To hand in:

1. Atkins 3.11(b)  
   **3.11(b)** Calculate the standard Gibbs energy of the reaction CO(g) + CH₃OH(l) → CH₃COOH(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 kₜ = 1.26 × 10⁻⁹ 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 Δ_r G°(375 K) for the reaction 2 CO(g) + O₂(g) → 2 CO₂(g) from the value of Δ_r G°(298 K), Δ_r H°(298 K), and the Gibbs–Helmholtz equation.

5. Atkins 3.26  
   **3.26** Use the Maxwell relations to express the derivatives (a) (∂S/∂V)ₚ and (∂V/∂S)ₚ, and (b) (∂p/∂S)ᵥ and (∂V/∂S)ᵥ in terms of the heat capacities, the expansion coefficient α, and the isothermal compressibility, κₜ.

6. Atkins 3.38  
   **3.38** In biological cells, the energy released by the oxidation of foods (*Impact* 12.2) is stored in adenosine triphosphate (ATP or ATP⁴⁻). The essence of ATP’s action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP³⁻):

   \[
   \text{ATP}^{4-}(aq) + H₂O(l) \rightarrow \text{ADP}^{3-}(aq) + \text{HPO}_₄^{2-}(aq) + H₂O⁺(aq)
   \]

   At pH = 7.0 and 37°C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are Δ_r H = −20 kJ mol⁻¹ and Δ_r G = −31 kJ mol⁻¹, respectively. Under these conditions, the hydrolysis of 1 mol ATP⁴⁻(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 pH = 7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 10⁶ ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre (1 W = 1 J s⁻¹)? A computer battery delivers about 15 W and has a volume of 100 cm³. 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

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, \( \text{HNO}_3 \cdot n\text{H}_2\text{O(s)} \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O(\text{g})} \), for \( n = 1, 2, \) and 3. Given \( \Delta_r G^\circ \) and \( \Delta_r H^\circ \) for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute \( \Delta_r G^\circ \) at 190 K.

<table>
<thead>
<tr>
<th>( n )</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_r G^\circ/(\text{kJ mol}^{-1}) )</td>
<td>46.2</td>
<td>69.4</td>
<td>93.2</td>
</tr>
<tr>
<td>( \Delta_r H^\circ/(\text{kJ mol}^{-1}) )</td>
<td>127</td>
<td>188</td>
<td>237</td>
</tr>
</tbody>
</table>

8. Engel P5.36

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

| Temperature (K) | Heat Capacity \( C_{P,m}^\circ \) (J K\(^{-1}\)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 $\Delta S$ 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:

$$\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2\text{O}(l) \rightarrow \text{NH}_3(aq) + \frac{3}{2} \text{O}_2(g)$$

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 $\Delta G_f^o (\text{NH}_3, \text{aq}) = -80.3 \text{ kJ mol}^{-1}$.

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)

1. Atkins 3.12 (b)
   \textbf{3.12(b)} The standard enthalpy of combustion of solid urea \((\text{CO(NH}_2)_2\)) is 
   \(-632\ \text{kJ mol}^{-1}\) at 298 K and its standard molar entropy is \(104.50\ \text{J K}^{-1}\ \text{mol}^{-1}\).
   Calculate the standard Gibbs energy of formation of urea at 298 K.

2. Atkins 3.16 (b)
   \textbf{3.16(b)} Suppose that 2.5 mmol Ar(g) occupies 72 dm\(^3\) at 298 K and expands
   to 100 dm\(^3\). Calculate \(\Delta G\) for the process.

3. Atkins 3.17 (b)
   \textbf{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 \(\Delta S\) for the process.

4. Atkins 3.21 (b)
   \textbf{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.

5. Atkins 3.24
   \textbf{3.24} Show that, for a perfect gas, \((\partial U/\partial S)_V = T\) and \((\partial U/\partial V)_S = -p\).

6. Atkins 3.25
   \textbf{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
   \((\partial T/\partial p)_S = (\partial V/\partial S)_p\).

7. Atkins 3.28
   \textbf{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?

8. Atkins 3.37
   \textbf{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, \(37^\circ\text{C}\).
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:

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}^+ (aq) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)
\]

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:

<table>
<thead>
<tr>
<th>( T = 298 \text{ K} )</th>
<th>( \text{CO}_2(g) )</th>
<th>( \text{H}_2\text{O}(l) )</th>
<th>( \text{C}<em>6\text{H}</em>{12}\text{O}_6(s) )</th>
<th>( \text{O}_2(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_f^\circ \text{kJ mol}^{-1} )</td>
<td>393.5</td>
<td>285.8</td>
<td>1273.1</td>
<td>0.0</td>
</tr>
<tr>
<td>( S^\circ \text{J mol}^{-1}\text{K}^{-1} )</td>
<td>213.8</td>
<td>70.0</td>
<td>209.2</td>
<td>205.2</td>
</tr>
<tr>
<td>( C_{p,m}^\circ \text{J mol}^{-1}\text{K}^{-1} )</td>
<td>37.1</td>
<td>75.3</td>
<td>219.2</td>
<td>29.4</td>
</tr>
</tbody>
</table>

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 \( \delta C_p^{trs} \) is the transition excess heat capacity (see Section 4.10). Using the equation for \( \Delta S_{den} \) 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 spreadsheet 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 \( \delta S_{den} \). Assume the denaturation occurs reversibly. (**Hint:** Determine \( \Delta H_{den} \) graphically then determine \( T_m' \)) [**Hint:** You can perform the integration numerically using either a spreadsheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.10).]
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 \( \Delta G \) and \( \Delta A \) 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 \( \Delta G \) and \( \Delta A \) 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:

\[
C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)
\]

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