxide):poly(styrene) block ratios, such that smaller poly(styrene) blocks gave larger pores when the poly(ethylene oxide) block size was held constant. Briefly describe the mechanism employed in this paper to create the regular pores in the nanoporous carbon material and rationalize the observed dependence of pore size on monomer ratios in the diblock copolymers used.



TEM images of mesoporous carbon prepared by pyrolysis of diblock copolymer/resol precursor films in N_2 at 800°C viewed from the (a) [100], (b) [110], (c,d) [211] directions.

Physical Chemistry Cume
December 8, 2007

1. Consider a single phased closed chemical system that can vary in chemical composition. The Gibbs function for the system, G, depends upon T, P, and mole numbers $G = G(T, P, n_i)$.

A. (15 pts.) Use the equation $dG = -SdT + VdP$ for a closed system of constant composition and the definition of chemical potential, μ_i, to show that

$$dG = -SdT + PdV + \Sigma\, \mu_i\, dn_i$$

where the sum includes all the constitutents of the mixture.

B. (15 pts.) If the mole numbers in (A) are constrained by the stoichiometry of a single chemical reaction, then we can write $n_i = n_i^o \pm \nu_i \xi$ where ξ is an extent of reaction variable. Using this information show that at constant T and P

$$\frac{dG_{T,P}}{d\xi} = \Sigma \mu_i \nu_i \equiv \Delta\mu$$

which is the change in Gibbs function per unit advancement of the reaction.

C. (15 pts.) For closed chemical systems in thermal and mechanical equilibrium the second law states that $dS \geq \frac{dq}{T}$. Use this information to demonstrate that the condition for the reaction to proceed spontaneously is $\Delta\mu < 0$.

2. Consider the dissociation of nitrogen tetroxide N_2O_4 $(g) \leftrightarrow 2\, NO_2$ (g) at 25°C. Suppose 1 mol of N_2O_4 is confined in a vessel under 1 atom pressure.

Given information:
ΔG_f^o $(NO_2; g) =$ 51.30 kJ/mol
ΔG_f^o $(N_2O_4; g) =$ 97.8 kJ/mol

A. (20 pts) Calculate the degree of dissociation.
B. (10 pts) If 5 mol of argon are introduced and the mixture is confined under 1 atm total pressure, what is the degree of dissociation?
C. (5 pts) The system comes to equilibrium as in part A. If the temperature and volume of the vessel are then kept constant and 5 mol of argon are introduced, what will be the degree of dissociation?

3. (5 pts. each) Define the four following terms in <u>words and equations</u> (or symbols).

A. Energy; B. Chemical potential; C. Spontaneity (as used in thermodynamics)
D. Equilibrium

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.)