Department of Chemistry
Cumulative Examinations
February 8, 2003

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, Page 4
4) Organic Cumulative Examination, Pages 5-6
5) Physical Cumulative Examination, Page 7

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.
The following questions relate to the limit of detection and sensitivity in IR and NMR spectroscopy.

1. What are the general strengths and weaknesses of carrying out qualitative and quantitative analyses using IR or NMR spectroscopy? Are both methods good at structure identification? Can either be used to analyze mixtures?

2. Give two reasons why IR spectroscopy is more sensitive than NMR.

3. Suppose you had a very small liquid sample whose concentration you wanted to determine using transmission IR. Assume that the sample was contained in a square capillary tube whose inner dimension was 50 \( \mu \text{m} \), and the IR light, which was incident at right angles to the capillary, illuminated a spot that was 50 \( \mu \text{m} \) wide. If the sample has a carbonyl group with a strong molar absorptivity of 2000 \( \text{cm}^2 \text{M}^{-1} \), what is the minimum concentration that could be detected, assuming the standard deviation of the blank measurement is 0.005 absorption units. What is the difference between the limit of detection and the limit of quantitation? What difficulties might arise in determining the concentration of smaller volumes using this method?

4. Now imagine that because of the glowbar’s large source dimensions, you cannot focus the IR light down to this spot size without losing too much light intensity. As a result, 50\% of this light leaks past the sample into the detector. What happens quantitatively to the signal? Draw a qualitative picture of the effect of stray light on a calibration plot of absorption vs. concentration.

5. Now consider detecting the same sample using NMR. A recent commercial version of a microcoil NMR probe has appeared with a concentration limit of detection of 2.7 \( \text{mM} \) for a 1 \( \mu \text{L} \) sample at 600 MHz for a single, 1 sec data acquisition. Signal averaging for 10 min would reduce this LOD to what value?

6. Roughly speaking, the NMR signal-to-noise ratio (S/N) is inversely proportional to the detection coil diameter, and proportional to the sample’s length. What happens quantitatively to the S/N when the sample is reduced from 1 mL to 10 nL, assuming the sample dimensions are reduced equally? The NMR signal is proportional to the number of spins located in the detection coil region. Is there a way to improve the S/N?

7. The analytical sensitivity is given by: \( \gamma = m/\sigma \), where \( m \) is the slope of the calibration curve, and \( \sigma \) is the standard deviation of the measurement, or blank. The units for the analytical sensitivity are \( \text{M}^{-1} \). The calibration curve signal is given by \( S = mc + S_{\text{bl}} \), where \( m \) is the slope, \( c \) is the concentration, and \( S_{\text{bl}} \) is the signal of the blank. Calculate the analytical sensitivity for both the IR and NMR experiments at the respective LOD’s using the data given in Questions 3 and 5. You can assume \( S_{\text{bl}} = 0 \). To get started on the
IR problem, remember that σ is related to the LOD by a numerical factor, and m is related to both the molar absorptivity and the sample length given in Question 3. Is there an equivalent expression for the NMR experiment? (Hint, write the signal intensity as a function of the concentration LOD given in Question 5 above.) Comment on the relative sizes of the two sensitivities, as well as the factors that affect the sensitivity. Which technique can detect fewer analyte molecules?
This cumulative examination deals with the biochemical processes utilized for the replication of genetic information. Part A counts 60 points; parts B and C count 20 points each.

(A) Describe in detail the mechanisms of DNA replication in *Escherichia coli*. Your response should include clear descriptions of the role, functional significance and important properties of each of the major enzymes and proteins involved in replication. Clearly describe how directionality is dealt with during replication. Sketch appropriate diagrams to illustrate your answer.

(B) The replication and transmission of genetic information by HIV differs in several very fundamental ways from that utilized by *E. coli*. What are the major differences? Describe the most important points.

(C) DNA is the only biological molecule that is subject to repair in the cell. Why is this an efficient strategy? What are the most important types of repair mechanisms? Briefly discuss their action in molecular terms.
Transition Metal Alkyl and Carbonyl Chemistry

1. (24 points)
   (i) Indicate which of the following transition metal alkyls are stable (in the absence of O₂ and H₂O) to the so-called α- or β- hydride abstraction mechanisms. Explain the origin of the stability for those that are stable, and give the known products (or likely products) for those that are unstable.

   (a) Ti(CH₂Ph)₄
   (b) [(NH₃)₂RhEt]Cl₂
   (c) V(CH₂SiMe₃)₄
   (d) Ta(CH₂CMc₃)₅
   (e) W(CH₂CMc₃)₆

   (ii) Give balanced equations showing how Ti(CH₂Ph)₄ reacts with H₂O and with ethanol.

