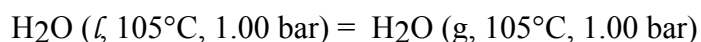


20.110/5.60/2.772 Fall 2005
Homework #3
Due Friday September 30

1. **What is constant?** For each of the following processes, specify which of q , w , ΔU , ΔH , ΔS are zero (give **all** of the ones that are zero).
- (a) A nonideal gas is taken around a Carnot cycle.
 - (b) A nonideal gas is adiabatically expanded through a throttling valve in a Joule-Thomson experiment
 - (c) Liquid water is vaporized at 100 °C and 1 atm.
 - (d) H₂ and O₂ react to form H₂O in a thermally isolated bomb calorimeter.
 - (e) One mole of an ideal gas is compressed along a reversible adiabat.
2. **Entropy and spontaneous change.** Calculate the change in entropy when one mole of water undergoes the following irreversible change in state.



In order to do this, you must devise a reversible path to go from the initial to the final state. You have the following information: the ΔH of vaporization of liquid water is 40,508 J mol⁻¹ at 100.0 °C; the molar heat capacity of H₂O (l) is 75.3 J K⁻¹ and that of H₂O (g) is 37.5 J K⁻¹. Both of these heat capacities can be taken as independent of T in the range 100-105 °C.

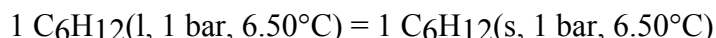
3. **Entropy changes in thermodynamic processes.** Physical data for water are given below. Use this information to calculate the entropy change when:
- a. Two moles of H₂O (g) are cooled at constant pressure from 120°C to 100°C by placing the container of steam initially at 120°C in a large room that has a constant temperature of 100°C.
 - b. One mole of H₂O (g) is expanded at constant pressure of 2 bar from an original volume of 20 L to a final volume of 25 L. You can consider the gas to be ideal.
 - c. One hundred grams of H₂O (s) at -10°C and 1 bar are heated to H₂O (l) at 10°C and 1 atm.

$$C_{p,\text{H}_2\text{O}(\text{s})} = 38.07 \frac{\text{J}}{\text{mole} \cdot \text{K}} \qquad C_{p,\text{H}_2\text{O}(\text{l})} = 75.31 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$
$$C_{p,\text{H}_2\text{O}(\text{g})} = 33.76 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$
$$\Delta H_{m,\text{H}_2\text{O}} = 6006.5 \frac{\text{J}}{\text{mole}}$$

(from problem 3.21 p. 120 Tinoco, Sauer, and Wang, *Physical Chemistry: Principles and Applications in Biological Sciences*, 3rd ed., Prentice-Hall, Englewood Cliffs, New Jersey (1995))

- 4. Entropy change and the system.** A flask initially containing several moles of liquid cyclohexane ($\Delta H_{\text{fus}} = 2630 \text{ J mol}^{-1}$) at its normal (1 bar) freezing point of 6.50°C is placed in thermal contact with an ice water bath (at 0.00°C) until 1.00 mole of cyclohexane has frozen, and the flask is then removed from the bath. ($\Delta H_{\text{fus}} = 5980 \text{ J mol}^{-1}$ for H_2O).

(a) the change in state which occurs in the flask of cyclohexane is



Calculate ΔS for the cyclohexane during the above process.

(b) Give the change in state that occurs in the ice water bath during the above process and calculate ΔS for this change in state. Assume that the combined system of the cyclohexane and the ice water bath forms an isolated system that is adiabatically decoupled from all surroundings.

(c) Calculate ΔS_{total} for the combined isolated system during the above process. Does the process described above occur reversibly or irreversibly?

- 5. Entropy always increases... or does it?** A sealed container of 1 mole of water at 4°C (beaker (A)) is placed in contact with a second container of water (also 1 mole) that has an initial temperature of 60°C (beaker (B)), and the two are enclosed by thermal insulation so that they form an approximately isolated system at a constant pressure (1 bar). The molar heat capacity of water is approximately constant during the ensuing changes in the system with a value of $75 \text{ J mole}^{-1} \text{ K}^{-1}$.

d. What is the final temperature of the water in beaker (A)? In beaker (B)?

e. What is the entropy change in the water in beaker (B)?

f. Show quantitatively why the result in part b does not violate the second law.

g. Suppose now that we were to take the sealed beaker (B) at 60°C and instead immerse it in a very large heat bath equilibrated at a temperature of 4°C . What is the final temperature of the water in beaker (B) at equilibrium? What is the entropy change in beaker (B)?

h. Show quantitatively that the result in part d does not violate the second law.

- 6. Expansions, entropy, and free energy.** One mole of ideal gas is expanded at 400.0 K isothermally from a pressure of 10.0 bar to 3.0 bar .

(a) calculate w , q , ΔU , ΔH , ΔS , ΔG for this change of state if done reversibly.

(b) calculate w , q , ΔU , ΔH , ΔS , ΔG for this change of state if done irreversibly against zero external pressure (i.e. a "free" expansion).

