

## Department of Chemistry Cumulative Examinations September 24, 2005

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 3-5
- 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.

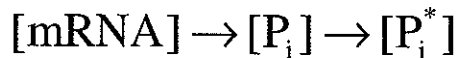
When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

**PURDUE**  
UNIVERSITY

Analytical Chemistry Cumulative Exam  
September 24, 2005

1. On September 13, Prof. Bakker presented a seminar on the state of the science of ion-selective membrane electrodes. A conventional pH glass electrode is an ion-selective electrode (ISE). Describe with as much detail as you can how a glass pH electrode functions. Describe the process that is responsible for development of the potential across the glass membrane. Describe specifically how you would go about selecting and preparing a buffer solution to be used to calibrate a pH electrode.
2. For ion selective electrodes, the electrode response depends on ion activity. Define ion activity, in quantitative terms. Since the ideal Nernstian-response ISE responds directly to one ion activity in solution, how does one deal practically with the thermodynamic requirement that only a potential difference can be measured?
3. Draw a cell diagram for a functional liquid membrane ion selective electrode. Label all components clearly.
4. Imagine that you have designed a membrane ISE for cations in aqueous solution. Write the equation that describes the phase boundary potential at the membrane-sample solution interface that forms the basis of quantitative measurements. Use this equation (or discuss as well as you can) to describe how an ionophore (complexing agent) influences the phase boundary potential and thus the response of the electrode to analyte cations. Describe and discuss the nature of the optimum membrane characteristics, in order to yield Nernstian response, and indicate a commonly used membrane material that would be appropriate.
5. A very important characteristic of ion selective electrodes used as sensors is their selectivity. Describe quantitatively what is meant by the term selectivity. For an ion-carrier-based ISE to be used, for example, for determination of  $\text{Ca}^{2+}$  in the presence of  $\text{Mg}^{2+}$ , discuss how selectivity relates to the respective complex formation constants, and what other factors also play a role, if any. How can these complex formation constants be altered to optimize the selectivity in this case?
6. Describe two factors that contribute to determining the magnitude of the lower limit of detection of analyte ions for your ISE.

Proteins can change in concentration and the degree to which they are post-translationally modified in response to regulatory stimuli, i.e.



where  $P_i$  is a specific protein and  $P_i^*$  is the post-translationally modified form of that protein. The concentration of either may increase or decrease as a consequence of the regulatory stimulus. This means that expression, degradation, and the rate of interconversion between  $P_i$  and  $P_i^*$  all play a role in the concentration of a protein at any moment in time.

1. How would you determine the degree to which  $P_i$  and  $P_i^*$  changed in concentration as a result of a stimulus. If your answer is based on the use of a separation system to separate the two forms of the protein, explain whether the method you propose will work with all forms of post-translational modification.
2. Assuming that  $P_i$  increased in concentration and  $P_i^*$  decreased in concentration as a result of a stimulus, explain all the ways this could have occurred.

# Inorganic Chemistry Cumulative Exam

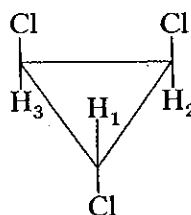
Purdue University

September 24, 2005

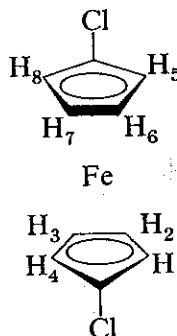
There are 100 possible points in this exam.

1. (20 points) Determine the point groups of the following molecules, and find the requested equivalent atoms within these molecules.

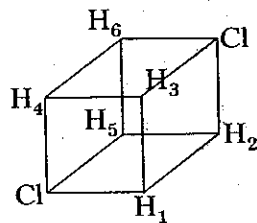
(a) Which protons, if any, are equivalent to  $H_1$



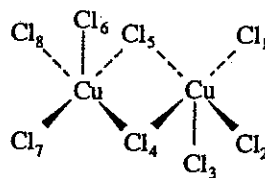
(b) Which protons, if any, are equivalent to  $H_6$ ?



