

Department of Chemistry Cumulative Examinations October 21, 2006

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 4-7
- 4) Organic Cumulative Examination, Page 8
- 5) Physical Cumulative Examination, Page 9

On your examination booklet:

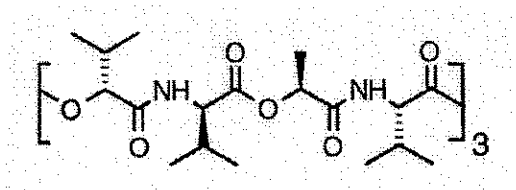
- 1) Print your student ID number.
- 2) Print this Exam Booklet number: _____
- 3) Print the question number you are answering.
- 4) Print the Exam Date.

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

1. Consider the structure of a well known potassium ion-selective receptor, valinomycin:



The complex formation constant of this receptor with K^+ has been determined *in water* as $\log K_1(\text{aq}) = 0.3$ and in plasticized poly(vinyl chloride), a hydrophobic polymeric solvent ordinarily used as a sensing material, as $\log K_1 = 10.0$.

Please explain this very large discrepancy in stability constants.

2. Valinomycin was one of the first receptors to be used in solvent polymeric ion-selective electrodes for the determination of potassium ions by direct potentiometry.

Ideally, such potentiometric sensors function according to the Nernst equation, written in simplified form as:

$$emf = K + s \log a_K$$

a) Such sensors are responsive to the ion activity. Write down the relationship between the ion activity and the molar ion concentration.

b) Explain the role of the reference electrode in this measurement, and assess how an error of 2 mV affects the measured potassium levels (assume an electrode slope, s , of 59.2 mV).

3. The selectivity of these types of sensors over other monovalent ions such as sodium is described by an ion-exchange equilibrium. The resulting electrode function is an extension of the Nernst equation, called the Nicolsky equation:

$$emf = K + s \log \left(a_K + K_{K,Na}^{pot} a_{Na} \right)$$

a) For a selectivity coefficient, $K_{K,Na}^{pot}$, of 0.00010, predict the *percent error* when measuring 0.0030 M potassium activity in the presence of 0.10 M sodium activity.

b) The selectivity coefficient can be related to the formation constants of the receptor in the membrane. Only one of the following relationships is correct. Please pick the correct equation and defend your choice. In the equations, $\beta_1(\text{ValK})$ and $\beta_1(\text{ValNa})$ are the 1:1 formation constants for the indicated complexes in the membrane phase and $K_{K,Na}$ the

ion-exchange constant for the exchange of *uncomplexed* potassium by sodium from the membrane.

$$K_{K,Na}^{pot} = K_{K,Na} \frac{\beta_1(ValK)}{\beta_1(ValNa)} \quad (1)$$

$$K_{K,Na}^{pot} = K_{K,Na} \frac{\beta_1(ValNa)}{\beta_1(ValK)} \quad (2)$$

$$K_{K,Na}^{pot} = \frac{\beta_1(ValNa)}{\beta_1(ValK)} \quad (3)$$

$$K_{K,Na}^{pot} = K_{K,Na} \beta_1(ValK) \quad (4)$$

4. Modern potentiometric sensors for potassium still largely rely on valinomycin in the routine clinical analysis of whole blood samples. The membranes contain a lipophilic cation-exchanger in addition to valinomycin.

a) Discuss the role of this ion-exchanger and the nature of its counterion in the membrane.

b) Postulate how the sensors would behave without any such ion-exchanger present in the membrane. Would you still expect the membrane to behave according to the Nernst equation? Please discuss.

1. In 2006, Andrew Fire and Craig Mello were awarded the Nobel Prize in Physiology or Medicine "for their discovery of RNA interference - gene silencing by double-stranded RNA".
 - A. What is RNA interference?
 - B. What does gene silencing mean?
 - C. Provide an example of gene silencing that could potentially be used as a therapeutic procedure (for example killing of certain type of cancerous cells).

2. In 2006, Roger D. Kornberg was awarded the Nobel Prize in Chemistry "for his studies of the molecular basis of eukaryotic transcription".

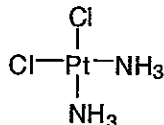
What is transcription and why is it important?

