

Chemistry 453

Enter answers in a Blue Book

Final Examination

There are 6 parts to this exam. Parts 1-3 deal with material covered since the midterm exam. Part 4-6 cover all course material.

- Enter all answers into your Composition Book (i.e. Blue or Green book)
- Enter your name, Chem 453 section (A or B) and student number on the front page.
- You will get most of the Credit if you set up the equations correctly and substitute in the correct values. Final numerical answers are only worth 1-2 points.
- Units required: distances in meters m, volume in meters cubed m^3 , time in seconds s, energy in Joules J, temperature in degrees K, pressure in Pascals Pa, force in Newtons N, mass in kilograms kg.

- Useful Constants and Conversions:

Universal Gas Constant $R = 8.31 JK^{-1} mol^{-1}$

Avogadro's number $N_A = 6.02 \times 10^{23} mol^{-1}$

Boltzmann's constant $k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} JK^{-1}$

Planck's constant $h = 6.62 \times 10^{-34} Js$

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} Js$$

Rydberg constant $\mathcal{R} = 2.18 \times 10^{-18} J$

Speed of light $c = 3.00 \times 10^8 m s^{-1}$

Mass of electron $m_e = 9.1 \times 10^{-31} kg$

Pressure: Pascal = Pa = $N m^{-2}$

Force: Newton = N = $kg m s^{-2}$

Energy: Joule = J = $N m = kg m^2 s^{-2}$

Viscosity: Poise = 0.10 Pa s = $0.100 kg m^{-1} s^{-1}$

1 Angstrom = $1 \text{Å} = 10^{-10} m$.

1000L = $1.00 m^3$

1 atmosphere = 101325 Pa

Part 1 (28 points): Answer FOUR out of the six questions.

1.1) State the A Priori Probability Principle. Explain how this principle is used in a statistical calculation..

1.2) Describe the reaction mechanism for diffusion-controlled kinetics.

1.3) Consider a diatomic molecule in the gas phase. Assuming the vibrational temperature is much **greater** than the actual temperature i.e. $\theta_{vib} \gg T$ but the rotational; temperature $\theta_{rot} \ll T$ what is the approximate heat capacity per mole for this molecule? Explain.

1.4) Describe the two forces that are involved in Brownian motion. Give two examples of physical processes that can be described as Brownian motion.

1.5) Arrange the following motions in the order of the importance of quantum effects. Assume $T=300K$ and $V=1m^3$. Explain your reasoning.

- Molecular Translation: $\Lambda = 10^{-10} m$
- Rigid Rotation of a molecule: $\theta_{rot} = 10K$
- Atomic Vibrations: $\theta_{vib} = 2000K$
- Electronic Motions in hydrogen atoms

1.6) Define the thermal wavelength. How does this parameter reflect the degree to which quantization is important in translational motions?

Part 2. (36 points) Perform THREE of the following FIVE calculations. These calculations consist of solving at least one or two equations. They vary in the amount of work...so chose wisely.

2.1) Calculate the quantum mechanical rotational energy, total angular momentum L , and the z angular momentum L_z for a HCl molecule in the $J=1, m=1$ state, where the rotation of the molecule is modeled as a quantized rigid rotation. Assume the bond length of HCl is 136 pm.

2.2) The hemoglobin (Hb) protein is responsible for O_2 transport. The diffusion coefficient for Hb is $6.9 \times 10^{-11} m^2 s^{-1}$ at $T=298K$. Assuming a viscosity of $\eta = 0.891 \times 10^{-3} kg m^{-1} s^{-1}$ and assuming Hb behaves as a hydrated sphere in solution, calculate the hydrodynamic radius of Hb

2.3) Calculate the contribution to the molar heat capacity from the bond vibration in N_2 . Assume $T=1000K$ and for N_2 $\theta_{vib} = 3374K$.

2.4) Calculate the thermal wavelength and the translational partition function for water vapor at $T=500K$ assuming $V=0.001m^3$.

2.5) 1,3-butadiene ($H_2C=CH-CH=CH_2$) has two conjugated double bonds and 4π electrons that are delocalized along the four carbon chain. Assume the molecule is about $6.26 \times 10^{-10} m$ in length. Suppose we approximate the π electron energies using the particle in a one dimensional box model. If 1,3-butadiene absorbs light, an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Calculate the change in energy that occurs when a π electron is

promoted from the HOMO to the LUMO. Calculate also the wavelength of light that is absorbed in making this energy change.

