Chemistry 130A - Midterm 1

50 minute open book exam

September 26, 1994

Read the whole test, then do the easiest parts first.

1. (30 points)

a). How much heat is evolved or absorbed when 1 mol of the peptide glycylglycine is hydrolyzed to 2 mol of glycine at a pressure of 1 atm at 25°C? You may assume that the molar enthalpies of the molecules are the same in the solid and in solution.

b) How much heat is evolved or absorbed if the reaction involves 10 mL of a 0.10 M solution of glycylglycine? All other conditions are the same as in part (a).

c) Write the equation you would use to calculate the heat effect at 37°C. Define the parameters in your equation, but do not calculate.

d) If heat is evolved in a reaction at constant P, will the equilibrium constant K, increase or decrease with increasing T? Write the equation that would allow you to calculate the change in K with temperature.

e) For the reaction in part (a), the K can be written as $$K = \frac{[Gly]^2}{[Glygly]}$$

Name _____ 2

If we assume that equilibrium activities can be replaced by equilibrium concentrations, what is the change in K when we double the concentrations of Glygly and Gly in the experiment? What is the change in $\Delta G°$? What is the change in ΔG? You do not have to calculate $\Delta G°$ to answer this question.

2. (25 points)

a) If a molecule, such as butyric acid, forms a hydrogen-bonded dimer in the gas phase (2 butyric acid $\rightarrow$ dimer), we know that the entropy decreases. Explain in one or two sentences why we can not predict the sign of the entropy change, if butyric acid forms a dimer in aqueous solution.

b) Describe what experimental measurements we could make to obtain the standard entropy change when 2 butyric acid (aqueous) $\rightarrow$ dimer (aqueous) at 25°C. State what you measure (not calculate) and how it is related to $\Delta S°$ for the reaction.

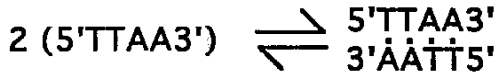
c) Calculate the change in entropy, in J K^{-1} when 2 mol of liquid ethanol is heated irreversibly at 1 atm from 20°C to 30°C.

d) State the second law of thermodynamics precisely in one sentence. If we consider the earth and its atmosphere as a system, can the entropy of this system decrease?

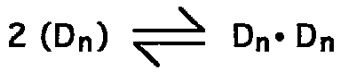
Name _____ 3

3. (30 points)

a) Use the nearest-neighbor values in the handout sheet to calculate the equilibrium constant at 25°C for the reaction



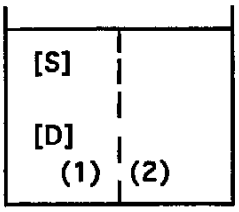
b) The melting temperature for a different self-complementary deoxyoligonucleotide, D_n, was found to be 65°C for a solution of 1.00×10^{-4} M strands. The melting temperature is defined as the temperature for which half the strands are in the double-stranded helix. Calculate K at 65°C for the reaction



c) At 45°C the equilibrium constant (K_{45}) is 2 times the equilibrium constant at 65°C (K_{65}). Calculate $\Delta H°$ for the reaction. You don't need to do (b) to do (c).

Name _____ 4

d) A semi-permeable membrane can be obtained which allows the single strands and solvent to pass, but prevents passage of the double-stranded molecules. We start an experiment with the membrane separating equal volumes of solvent and add oligonucleotide to one side of the compartment. An equilibrium mixture of single strands [S] and double strands forms.



(initial state)

After 24 hours at constant T, P, equilibrium is reached across the membrane. What are the concentrations of single strands and double strands on each side at equilibrium? (Final state)

$[S]_1 =$ $[D]_1 =$

$[S]_2 =$ $[D]_2 =$

Does G (final state) - G (initial state) increase, decrease or remain the same? Does S (final state) - S (initial state) increase, decrease or remain the same?

4. (15 points)

a) Calculate the standard free energy (kJ mol^{-1}) of ionization of pyruvic acid in aqueous solution at 25°C. Use solute standard states with concentrations in molarities.

b) Calculate the change in the actual free energy of ionization when 1 mol of 1.00×10^{-3} M pyruvic acid ionizes to give 1.00×10^{-4} M H^+ and 1.00×10^{-4} M pyruvate. You can do (b) without doing (a).

c) Write the chemical reaction that corresponds to the standard free energy of ionization. What are the standard states for each species?