University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015
Midterm Key

- **Enter all answers into your Bluebook.**
- **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, 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 $h = 6.62 \times 10^{-34} Js$
Pa=N m^{-2}
N=kg m s^{-2}
J=N m= kg m^2 s^{-2}

Section 1(Total points=28. Answer 4 out of 6 questions).

1.1) Explain the Ergodic Postulate. What basic purpose does this postulate serve in statistical mechanics?

Answer: The ergodic postulate states that if an ensemble contains all microstates encountered in the course of a time average, then the ensemble average and time average are equivalent.

1.2) Describe two ways to measured the enthalpy of denaturation of a protein. When will these two measurements agree and when will they disagree. Explain your answer.

Solution

First, the heat capacity as a function of temperature is measured over a temperature range $\Delta T = T_2 - T_1$ using differential scanning calorimetry. The enthalpy is obtained from $\Delta H_{DSC} = \int_{T_1}^{T_2} C_P(T) dT$. Second, the fraction of structured protein f_N is measured at a given temperature to obtain and equilibrium constant $K = \frac{f_D}{f_N} = \frac{1 - f_N}{f_N}$ where f_D is the fraction of denatured protein. The enthalpy is obtained by measuring the equilibrium temperatures and the equilibrium constant

1.3) Consider the following two expressions for the statistical internal energy:

$$\frac{U}{N} = \sum_{j=1}^{M} P_j E_j; \quad U = k_B T^2 \frac{\partial \ln Q}{\partial T};$$

Explain and define all the terms in these equations. Without necessarily doing a detailed derivation, explain how these two expressions are related.

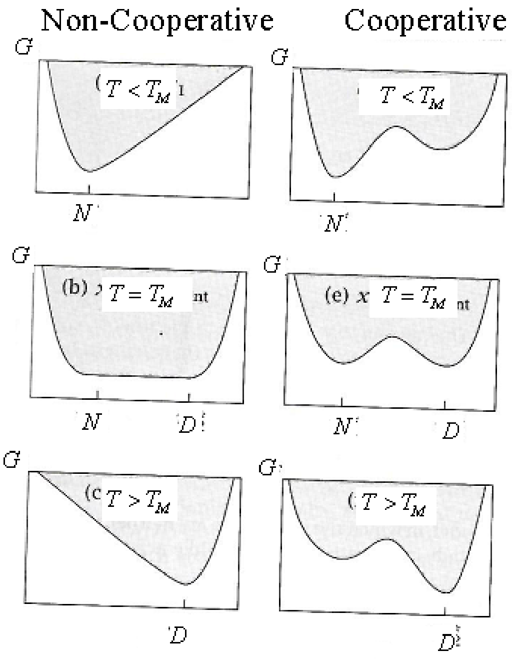
Answer: $\frac{U}{N} = \sum_{j=1}^{M} P_j E_j$; P$_j$ is the Boltzmann Distribution Law probability that a particle occupies energy state E$_j$. If the Boltzmann Law probability $P_j = \frac{w_j e^{-E_j/k_BT}}{Q}$ is substituted into $\frac{U}{N} = \sum_{j=1}^{M} P_j E_j$; we obtain $U = k_B T^2 \frac{\partial \ln Q}{\partial T}$ where $Q = \sum_{j=1}^{M} w_j e^{-E_j/k_BT}$ is the partition function. The term w$_j$ is the degeneracy of the energy state E$_j$.

1.4) In this course, two forms for the partition function Q for a system of N non-interacting particles has been given: $Q = q^N$ and $Q = \frac{q^N}{N!}$. Explain the purpose of the N! term. Would the N! term be important in the calculation of the internal energy U of an ideal gas? Would it be important in the calculation of the entropy S of an ideal gas? Explain.

Answer: N! corrects for overcounting of states in the partition function due to particle indistinguishability: i.e. particles switch between microstates faster than the rate of observation. The constant N! term does not contribute to the internal energy of an ideal gas $U = k_B T^2 \frac{\partial \ln Q}{\partial T}$ because it is removed by the temperature differentiation. However it does contribute to the entropy which is defined as $S = \frac{U}{T} + k_B \ln Q$.

