

**Department of Chemistry  
Cumulative Examinations  
September 22, 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, Page 2
- 3) Inorganic Cumulative Examination, Pages 3-4
- 4) Organic Cumulative Examination, Page 5-6
- 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**  

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**U N I V E R S I T Y**

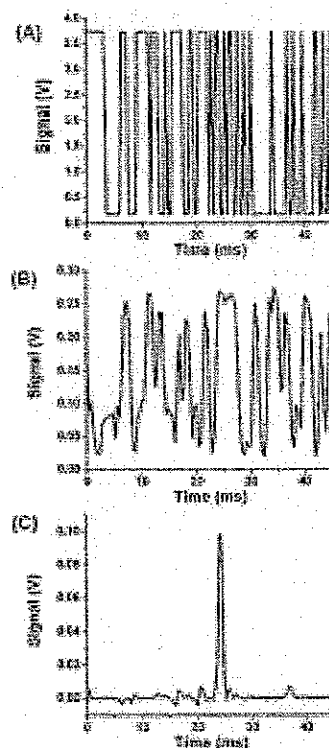
## Analytical Chemistry Cume, Sept. 22, 2007

### *Analytical Chemistry Cume Based on the Announced Publications:*

1. "Hadamard Transform Ion Mobility Spectrometry" by Andrew W. Szumlas, Steven J. Ray, and Gary M. Hieftje, *Anal. Chem* **2006**, *78*, 4474-4481.
2. "Hadamard Transform Ion Mobility Spectrometry" by Brian H. Clowers, William F. Siems, Herbert H. Hill, and Steven M. Massick, *Anal. Chem* **2006**, *78*, 44-51.

**Please be sure to completely answer each question that is asked!**

1. In ion mobility spectrometry, what are the physical properties of the molecules that provide separation?
2. Both papers observe average S/N enhancements of up to ~7 when applying Hadamard transform detection compared to traditional sampling. In terms of the differences in duty cycle alone, explain why this 7-fold enhancement is not surprising in retrospect. (hint: what was the approximate difference in duty cycle in traditional vs. Hadamard IMS?)
3. What is the primary origin of the multiplex advantage in these instruments? What is the primary origin of the multiplex disadvantage in these instruments? Which one is more significant in these measurements, and why?
4. Both papers used a Faraday plate as the detector for measuring ion fluxes through the drift tubes. Draw both a physical schematic and an electronic schematic of a Faraday plate and describe the basics of its operation.
5. Faraday plates are not particularly sensitive ion detectors. For example, in most mass spectrometry applications, microchannel plates provide much lower ion detection limits with much greater sensitivities. Why were they not used in either experimental configuration?
6. Both papers used a Bradbury-Neilson (B-N) ion gate to modulate the incident ion flux in the Hadamard transform measurements. What is a B-N gate, and how does it operate? What particular aspect of the gate is most important in dictating S/N in both of the present studies?
7. Explain the significance of the figure to the right, taken from the Szumlas paper. Specifically, what is the relationship between the top panel and the middle panel? The middle panel and the bottom panel?
8. Will HT-IMS have an impact? What are the pros and cons of the method relative to existing technologies, and can it be competitive with IMS and with atmospheric sampling MS? Defend your answers! (The argument is the only thing that matters in this question).



**Figure 2.** Three panels that demonstrate the conversion of a pseudo-random binary sequence to an ion mobility spectrum: (A) pseudo-random binary sequence applied to the ion gate, (B) raw data for the analyte that (at first) appears obscured at the detector prior to the transform, and (C) spectrum of T16 reconstructed from the background-subtracted data shown in panel B. The data in these three frames cover only the first 40 ms of the entire series, which is over 400 ms long.

## Biochemistry Cumulative Exam

### Title: Transcription and Translation

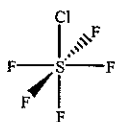
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1. (20 points). What are the functions of the following?  
(a) EF-Tu (b) EF-Ts (c) t-RNA synthetase (d) mRNA
2. (5 points) What are the approximate transcription and translation rates in *E. coli*?
3. (10 points). What is the role of sigma subunit? Why is it advantageous to have sigma subunits?
4. (10 points) Provide any two differences between promoters and enhancers.
5. (15 points) Provide any three major identity elements of t-RNA?
6. (20 points) Define the following terms in two to three sentences:  
(a) Anticodon (b) Shine Dalgarno sequence (c) RNA editing (d) RNAi
7. (15 points) What are the three major differences between prokaryotic and eukaryotic mRNA?
8. (5 points) What is the biggest difference between a typical protein enzyme and ribosome?