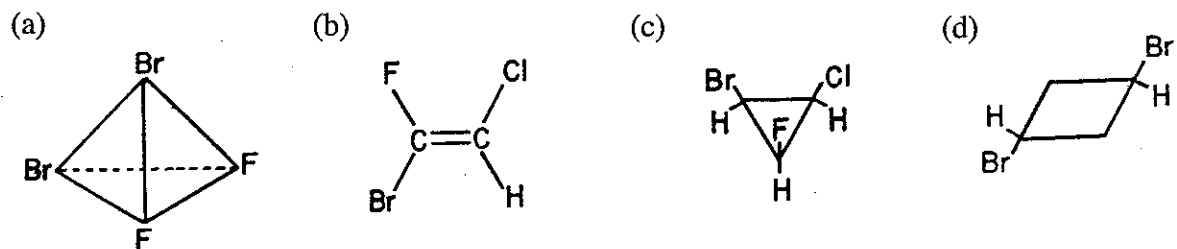
(c) Which protons, if any, are equivalent to  $H_1$ ?



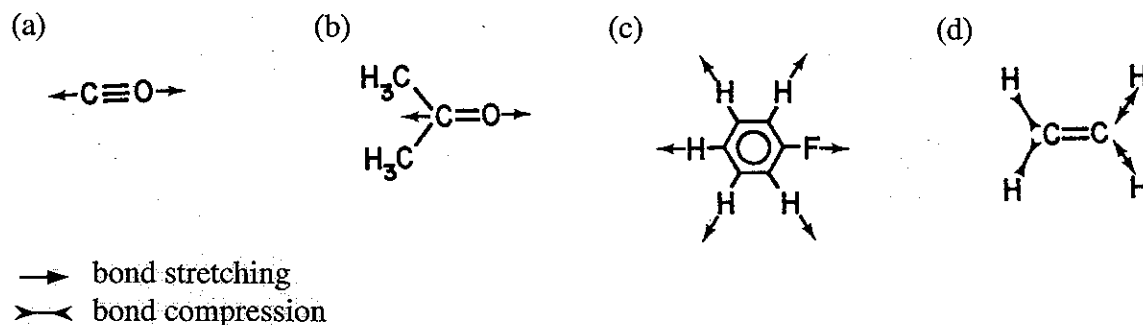
(d) Which chlorides, if any, are equivalent to  $Cl_1$ ?



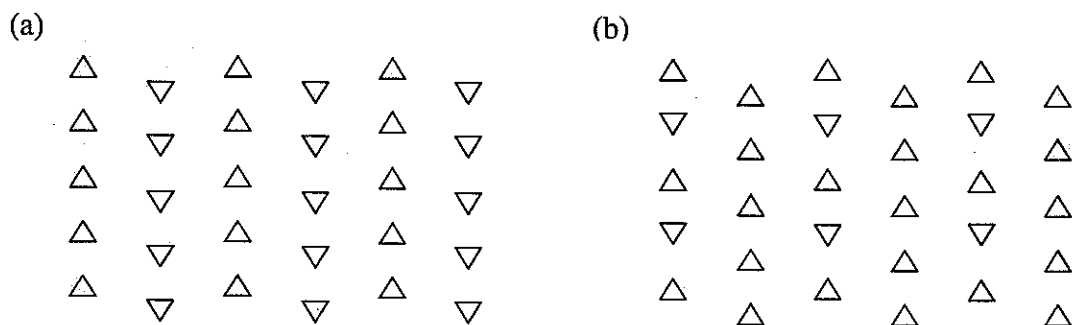
2. (10 points) Molecules with a mirror plane, center of inversion, or improper axis of rotation cannot be optically active. Molecules without such symmetry elements can be active. Using these criteria, determine whether or not each of the following molecules is optically active.



3. (10 points) In order that a molecular vibration may give rise to IR absorption, the dipole moment of the molecule must change during the vibration. Determine whether or not each of the following molecular vibrations is IR active.

