You may use a calculator, a one page reminder sheet, but no other aides during the examination. Read the examination over before beginning. There are 6 questions worth a total of 100 points. It may be prudent to begin with the questions about which you are most confident. Then of the remaining questions work the ones you are most confident, etc. If you need more space, use the back of these sheets. Please indicate you are doing so in the space provided for the answer.

Some questions have multiple parts. If you do not know the answer to the first part, you can receive significant partial credit on later parts by indicating how you would use the earlier answer if you had it, for example by using a variable to represent that answer.

You must show work to receive full credit

NOTES FOR MIDTERM 2, 1999: The exam given in 1996 covers only up to the phase equilibrium part of Chapter 6. I will assign some problems that cover phase equilibrium on Wednesday Feb. 17. The exam next week (Tuesday Feb. 23) will cover the material covered through lecture on Friday Feb. 19. This will likely go through the first four of five sections of Chapter 7 of Chang’s text. More details will be provided on Friday.
1. (20 points) Consider the reaction

\[ 2\text{C}_2\text{H}_2(g) + 5 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \]

With thermodynamic data for the standard states of the reactants and products at 298 K:

<table>
<thead>
<tr>
<th></th>
<th>( \Delta_f H^0 ) (kJ mol(^{-1}))</th>
<th>( S^0 ) (J mol(^{-1})K(^{-1}))</th>
<th>( C_{p,m} ) (J mol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_2)</td>
<td>226.73</td>
<td>200.94</td>
<td>43.93</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>-393.51</td>
<td>213.74</td>
<td>37.11</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-241.82</td>
<td>188.83</td>
<td>33.58</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.00</td>
<td>205.14</td>
<td>29.36</td>
</tr>
</tbody>
</table>

(a) (15 points) Using the information given above to calculate \( \Delta H \) and \( \Delta S \) for the reaction at 398 K, 1 bar. Assume all heat capacities are constant with temperature.

(b) (5 points) Will this process occur spontaneously? Justify your answer.
2. (20 points) For the following processes, determine whether each of the thermodynamic quantities listed are greater than, less than or equal to zero for the system described. Consider all gases to behave ideally. Indicate your reasoning and state explicitly any assumptions or approximations you need to make. Also indicate when answer is based on another part of the same question.

(a) (6 points) A sample of gas is carried through a complete Carnot cycle (isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression - all reversible).

i. \( w \)

ii. \( \Delta S \)

iii. \( \Delta G \)

(b) (8 points) A sample (A) of iron at temperature \( T_h \) is brought in contact with a second identical sample (B) of iron at a lower temperature \( T_c \) in a thermally isolated container. The final temperature is \( (T_h + T_c)/2 \). You may assume that the heat capacity of the iron is independent of temperature and \( m_A = m_B \).

Subscripts \( A \) and \( B \) indicate the separate pieces of iron. Quantities without subscripts are for the system (both samples A and B)

i. \( \Delta H \)

ii. \( \Delta S_A \)

iii. \( \Delta S_B \)

iv. \( \Delta S \)
(c) (6 points) When a rubber band is stretched, the polymer molecules which make it up are stretched [compare Figures (b) for the unstretched state and Figure (c) for the stretched state, below]. When it contracts it cools (i.e. heat is absorbed). To a first approximation, $\Delta U = 0$. What are the signs of $\Delta S$, $\Delta G$ and $\Delta H$ when a rubber band is allowed to contract?
3. (13 points)

(a) (8 points) Show that the expression for the volume dependence of $C_V$, at constant $T$, is given by:

$$\left( \frac{\partial C_V}{\partial V} \right)_T = T \left( \frac{\partial^2 p}{\partial T^2} \right)_V$$

(1)

where, $U = U(T, V)$ and

$$dU = C_V dT + \pi_T dV$$

(2)

(b) (5 points) Show that, at constant $T$, $C_V$ for a van der Waals gas

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

(3)

is not a function of volume.
4. (20 points) Consider the reversible adiabatic expansion of air from an initial pressure of 5.0 atm to a final pressure of 1.0 atm, \( C_{\text{V,m}} = 5/2R \) and is independent of temperature (for the purpose of this problem, you can assume that air behaves like a perfect gas).

(a) (4 points) What is \( C_{\text{p,m}} \) for air?

(b) (11 points) If the initial temperature and volume are \( T_i = 298 K \) and \( V_i = 10. L \), what are the final temperature and volume?

(c) (4 points) What are \( \Delta S \) of the system and surroundings for this process?
5. (15 points) Hydrogen bonding plays an extremely important role in biochemistry. For example, it is what determines the secondary structure in proteins and what holds together the two strands of DNA. One of the simplest examples of hydrogen bonding is the formation of dimers of malanaldehyde (HCO$_2$H) in the gas phase, where dotted lines represent hydrogen bonds:

The thermodynamic data for this reaction at 298K is provided below

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_f H^0$ (kJ mol$^{-1}$)</th>
<th>$S^0$ (J mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH($g$)</td>
<td>-362.63</td>
<td>251.0</td>
</tr>
<tr>
<td>(HCOOH)$_2$($g$)</td>
<td>-785.34</td>
<td>347.7</td>
</tr>
</tbody>
</table>

(a) (15 points) Evaluate $\Delta G$ and $\Delta S$ for this reaction at 298 K and 1 bar.

(b) (5 points) To determine the approximate bond enthalpy of a hydrogen bond from this reaction, one would divide $\Delta_f H$ by two. Would the analogous procedure be appropriate to determine the bond entropy? In other words, does the entropy decrease linearly with the number of hydrogen bonds? Why or why not?
6. (12 points, 3 points each) For each of the following equations, provide the conditions under which they apply (i.e. adiabatic, reversible, constant T, perfect gas, etc.)

(a) \( \Delta G = \Delta H - T \Delta S \)

(b) \( \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \)

(c) \( \Delta S = C_p \ln \left( \frac{T_f}{T_i} \right) \)

(d) \( \frac{dq}{T} \geq \frac{dq}{T} \)