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 $N_A = 6.02\times10^{23} mol^{-1}$
  Boltzmann's constant $k_B = \frac{R}{N_A} = 1.38\times10^{-23} JK^{-1}$
  Planck's constant $h = 6.62\times10^{-34} Js$
  $\hbar = \frac{h}{2\pi} = 1.05\times10^{-34} Js$
  Rydberg constant $\Re = 2.18\times10^{-18} J$
  Speed of light=c=3.00x10^8 m s^{-1}

  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=1Å=10^{-10} m.
  1000L=1.00m^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.

Answer: In an isolated system characterized by fixed values of N, V, and E, and possessing Ω(N,V,E) microstates, has equal probability of being found in any of its Ω(N,V,E) microstates, i.e. P=1/ Ω(N,V,E).

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

Answer: Two Brownian diffusors A and B with diffusion coefficients D_A and D_B, react when they encounter one another. If they are spheres with radii R_A and R_B a reaction occurs when the centers of these spheres come within R_A+R_B of one another. In such a case the molar rate constant has the form: $k_m = 4\pi N_A\left(D_A + D_B\right)\left(R_A + R_B\right)$

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

Answer: If $\theta_{rot} << T$, then $C_{V,rot} \approx R$ (2 dof's). But if $\theta_{vib} >> T$ then $0 \le C_{V,vib} \ll R$. In addition we can safely assume $C_{V,trans} = \frac{3R}{2}$. Then

$$C_V = C_{V,trans} + C_{V,rot} + C_{V,vib} \approx \frac{3R}{2} + R + 0 = \frac{5R}{2}$$

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.

Answer: The driving force arising from the gradient in the chemical potential resisted by the frictional force gives rise to 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

Answer: Electron motions>vibrations>rotations>translations

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

Answer: $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$. This is the thermally averaged wavelength of a confined quantum particle. If we use particle-in-a-box energy levels then $\Delta E = \left(2n+1\right)\frac{h^2}{8mL^2}$. When the size of the box L approaches Λ, ΔE becomes large and quantum effects in translation are observed.

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 Lz 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.

$$E_J = J\left(J+1\right)\frac{\hbar^2}{2I}$$

$$I = \mu R^2$$

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{M_H M_{Cl}}{M_H + M_{Cl}}\frac{1}{N_A} = \frac{\left(0.001 kg\, mol^{-1}\right)\left(0.0355 kgmol^{-1}\right)}{0.001 kg\, mol^{-1} + 0.0355 kgmol^{-1}}\frac{1}{6.022\times10^{23} mol^{-1}}$$

$$= \frac{0.972\times10^{-3} kg}{6.022\times10^{23}} = 1.61\times10^{-26} kg$$

$$I = \left(1.61\times10^{-26} kg\right)\left(1.36\times10^{-10} m\right)^2 = 2.98\times10^{-46} kgm^2$$

$$\therefore E_{J=1} = \frac{\left(2\right)\left(1.05\times10^{-34} Js\right)^2}{\left(2\right)\left(2.98\times10^{-46} kgm^2\right)} = 3.70\times10^{-69+46} J = 3.70\times10^{-23} J$$

2.2) The hemoglobin (Hb) protein is responsible for O_2 transport. The diffusion coefficient for Hb is 6.9x$10^{-11}m^2$ s^{-1} at T=298K. Assuming a viscosity of $\eta = 0.891\times10^{-3} kgm^{-1}s^{-1}$ and assuming Hb behaves as a hydrated sphere in solution, calculate the hydrodynamic radius of Hb

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R}$$

$$\therefore R = \frac{k_B T}{6\pi\eta D} = \frac{\left(1.38\times10^{-23} JK^{-1}\right)\left(298K\right)}{\left(6\right)\left(3.14\right)\left(0.891\times10^{-3} kgm^{-1}s^{-1}\right)\left(6.9\times10^{-11} m^2 s^{-1}\right)} = 3.55\times10^{-9} m$$

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

$$C_{V,m} = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^2} = \left(8.31 JK^{-1}mol^{-1}\right)\left(\frac{3374}{1000}\right)^2 \frac{e^{-3374/1000}}{\left(1-e^{-3374/1000}\right)^2}$$

$$= \left(8.31 JK^{-1}mol^{-1}\right)\left(11.4\right)\frac{e^{-3.374}}{\left(1-e^{-3.374}\right)^2} = \left(94.7 JK^{-1}mol^{-1}\right)\frac{0.034}{0.933} = 3.45 JK^{-1}mol^{-1}$$