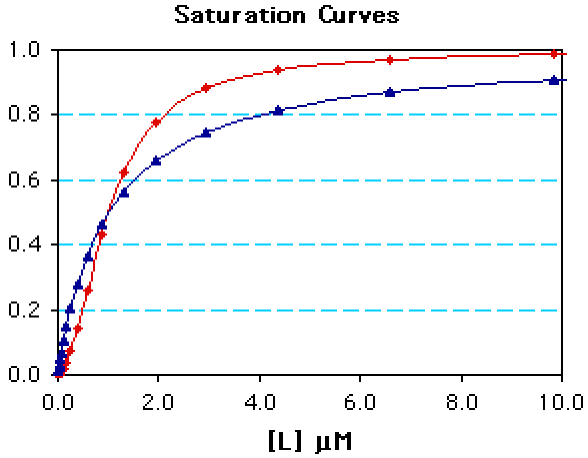
1.5) Explain the difference between fully cooperative versus non-cooperative models for helix-coil transitions. In particular sketch how the free energy changes as a function of temperature for a non-cooperative versus a fully cooperative helix-coil transition.

Answer: in non-cooperative helix-coil (i.e. h-c) transitions, monomers undergo h-c transitions independently. The change from fully helical N to random coil D involves the formation of partially structured intermediates. In a cooperative h-c transition the monomers do not change structural state independently. For a fully cooperative h-c transition an equilibrium exists between D state proteins and N state proteins and no partially structured intermediates occur. For a non-cooperative transition the free energy G surface always has a single minimum: at the N state at low temperatures, at the D state for high temperatures. At intermediate temperatures the minimum broadens and shifts from N to D. For fully cooperative transitions two free energy minima exist



for N and D, and the global minimum changes from N to D as temperature is increased. (129 words)

1.6) Sketch binding curves for non-cooperative and cooperative ligand binding reactions. Explain in detail the reasons for the different features of these curves.



Answer: Binding or Saturation Curves are shown at right: cooperative is red and non-cooperative is blue. For non-cooperative the equation is $f_B = \dfrac{k[L]}{1+k[L]}$. This hyperbolic curve rises rapidly at first due to addition of partly filled intermediates as ligand L is added. For fully cooperative the red curve follows $f_B = \dfrac{k[L]^N}{1+k[L]^N}$ and rises more slowly than the blue non-cooperative curve at low [L] because no partially filled intermediates occur. As [L] increases the red curve rises rapidly due to addition of fully bound polymer to the solution. Both curves level off at f_B=1, i.e. fully bound polymer.

Section 2 (Total points=36. Answer three out of five problems)

2.1) Calculate the partition function and the helix fraction f_H for a tetramer using the zipper model assuming s=1.5 and σ=0.001. If necessary assume q_0=1.

$$q_{zipper} = q_0\left(1+\sigma\sum_{k=1}^{4}(N+1-k)s^k\right)$$

$$= q_0\left(1+\sigma\left(4s+3s^2+2s^3+s^4\right)\right)$$

$$= 1 + 0.001\left(4(1.5)+3(1.5)^2+2(1.5)^3+1.5^4\right) = 1+(0.001)(24.6) = 1.025$$

$$\frac{\partial q}{\partial s} = \frac{\partial}{\partial s}\left(1+\sigma(4s+3s^2+2s^3+s^4)\right) = \sigma\left(4+6s+6s^2+4s^3\right)$$
$$= 0.001(4+9+13.5+13.5) = 0.04$$
$$\therefore f_H = \frac{1}{N}\frac{s}{q}\frac{\partial q}{\partial s} = \frac{1.5}{4(1.025)}(0.04) = 0.0146$$

2.2) Using the Bragg-Zimm model calculate the fractional helicity f_H for a polymer for which N=10000 if σ=0.01 and s=0.6.

