

Problem Set #7, Chem 340, Fall 2013

– Due Friday, Oct 18, 2013

Please show all work for credit

To hand in :

1. Atkins 3.11(b)

3.11(b) Calculate the standard Gibbs energy of the reaction $\text{CO(g)} + \text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{COOH(l)}$ at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

2. Atkins 3.18 (b)

3.18(b) Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm^{-3}) when the pressure is increased isothermally from 100 kPa to 100 MPa. Take $k_T = 1.26 \times 10^{-9} \text{ Pa}^{-1}$.

3. Atkins 3.19 (b)

3.19(b) Calculate the change in chemical potential of a perfect gas that its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50°C .

4. Atkins 3.16

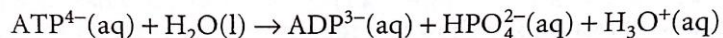
3.16 Calculate $\Delta_r G^\circ(375 \text{ K})$ for the reaction $2 \text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$ from the value of $\Delta_r G^\circ(298 \text{ K})$, $\Delta_r H^\circ(298 \text{ K})$, and the Gibbs–Helmholtz equation.

5. Atkins 3.26

3.26 Use the Maxwell relations to express the derivatives (a) $(\partial S/\partial V)_T$ and $(\partial V/\partial S)_p$ and (b) $(\partial p/\partial S)_V$ and $(\partial V/\partial S)_p$ in terms of the heat capacities, the expansion coefficient α , and the isothermal compressibility, κ_T .

6. Atkins 3.38

3.38 In biological cells, the energy released by the oxidation of foods (*Impact I2.2*) is stored in adenosine triphosphate (ATP or ATP^{4-}). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP^{3-}):



At $\text{pH} = 7.0$ and 37°C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are $\Delta_r H = -20 \text{ kJ mol}^{-1}$ and $\Delta_r G = -31 \text{ kJ mol}^{-1}$, respectively. Under these conditions, the hydrolysis of 1 mol $\text{ATP}^{4-}(\text{aq})$ results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at $\text{pH} = 7.0$ and 310 K. (b) Suppose that the radius of a typical biological cell is $10 \mu\text{m}$ and that inside it 10^6 ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre ($1 \text{ W} = 1 \text{ J s}^{-1}$)? A computer battery delivers about 15 W and has a volume of 100 cm^3 . Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol^{-1} of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

7. Atkins 3.40

3.40† Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Worsnop *et al.* investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (*Science* 259, 71 (1993)). They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours, $\text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O}(\text{g})$, for $n = 1, 2$, and 3 . Given $\Delta_r G^\ominus$ and $\Delta_r H^\ominus$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^\ominus$ at 190 K.

n	1	2	3
$\Delta_r G^\ominus / (\text{kJ mol}^{-1})$	46.2	69.4	93.2
$\Delta_r H^\ominus / (\text{kJ mol}^{-1})$	127	188	237

8. Engel P5.36

P5.36 From the following data, derive the absolute entropy of crystalline glycine at $T = 300$ K. [*Hint*: You can perform the integration numerically using either a spread sheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.10).]

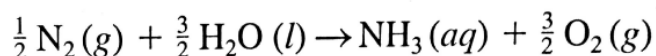
Temperature (K)	Heat Capacity $C_{P,m}^\ominus$ ($\text{J K}^{-1} \text{mol}^{-1}$)
10	0.3
20	2.4
30	7.0
40	13.0
60	25.1
80	35.2
100	43.2
120	50.0
140	56.0
160	61.6
180	67.0
200	72.2
220	77.4
240	82.8
260	88.4
280	94.0
300	99.7

9. Engel P5.45

P5.45 From a DSC experiment it is determined that for the denaturation of a protein $\Delta H = 640.1 \text{ kJ mol}^{-1}$ at $T_m = 340 \text{ K}$ and $P = 1 \text{ bar}$. Calculate ΔS for this denaturation at $T = 340 \text{ K}$ and $P = 1 \text{ atm}$. Determine the entropy and enthalpy changes at $T = 310 \text{ K}$ assuming $\Delta C_p = 8.37 \text{ kJ K}^{-1} \text{ mol}^{-1}$ is independent of temperature between $T = 310. \text{ K}$ and $T = 340. \text{ K}$.

10. Engel P6.13

P6.13 Nitrogen is a vital element for all living systems; except for a few types of bacteria, blue-green algae, and some soil fungi, organisms cannot utilize N_2 from the atmosphere. The formation of “fixed” nitrogen is therefore necessary to sustain life and the simplest form of fixed nitrogen is ammonia NH_3 . Living systems cannot fix nitrogen using the gas-phase components listed in Problem P6.12. A hypothetical ammonia synthesis by a living system might be:



where (aq) means the ammonia is dissolved in water.

Calculate the standard free energy change for the biological synthesis of ammonia and calculate the equilibrium constant as well. Based on your answer, would the biological synthesis of ammonia occur spontaneously? Note that $\Delta G_f^\circ(\text{NH}_3, aq) = -80.3 \text{ kJ mol}^{-1}$.

11. Engel P6.20

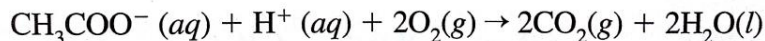
P6.20 Calculate the Gibbs energy change for the protein denaturation described in Problem 5.45 at $T = 310. \text{ K}$ and $T = 340. \text{ K}$.