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

$$\Lambda = \frac{h}{\sqrt{2\pi m_{H_2O} k_B T}} \frac{h\sqrt{N_A}}{\sqrt{2\pi M_{H_2O} k_B T}} = \frac{\left(6.626\times10^{-34}\,Js\right)\left(60.22\times10^{-24}\,mol^{-1}\right)^{1/2}}{\left(\left(6.28\right)\left(0.018 kgmol^{-1}\right)\left(1.38\times10^{-23}\,JK^{-1}\right)\left(5.00\times10^{2}\,K\right)\right)}$$

$$= \frac{51.4\times10^{-22}\,Js}{2.79\times10^{-11}\,kgms^{-1}} = 1.84\times10^{-10}\,m$$

$$q_{trans} = \frac{V}{\Lambda^3} = \frac{0.001m^3}{\left(1.84\times10^{-10}\,m\right)^3} = 1.61\times10^{26}$$

2.5) 1,3-butadiene ($H_2C{=}CH{-}CH{=}CH_2$) has two conjugated double bonds and 4 π electrons that are delocalized along the four carbon chain. Assume the molecule is about 6.26x10^{-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.

If there are 4 electrons the n=1 and n=2 levels are filled. Then the HOMO is n=2 and the LUMO is n=3.

$$\Delta E = \left(3^2 - 2^2\right)\frac{h^2}{8mL^2} = \frac{\left(5\right)\left(6.626\times10^{-34}\,Js\right)^2}{\left(8\right)\left(9.1\times10^{-31}\,kg\right)\left(6.26\times10^{-10}\,m\right)^2} = \frac{2.20\times10^{-66}\,J}{2.85\times10^{-48}} = 7.72\times10^{-19}\,J$$

$$\Delta E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{\left(6.626\times10^{-34}\,Js\right)\left(3\times10^{8}\,ms^{-1}\right)}{7.72\times10^{-19}\,J} = 2.57\times10^{-7}\,m$$

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.

a) Calculate the vibrational and rotational partition functions for CO at T=1000K

$$q_{rot} = \frac{T}{\sigma\theta_{rot}} = \frac{1000}{2.77} = 361$$

$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} = \frac{e^{-1.55}}{1-e^{-3.103}} = \frac{0.212}{0.955} = 0.222$$

b) 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.

The translational and rotational motions can be treated classically because $T \gg \theta_{rot}$ and $V \gg \Lambda^3$. Therefore:

$$U = \frac{5RT}{2} + R\theta_{vib}\left(\frac{1}{2} + \frac{1}{e^{\theta_{vib}/T} - 1}\right) - D_e$$

$$= 20775 Jmol^{-1} + 25786 Jmol^{-1}\left(0.50 + 0.05\right) - 185000 Jmol^{-1}$$

$$= 20775 Jmol^{-1} + 14182 Jmol^{-1} - 185000 Jmol^{-1} = -150043 Jmol^{-1}$$

c) 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.

Again we assume the translational and rotational motions make their classical contributions to the heat capacity:

$$C_V = \frac{5R}{2} + R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1 - e^{-\theta_{vib}/T}\right)^2}$$

$$= 20.775 JK^{-1}mol^{-1} + \left(8.31 JK^{-1}mol^{-1}\right)\left(3.103\right)^2 \frac{e^{-3.103}}{\left(1 - e^{-3.103}\right)^2}$$

$$= 20.775 JK^{-1}mol^{-1} + \left(80.01 JK^{-1}mol^{-1}\right)\frac{0.045}{0.912} = 24.723 JK^{-1}mol^{-1}$$

The classical prediction is $C_V = \frac{7R}{2} = \left(3.5\right)\left(8.31 JK^{-1}mol^{-1}\right) = 29.09 JK^{-1}mol^{-1}$

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 questions 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) A nucleosome particle was found to have a diffusion coefficient of 4.73x10^{-11} m^2 s^{-1}. at T=293K. Assuming a viscosity of 1.00x10^{-3} kg m^{-1} s^{-1}, calculate the radius of the nucleosome particle.