3. Can you think of a link between transcription and gene silencing by RNAi? Give the reasons for your answer.

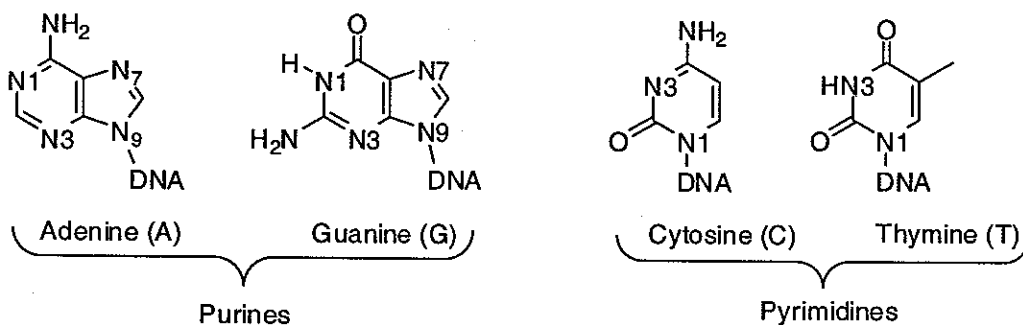
4. Provide three different types of structures that RNA molecules can form.

5. Can these structures also form in DNA? Give the reason(s) for your answer.

Cisplatin or Cis-DDP, cis-diaminodichloroplatinum(II), is an anticancer drug that falls into the class of DNA-damaging agents. It acts in a similar mechanism to that of bifunctional alkylating agents. Its structure is shown below.



- (a). Do you expect this molecule to be diamagnetic or paramagnetic? Explain your answer by showing electron occupancy in the metal d-orbitals in this symmetry (ligand field)?
- (b). It is believed that the active species results from reaction with water. Show the structure of the product.
- cis-PtCl₂(NH₃)₂ + H₂O (excess) →
- (c). Cisplatin is soluble in water at 1 mg/mL. What is the concentration in molarity of a saturated aqueous solution of cisplatin?
- (d). The active aquated species of cisplatin is a bifunctional electrophilic agent and is therefore able to bind any nucleophilic site present on DNA. Suggest which position on the purines and pyrimidines would be most probable for binding cisplatin.



- (e). The trans isomer of cisplatin is ineffective as a drug. Suggest a mechanism for cisplatin's action on DNA strand that would account for reduced activity of the trans analogue.
- (f). Assign the point group symmetry for each isomer, cis and trans-platin.
- (g). Deduce the number of IR active Pt-Cl stretching modes that would be expected for each isomer.
- (h). One of the mechanisms by which cells develop resistance to cisplatin is via an increase in production of glutathione and metallothioneins. Explain how these molecules would inhibit the action of cisplatin.

PERIODIC TABLE OF THE ELEMENTS

Table of Selected Radioactive Isotopes

Naturally occurring radioactive isotopes are designated by a mass number in blue (though some are also manufacturer's). Later in the table, isotopes of elements with a half-life of less than 100 years are designated by a letter in red. The table includes many of the long-lived radioactive isotopes; many others are not included because their half-lives are so long that they are not considered to be significant. The principal mode of decay is as follows: α - alpha particle emission; β^- - beta minus particle emission; β^+ - beta plus particle emission; EC - orbital electron capture; IT - isomeric transition from upper to lower isomeric state; SF - spontaneous fission.

Selected Radioactive Isotopes

1 (15.3 min) β^-
2 (12.32 yr) β^-
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GROUP IA	1 H 1.0079	2 He 4.00260	VIII																10 Ne 20.179	11 Na 22.98976928	12 Mg 24.304	IIA																20 Ca 40.078	21 Sc 44.955912	22 Ti 47.88	23 V 50.9415	24 Cr 51.9959	25 Mn 54.938045	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	IIB																48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.90545	54 Xe 131.29	86 Rn 222
GROUP IIA	3 Li 6.941	4 Be 9.01218	5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.179	11 Na 22.98976928	12 Mg 24.304	13 Al 26.9815386	14 Si 28.0855	15 P 30.973762	16 S 32.06	17 Cl 35.453	18 Ar 39.948	19 K 39.0983	20 Ca 40.078	21 Sc 44.955912	22 Ti 47.88	23 V 50.9415	24 Cr 51.9959	25 Mn 54.938045	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc 98.90625	44 Ru 101.07	45 Rh 101.07	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.90545	54 Xe 131.29	86 Rn 222																			
GROUP IIIA	13 Al 26.9815386	14 Si 28.0855	15 P 30.973762	16 S 32.06	17 Cl 35.453	18 Ar 39.948	19 K 39.0983	20 Ca 40.078	21 Sc 44.955912	22 Ti 47.88	23 V 50.9415	24 Cr 51.9959	25 Mn 54.938045	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc 98.90625	44 Ru 101.07	45 Rh 101.07	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.90545	54 Xe 131.29	86 Rn 222																													
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C_{nv} GROUPS