Part 3. Multi-step calculations (36 points) Perform ONE of the two multi-step problems

3.1) For carbon monoxide CO the following data are available:

$\theta_{vib} = 3103K$, $\theta_{rot} = 2.77K$, $D_e = 185kJmol^{-1}$, $g_1 = 1$. Assume 1 mole of CO molecules are contained in a volume $V=1m^3$.

- Calculate the vibrational and rotational partition functions for CO at $T=1000K$
- Calculate the total internal energy at $T=1000K$. Include translational, rotational, vibrational, and electronic contributions. If you treat any energy contribution classically, justify these approximations.
- Calculate the heat capacity at $T=1000K$. Again justify any approximations you make and compare your final result to the classical prediction derived from the equipartition theorem.

3.2) Chromatin is a complex of DNA and proteins called histones. Chromatin has the appearance of a string of beads where each “bead” is a spherical particle called the nucleosome. Individual nucleosomes have been isolated and studied. A long-standing question was: Is the DNA tightly packed inside the nucleosome within a shell of histone proteins or are the histones and DNA dispersed evenly throughout the particle?

- A nucleosome particle was found to have a diffusion coefficient of $4.73 \times 10^{-11} m^2 s^{-1}$. at $T=293K$. Assuming a viscosity of $1.00 \times 10^{-3} kg m^{-1} s^{-1}$, calculate the radius of the nucleosome particle.
- Within the nucleosome is a complex of eight histone proteins. This histone octamer has a total molecular weight of $M_2=138 kg mol^{-1}$ and a specific volume of $\bar{V}_2 = 0.74 mL g^{-1}$. Assuming the histone octamer is an unhydrated sphere, calculate its radius.
- The DNA in the nucleosome is 200 base pairs in length where adjacent base pairs are separated by $3.4 \times 10^{-10} m$. Assuming this DNA is a random coil polymer, calculate its root mean square end-to-end distance. Compare your answers to parts b and c and determine how the DNA and proteins are packed within the nucleosome.

Start of Cumulative Exam: 100 points Total

Part 4. (28 points): Answer FOUR out of the six questions

4.1) In each case, does the heat capacity agree with the predictions of the classical Equipartition Principle? In each case describe the mechanical model upon which your

answer is based. If any system deviates from classical behavior, explain the origin of the deviation:

- For hydrogen (H_2) gas, C_V is $20.75 \text{ J K}^{-1} \text{ mole}^{-1}$
- For argon (Ar) gas, $C_V = 12.5 \text{ J K}^{-1} \text{ mole}^{-1}$
- For solid silver (Ag), $C_V = 25.5 \text{ J K}^{-1} \text{ mole}^{-1}$
- For solid iron (Fe), $C_V = 24.8 \text{ J K}^{-1} \text{ mole}^{-1}$

4.2) Explain the similarities and differences between the Bragg-Zimm and zipper models for helix-coil structural transitions.

4.3) State the Correspondence Principle. Give an example of how a quantum system displays this principle. Include a sketch to illustrate your example.

4.4) Sketch the Scatchard plot for a protein that binds two substrate molecules non-cooperatively. Assume the binding constant is $K=10^3$. On your plot indicate the value of the slope, the y-intercept, and the x-intercept. Explain your sketch using the Scatchard equation.

4.5) Consider a polymer undergoing a helix-coil transition. Make a sketch of how the helical fraction f_H changes with $s = e^{-\Delta G^0/RT}$ for a fully cooperative and a non-cooperative helix-coil transition. Explain why these graphs differ.

4.6) What is the difference between activated and diffusion-controlled kinetics? You can use equations for the rate constants in your explanation.

Part 5) (36 points) Perform THREE of the following FIVE calculations. These calculations consist of solving at least one or two equations. They vary in the amount of work...so chose wisely.

5.1) Consider a particle of mass $m=10^{-25} \text{ kg}$ in a three dimensional cubic box with lengths $L=10\text{\AA}$. Calculate the frequency of radiation required to excite the particle from its ground state to the next higher energy state.