$$D = \frac{k_B T}{6\pi\eta R}$$

$$\therefore R = \frac{k_B T}{6\pi\eta D} = \frac{\left(1.38\times10^{-23}JK^{-1}\right)\left(293K\right)}{\left(18.84\right)\left(0.001kgm^{-1}s^{-1}\right)\left(4.73\times10^{-11}m^2s^{-1}\right)}$$

$$= \frac{4.04\times10^{-21}J}{8.91\times10^{-13}kgms^{-2}} = 4.53\times10^{-8}m$$

b) 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 $\overline{V}_2 = 0.74\text{mL g}^{-1}$. Assuming the histone octamer is an unhydrated sphere, calculate its radius.

$$\frac{M_2\overline{V}_2}{N_A} = \frac{4\pi R_0^3}{3}$$

$$\therefore R_0 = \left(\frac{M_2\overline{V}_2}{N_A}\frac{3}{4\pi}\right)^{1/3} = \left(\frac{\left(138000gmol^{-1}\right)\left(0.74mLg^{-1}\right)\left(0.239\right)}{6.022\times10^{23}mol^{-1}}\right)^{1/3}$$

$$= \left(4.05\times10^{-20}mL\right)^{1/3} = \left(4.05\times10^{-23}L\right)^{1/3} = \left(4.05\times10^{-26}m^3\right)^{1/3} = 3.43\times10^{-9}m$$

c) The DNA in the nucleosome is 200 base pairs in length where adjacent base pairs are separated by 3.4x10^{-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.

$$r_{rms} = \left(3.4\times10^{-10}m\right)\left(200\right)^{1/2} = 4.8\times10^{-9}m$$

DNA is wrapped around the histone octamer.

.

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 J K^{-1} mole^{-1}
  - Answer: Disagrees. For a classical diatomic molecule
    $$C_V = \frac{7R}{2} = 29.09JK^{-1}mol^{-1}$$
- For argon (Ar) gas, C_V=12.5 J K^{-1} mole^{-1}

  - Answer; Agrees. . For a classical monatomic molecule $C_V = \frac{3R}{2} = 12.47 JK^{-1}mol^{-1}$
- For solid silver (Ag), C_V= 25.5 J K^{-1} $mole^{-1}$
  - Classically: Agrees well. $C_V = 3R = 24.93 JK^{-1}mol^{-1}$
- For solid iron (Fe), C_V= 24.8 J K^{-1} $mole^{-1}$
  - Agrees well. $C_V = 3R = 24.93 JK^{-1}mol^{-1}$

.

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

Answer: The zipper model assumes that once helix nucleation occurs, propagation can only occur from pre-existing helical segments. The Bragg-Zimm model allows multiple helix nucleations.

.

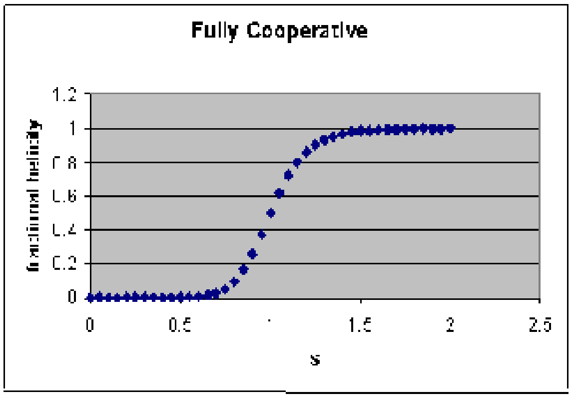
4.3) State the Correspondence Principle. Give an example of how a quantum system displays this principle. Include a sketch to illustrate your example.

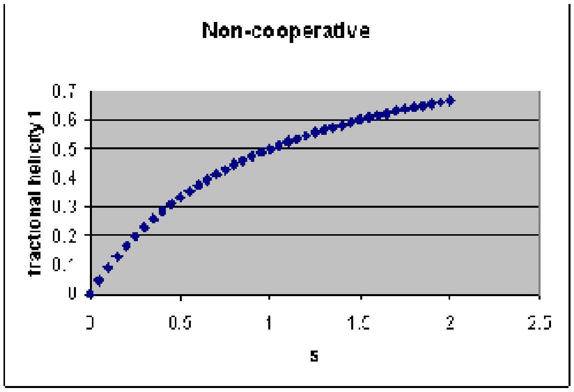
Answer: The behavior of systems described by quantum mechanics will approach classical mechanics as the energy increases.

