The Final exam is scheduled for Monday, June 10, begins at 2:30 pm in Bagley 131, and ends at 4:20.

The final exam consists of two parts. The first half of the exam deals with material covered since the Midterm Exam. The second half of the final exam is a cumulative examination of all the course material.

- **First Half of the Final Exam will cover**
  - Chapters 5-8 and 11 in the text
  - Lectures 16-37
  - All Problems in Homework Assignments 5-10

- **Second Half of the Final exam will cover**
  - All material covered up to examination 2 including
    - Text chapters 1-6
    - Lectures 1-21
    - All problems in Homework assignments 1-6

- **Bring**
  - Calculator (any type)
  - Pencil/Pen
  - Straight Edge (for drawing graphs)
  - Blue/Green Book
  - 2 pages of notes (double-sided, see below)

- **Format:**
  - Closed Book.
  - Open Notes.
    - Two pages, double-sided.

- **Grading:** Grading of the examination will be based on the standards stated in the Chemistry 355 course syllabus. Please review the standards section of the syllabus. Important points to keep in mind:
  - Partial credit is **USUALLY** given in units of 3-5 points.
  - Obtaining the correct numerical answer is counted in partial credit grading. An answer that is within 10% of the correct answer will be fully credited.
  - Calculations must include physical units and a proper dimensional analysis must be included in the calculation.
  - Students are expected to understand how to use their calculators properly. Students will **NOT** be forgiven for mistakes resulting from calculator errors.
  - When you are asked to explain an answer or are asked to define a term, a worded statement *in complete sentences* is required.
• If you are given the option to choose from a list of problems (e.g. answer three of the following five questions) you will NOT be credited for answering more than the requested number. For example, if you are allowed to select three problems out of five for answering…and you answer all five… the graders will NOT credit you for the highest three scoring problems out of five. The first three problems presented on the blue book will be graded.

Examination Study Guidelines: Here is a general outline of the examination that will be presented to you on 5 June.

Problem 1 (20 pts) Define 2 out of 6 Terms.
• Osmotic Pressure
• Membrane Equilibria
• Chemiosmotic Theory of Membrane Transport
• Goldman Equation
• Donnan Effect
• Transport Concepts:
  • Frictional Forces and Buoyancy
  • Steady State and Steady State Velocity (terminal velocity)
  • Ficks’ Laws
  • Random Walk
  • Frictional Coefficient and Molecular Shapes (Spheres (Stokes’ Law)
  • Non-spherical Molecules: Ellipsoids, Rods, Random Coil Polymers
• Centrifugation/Sedimentation
  • Velocity Centrifugation
  • Equilibrium Centrifugation
  • Centrifugation in a gradient
• Viscosity
  • Poiseuille Flow
  • Turbulence
  • Viscosity of Polymer Solutions: Intrinsic Viscosity, etc.
• Biology at Surfaces
  • Surface Tension
  • Capillary Action
  • Surfactants
  • Surface Adsorption
• Quantum Mechanics & Spectroscopy:
  • Quantum vs. Classical Linear Harmonic Oscillator
  • Heisenberg Uncertainty Principle
  • Wave Functions & Wave Mechanics: Particle in a Box
  • UV-Vis, Fluorescence, Light Scattering, IR Spectroscopy
Problem 2 (20 pts)
- Qualitative Problems involving any of the concepts above
- Examples:
  a) Dipalmitoyl lecithin is a naturally-occurring detergent that is found at the air-water interface of the alveoli, which are the smallest air compartments in the lung. Explain the function of dipalmitoyl lecithin in the lung. Explain your answer in terms of surface tension and the effect of detergents on the surface tension of water.

  **Answer:** Dipalmitoyl lecithin is a surfactant that forms a bilayer structure at the air-water interface of the lung. It lowers the surface tension of water from 0.7275 N/m to almost zero, which in turn diminishes the amount of work required to expand the surface area of the lung during breathing.

  b) The energy for a quantum mechanical linear harmonic oscillator (LHO) is given by $E_n = \hbar \nu (n + \frac{1}{2}) \ldots n = 0, 1, 2, 3, \ldots$. Sketch the allowed energy levels on a graph of the classical potential $V(x) = \frac{1}{2} \kappa x^2$. The lowest energy state of the LHO corresponds to $n=0$. Where is it located relative to the classical potential?

