

Answer at least 8 (any 8) of the following 10 questions. The two remaining questions will be graded for extra credit. Please show your work clearly. Feel free to use the back of the pages of the exam if necessary, but be concise. No credit will be given for unnecessary information.

1. A protein is shown to unfold with a ΔH of 100 kcal/mol at a T_m of 50 °C. What is the change in entropy at 50°C?
2. The ΔC_p for unfolding of the protein in problem 1 is shown to be 1000 cal/deg/mol by DSC. Plot what you would expect the DSC data to look like given the information provided here and in problem 1. Indicate clearly those aspects of the DSC plot which are determined by the information provided.
3. Given the information in problems 1 and 2, calculate the ΔH for unfolding the protein at room temperature (25 °C).
4. Define “chemical potential” mathematically. What is the relationship between the chemical potentials of two species at equilibrium?
5. The association constant for ATP binding to myosin is 10^{11} M. What is the standard state free energy of binding? What can you say about the enthalpy of binding given this information?
6. What is the difference between a van’t Hoff enthalpy and a calorimetric enthalpy? How are the two determined?
7. The association of two hydrophobic groups in water is associated with a positive change in enthalpy, an increase in entropy, a decrease in free energy, and a decrease in heat capacity. Rationalize these changes in terms of solvent and solute interactions.
8. Consider one liter of 1 mole of an ideal monatomic gas at 25 °C. Compress the gas reversibly and isothermally to 0.5 liter. What is the change in entropy?
9. Describe the four steps in a Carnot cycle. What is the heat change in each? Discuss the importance of the Carnot cycle in the development of the second law of thermodynamics.

Fundamental constants and conversion factors

$$1 \text{ cal} = 4.184 \text{ J} \quad (\text{the mechanical equivalent of heat})$$

$$1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm}$$

$$1 \text{ erg} = 1 \text{ g cm}^2 \text{ s}^{-2}$$

$$1 \text{ joule} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ atm} = 1.013 \text{ newton m}^{-2}$$

$$1 \text{ watt} = 1 \text{ J s}^{-1}$$

$$1 \text{ L atm} = 101.3 \text{ J} = 24.22 \text{ cal}$$

$$\text{Boltzmann's constant } k \quad 1.38066 \times 10^{-23} \text{ J/K}$$

$$\begin{array}{l} \text{Gas constant} \quad R \quad 8.3144 \text{ J/(K mole)} \\ \quad \quad \quad \quad \quad \quad 1.99 \text{ cal/(K mole)} \\ \quad \quad \quad \quad \quad \quad 0.082 \text{ L atm/(deg mole)} \end{array}$$

$$C_v \text{ (ideal, monatomic gas)} \quad 3/2nR \quad 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p \text{ (ideal, monatomic gas)} \quad 5/2nR \quad 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Fundamental equations

$$PV = nRT$$

$$\Delta E = q + w$$

$$\Delta S = q_{\text{rev}}/T$$

$$H = E + PV$$

Hints:

1. ΔG° at the T_m is zero.
2. Use the ΔH at the T_m , the T_m and the ΔC_p to sketch a DSC curve given the information in the DSC handout.
3. $\Delta H(T) = \Delta H(T_m) + \Delta C_p (T - T_m)$
4. See the textbook and your notes.
5. $\Delta G^\circ = -RT \ln K$. You cannot say anything about ΔH given this information.
6. A van't Hoff enthalpy is obtained indirectly from the temperature dependence of an equilibrium constant. A calorimetric enthalpy is obtained from a direct measurement of a heat change.
7. The association of two hydrophobes leads to a decrease in organized ("ice berg") water around the hydrophobes. The increase in enthalpy presumably indicates that the organized waters had a stronger enthalpy of association. The increase in entropy results from the release of the organized water. The decrease in ΔG indicates that $T\Delta S$ is greater than the increase in ΔH . The decrease in DCP results from the decrease in organized water around the separated hydrophobes when they associate.
8. Calculate the heat change for the isothermal compression (-411 cal). The entropy change is q/T .
9. See your text and notes.