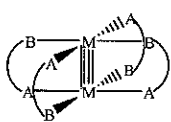
# Inorganic Cumulative Exam

September 22, 2007

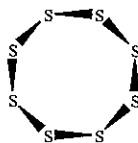
1 (25 pt) Assign symmetry point groups for the following molecules/objects (mark symmetry elements clearly)



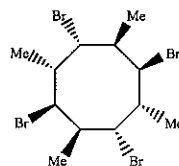
1a



1b



1c



1d



1e

(tetrahedron with one pair of opposite edges painted bold)

2 (25pt) Use a two dimensional lattice to prove that the only rotation symmetry elements allowed by lattice translation are  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_6$ .

3 (30 pt) (i) Use the symmetry and LCAO (linear combination of atomic orbitals) to analyze the  $\sigma$ -bonding MOs in  $\text{PtCl}_4^{2-}$  (use XY plane as the molecular plane) and determine which of Pt valence orbitals are involved in the  $\sigma$ -bonding. Character table can be found from the following page. (ii) By further considering the  $\pi$ -type lone pairs on the Cl ligands, sketch *qualitatively* the energy levels of the Pt  $d$ -orbitals (symmetry unnecessary for this part).

4 (20 pt) Sketch the structures of the following “famous” inorganic compounds (complex ions).

(a) ferrocene

(b)  $[\text{Re}_2\text{Cl}_8]^{2-}$

(c)  $[\text{Ru}(\text{bipy})_3]^{2+}$

(d) Zeiss's salt

(e) Grubbs first generation catalyst

Character tables – choose **one** suitable for problem #3

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$A_1$	1	1	1	1	1	-	$x^2+y^2+z^2$
$A_2$	1	1	1	-1	-1	-	-
E	2	-1	2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	-
$T_2$	3	0	-1	-1	1	$(x, y, z)$	$(xy, xz, yz)$

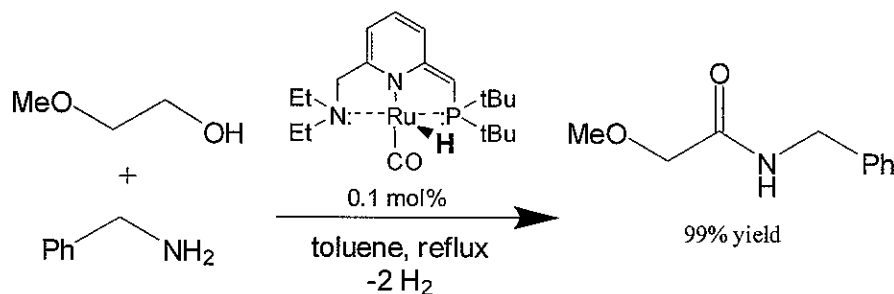
$C_{4v}$	E	$2C_4(z)$	$C_2$	$2\sigma_v$	$2\sigma_d$		
$A_1$	1	1	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$	-
$B_1$	1	-1	1	1	-1	-	$x^2-y^2$
$B_2$	1	-1	1	-1	1	-	xy
E	2	0	-2	0	0	$(x, y)$ $(R_x, R_y)$	$(xz, yz)$

$D_{4h}$	E	$2C_4(z)$	$C_2$	$2C'_2$	$2C''_2$	i	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	-	$x^2+y^2, z^2$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	$R_z$	-
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1	-	$x^2-y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1	-	xy
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	-	-
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	z	-
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1	-	-
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1	-	-
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$	-

$D_{3h}$	E	$2C_3$	$3C'_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A'_1$	1	1	1	1	1	1	-	$x^2+y^2, z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$	-
E'	2	-1	0	2	-1	0	$(x, y)$	$(x^2-y^2, xy)$
$A''_1$	1	1	1	-1	-1	-1	-	-
$A''_2$	1	1	-1	-1	-1	1	z	-
E''	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

## Green synthesis: Saving the world, one atom at a time

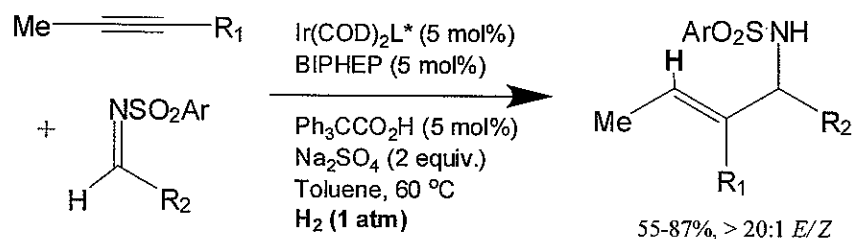
1. Milstein and coworkers reported a remarkably direct synthesis of amides from alcohols and amines, with liberation of  $H_2$  (*Science* 2007, 317, 790-792).