5.2) The reaction between two spherical molecules obeys diffusion-controlled kinetics. Assume $T=300\text{K}$, $\eta=0.1 \text{ kg m}^{-1} \text{ s}^{-1}$, and the molecular radii are 10\AA and 20\AA . Calculate the rate constant and give your answer in units of $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

5.3) The molecule HCl vibrates as a quantized linear harmonic oscillator. The bond force constant of $^1\text{H}^{35}\text{Cl}$ is $\kappa = 481 \text{ Nm}^{-1}$. Calculate the energy, the average momentum squared momentum $\langle p^2 \rangle$ and the average squared displacement $\langle x^2 \rangle$ if the wave

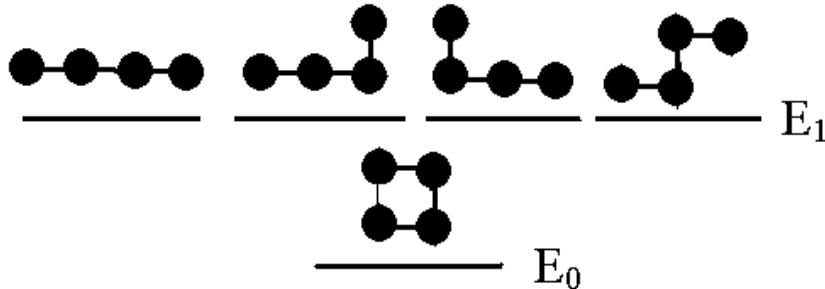
function is $\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$. Note: You do NOT have to do any calculus to

answer this question.

5.4) Calculate the fractional helicity f_H for a Bragg-Zimm trimer (i.e. a peptide composed of three monomers) if $\sigma=0.01$ and $s=100$.

5.5) A monatomic ideal gas has a thermal wavelength of $\Lambda = 2.00 \times 10^{-11} m$ at $T=1000K$. If the volume of the gas is $8.00m^3$, calculate the single particle translational partition function. Calculate also the molar entropy associated with this motion assuming the atoms are indistinguishable.

Part 6. Perform ONE of the TWO multi-step calculations given below.



6.1) In the figure at the right we model the energetics of a small polymer composed of four monomeric units or “beads” connected by chemical bonds. The polymer has two energy states. In the “structured state” the polymer is folded upon itself forming a hydrogen bond (thin line) between the two end beads. This structured state has an energy E_0 . There are four “unstructured” states each with energy E_1 . We assume $E_1 > E_0$ because the hydrogen bond must be broken to go from the structured to any of the unstructured states.

a) Assume $E_0=0$ and $E_1=1.00 \times 10^{-20}J$. Calculate the partition function at $T=250K$. What fraction P_0 of the polymers are structured at this temperature?

b) Calculate the molar internal energy and the molar entropy of the polymer at $T=250K$.

c) Calculate the partition function for the same system at $T=350K$. What fraction of polymers are structured at this temperature?

d) Calculate the change in molar internal energy and entropy when the temperature of the polymer changes from $T=250K$ to $T=350K$.

6.2) Consider a polymer composed of N monomers which undergo helix-coil transitions non-cooperatively. Define the equilibrium constant $s = \frac{q_H}{q_C} = e^{-\Delta G^0/RT}$, where ΔG^0 is the

Gibbs energy change when a coil monomer changes to helix. Note q_H is the partition function for the monomer if it is helical and q_C is the partition function for the monomer if it is coil. Let $q_C=1$. Note also that the monomers are distinguishable.

a) Write out the expression for the partition function of the entire polymer in terms of s and N . Use your expression for the partition function to calculate the change in helical fraction f_H when s changes from $s=1.00$ to $s=4.00$

b) Calculate the entropy change for a polymer composed of $N=10,000$ monomers when s changes from $s=1.00$ to $s=4.00$. Calculate also the entropy change when one mole of polymers, each composed of $N=10000$ monomers, changes from $s=1$ to $s=4.00$.

c) At the melting temperature T_M , $\Delta G^0 = 0$ and $s=1.00$. For temperatures $T < T_M$, the helix structure dominates, so $\Delta G^0 < 0$ and $s > 1$. Suppose the melting temperature for this polymer is $T_M=330\text{K}$ and at $T=312\text{K}$, $s=4.00$. Assuming the molar enthalpy change ΔH^0 is constant between $T=312\text{K}$ and $T=330\text{K}$, calculate the molar enthalpy change that occurs when s changes from 1.00 to 4.00. Hint: Recall the van't Hoff equation from

Chem 152 and 452:
$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

d) Based on your answers to parts a-c, for $T < T_M$, is $\Delta G^0 < 0$ for the transition from coil to helix because of the entropy change or because of the enthalpy change? Explain.