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.

Answer: The plot should be a straight line, slope=-K=-1000, the y-intercept should be KxN=1000x2=2000, and the x-intercept should be N=2.

4.5) Consider a polymer undergoing a helix-coil transition. Make a sketch of the 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.





The non-cooperative curve results from increase in the populations intermediate species that contain larger amounts of helical sequences**.** The non-cooperative curve results from increase in the population of fully structured helices. No partly structured intermediates occur so the slope of the curve is steeper than for the non-cooperative curve.

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

Answer: In activated kinetics, encounters between reactants A and B form an transition state $AB^{\dagger}$ if the reactants collide with sufficient energy to reach the activation energy Ea. In activated kinetics the rate constant k depends exponentially on temperature: $k = Ae^{-E_a/RT}$. In contrast we can idealize diffusion-controlled kinetics as encounters between spherical molecules A and B with radii R_A and R_B and coefficients of translational diffusion D_A and D_B. The molecules react whenever their centers come within R_A+R_B of each other and the kinetic constant is: $k_{diffusion} = 4\pi\left(D_A + D_B\right)\left(R_A + R_B\right)$.

Because the diffusion coefficient is linear in T: $D = \dfrac{k_B T}{f}$ the dependence of diffusion-controlled kinetics on T is linear.

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} kg in a three dimensional cubic box with lengths L=10Å,. Calculate the frequency of radiation required to excite the particle from its ground state to the next higher energy state.

The ground state is $\left(n_x, n_y, n_z\right) = \left(1,1,1\right)$. The next excited state is triply degenerate:

$$\left(n_x, n_y, n_z\right) = \left(2,1,1\right) = \left(1,2,1\right) = \left(1,1,2\right)$$

$$E = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8mL^2}$$

$$\therefore \Delta E = \left(6-3\right)\frac{h^2}{8mL^2} = \frac{\left(3\right)\left(6.626\times10^{-34}\,Js\right)^2}{\left(8\right)\left(10^{-25}\,kg\right)\left(10^{-9}\,m\right)^2} = \frac{3\times43.9\times10^{-68}\,J}{8\times10^{-43}} = 1.65\times10^{-24}\,J$$

$$\Delta E = h\nu \Rightarrow \nu = \frac{\Delta E}{h} = \frac{1.65\times10^{-24}\,J}{6.626\times10^{-34}\,Js} = 2.49\times10^{9}\,s^{-1}$$

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

$$k_{diffusion} = 4\pi N_A \left(D_A + D_B\right)\left(R_A + R_B\right)$$

$$= 4\pi N_A \frac{k_B T}{6\pi\eta}\left(\frac{1}{R_A} + \frac{1}{R_B}\right)\left(R_A + R_B\right) = \frac{2RT}{3\eta}\left(\frac{1}{R_A} + \frac{1}{R_B}\right)\left(R_A + R_B\right)$$

$$= \frac{2\left(8.31JK^{-1}mol^{-1}\right)\left(300K\right)}{3\left(0.1kgm^{-1}s^{-1}\right)}\left(10^9 m^{-1} + 0.5\times10^9 m^{-1}\right)\left(1\times10^{-9} m + 2\times10^{-9} m\right)$$

$$\frac{2\left(8.31JK^{-1}mol^{-1}\right)\left(300K\right)}{3\left(0.1kgm^{-1}s^{-1}\right)}\left(1.5\times10^9 m^{-1}\right)\left(3\times10^{-9} m\right) = 7.47\times10^4 m^3 mol^{-1}s^{-1}$$

5.3) The molecule HCl vibrated as a quantized linear harmonic oscillator. The bond force constant of ^{1}H^{35}Cl is $\kappa = 481Nm^{-1}$. Calculate the energy, the average momentum squared momentum $\left\langle p^2 \right\rangle$ and the average squared displacement $\left\langle x^2 \right\rangle$ if the wave function is $\psi_1\left(x\right) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$. Note: You do NOT have to do any calculus to answer this question. **Note: Students were told only to calculate the energy. Too long otherwise.**

For the energy n=1.