- 7. Gibbs free energy and irreversibility.** Calculate the molar Gibbs energy G of fusion when supercooled water at -3°C freezes at constant T and P . The enthalpy of fusion of ice is 6000 J mol^{-1} at 0°C . The heat capacities of water and ice in the vicinity of the freezing point are 75.3 and $38 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.
- 8. Gibbs free energy and mixing.** Calculate ΔG_{mix} and ΔS_{mix} (a) for the formation of a quantity of air containing 1 mole of gas by mixing nitrogen and oxygen at 298.15 K . Air may be taken to be 80% nitrogen and 20% oxygen; (b) for mixing 2 mol of H_2 with 1 mol of O_2 at 25°C under conditions where no chemical reaction occurs.
- 9. ‘Melting’ secondary structures in biopolymers.** Given below are thermodynamic data for the transformation of DNA from double-stranded to single-stranded (denaturation) and the transformation of a synthetic polypeptide, poly(benzyl L-glutamate), from an ordered helix structure to a disordered random coil- each in the stated solvent and temperature conditions.
- What is the free energy for denaturation of DNA at 37°C ? Will DNA denaturation occur spontaneously at this temperature?
 - If the enthalpy and entropy changes of denaturation vary only weakly with temperature, can we cause this denaturation reaction to become spontaneous by raising the temperature? How do you know?
 - Consider now the helix to coil transition given below for poly(benzyl L-glutamate). Is this transition spontaneous at 39°C ?
 - Give a possible explanation for the signs of ΔH° and ΔS° for the poly(benzyl L-glutamate transition). Does increasing the temperature favor the helix-to-coil transition?
 - Assuming the enthalpy and entropy changes for the helix-to-coil transition are approximately constant over a significant temperature range, at what temperature would the helix and coil forms of the polypeptide be in equilibrium?

Transition	ΔH°	ΔS°
DNA double-strand to single-strand in 1 M NaCl at 37°C , 1 atm	$\sim 35 \text{ kJ/mole base pairs}$	$\sim 88 \text{ J/(mole base pairs K)}$
Poly(benzyl L-glutamate) helix-to-disordered coil in ethylene dichloride/dichloroacetic acid solvent at 39°C , 1 atm	$-4.0 \text{ kJ/mole amide bonds}$	$-12 \text{ J/(mole amide bonds K)}$

(based on problem 3.17, p. 119 Tinoco, Sauer, and Wang, *Physical Chemistry: Principles and Applications in Biological Sciences*, 3rd ed., Prentice-Hall, Englewood Cliffs, New Jersey (1995))

- 10. Disease and thermodynamics.** It is believed that the dimerization of a certain protein “A” controls the signaling by growth factor, and that a disease that is associated with two amino

acid mutations in protein “A” is related to a change in the dimerization equilibrium. The dimerization reaction can be written: $2A = A-A$ where A-A represents the dimer. The standard enthalpy changes and entropy changes for the dimerization reaction for the WT protein (A_{WT}) and the mutant protein (A_M) are as follows:

Protein	ΔH^0 , Kcal/mol	ΔS^0 , Kcal/(mol-K)
A_{WT}	57.0	0.185
A_M	39.0	0.105

- Does either protein spontaneously dimerize at 37°C under standard conditions?
- For each protein, at what temperature does the dimerization process become spontaneous under standard conditions? If body temperature is 335K, then is the

Additional Practice Problems (not graded):

- Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is $146.22 \text{ JK}^{-1} \text{ mol}^{-1}$ at 298 K. (Assume ideal gas if needed).
- A sample consisting of 1.00 mol of a monatomic ideal gas with $\bar{C}_V = \frac{3}{2}R$ is heated from 100°C to 300°C at constant pressure. Calculate ΔS (for the system).
- Show that
$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \quad \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$
- A sample of 3.00 mol of a diatomic ideal gas at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5 \text{ JK}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS .
- A system undergoes a process in which the entropy change is $+2.41 \text{ JK}^{-1}$. During the process, 1.00 kJ of heat is added to the system at 500 K. Is the process thermodynamically reversible? Explain your reasoning.
- Calculate the change in entropy when 50 g of water at 80°C is poured into 100 g of water at 10°C in an insulated vessel given that $C_{p,m} = 75.5 \text{ JK}^{-1} \text{ mol}^{-1}$
- Consider a system consisting of 2.0 mol $\text{CO}_2(\text{g})$, initially at 25°C and 10 bar and confined to a cylinder of 10 cm^2 cross-section. It is allowed to expand adiabatically against an external pressure of 1.0 bar until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered an ideal gas with $C_{V,m} = 28.8 \text{ JK}^{-1} \text{ mol}^{-1}$ and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , and (e) ΔS .

8. Calculate the Carnot efficiency of a primitive steam engine operating on steam at 100°C and discharging at 60°C . Repeat the calculation for a modern steam turbine that operates with steam at 300°C and discharges at 80°C .

9. Helium is compressed isothermally and reversibly at 100°C from a pressure of 2 to 10 bar. Calculate (a) q per mole, (b) w per mole, (c) $\Delta\bar{G}$, (d) $\Delta\bar{A}$, (e) $\Delta\bar{H}$, (f) $\Delta\bar{U}$, (g) $\Delta\bar{S}$, assuming that helium is an ideal gas.

10. Toluene is vaporized at its boiling point, 111°C . The heat of vaporization at this temperature is 361.9 g^{-1} . For the vaporization of toluene, calculate (a) w per mole, (b) q per mole, (c) $\Delta\bar{H}$, (d) $\Delta\bar{U}$, (e) $\Delta\bar{G}$, (f) $\Delta\bar{S}$.