  **Answer:**

  ![Graph of allowed energy levels](image)

  The ground state energy, corresponding to $n=0$ is $E_0 = \frac{\hbar \nu}{2}$ where $\nu$ is the frequency of the oscillator. It is NOT located at the bottom of the classical potential. At the bottom of the classical potential both the momentum and displacement are zero, exactly. This situation is forbidden by the Heisenberg Uncertainty Principle.

Problems 3 and 4 (30 pts each) Multi-Step calculation
Transport
- Calculation of friction coefficients and diffusion coefficients (Stoke’s Law, Non-spherical Molecules)
- Calculation of hydrodynamic radius from diffusion coefficient
• Calculation of radius of non-hydrated molecule from specific volume and molecular weight
• Calculation of degree of hydration
• Rms displacement from Diffusion Coefficient
• Calculate sedimentation coefficient from data (i.e. by graphing ln(r) versus time)
• Calculate molecular mass from sedimentation coefficient
• Molecular Shape from Viscosity Measurements

Example:

a) E. coli DNA ligase, an enzyme that catalyzes the formation of phosphodiester bonds in DNA, has a specific volume of 0.737 cm$^3$/g at 293K. A velocity sedimentation experiment performed at a speed of 56,050 rpm yielded the following data:

<table>
<thead>
<tr>
<th>Elapsed time (min)</th>
<th>Boundary Position (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.91</td>
</tr>
<tr>
<td>40</td>
<td>6.11</td>
</tr>
<tr>
<td>80</td>
<td>6.30</td>
</tr>
<tr>
<td>120</td>
<td>6.51</td>
</tr>
</tbody>
</table>

• From a graph of the data obtain the sedimentation coefficient $s$.
• Determine the molecular weight of E. coli DNA ligase. Assume the density of the solution is 1 g/cm$^3$. Assume the frictional factor at 293K is $8.24 \times 10^{-8}$ g/s.
• Determine the diffusion coefficient at T=293K.

Solution:

\[
S = \text{Slope} = 1.34 \times 10^{-5} \text{ s}^{-1}
\]

\[
\omega = 2\pi \times 56,050 \text{ rpm} = 1 \text{ min}/60 \text{s} = 5.870 \times 10^{3} \text{ rad/s}
\]

\[
\therefore \ s = \frac{\text{Slope}}{\omega^2} = \frac{1.34 \times 10^{-5} \text{ s}^{-1}}{5.870 \times 10^{3} \text{ rad/s}^2} = 3.81 \times 10^{-13} \text{ s} = 3.81S
\]
Chemiosmotic Problem

- Calculate Work required to move ions across a membrane in the presence of a transmembrane electrostatic potential
- Calculate degree of hydrolysis of ATP required to accomplish ion transport across a membrane
- Calculate transmembrane potential using the Goldman equation
- Example:

  **Bovin serum albumin (BSA)** has a molecular weight of M=66,500 g/mole and a specific volume of $\bar{V}_2 = 0.734 \text{ cm}^3 / \text{g}$.

  a) In a velocity centrifugation experiment, the sedimentation coefficient $s_{20,w}$ is determined to be 4.31 S. Determine the friction coefficient $f$ of BSA. Assume the density of the solution is 1 g/cm$^3$.

  Solution: $s_{20,w} = \frac{M_2 \left(1 - \bar{V}_2 \rho\right)}{N_A f} \Rightarrow f = \frac{M_2 \left(1 - \bar{V}_2 \rho\right)}{N_A s_{20,w}}$

  \[
  f = \frac{66,500 \text{ g/mole}}{6.02 \times 10^{23} \text{ mole}^{-1}} \times \frac{1 - 0.734}{4.31 \times 10^{-13} \text{ S}} = 6.82 \times 10^{-8} \text{ g/s}
  \]

  b) Assuming that BSA is spherically shaped in solution, calculate the effective Stokes radius. Assume the viscosity $\eta = 0.01 \text{ g cm}^{-1} \text{ s}^{-1}$.