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{M_H M_{Cl}}{M_H + M_{Cl}}\frac{1}{N_A} = \frac{\left(0.001kgmol^{-1}\right)\left(0.0355kgmol^{-1}\right)}{0.001kgmol^{-1} + 0.0355kgmol^{-1}}\frac{1}{6.022\times10^{23} mol^{-1}}$$

$$= \frac{\left(0.001kgmol^{-1}\right)\left(0.0355kgmol^{-1}\right)}{0.0365kgmol^{-1}}\frac{1}{6.022\times10^{23} mol^{-1}} = 1.62\times10^{-26} kg$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} = \frac{1}{6.28}\sqrt{\frac{481Nm^{-1}}{1.62\times10^{-26} kg}} = \left(2.51\right)\left(17.2\times10^{13} s^{-1}\right) = 4.33\times10^{14} s^{-1}$$

$$\therefore E = h\nu\left(1 + \tfrac{1}{2}\right) = \left(1.5\right)\left(6.626\times10^{-34} Js\right)\left(4.33\times10^{14} s^{-1}\right) = 4.30\times10^{-19} J$$

Students do NOT have to do the next two calculations

$$\left\langle V\left(x\right)\right\rangle = \frac{E}{2} = \frac{\kappa}{2}\left\langle x^2\right\rangle \Rightarrow \left\langle x^2\right\rangle = \frac{E}{\kappa} = \frac{4.30\times10^{-19} J}{481Nm^{-1}} = 8.94\times10^{-22} m^2$$

$$\left\langle K\left(p\right)\right\rangle = \frac{E}{2} = \frac{\left\langle p^2\right\rangle}{2\mu} \Rightarrow \left\langle p^2\right\rangle = \mu E = \left(4.30\times10^{-19} J\right)\left(1.62\times10^{-26} kg\right) = 6.97\times10^{-45} kgJ$$

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

Trimers: CCC, CCH, CHC, HCC, HHC, HCH, CHH, HHH

$$q = q_0\left(1+3\sigma s+2\sigma s^2+\sigma^2 s^2+\sigma s^3\right)$$

$$f_H = \frac{s}{3q}\frac{\partial q}{\partial s} = \frac{3\sigma s+4\sigma s^2+2\sigma^2 s^2+3\sigma s^3}{3\left(1+3\sigma s+2\sigma s^2+\sigma^2 s^2+\sigma s^3\right)} = \frac{3+40+2+30000}{3\left(1+3+20+1+10000\right)} = \frac{30045}{30075} = 0.999$$

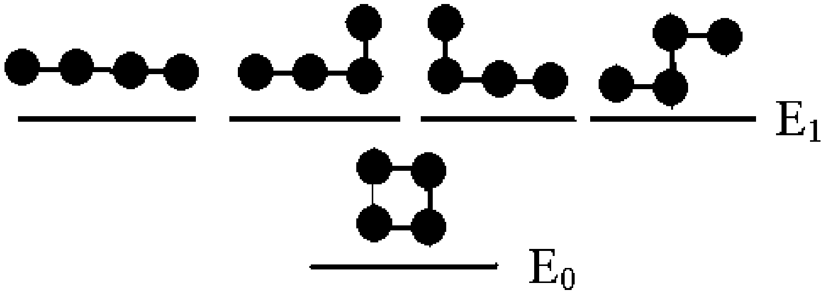
5.5) A monatomic ideal gas has a thermal wavelength of $\Lambda = 2.00\times10^{-11}m$ at T=1000K. If the volume of the gas is 8.00m^3, calculate the single particle translational partition function. Calculate also the molar entropy associated with this motion assuming the atoms are indistinguishable.

$$q_{trans} = \frac{V}{\Lambda^3} = \frac{8.00m^3}{\left(2.00\times10^{-11}m\right)^3} = 10^{33}$$

$$S = R\ln\left(\frac{qe^{5/2}}{N_A}\right) = \left(8.31JK^{-1}mol^{-1}\right)\ln\left(\frac{12.2\times10^{33}}{6.022\times10^{23}}\right) = \left(8.31JK^{-1}mol^{-1}\right)\ln\left(2.03\times10^{10}\right)$$

$$= \left(8.31JK^{-1}mol^{-1}\right)\left(0.708+10\ln10\right) = 197JK^{-1}mol^{-1}$$

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 x10^{-20}J. Calculate the partition function at T=250K. What fraction P_0 of the polymers are structured at this temperature?