$$\lambda_1 = \frac{s+1+\sqrt{(s-1)^2+4\sigma s}}{2} = \frac{0.6+1+\sqrt{(0.6-1)^2+4(0.01)(0.6)}}{2}$$
$$= \frac{1.6+\sqrt{0.160+0.024}}{2} = \frac{1.60+0.429}{2} = 1.01$$
$$\frac{\partial \lambda_1}{\partial s} = \frac{1}{2}\left(1+\frac{s-1+2\sigma}{\sqrt{(s-1)^2+4\sigma s}}\right) = \frac{1}{2}\left(1+\frac{0.6-1+0.02}{0.429}\right) = 0.057$$
$$f_H = \frac{\langle n\rangle}{N} = \frac{s}{N}\frac{\partial \ln \lambda_1^N}{\partial s} = \frac{s}{\lambda_1}\frac{\partial \lambda_1}{\partial s} = \frac{0.6}{1.01}(0.057) = 0.034$$

2.3) Calculate the single particle partition function for a two level system if the spacing between the energy levels is $\varepsilon = 5.00\times10^{-21}\,J$ and T=1000K. Calculate the internal energy U per mole and the molar entropy.. Assume the particles are distinguishable

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Distinguishable means $Q = q^N$

$$q = 1+e^{-\varepsilon/k_BT} = 1+\exp\left(-\frac{5\times10^{-21}\,J}{(1.38\times10^{-23}\,J)(1000K)}\right) = 1+e^{-0.362} = 1.70$$
$$U = \frac{N_A\varepsilon e^{-\varepsilon/k_BT}}{1+e^{-\varepsilon/k_BT}} = \frac{N_A\varepsilon}{1+e^{\varepsilon/k_BT}} = \frac{(6.02\times10^{23}mol^{-1})(5\times10^{-21}J)}{1+e^{0.362}} = \frac{3.01\times10^3\,Jmol^{-1}}{2.44} = 1.24kJmol^{-1}$$
$$S = \frac{U}{T}+k_B\ln Q = \frac{U}{T}+k_BN_A\ln q = \frac{1.24kJmol^{-1}}{1000K}+8.31JK^{-1}mol^{-1}\ln(1.70)$$
$$= 1.24JK^{-1}mol^{-1}+4.41JK^{-1}mol^{-1} = 5.65JK^{-1}mol^{-1}$$

2.4) The variance σ^2 of a physical property X is a measure of the width of the distribution of X. The variance of X is defined as $\sigma^2 = \langle X^2\rangle - \langle X\rangle^2$. The standard deviation σ is the square root of the variance. Calculate the variance and the standard deviation of the velocity (i.e. X=v) distribution for helium gas at T=1000K. Assume helium behaves ideally at this temperature.

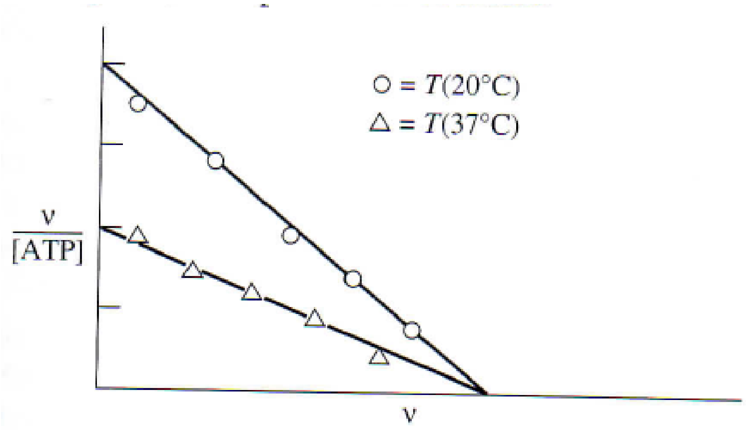
Solution:

$$\sigma^2 = \left\langle v^2 \right\rangle - \left\langle v \right\rangle^2 = \frac{3RT}{M} - \frac{8RT}{\pi M} = \frac{RT}{M}\left(3 - \frac{8}{\pi}\right)$$

$$\therefore \sigma^2 = \frac{\left(8.31JK^{-1}mol^{-1}\right)\left(1000K\right)}{0.004kgmol^{-1}}\left(3-2.55\right) = 9.34\text{x}10^5\text{m}^2\text{s}^{-2}$$

$\sigma = 9.67\text{x}10^2\ \text{ms}^{-1}$

2.5) The enzyme tetrahydrofolate synthetase has four identical binding sites to which its substrate ATP binds non-cooperatively. At T=293K (i.e. 20°C) the equilibrium binding constant is $K=1.00\text{x}10^4$. Scatchard plots of ATP binding to tetrahydrofolate synthetase are shown at the right for T=293K and 310K (i.e. 37°C).