Extra problems (do not hand in)

- Atkins 3.12 (b)
3.12(b) The standard enthalpy of combustion of solid urea ($\text{CO}(\text{NH}_2)_2$) is -632 kJ mol^{-1} at 298 K and its standard molar entropy is $104.60 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of urea at 298 K.
- Atkins 3.16 (b)
3.16(b) Suppose that 2.5 mmol Ar(g) occupies 72 dm^3 at 298 K and expands to 100 dm^3 . Calculate ΔG for the process.
- Atkins 3.17 (b)
3.17(a) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\text{J} = -85.40 + 36.5(T/\text{K})$. Calculate the value of ΔS for the process.
- Atkins 3.21 (b)
3.21(b) Estimate the change in the Gibbs energy of 1.0 dm^3 of water when the pressure acting on it is increased from 100 kPa to 300 kPa.
- Atkins 3.24
3.24 Show that, for a perfect gas, $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -p$.
- Atkins 3.25
3.25 Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.
- Atkins 3.28
3.28 Derive the thermodynamic equation of state
$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$
Derive an expression for $(\partial H/\partial p)_T$ for (a) a perfect gas and (b) a van der Waals gas. In the latter case, estimate its value for 1.0 mol Ar(g) at 298 K and 10 atm. By how much does the enthalpy of the argon change when the pressure is increased isothermally to 11 atm?
- Atkins 3.37
3.37 At 298 K the standard enthalpy of combustion of sucrose is $-5797 \text{ kJ mol}^{-1}$ and the standard Gibbs energy of the reaction is $-6333 \text{ kJ mol}^{-1}$. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37°C .

9. Engel P5.27

P5.27 In the Krebs cycle, degradation of the carbon skeleton of glucose is completed when acetate ion is oxidized to carbon dioxide and water. The net reaction for the Krebs cycle is:



Calculate the entropy change for this reaction at $T = 298 \text{ K}$.

10. Engel P5.20

P5.20 Consider the formation of glucose from carbon dioxide and water, that is, the reaction of the following photosynthetic process: $6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$. The following table of information will be useful in working this problem:

$T = 298 \text{ K}$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(l)$	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	$\text{O}_2(g)$
$\Delta H_f^\circ \text{ kJ mol}^{-1}$	-393.5	-285.8	-1273.1	0.0
$S^\circ \text{ J mol}^{-1} \text{ K}^{-1}$	213.8	70.0	209.2	205.2
$C_{p,m}^\circ \text{ J mol}^{-1} \text{ K}^{-1}$	37.1	75.3	219.2	29.4

Calculate the entropy and enthalpy changes for this chemical system at $T = 298 \text{ K}$ and $T = 330. \text{ K}$. Calculate also the entropy of the surrounding and the universe at both temperatures.

11. Engel P 5.41

P5.41 For protein denaturations, the excess entropy of

denaturation is defined as $\Delta S_{den} = \int_{T_1}^{T_2} \frac{\delta C_P^{trs}}{T} dT$, where δC_P^{trs} is

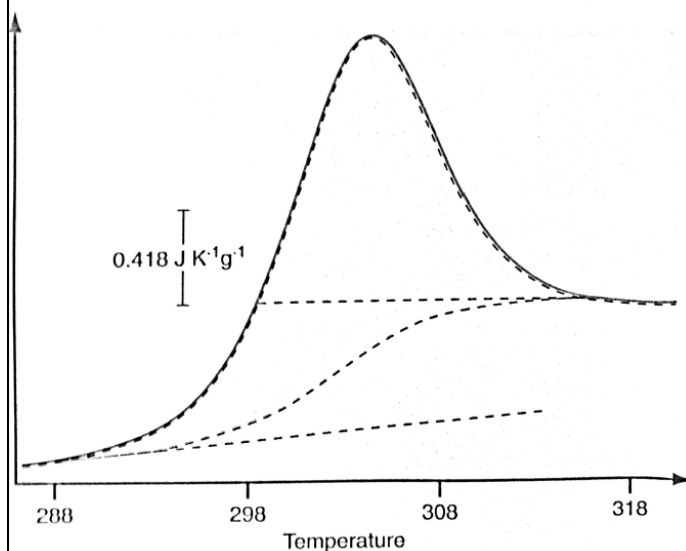
the transition excess heat capacity (see Section 4.10). Using the equation for ΔS_{den} given here, calculate the excess entropy of denaturation from the differential scanning calorimetry data given in Problem P4.31. Assume the molecular weight of the protein is 14000. grams. [Hint: You can perform the integration numerically using either a spread sheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.10).]

P5.42 Using the data in Problem P5.42 and the equation

$\Delta H_{den} = \int_{T_1}^{T_2} \delta C_P^{trs} dT$, calculate δS_{den} . Assume the denaturation

occurs reversibly. (Hint: Determine ΔH_{den} graphically then determine T_m .) [Hint: You can perform the integration numerically using either a spread sheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.10).]

P4.31 The figure below shows a DSC scan of a solution of a T4 lysozyme mutant. From the DSC data, determine T_m , the excess heat capacity δC_p , and the intrinsic and transition excess heat capacities at $T = 308$ K. In your calculations, use the extrapolated curves, shown as dashed lines in the DSC scan.

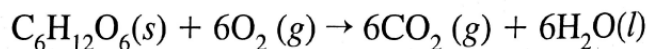


12. Engel P6.4

P6.4 A sample containing 2.50 mol of an ideal gas at 298 K is expanded from an initial volume of 10.0 L to a final volume of 50.0 L. Calculate ΔG and ΔA for this process for (a) an isothermal reversible path and (b) an isothermal expansion against a constant external pressure of 0.750 bar. Explain why ΔG and ΔA do or do not differ from one another.

13. Engel P6.9

P6.9 James Watt once observed that a hard-working horse can lift a 330.-lb weight 100. ft in 1 min. Assuming the horse generates energy to accomplish this work by metabolizing glucose:



calculate how much glucose a horse must metabolize to sustain this rate of work for 1 hour at $T = 298.15$ K?