

**Chapter 4 &5 Reading and Homework #3**

**READING ASSIGNMENT**

**Mon Oct. 3:** Chapter 4:pp. 108-115: activity, standard states, and the *real* K.  
**Tue Oct. 4:** bottom 126-129, Temperature Dependence of  $K_{eq}$ ; 140-43(DNA melting);  
**Thur Oct. 6** Chap. 2: p. 24 Equipartition; Chap. 5: p. 162 Boltzmann distribution;  
pp. 135-138, Thermodynamics of metabolism

**Homework Assignment #3**

**Chapter 4, Problems:** 2, 4\*, 8, 14a#, 20, and S1-S4 below. **Due Monday, Oct. 10, in class.**  
*Note that  $\Delta G^0$  for hydrolysis of ATP is given in the footnote of Table 4.3*

**Footnotes**

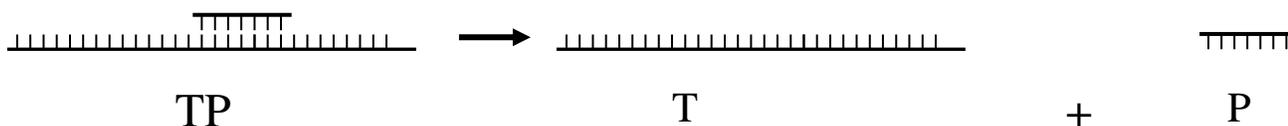
\* **4c:** Find the maximum concentration ratio of glucose(in)/glucose(out) using the stoichiometry of 4(a) if the activity coefficient for glucose(in) = **0.30**.

**#14a:** Do this for **pH 8 and 0.30 M for the total concentration of histidine**. *If* this cannot be done using NaOH, use HCl instead.

**Supplemental Problems**

**S1.** If  $\Delta G^0$  for hydrolysis of hypothetical compound BOH in the reaction:  
B-phosphate +  $H_2O \rightarrow BOH$  + phosphate is -15.0 kJ/mol, calculate the  $\Delta G^0$  for the phosphorylation of B-OH by ATP.  
Note that  $\Delta G^0$  for hydrolysis of ATP is given in the footnote of Table 4.3

**S2.** Consider the equilibrium constant for dissociation ( $K_d$ ) ("melting") of the double stranded probe (P) + target DNA (T) at **37 °C**:



where P (probe) is a small piece of DNA, complementary to a small part of the target (T).

(a) Write down the equilibrium constant,  $K_d$ , for this reaction in terms of [P] and the ratio,  $r$ , of free target, [T], and complexed target, [TP]. ( $r = [T]/[TP]$ ) This *is* as trivial as it sounds.

(b) Using the sequence **5'-TAGCG-3'** for the probe, and Table 4.4, calculate  $\Delta G^0$  and  $K_d$  for the reaction in (a) at 37°C. (Note: Table 4.4 is for *association* not dissociation. You will have to convert the numbers to values for dissociation.)

(c) Find the temperature ( $T_m$ ) for which 50% of the target is bound to probe, given that:  $C_{probe} = [P] + [TP] = 5 \times 10^{-4} M$  and  $C_{target} = [T] + [TP] = 3 \times 10^{-6} M$ . ( $T_m$  is called the "melting temperature"). (Note that  $[P] \cong C_{probe}$  because probe is in great excess and only a small fraction of it can bind).

**S3. The atmosphere closely obeys the Boltzmann distribution. (This math is exactly the same as  $K = \exp(-\Delta G^0/RT)$ ). For this problem  $K = p(\text{altitude } 2)/p(\text{altitude } 1)$ , i.e., the ratio of pressures at any two altitudes.**

Using the Boltzmann distribution, find the atmospheric pressure (bars) in Bozeman (elevation = 5000 feet above sea level), assuming  $T = 298$  K. Assume the degeneracy (**which is the  $W$  in  $S = k_B \ln W$** ) is effectively a constant for altitudes below 100,000 ft. Use the average molecular mass of the air molecules, which is  $0.2(32) + 0.8(28) = 28.8$  g/mol. (remember that the ratio of the pressures is the ratio of concentrations).

**S4.** From the Boltzmann distribution, find the ratio of probabilities to be in the first excited vibrational quantum state compared to being in the lowest (zero-point) state for  $N_2$  and  $I_2$  gases, given that for  $N_2$ , the vibrational energy level spacing is about **25 kJ/mole**, but for  $I_2$  the energy of the vibrational energy level spacing is only **2.4 kJ/mol**. How do your results show that it is reasonable that the vibrational degrees of freedom do not contribute significantly to heat capacity for  $N_2$  but they do for  $I_2$ . (The degeneracy of vibrational states = 1).

**Below is a summary of what is on page 24. Equipartition of energy and heat capacities.** Rereading *p. 24* you will find that a molecule soaks up  $\frac{1}{2} k_B T$  J per each molecular "degree of freedom", i.e.,  $\frac{1}{2} RT$  J/mol. All molecules have 3 translational degrees of freedom, and diatomic molecules have two rotational degrees of freedom at room temperature. They also have 1 vibration (which gives 2 more degrees, 1 kinetic energy and 1 for potential energy). This would seem to predict molar energies of  $\frac{7}{2} RT$ , and therefore  $C_{v,m} = \frac{7}{2} R$  and  $C_{p,m} = \frac{9}{2} R$ , but at room temperature most diatomics have  $C_{v,m}$  close to  $\frac{5}{2} R$  and  $C_{p,m}$  close to  $\frac{7}{2} R$ . This seemingly inexplicable behavior is understandable from a combination of the **Boltzmann distribution** combined with the basic result of **quantum mechanics**: Later in the semester you will learn that the vibrational quantum energy level spacing is proportional to the vibrational frequency, and is given by  $\Delta E = h\nu_{\text{vib}}$ . Strong bonds between low mass atoms have high vibrational frequencies and therefore a larger energy jump to reach the excited vibrational states. (Just for your further information that is not needed to work this problem, the vibrational energy level spacing =  $h\nu_{\text{vib}}$ .  $\nu_{\text{vib}}$  for  $N_2 = 2100 \text{ cm}^{-1}$ ;  $\nu_{\text{vib}}$  for  $I_2 = 200 \text{ cm}^{-1}$ ; the difference is because the N is a light atom and  $N_2$  bond is a very strong triple bond.  $I_2$  has a weak single bond and the atoms are much heavier.)

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**Exam 2 is on Friday, October 14, 7:55-8:55 am** in the usual meeting room. It is closed book and over chapters 3,4, ***plus*** p. 24 of Chapter 2 and p. 162 of Chapter 5, which are pertinent to this homework. ***You may have one 4 x 6" sheet of handwritten information (both sides) of your choosing for use on the exam.***