  \[
  f = 6\pi \eta R \Rightarrow R = \frac{f}{6\pi \eta} = \frac{6.82 \times 10^{-8} \text{ g/s}}{6\pi \times 0.01 \text{ g cm}^{-1} \text{ s}^{-1}} = 3.62 \times 10^{-7} \text{ cm}
  \]

  c) Assuming that BSA is a hydrated sphere in solution, calculate the number of water molecules of hydration associated with each BSA molecule. Assume the specific volume of water is 1 cm$^3$/g.

  \[
  \frac{4\pi}{3} R^3 = \frac{M_2 \bar{V}_2 + \delta \bar{V}_1}{N_A} \Rightarrow \delta = \frac{1}{\bar{V}_1} \frac{4\pi R^3}{3 M_2} \frac{N_A}{\bar{V}_2}
  \]
\[ \delta = \frac{1}{V_1} \frac{4\pi R^3}{3} \frac{N_A}{M_2} \bar{V}_2 = \frac{1}{1\text{cm}^3 / g} \frac{4\pi \times 3.62 \times 10^{-7} \text{cm}^3}{3} \frac{6.02 \times 10^{23} \text{mole}^{-1}}{66,500 \text{g/mole}} - 0.734 \text{cm}^3 / g \]

\[ \therefore \delta = 1.800 - 0.734 = 1.066 \text{ g of water / g BSA} \Rightarrow \frac{1.066 \text{ g}}{1 \text{g} / 66,500 \text{g mole}^{-1}} = 3.938 \text{ waters / BSA} \]

Solution: \[ s_{20,w} = \frac{M_2}{N_A f} \left( 1 - \bar{V}_2 \rho \right) \Rightarrow f = \frac{M_2}{N_A s_{20,w}} \left( 1 - \bar{V}_2 \rho \right) \]

\[ f = \frac{66,500 \text{ g/mole}}{6.02 \times 10^{23} \text{ mole}^{-1}} - 0.734 = 6.82 \times 10^{-8} \text{ g/s} \]

Or

Colligative Properties
- Osmotic Pressure: Calculate Molecular Weight from Osmotic Pressure data
- Donnan Effect: Determine equilibrium concentrations of ions on both sides of a semi-permeable membrane at equilibrium. Calculate osmotic pressure in presence of distributions of ions across a membrane.

Cumulative Exam

Problem 5 (20 pts) Define 2 out of 6 Terms
- First & Second Laws of Thermodynamics
- State Functions
- Free Energy Changes
- Calorimetry
- Quantization effects on entropy and heat capacity
- Colligative Properties (i.e. Osmotic Pressure)
- Biological Oxidation-Reduction Reactions
- Buffers
- Nernst Equation
- Scatchard and Hill plots: Independent, cooperative binding

Problem 6 (20 pts) Qualitative Problems Based on Topics Listed Under Problem 5

Problems 7 and 8 (30 pts each) Multi-step Calculation
- For a physical process determine \( \Delta H, \Delta S, \Delta E, q, \) and \( w \) for system, surroundings, universe.
- Calculate ionic strength \( I = \frac{1}{2} \sum c_i z_i^2 \)
- Calculate activity coefficients \( \log \gamma = -0.509 z_i^2 \sqrt{I} \)
• Biological Oxidation-Reduction Problem

• Determination of binding affinity, number of binding sites, mode of binding (independent/cooperative) from Hill or Scatchard Plot Data.

Examples from Last Chem 355 Final:

• The data below show the binding of a ligand to a macromolecule. Using an appropriate graphical technique, calculate both the number of binding sites \( n \) and the binding constant \( K \), and show that all sites are identical and independent. Note: whatever graphical technique you use, write the equation that it is based on.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Ligand Concentration (M)} & 0.0005 & 0.001 & 0.002 & 0.005 & 0.010 & 0.020 \\
\text{Number sites bound } \bar{v} & 1.6 & 2.5 & 3.2 & 4.0 & 4.1 & 4.8 \\
\hline
\end{array}
\]

Solution: Scatchard Equation:

\[
\frac{\bar{v}}{[L]} = K N - \bar{v}
\]

The slope is \( 2500/3 = 833.33 = K \)
The x intercept = \( N = 5 \)
The near-linearity of the plot indicates the binding is independent and to identical binding sites.