

## Molecular Biophysics, Physics 177, Spring 2008

# Homework # 1 Thermodynamics Review

Assigned February 7, 2008.

Due February 15, 2008 5 PM to Jeff or the drop box outside Birge 225.

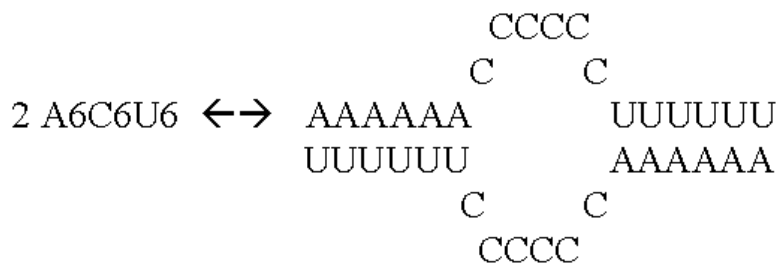
1. Photosynthesis by land plants leads to the fixation each year of about 1 kg of carbon on the average for each square meter of an actively growing forest. The atmosphere is approximately 20% O<sub>2</sub>, and 80% N<sub>2</sub>, but contains 0.046% of CO<sub>2</sub>.
  - a. What volume of air (25 °C and 1 atm) is needed to provide this 1 Kg. of carbon?
  - b. How much carbon is present in the entire atmosphere lying above each square meter of the earth surface?
  - c. At the current rate of utilization, how long would it take to use all the CO<sub>2</sub> in the entire atmosphere above the forest? (Obviously you will have to ignore atmospheric circulation and replenishment from the oceans, rocks, combustion of fuels, respiration of animals, and decay of biological material).
2. Biological organisms have been discovered living at great depths at the bottom of the ocean. The properties of common substances are greatly altered there because of the enormous hydrostatic pressures caused by the weight of the ocean lying above. The organisms need to equilibrate their internal pressures with this external hydrostatic pressure to prevent being crushed.
  - a. Calculate the hydrostatic pressure in the ocean at depth 2500 m.
  - b. Except near sources of heat, such as vents of hot gases coming from the earth's mantle, the temperature is close to 4°C. Calculate the percentage increase in density of the liquid water under these conditions compared with that at the surface. The isothermal compressibility of liquid water at 4°C is  $49.5 \times 10^{-6} \text{ atm}^{-1}$
  - c. Consider a balloon filled with O<sub>2</sub> at 1 atm pressure and occupying a 10 L volume at 293 K. Determine its volume at a depth of 2500 m below the ocean surface, at 277 K.
3. One mole of liquid water at 100 °C is heated until the water is converted entirely to vapor at 100 °C and 1 atm of pressure. Calculate q, w, ΔE and ΔH. For each of the following conditions:
  - a. The vaporization is carried out in a cylinder where the external pressure on the piston is maintained at 1 atm of pressure throughout.
  - b. The cylinder is first expanded against a vacuum ( $P_{\text{ext}} = 0$ ) to the same volume as in part (a) , and then sufficient heat is added to vaporize the liquid completely to 1 atm pressure.
4. Transitions from order, helical conformations of polypeptides and polynucleotides to disordered states are accompanied by positive enthalpy and entropy changes. However, when the synthetic polypeptide polybenzyl-L-glutamate undergoes a transition from an

ordered helix to a disordered coil in an ethylene dichloride-dichloroacetic acetic solvent at 39 °C and 1 atm,  $\Delta H^\circ = -4.0$  kJ (per mol amide) and  $\Delta S^\circ = -12$  J $^\circ$ K $^{-1}$  (per mol amide).

- Give a possible explanation for the experimental result that heat is released and entropy is decreased for this transition. Does increasing the temperature favor the helix-coil transition?
  - Is the reaction spontaneous at 39 °C? What thermodynamic criterion did you use to reach this conclusion?  
At what temperature (°C) will the helix-coil reaction be reversible? This temperature is often called the "melting" temperature of the helix. Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.
  - Can a reaction occur in an isolated system which leads to a decrease in the entropy of the system? If it can, give an example; if it cannot, state why not.
5. A single stranded polynucleotide that has complementary ends can form a base-paired hairpin loop:



- At 25 °C the equilibrium constant  $K_1 = 0.86$ . What are the concentrations of loop and single strand at equilibrium if the initial concentration of single strands is 1.00 mM? Will increasing the initial concentration of oligonucleotide increase or decrease the fraction of hairpin loop? Explain.
- At 37 °C the equilibrium constant  $K_1 = 0.51$ . Calculate,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ , at this temperature.
- As the concentration of oligonucleotide is increased, another reaction becomes possible. A double-stranded molecule with an internal loop can form:



At 25 °C,  $K_2 = 1.00 \times 10^{-2} \text{ M}^{-1}$  (and  $K_1 = 0.86$ ). Calculate the concentrations of all three species (single strands, ss, double strands, ds, and hairpin loop, h) at equilibrium in a solution of initial concentration of single strands of 0.100 M.

- Derive an expression for the equilibrium constant  $K$  as a function of  $c$ , the initial concentration of single strands, and  $f$ , the fraction of single strands that are in the double-stranded helix at equilibrium as:  $2S \leftrightarrow D$ . (With  $K = [D]/[S]^2$ ).