

Chapter 4 &5 Reading and Homework #3

READING ASSIGNMENT

Mon Oct. 2: Chapter 4:pp. 108-115: activity, standard states, and the *real* K.

Tue Oct. 3: bottom 126-129, Temperature Dependence of K_{eq} ; 140-43(DNA melting);

Thur Oct. 5 Chap. 2: p. 24 Equipartition; Chap. 5: p. 162 Boltzmann distribution;

pp. 135-138, Thermodynamics of metabolism

Homework Assignment #3 (CORRECTED!)

**Corrections are on problem 4(c): -5.7 changed to 10.00 at 25 °C, 20.00 at 35 °C;
on problem S4 : N₂ is changed to CO**

Chapter 4, Problems: 2, 4*, 8&, 14a#, 20, and S1-S4 below. **Due Monday, Oct. 9, in class.**

Exam 2 is on Friday Oct 13.

Note that ΔG^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) = **0.44**.

& **8 do this for compounds X and Y. Replace the word fumarate with X, and replace the word malate with Y.**

& 8a $K_{eq} = \frac{-5.7}{10.00}$ at 25°C

& 8e $K_{eq} = \frac{-5.7}{20.00}$ at 35°C

#14a: Do this for pH 7.6 and 0.15 M for the total concentration of histidine. *If* this cannot be done using NaOH, use HCl instead.

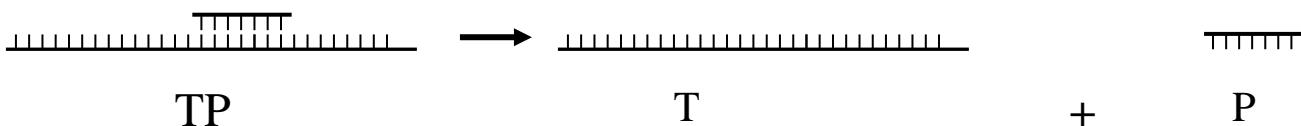
Supplemental Problems

S1. If ΔG^0 for hydrolysis of hypothetical compound X-OH in the reaction:

X-phosphate + H₂O → X-OH + phosphate is -20.0 kJ/mol, calculate the ΔG^0 for the phosphorylation of X-OH by ATP.

Note that ΔG^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'- CGCTA-3'** for the probe, and Table 4.4, calculate ΔG^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: $C_{\text{probe}} = [P] + [TP] = 5 \times 10^{-3} \text{ M}$ and $C_{\text{target}} = [T] + [TP] = 2 \times 10^{-6} \text{ M}$. (T_m is called the “melting temperature”). (Note that $[P] \approx C_{\text{probe}}$ 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 $K = \exp(-\Delta G^\circ/RT)$). 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 **Butte, MT (elevation = 5,538 feet above sea level)**, assuming $T=298 \text{ K}$. 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 $0.2(32) + 0.8(28) = 28.8 \text{ g/mol}$. (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 **CO and Br₂** gases, given that for **N₂ CO**, the vibrational energy level spacing is about **25.7 kJ/mole**, but for **Br₂** the energy of the vibrational energy level spacing is only **3.79 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 **CO** but they do for **Br₂**. (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 $\frac{1}{2} k_B T \text{ J}$ per each molecular "degree of freedom", i.e., $\frac{1}{2} RT \text{ J/mol}$. 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 $7/2 RT$, and therefore $C_{v,m} = 7/2 R$ and $C_{p,m} = 9/2 R$, but at room temperature most diatomics have $C_{v,m}$ close to $5/2 R$ and therefore $C_{p,m}$ close to $7/2 R$. 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 (but not needed to work this problem), the vibrational energy level spacing = $h\nu_{\text{vib}}$. ν_{vib} for CO = 2150 cm^{-1} ; ν_{vib} for Br₂ = 317 cm^{-1} ; the difference is because C and O are light atoms and CO bond is a very strong triple bond. Br₂ has a weak single bond and the atoms are much heavier.)

Exam 2 is on Friday, October 13, 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.