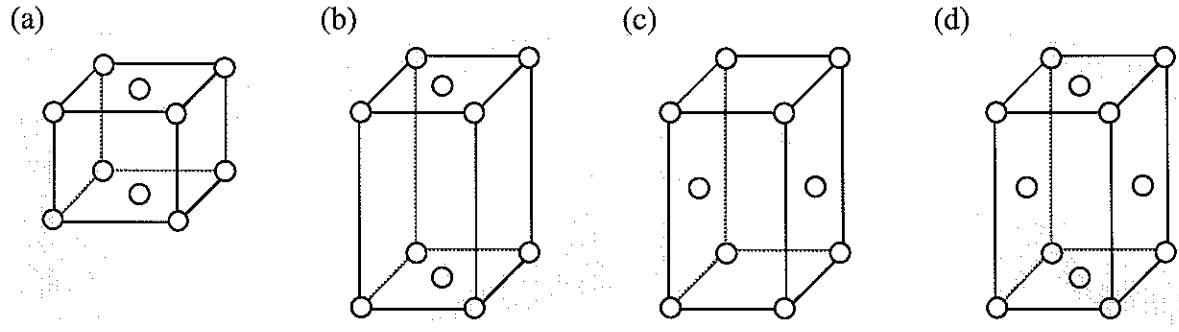


4. (10 points) A plane lattice is an infinite array of points in two dimensions such that every point is identical, having the same surroundings in the same orientation. A unit cell of a plane lattice is a parallelogram of two unit translations with lattice points at the corner and is perfectly representative of the lattice. Draw a unit cell for the following 2D patterns (Remember to draw your answers in your blue book!).



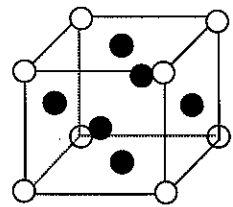
5. (20 points) The monoclinic system is characterized by one diad (2-fold rotation or mirror plane). The orthorhombic system is characterized by three mutually perpendicular diads.

tetragonal system is characterized by one tetrad (4-fold axis). The cubic system is characterized by four triads (3-fold rotational axis). To which crystal system must each of the following belong?



6. (10 points) What is the lattice type of the following structure (white circles at 8 corners of a cube and black circles at the centers of 6 faces)? Explain your answer.

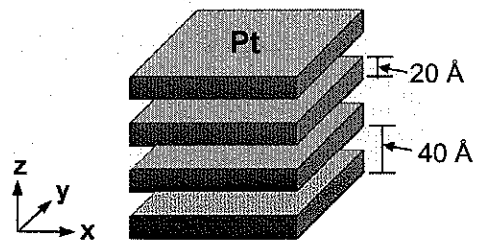
- (1) Primitive cubic
- (2) Body-centered cubic
- (3) Face-centered cubic
- (4) Primitive orthorhombic
- (5) Face-centered orthorhombic



7. (10 points) Material A crystallizes in the primitive cubic structure with  $a = 4.0 \text{ \AA}$ . Calculate the  $2\theta$  position for (200) reflection when Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) is used.

[Bragg's equation:  $\lambda = 2d_{hkl} \sin\theta$ ]

8. (10 points) Platinum metal shows typical X-ray diffraction patterns for a face-centered cubic structure ( $a = 3.92 \text{ \AA}$ ). Suppose that this material is prepared as a 2 nm thick layer that repeats every 4 nm along the direction that is perpendicular to the layers. Sketch (or describe) the expected XRD patterns resulting from this nanostructure.



(Bonus, 10 points) Calculate the  $2\theta$  position for the first x-ray reflection (with the largest d-spacing) created by this nanostructure ( $\lambda = 1.54 \text{ \AA}$ ).

# Organic Cumulative Exam: Stereochemistry and Conformational Analysis 09/24/05

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**I.1 (18 pts)** Provide general definitions (with aid of illustrations, if necessary) for the following terms:

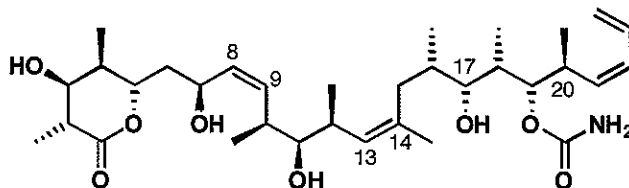
- i.* 'allylic 1,3-strain'
- i.* 'meso compound'
- i.* 'optically active'
- i.* 'prochiral'
- i.* 'staggered conformation'
- i.* 'syn-pentane interaction'