From the plot calculate K at T=310K and then calculate ΔG° also at T=310K. Assume the y-intercept is graduated linearly. Also, calculate ΔH° for ATP binding to tetrahydrofolate synthetase. Assume ΔH° is constant between 293K and 310K. Finally calculate ΔS° at T=310K.

Solution: The Scatchard equation is $\frac{\langle v \rangle}{[L]} = KN - K\langle v \rangle$. The y intercept is $\frac{\langle v \rangle}{[L]} = KN = 4\times10^4$. If the y axis is graduate linearly the the intercept at T=310K is half of its value at T=293K. Then $K_{310} = \frac{K_{293}}{2} = \frac{10^4}{2} = 5\times10^3$.

$$\therefore \Delta G^\circ = -RT\ln K = -\left(8.31JK^{-1}mol^{-1}\right)\left(310K\right)\ln\left(5\times10^3\right) = -21{,}900Jmol^{-1}$$

To calculate the enthalpy of binding:

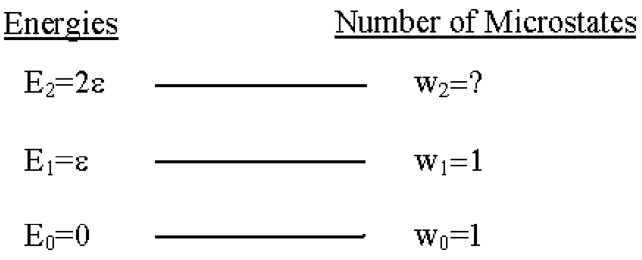
$$\ln\left(\frac{K_{293}}{K_{310}}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{310K} - \frac{1}{293K}\right) = \frac{\Delta H^\circ}{8.31JK^{-1}mol^{-1}}\left(-0.000187K^{-1}\right)$$

$$\Delta H^\circ = -\frac{\ln 2\left(8.31Jmol^{-1}\right)}{0.000187} = -30802Jmol^{-1}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ_{310}}{T} = \frac{-30802Jmol^{-1} + 21900Jmol^{-1}}{310K} = -28.7JK^{-1}mol^{-1}$$

Section 3 (Total points=36. Answer one of the two problems)

3.1) The simplest system that displays cooperativity is the three energy level system shown at the right.



The energy levels are spaced equally apart by $\Delta E=\varepsilon$. The lowest two energy levels have one microstate each ($w_0=w_1=1$).

a) Assume $w_2=1$, $\varepsilon = 1.38\times10^{-20}\,J$, and T=1000K. Compute the partition function, the three probabilities p_0, p_1, and p_2.

$$q = 1+e^{-1}+e^{-2} = 1+0.368+0.135 = 1.50$$

$$p_0 = \frac{1}{q} = \frac{1}{1.50} = 0.667; \quad p_1 = \frac{e^{-1}}{q} = \frac{0.368}{1.50} = 0.245 \quad p_2 = 1-0.667-0.245 = 0.088$$

b) Now change the conditions. Assume $w_2=1000$ and assume $\varepsilon = 1.38\times10^{-20}\,J$. Determine the temperature T at which $p_0=p_2$, i.e. the temperature at which $\frac{p_0}{p_2}=1$.