$$\frac{E_1}{k_B T} = \frac{10^{-20} J}{\left(1.38\times10^{-23} JK^{-1}\right)\left(250K\right)} = 2.90$$

$$q = 1 + 4e^{-E_1/k_B T} = 1 + 4e^{-2.9} = 1.22$$

$$P_0 = \frac{1}{q} = \frac{1}{1.22} = 0.820$$

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

$$U = \frac{N_A E_1 e^{-E_1/k_B T}}{q} = \left(6.022\times10^{23} mol^{-1}\right)\left(10^{-20} J\right)\frac{4e^{-2.9}}{1.22} = 1086 Jmol^{-1}$$

$$S = \frac{U}{T} + R\ln q = \frac{1086 Jmol^{-1}}{250K} + 8.31 JK^{-1}mol^{-1}\ln\left(1.22\right) = 6.00 JK^{-1}mol^{-1}$$

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

$$\frac{E_1}{k_B T} = \frac{10^{-20} J}{\left(1.38\times10^{-23} JK^{-1}\right)\left(350K\right)} = 2.07$$

$$q = 1 + 4e^{-E_1/k_B T} = 1 + 4e^{-2.07} = 1.50$$

$$P_0 = \frac{1}{q} = \frac{1}{1.50} = 0.665$$

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

$$U = \frac{N_A E_1 e^{-E_1/k_B T}}{q} = \left(6.022\times10^{23} mol^{-1}\right)\left(10^{-20} J\right)\frac{4e^{-2.07}}{1.50} = 2026 Jmol^{-1}$$

$$S = \frac{U}{T} + R\ln q = \frac{2026 Jmol^{-1}}{350K} + 8.31 JK^{-1}mol^{-1}\ln\left(1.50\right) = 9.16 JK^{-1}mol^{-1}$$

$$\Delta U = 2026 Jmol^{-1} - 1086 Jmol^{-1} = 940 Jmol^{-1}$$

$$\Delta S = 9.16 JK^{-1}mol^{-1} - 6.00 JK^{-1}mol^{-1} = 3.16 JK^{-1}mol^{-1}$$

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

For a non-cooperative transition: $q=\left(1+s\right)^N$ and $f_H=\frac{s}{Nq}\frac{\partial q}{\partial s}=\frac{s}{1+s}$

$$\therefore \Delta f_H=\frac{4}{1+4}-\frac{1}{1+1}=\frac{4}{5}-\frac{1}{2}=\frac{3}{10}=0.30$$

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.

$$U=-\frac{Nk_BTs\ln s}{1+s}$$

$$\therefore S=\frac{U}{T}+Nk_B\ln\left(1+s\right)=Nk_B\left(-\frac{s\ln s}{1+s}+\ln\left(1+s\right)\right)$$

$$\Delta S=S_4-S_1=\left(10000\right)\left(1.38\times10^{-23}JK^{-1}\right)\left[-\frac{4\ln4}{1+4}+\ln\left(1+4\right)+\frac{\ln1}{1+1}-\ln\left(1+1\right)\right]$$

$$=\left(1.38\times10^{-19}JK^{-1}\right)\left(-1.11+1.61-0.69\right)=-2.62\times10^{-20}JK^{-1}$$

$$\Delta S_m=N_A\Delta S=\left(6.022\times10^{23}mol^{-1}\right)\left(-2.62\times10^{-20}JK^{-1}\right)=-1.58\times10^{4}JK^{-1}mol^{-1}$$

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=330K and at T=312K, s=4.00. Assuming the molar enthalpy change ΔH^0 is constant between T=312K and T=330K, 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: $\ln\left(\frac{K_2}{K_1}\right)=-\frac{\Delta H^0}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

$$\ln\left(\frac{4}{1}\right)=1.39=-\frac{\Delta H^0}{R}\left(\frac{1}{312K}-\frac{1}{330K}\right)$$

$$-\left(1.39\right)\left(8.31JK^{-1}mol^{-1}\right)=\Delta H^0\left(0.0032K^{-1}-0.0030K^{-1}\right)$$

$$\Delta H^0=-57755Jmol^{-1}$$

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.

The entropy decreases because the amount of helix increases (i.e. s increases) when the temperature decreases from T=330K to T=312K. On the other hand as the temperature decreases the enthalpy decreases so the process is exothermic. Because $\Delta G^0 < 0$ the reaction is driven by the enthalpy change.