C _{2v}	E	C ₂	σ _v (xz)	σ _{v'} (yz)		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz

C_{nh} GROUPS

C _{2h}	E	C ₂	i	σ _h		
A _g	1	1	1	1	R _z	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	R _x , R _y	xz, yz
A _u	1	1	-1	-1	z	
B _u	1	-1	-1	1	x, y	

D_{nd} GROUPS

D _{2d}	E	2S ₄	C ₂	2C _{2'}	2σ _d		
A ₁	1	1	1	1	1		x ² + y ² , z ²
A ₂	1	1	1	-1	-1	R _z	x ² - y ²
B ₁	1	-1	1	1	-1		xy
B ₂	1	-1	1	-1	1	z	yz
E	2	0	-2	0	0	(x, y), (R _x , R _y)	(xz, yz)

D_{nh} GROUPS

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

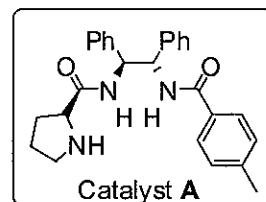
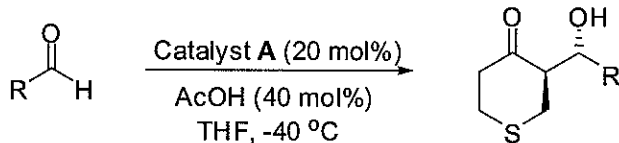
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		$(2z^2 - x^2 - y^2, x^2 - y^2)$
E	2	-1	2	0	0		
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3\sigma_h$		
A_g	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_u	1	1	1	1	-1	-1	-1	-1		
E_g	$\begin{Bmatrix} 1 & \epsilon & \epsilon^* & 1 & 1 & \epsilon & \epsilon^* & 1 \\ 1 & \epsilon^* & \epsilon & 1 & 1 & \epsilon^* & \epsilon & 1 \end{Bmatrix}$									$(2z^2 - x^2 - y^2, x^2 - y^2)$
E_u	$\begin{Bmatrix} 1 & \epsilon & \epsilon^* & 1 & -1 & -\epsilon & -\epsilon^* & -1 \\ 1 & \epsilon^* & \epsilon & 1 & -1 & -\epsilon^* & -\epsilon & -1 \end{Bmatrix}$									
T_g	3	0	0	-1	3	0	0	-1	(R_x, R_y, R_z)	(xy, xz, yz)
T_u	3	0	0	-1	-3	0	0	1	(x, y, z)	

$\epsilon = e^{(2\pi i)/3}$

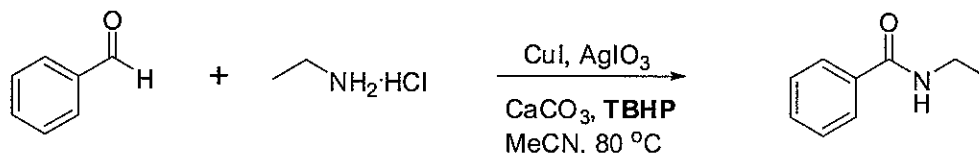
ORGANIC CUME, OCTOBER 2006

Q 1. (20 pts) Reference: *J. Org. Chem.* **2006**, *71*, 8198
Graphical Abstract of this paper shows the following reaction.



Is there any reactant missing in this equation? What is it? What reaction is being discussed in the paper? Provide the mechanism for the general reaction (ignore the stereochemistry).

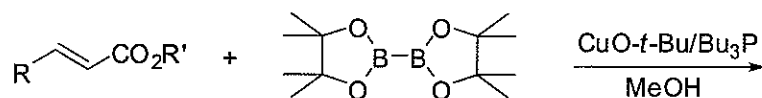
Q 2. (20 pts) Reference: *J. Am. Chem. Soc.* **2006**, *128*, 13064



What is **TBHP**? Provide a mechanism for the above reaction.

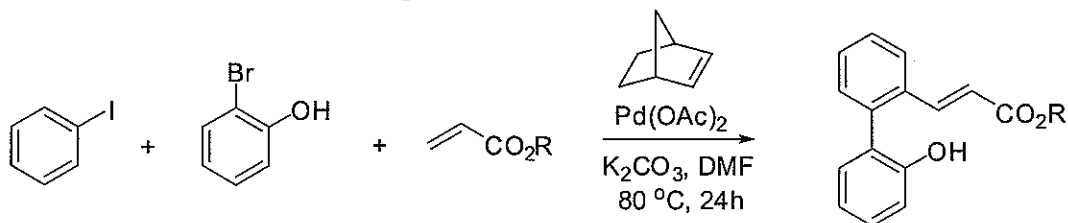
Q 3. (20 pts) Reference: *Org. Lett.* **2006**, *8*, 4887.