**I.2 (6 pts)** An object or a molecule is *achiral* if it possesses a plane of symmetry. Rank the following molecules by the number of symmetry planes that they possess:

- i.* H<sub>2</sub>
- i.* methane
- i.* chloroform
- i.* dichloromethane
- i.* *trans*-1,2-dimethylcyclopentane
- i.* *cis*-1,2-dimethylcyclopentane

**I.3 (16 pts)** Draw schematic <sup>1</sup>H-NMR spectra for both *cis*- and *trans*-1,2-dichlorocyclopropanes, assuming sufficient resolution to provide well-resolved multiplets. Indicate integration values and label *diastereotopic* protons.

**I.4 (40 pts)** (+)-Discodermolide is a marine metabolite possessing potent anticancer activity due to its tubulin-stabilizing property.

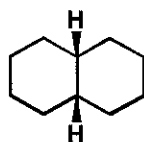


- a) **(13 pts)** Please indicate configurations of all of the asymmetric centers in (+)-discodermolide according to the Cahn-Ingold-Prelog rules.

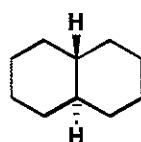
- b) (7 pts) Rationalize the preference for a boat-like conformation of the tetrasubstituted  $\delta$ -lactone fragment (*JACS* 2001, 123, 9535).
- c) (20 pts) The solution structure of (+)-discodermolide suggests that nonbonded (*e.g.*, allylic 1,3-strain, *syn*-pentane, etc.) interactions play a major role in defining the overall helical-like configuration of the natural product (*Org. Lett.* 2001, 3, 696). Propose and briefly explain conformational preferences for the  $C^7-C^{10}$ ,  $C^{10}-C^{12}$ ,  $C^{12}-C^{15}$ ,  $C^{16}-C^{20}$ , and  $C^{21}-C^{24}$  fragments.

**I.4 (20 pts)** Fused ring systems are ubiquitous in nature, most notably in steroids. With a few exceptions, all steroidal ring junctions are *trans*. Synthetic approaches to fused systems, however, can lead to different stereochemical outcomes, and therefore it is important to consider the energetic parameters involved.

- a) (5 pts) Draw all available all-chair conformations for both *cis*- and *trans*-decalins and comment about their relative energetic stability.



*cis*-decalin



*trans*-decalin

- b) (5 pts) *trans*-Decalin, but not the *cis* isomer, can serve as a good model system to determine differences in reactivity of functional groups in axial vs equatorial environments. Explain.
- c) (10 pts) Perform an energy analysis on both *cis*- and *trans*-decalins in their lowest energy forms, using the following enthalpy costs: anti butane: 0 kcal/mol, gauche butane: 0.9 kcal/mol, *syn*-pentane interaction: 3.7 kcal/mol, eclipsed butane ( $120^\circ$ ): 3.7 kcal/mol, eclipsed butane ( $0^\circ$ ): 4.5 kcal/mol.

*Hint:* A systematic carbon-by-carbon “walk” may be helpful in identification of nonbonded interactions, which are only present in one system and not in the other.

Physical Cumulative Examination

September 24, 2005

1. A Gaussian random variable  $x$  is one whose normalized probability distribution  $P(x)$  is of the form

$$P(x) = \left( \frac{1}{2\pi\sigma^2} \right)^{1/2} \exp \left[ -\frac{1}{2} \left( \frac{x - \bar{x}}{\sigma} \right)^2 \right]. \quad (1.1)$$

From Eq. (1.1), one may show that

$$\int_{-\infty}^{\infty} P(x) dx = 1 \quad (1.2a)$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \bar{x} \quad (1.2b)$$

$$\langle [x - \langle x \rangle]^2 \rangle = \int_{-\infty}^{\infty} [x - \langle x \rangle]^2 P(x) dx = \sigma^2. \quad (1.2c)$$

Eqs. (1.1) and (1.2) will be used in the remainder of this problem, which will deal with the quantum mechanics of a one-dimensional harmonic oscillator of mass  $m$  and circular frequency  $\omega$  which is in its **ground state**.