The authors propose that the dehydrogenation (oxidation) occurs in two separate steps. The first step of the catalytic cycle involves coordination of the alcohol with the Ru center.

- a) (25 pts.) Suggest a catalytic cycle for this reaction. Show all intermediates, and be sure to keep track of all hydrogens. *Hint*: the catalyst is indeed correctly drawn.
- b) (10 pts.) Provide an alternative reaction condition (with reagents) for converting the starting materials into the amide above. How many extra atoms are involved (not counting catalysts or solvent)?
- c) (15 pts.) This reaction can also efficiently convert 2 equivalents of primary alcohol and diamine into a single product. What do you think would happen if a diol were used? Starting with 1 equiv. of 1,6-hexanediol and 1 equiv. 1,6-diaminohexane, propose the final outcome.

2. (25 pts.) Krische and coworkers could use the H<sub>2</sub> generated by Milstein in the reaction below! A “hydroalkynylation” reaction involving internal (unconjugated) alkynes and *N*-sulfonylimines produced highly substituted allylamines in good to high yields (*J. Am. Chem. Soc.* **2007**, *129*, 8432-33):

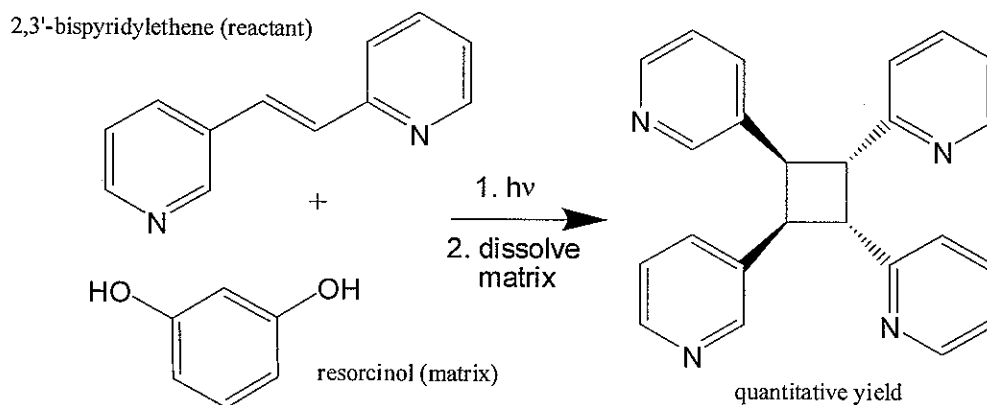


COD = cyclooctadiene; L\* = surrogate ligand; BIPHEP = 2,2'-bis(diphenylphosphine)

Replacing H<sub>2</sub> with D<sub>2</sub> resulted in 83% D incorporation at the vinylic position, and < 5% D in Me or R<sub>1</sub>. The sulfonamide position was found to incorporate a mixture of H and D, after isolation.

Propose a working mechanism for this reaction (don't worry about the coordinating ligands). Explain the use of triphenylacetic acid for full credit.

3. (25 pts.) Saving the world one atom at a time is kind of slow. How about organic reactions in a solventless system? MacGillivray and coworkers developed a photochemical solid-state reaction which proceeds in quantitative yield and with complete stereoselectivity, starting from a 1:1 solid mixture of resorcinol and 2,3'-bispyridylethene (*ChemComm* **2007**, 1603-04). The resorcinol is critical for the synthetic outcome.



- (a) (20 points) Provide a reasonable explanation for this remarkable result (please illustrate with a drawing).
- (b) (5 points) Is the product chiral?