Write the product for the following reaction and provide a mechanism for its formation?



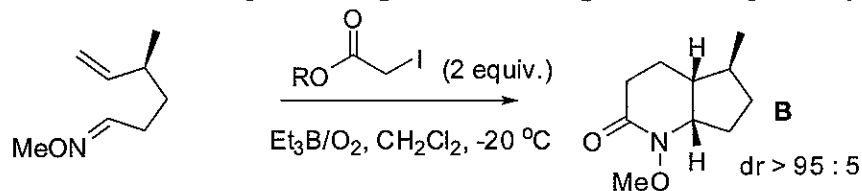
Q 4. (20 pts) Reference: *Org. Lett.* **2006**, *8*, 3967

Provide a mechanism for the following reaction?



Q 5. (20 pts) Reference: *Org. Lett.* **2006**, *8*, 4871

(A Stereocontrolled Access to Ring-Fused Piperidines through a Formal [2+2+2] Process)



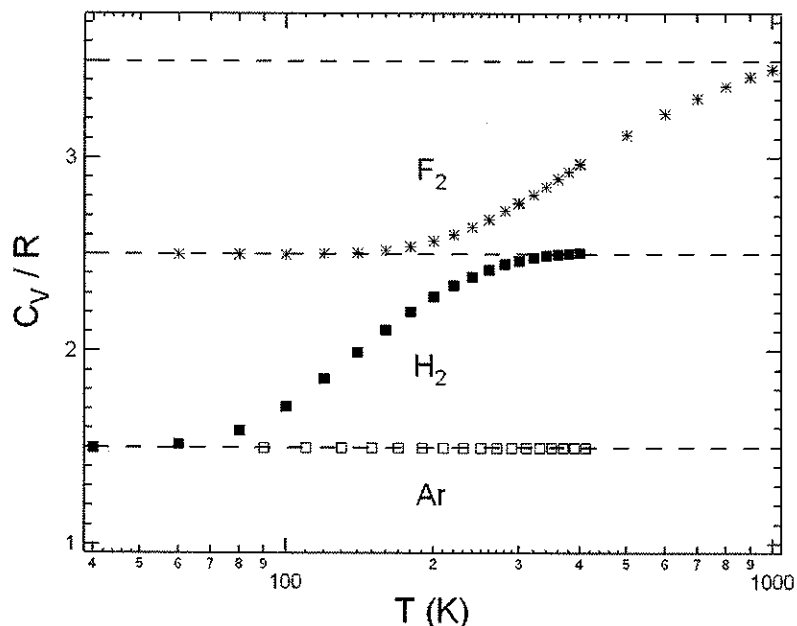
Provide a mechanistic cycle for the formation of the lactam **B**. Explain the term dr.
(**Hint:** $\text{Et}_3\text{B} + \text{O}_2$ provides Ethyl radical).

Extra credit.

(5 pts): Who won the Nobel Prize for Chemistry in 2006? What was it awarded for?

(5pts.): Name two of the 14 non-Purdue speakers at the inaugural Negishi-Brown Lectures and three of the 10 speakers at the recent Catalysis Symposium.

- 1) (10 points) Express C_V as a partial derivative of U and also in terms of a partial derivative of S .
- 2) (10 points) How do the first and second laws of thermodynamics help explain the connection between the above two expressions for C_V ?



- 3) (20 points) Consider the experimental values of C_V for argon which are shown in the above graph.
 - a. What is the energy, U , of argon that is implied by the above data?
 - b. How are the experimental values of C_V related to the number of degrees of freedom available to argon and what are the relevant degrees of freedom?
- 4) (30 points) Consider the experimental values of C_V for hydrogen (H_2) gas which are shown in the above graph.
 - a. Why is the C_V of hydrogen the same as that of argon at low T ?
 - b. What does the C_V of hydrogen at 400 K tell you about the number of degrees of freedom available to hydrogen at that temperature (and what are those degrees of freedom)?
 - c. What do you expect to happen to the C_V of hydrogen at higher temperatures (assuming it does not decompose).
- 5) (30 points) Consider the experimental values of C_V for fluorine (F_2) gas which are shown in the above graph.
 - a. Why is the C_V of fluorine at 100 K the same as that of hydrogen at 400 K?
 - b. What does the C_V of fluorine at ~ 1000 K tell you about the number of degrees of freedom available to fluorine at that temperature (and what are those degrees of freedom)?
 - c. What do you expect to happen to the C_V of fluorine at higher temperatures (assuming it does not decompose).