$$\frac{1}{1000e^{-\varepsilon/k_BT}} = 1 \Rightarrow e^{-2\varepsilon/k_BT} = \frac{1}{1000} \Rightarrow -2\varepsilon/k_BT = \ln\left(\frac{1}{1000}\right)$$

$$\therefore 2\varepsilon/k_BT = \ln(1000) \Rightarrow T = \frac{2\varepsilon}{k_B\ln 1000} = \frac{2\times1.38\times10^{-20}\,J}{\left(1.38\times10^{-23}\,JK^{-1}\right)(6.91)} = 289K$$

c) Using the temperature determined in part b, compute the partition function and the three probabilities p_0, p_1, and p_2. Explain how this system behaves cooperatively.

$$\frac{\varepsilon}{k_BT} = \frac{1.38\times10^{-20}\,J}{\left(1.38\times10^{-23}\,JK^{-1}\right)(289K)} = 3.46$$

$$q = 1+e^{-3.46}+1000e^{-6.92} = 1+0.031+1.00 = 2.03$$

$$\therefore p_0 = p_2 = \frac{1}{2.03} = 0.493; \quad p_1 = 1-0.986 = 0.014$$

When the statistical weights of the three levels are equal, all three levels are populated, albeit unequally. The populations change smoothly and the middle level is populated appreciably. However, when the statistical weight of the third level is increased, there exists a temperature at which the ground state and the highest level are equally populated and the middle level is virtually unpopulated. This resembles cooperativity because the population of the middle "intermediate level" is diminished.

3.2) An energy ladder has a ground state energy $\varepsilon_0 = 0$ and spacing between the energy levels of $\varepsilon = 3.76\times10^{-21}\,J$. The temperature is T=500K.

a) Evaluate the single particle partition function under these conditions.

$$\frac{\varepsilon}{k_B T} = \frac{3.76\times 10^{-21} J}{\left(1.38\times 10^{-23} JK^{-1}\right)\left(500K\right)} = \frac{3.76\times 10^{-21}}{6.90\times 10^{-21}} = 0.545$$

$$q = \frac{1}{1-e^{-\varepsilon/k_B T}} = \frac{1}{1-e^{-0.545}} = \frac{1}{1-0.58} = 2.38$$

b) Assume the number of particles in the system is 10^{24}. How many particles are in the ground state? How many are in first excited state? How many particles are in the rest of the excited states?

$$N_0 = NP_0 = N\frac{e^{-\varepsilon_0/k_B T}}{q} = \frac{Ne^0}{q} = \frac{10^{24}}{2.38} = 4.20\times 10^{23}$$

$$N_1 = NP_1 = N\frac{e^{-\varepsilon_1/k_B T}}{q} = \frac{Ne^{-.545}}{q} = \frac{0.580\times 10^{24}}{2.38} = 2.44\times 10^{23}$$

$$N_{rest} = 10^{24} - N_0 - N_1 = \left(10-4.20-2.44\right)\times 10^{23} = 3.36\times 10^{23}$$

c) Calculate the internal energy U per mole and the molar heat capacity C_v.

$$U = \frac{N_A \varepsilon e^{-\varepsilon/k_B T}}{1-e^{-\varepsilon/k_B T}} = \frac{N_A \varepsilon}{e^{\varepsilon/k_B T}-1} = \frac{\left(6.02\times 10^{23} mol^{-1}\right)\left(3.76\times 10^{-21} J\right)}{e^{0.545}-1}$$

$$= \frac{2.26 kJmol^{-1}}{1.725-1} = \frac{2.26 kJmol^{-1}}{0.725} = 3.12 kJmol^{-1} = 3120 Jmol^{-1}$$

$$C_V = N_A k_B \left(\frac{\varepsilon}{k_B T}\right)^2 \frac{e^{\varepsilon/k_B T}}{\left(e^{\varepsilon/k_B T}-1\right)^2} = \left(8.31 JK^{-1}mol^{-1}\right)\left(0.545\right)^2 \frac{e^{0.545}}{\left(e^{0.545}-1\right)^2}$$

$$= \left(2.47 JK^{-1}mol^{-1}\right)\frac{1.73}{\left(0.725\right)^2} = \frac{4.27 JK^{-1}mol^{-1}}{0.525} = 8.14 JK^{-1}mol^{-1}$$