Physical Chemistry  
Cumulative Exam  
Fall 2007

In this problem, you will study ideal gas volume changes. The following equations may prove helpful:

**General Equations**

$$dU = dq + dw.$$

$$dw = -P_{\text{ext}} dV.$$

For a composite system composed of subsystems 1 and 2

$$dU = dU_1 + dU_2.$$

**Ideal Gas Equations**

$$PV = nRT.$$

$$dU = C_v dT.$$

$$C_v = ynR \text{ where } y = \begin{cases} 3/2 & \text{monatomic gas} \\ 5/2 & \text{diatomic gas} \end{cases}$$

**Part A.** This part deals with the situation shown in Fig. 1.

		Compartment 2								
	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border: none; padding: 5px;">monatomic gas</td> <td style="border: none; padding: 5px;">diatomic gas</td> </tr> <tr> <td style="border: none; padding: 5px;"><math>n_{1i} = \frac{3}{4}n</math></td> <td style="border: none; padding: 5px;"><math>n_{2i} = \frac{1}{4}n</math></td> </tr> <tr> <td style="border: none; padding: 5px;"><math>T_{1i} = \frac{5}{4}T_i</math></td> <td style="border: none; padding: 5px;"><math>T_{2i} = T_i</math></td> </tr> <tr> <td style="border: none; padding: 5px;"><math>V_{1i} = \frac{1}{4}V</math></td> <td style="border: none; padding: 5px;"><math>V_{2i} = \frac{3}{4}V</math></td> </tr> </table>	monatomic gas	diatomic gas	$n_{1i} = \frac{3}{4}n$	$n_{2i} = \frac{1}{4}n$	$T_{1i} = \frac{5}{4}T_i$	$T_{2i} = T_i$	$V_{1i} = \frac{1}{4}V$	$V_{2i} = \frac{3}{4}V$	
monatomic gas	diatomic gas									
$n_{1i} = \frac{3}{4}n$	$n_{2i} = \frac{1}{4}n$									
$T_{1i} = \frac{5}{4}T_i$	$T_{2i} = T_i$									
$V_{1i} = \frac{1}{4}V$	$V_{2i} = \frac{3}{4}V$									
Compartment 1										

Figure 1

Namely, an *isolated system* of volume  $V$  is divided into compartment 1 (left) and compartment 2 (right) separated by a moveable thermally conducting partition. Compartments 1 and 2 contain, respectively, a monatomic and a diatomic ideal gas. The initial thermodynamic states of the two gases are indicated in Fig. 1. Suppose the partition is initially held fixed but is released at  $t=0$ . The system will eventually reach a final equilibrium state characterized by the following values of the state variables:

$$T_{1f}, P_{1f}, V_{1f}, n_{1f} = \frac{3}{4}n \text{ for compartment 1} \quad (\text{A.1a})$$

and

$$T_{2f}, P_{2f}, V_{2f}, n_{2f} = \frac{1}{4}n \text{ for compartment 2} \quad (\text{A.1b})$$

- a. Explain why in the final equilibrium state

$$T_{1f} = T_{2f} \equiv T_f \text{ and } P_{1f} = P_{2f} \equiv P_f. \quad (\text{A.2})$$

- b. Find expressions in terms of  $T_i, V, n,$  and  $R$  for:

(i)  $T_f$

(ii)  $P_f$

**Part B.** This part deals with the situation shown in Fig. 2

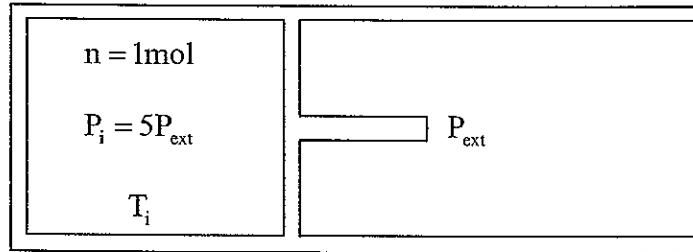


Figure 2

Namely, an *isolated system* is split into two parts by a piston which exerts a pressure  $P_{\text{ext}}$  on the left hand part. The latter is filled with 1 mol of an ideal monatomic gas with initial pressure  $P_i = P_{\text{ext}}$ , initial temperature  $T_i$ , and initial volume  $V_i = \frac{RT}{P_i}$ . Since  $P_i = 5P_{\text{ext}} > P_{\text{ext}}$  the gas expands adiabatically until its pressure drops to  $P_{\text{ext}}$ , at which time the final equilibrium state is reached and the expansion halts. Find expressions in terms of  $T_i, P_{\text{ext}}$  and  $R$  for:

- (i) The final gas temperature  $T_f$ .
- (ii) The final gas volume  $V_f$ .
- (iii) The work  $w$  done *on* the gas (it is negative).
- (iv) The change in internal energy of the gas  $\Delta U = U_f - U_i$ .
- (v) The change in enthalpy of gas  $\Delta H = H_f - H_i$ .

# Periodic Classification of the Elements

0

IA		IIA		IIIA		IVA		VA		VIA		VIIA		0			
1 H 1.00797	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 Act (227)															

*Lanthanides		†Actinides											
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
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.)