- a. The position observable  $y$  of the one-dimensional oscillator is a Gaussian random variable. Moreover, the average value  $\langle y \rangle$  and the uncertainty  $\Delta y$  of  $y$  are given by

$$\langle y \rangle = 0 \quad (1.3a)$$

and

$$\Delta y \equiv \left[ \langle y^2 \rangle - \langle y \rangle^2 \right]^{1/2} = \left( \frac{\hbar}{2m\omega} \right)^{1/2}. \quad (1.3b)$$

Given this information solve the following two problems.

- (i) Find the form of the normalized probability distribution  $P(y)$  of  $y$  in terms of  $m$ ,  $\omega$  and standard constants (for example,  $\pi$ ,  $\hbar$ , and so forth).
- (ii) From your result for  $P(y)$  find the form of the oscillator's wavefunction  $\psi(y)$  in terms of  $m$ ,  $\omega$ , and standard constants. State any assumptions that you need to make in order to obtain  $\psi(y)$ .

b. Using your result for  $\psi(y)$  found in problem 1a, solve the following two problems.

(i). Show that the average value  $\langle p_y \rangle$  of the momentum observable  $p_y$  of the oscillator is

$$\langle p_y \rangle = 0. \quad (1.4a)$$

(ii). Show that the uncertainty  $\Delta p_y$  of the momentum observable  $p_y$  is

$$\Delta p_y \equiv \left[ \langle p_y^2 \rangle - \langle p_y \rangle^2 \right]^{1/2} = \left( \frac{m\hbar\omega}{2} \right)^{1/2}. \quad (1.4b)$$

c. Given that  $p_y$  is a Gaussian random variable, find its probability distribution  $P(p_y)$  from the results of problem 1b. Express  $P(p_y)$  in terms of  $m$ ,  $\omega$ , and standard constants.

2. The 3s and 3d orbitals of a hydrogen atom have the following forms (where  $a_0$  is the Bohr radius)

### 3s orbital

$$\Psi_{n=3,\ell=0,m=0}(r, \theta, \phi) = R_{n=3,\ell=0}(r) Y_{\ell=0,m=0}(\theta, \phi)$$

where

$$R_{n=3,\ell=0}(r) = \left( \frac{1}{a_0} \right)^{3/2} \frac{2}{9\sqrt{3}} \left( 3 - \frac{2r}{a_0} + \frac{2r^2}{9a_0^2} \right) \exp(-r/3a_0)$$

and

$$Y_{\ell=0,m=0}(\theta, \phi) = \left( \frac{1}{4\pi} \right)^{1/2}$$

and

### 3d orbital

$$\Psi_{n=3,\ell=2,m=0}(r, \theta, \phi) = R_{n=3,\ell=2}(r) Y_{\ell=2,m=0}(\theta, \phi)$$

where

$$R_{n=3,\ell=2}(r) = \left( \frac{1}{a_0} \right)^{3/2} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} \exp(-r/3a_0)$$

and  $Y_{\ell=2,m=0}(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1)$ .

Show that the 3s and 3d orbitals are orthogonal. That is, show that

$$\int_0^{\infty} r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \Psi_{n=3,\ell=2,m=0}^*(r, \theta, \phi) \Psi_{n=3,\ell=0,m=0}(r, \theta, \phi) = 0.$$

(Hint: let  $x = \cos\theta$ .)

# Periodic Classification of the Elements

0

IA		IIA		IIIB		IVB		VB		VIB		VIIB		VIII		IIB		IIIA		IVA		VA		VIA		VIIA		0																														
1 H 1.00797	3 Li 6.939	4 Be 9.0122	11 Na 22.9898	12 Mg 24.312	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	53 I 126.9044	54 Xe 131.30	55 Cs 132.905	56 Ba 137.34	57 La* 138.91	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	87 Fr (223)	88 Ra (226)	89 Act (227)	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)

\*Lanthanides

†Actinides

(Numbers in parentheses are the mass numbers of the most stable isotopes.)