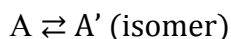


Biophysical Chemistry – CH 4404 01
Assignment 5

Due Friday, October 4, at 5:00 pm

Please complete the answers to this assignment on a separate page (or pages), showing your work and sources (if you referred elsewhere for constants, enthalpies, etc.).

1. Tinoco chapter 4, question 4. (6 points)
2. Tinoco chapter 4, question 9, parts (a) and (b). The value of $\Delta\bar{G}^{\circ}$ hydrolysis of ATP is given question 4.4 (above), and you can use your K from that question. (6 points)
3. Consider two reactions: the first has an equilibrium constant that is 8.4 times the equilibrium constant of the second. If the standard state Gibbs energy of the first at standard temperature and pressure is -250 kJ mol^{-1} , what is the standard state Gibbs energy of the second? (4 points)
4. The pK_A of ammonia is 9.25. What is the pH of the solution when 2.75 g of ammonium chloride (NH_4Cl , FW 53.491) are added to 100 mL of water? (4 points)
5. Consider two isomers of a compound that exist in equilibrium in solution:

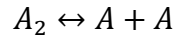


The following data was obtained for this reaction at multiple temperatures at 1 atm and pH 7.

T (°C)	0	20	30	45
K	0.1023	0.1000	0.0990	0.0976

- a. Assuming that $\Delta\bar{H}^{\circ}$ and $\Delta\bar{S}^{\circ}$ are constant over this temperature range, create a van't Hoff plot and determine $\Delta\bar{H}^{\circ}$ for this reaction. Submit a plot (with clearly labeled axes, legible axis labels, etc.) along with your work. Is this reaction endothermic or exothermic? (8 points)
- b. What is $\Delta\bar{G}^{\circ}$ at 25 °C? (4 points)
- c. If the total concentration of A is 100 mM, what is the concentration of each isomer at equilibrium at STP? (4 points)

6. It is common for DNA-binding proteins to form homodimers in their functional form. These dimers are stabilized by noncovalent interactions like hydrophobic packing and hydrogen bonding. The following equilibrium must be established:



- (a) If the total amount of protein A in solution is $50 \mu\text{M}$, and the equilibrium constant (K_{eq} , also called K_D for “dissociation constant”) for the reaction is 75×10^{-6} , what are the final concentrations of A and A_2 ? Note that successive approximations will not work for this problem; you will have to solve the quadratic equation. (4 points)

In the literature, K_D values are often expressed with units of concentration, i.e. K_D would be given as $75 \mu\text{M}$ in the example above. Even though K_{eq} values are defined to be unitless (since activities have no units), this can be a useful convention, because at $[A] = K_D$, the population of monomers and dimers is equal. We’ll explore this idea below.

- (b) It is very difficult to estimate the concentration of proteins in a cell, but suppose A has a total concentration of 1 nM . At this concentration, what is the K_D required so that 95% of A is dimeric? (4 points)

Hint: The fraction of A in dimeric form is given by $f = \frac{2[A_2]}{A_{\text{tot}}} = \frac{2[A_2]}{[A] + 2[A_2]}$. Combine this equation with the equation for the equilibrium constant to obtain an expression for K_D in terms of A_{tot} and f . You can check your work using the property of the K_D given above.

- (c) **Bonus Question:** Explain why when $[A] = K_D$, $f = 2/3$ and not $1/2$, even though the population of monomers and dimers is equal. (2 points)
7. Tinoco chapter 4, question 32. For part (a), you will have to develop a “fraction bound” expression similar to you were given in question 6, part (b). Obviously, it is *not* identical to the expression there, but the derivation is similar. As a hint, you may wish to set up a “mass balance table” for the equilibrium and express the fraction bound in terms of the variables you use there. (10 points)
8. Tinoco chapter 4, question 19. (8 points)