2. (16 points)
   (i) Describe the synthesis of salts of the [V(CO)₆]⁻ anion.
   (ii) Which homoleptic carbonyl species of Ti, Cr and Mn are isoelectronic with [V(CO)₆]⁻?
   (iii) Rank these four species in order of increasing values of the v(CO) modes (use > or < signs).
   (iv) Explain the trend in v(CO) values you have given in (iii) in terms of M-CO σ and π-bonding effects.

3. (20 points)
   Transition metal carbonyl clusters are examples of compounds that usually (although not always) contain M-M single bonds. Sketch the structures of the following carbonyls and show through electron counting procedures the M-M bond order(s) in each:

   [Fe₂(CO)₈]²⁻, Ru₂(CO)₁₂, Ir₄(CO)₁₂, Os₃(CO)₁₀H₂ and (Cp)₂Mo₂(CO)₄
   (Cp = cyclopentadienyl C₅H₅)

Note: The total of points allocated to these three questions is 60. Your score will then be converted to a %.
Please provide a detailed mechanism for the reactions below.


\[
\begin{align*}
\text{Br} & \quad \text{Ph}_3\text{CuLi} \\
tBuO & \quad \text{65\%} \\
\xrightarrow{\text{TEA (1.1 eq), TFE}} \quad \text{reflux, 1 h, 65\%} \\
tBuO & \quad \text{Ph}
\end{align*}
\]


\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{HO} & \quad \text{N}_3 \\
\xrightarrow{2} \text{80\%} \\
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{HO} \\
\text{OH} & \quad \text{N} = \text{N} \\
\text{N} & \quad \text{NHC}_{14}\text{H}_{29}
\end{align*}
\]


\[
\begin{align*}
\text{Bacterial Squalene Cyclase} \\
\text{Enz-AH}^{+}
\end{align*}
\]

\[
\text{BnO} \quad \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \quad \text{Bn} + \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \quad \text{OPg} \quad \xrightarrow{1 \text{ equiv MgI}_2} \quad \text{THF, 80 °C} \\
12 \text{ h} \quad \text{55% over 2 steps}
\]


\[\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{N}
\end{array} \quad \text{NH}_2 \quad \text{H} \quad \text{CH}_3 \quad \text{OP} \quad \text{CO}_2 \quad \xrightarrow{\text{general base}} \quad \text{general base}
\]

\[\text{a}, \text{R}=\text{CH}_2\text{CH}_2\text{OP}_2\text{O}_6^{2-} \quad \text{b}, \text{R}=\text{CH}_2\text{CH}_2\text{OH}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{N}
\end{array} \quad \text{NH}_2 \quad \text{H} \quad \text{CH}_3 \quad \text{OP} \quad \text{CO}_2
\]
(a) The dipole moment of the HF molecule at its equilibrium bond length of 0.92 Å is about 1.9 Debyes. Indicate what must be the qualitative behavior of the dipole moment function of HF by making a sketch that shows the dipole moment as a function of the H-to-F separation distance, going from slightly less than the equilibrium distance to a distance where the molecule has dissociated into neutral atoms. (This is asking you to show graphically—to a qualitative extent—the functional form of the dipole moment of HF based on what you know about diatomic molecules and their electronic structure from the bonding region to dissociation.)

(b) Explain one spectroscopic means for obtaining a value for the ground vibrational state dipole moment of HF in a low density gas sample. (Be concise. It is what has to happen at the molecular level in order to arrive at dipole information that needs to be explained, not the instrumental set-up.)

(c) Give one reason why the dipole moment of HF at its equilibrium bond length will differ from the spectroscopically measured dipole moment for HF in its ground vibrational state.

(d) The dipole moment of LiH in its lowest three vibrational states has been found to be 5.900 (n=0), 6.012 (n=1), and 6.116 (n=2) Debyes. (i) On the basis of this information alone, determine the most accurate value you can for the dipole moment of LiH at its equilibrium separation distance. Be very clear to indicate the basis for your determination. (ii) Predict a value for the dipole moment in the n=3 vibrational state.

(e) One of the ways in which overtone vibrational transitions in polar diatomic molecules, i.e. Δn >1 transitions, can be dipole allowed is anharmonicity in the stretching potential. If somehow a certain polar diatomic molecule could be constrained in an environment such that its stretching potential were strictly harmonic (no anharmonicity), is there any molecular feature that could make overtone vibrational transitions allowed? If not, an answer of "no" is sufficient, but if so, explain.