1. Why is some energy unavailable to do work?

In every process some of the energy that might be used for work is dissipated instead as heat.

2. What is a spontaneous process? How this is related to chemical potential?

A spontaneous process proceeds without intervention it may need a start.

Mechanical processes are driven spontaneously to the lowest physical potential energy.

Chemical processes proceed in the direction of increasing \(\Delta S_{\text{univ}}\) or decreasing \(\Delta G\).

More ordered \(\rightarrow\) less ordered

(salt crystal) \(\rightarrow\) (aqueous solution)

Less random \(\rightarrow\) more random

Smaller volume \(\rightarrow\) larger volume

Higher chemical potential \(\rightarrow\) lower chemical potential

3. Which of the substances will have higher Entropy? Explain Why

a. \(\text{NO}_2(g)\) or \(\text{N}_2\text{O}_5(g)\)  
   Absolute Entropy of larger molecules is greater
   or gas is greater.

b. \(I_2(g)\) or \(I_2(s)\)

c. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(g)\) or \(\text{CH}_3\text{CH}_3(g)\)

4. For each process, tell whether entropy of the system increases or decreases and explain.

d. \(2\text{CO}_2(g) \rightarrow 2\text{CO}(g) + \text{O}_2(g)\) \(\Delta S_{\text{sys}}^\circ = +\) more molecules of gas products

e. \(\text{NaCl}(s) \rightarrow \text{NaCl(aq)}\) \(\Delta S_{\text{sys}}^\circ = +\) crystal (NaCl) more ordered

f. \(\text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g)\) \(\Delta S_{\text{sys}}^\circ = +\) product has a gas \(\Rightarrow\) matter is more spread out, less ordered in products, As matter spreads out so does its energy.
5. For each process tell whether the entropy of the system increases or decreases.
   g. water is heated from 5°C to 55°C. \( \Delta S_{sys} = + \)  absolute entropy increases with temp.
   h. steam is condensed to water at 100°C. \( \Delta S_{sys} = - \) liquid has less entropy than gas.
   i. the volume of a container of a gas is doubled without adding any gas.
      Increasing volume \( \Rightarrow \) gas expanding \( \Rightarrow \) spreading out
      \( \Delta S_{sys} = + \)

6. The reaction \( \text{CO}(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l) \) is being evaluated as a possible way to manufacture liquid methanol \( \text{CH}_3\text{OH}(l) \), for use in motor fuel. Calculate \( \Delta S^0 \) for the reaction

   always Balance \( \rightarrow \) \( \text{CO}(g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l) \) \( \text{SYSTEM} = \text{Rxn} \)

   \[
   \begin{array}{|c|c|}
   \hline
   \text{Compound} & S^0 \text{(J mol}^{-1} \text{K}^{-1}) \\
   \hline
   \text{CO}(g) & 197.7 \\
   \text{H}_2(g) & 126.8 \\
   \hline
   \end{array}
   \]

   \[
   \Delta S_{\text{Rxn}}^0 = (1) S^0_{\text{CH}_3\text{OH}(l)} - \left\{ (1) S^0_{\text{CO}(g)} + (2) S^0_{\text{H}_2(g)} \right\} \\
   = (1)(126.8) - \left\{ (1)(197.7) + (2)(130.7) \right\} \text{ J mol}^{-1} \text{ K}^{-1} \\
   \Delta S_{\text{Rxn}}^0 = -332.3 \text{ J mol}^{-1} \text{ K}^{-1}
   \]

7. Calculate \( \Delta S^0_{\text{universe}} \) for the reaction of methane in air, and from your result confirm that this reaction is product favored. The reaction was done at 25°C.

   \( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \) \( \text{SYSTEM} = \text{Rxn} \)

   \[
   \begin{array}{|c|c|c|}
   \hline
   \text{Compound} & S^0 \text{(J mol}^{-1} \text{K}^{-1}) & H^0 \text{(kJ mol}^{-1}) \\
   \hline
   \text{CH}_4(g) & 186.264 & -74.81 \\
   \text{O}_2(g) & 205.138 & 0 \\
   \text{CO}_2(g) & 213.74 & -393.509 \\
   \text{H}_2\text{O}(l) & 69.91 & -285.830 \\
   \hline
   \end{array}
   \]

   \[
   \Delta S^0_{\text{universe}} = \Delta S^0_{\text{Rxn}} + \Delta S^0_{\text{universe}} \text{ Calc } \Delta S^0_{\text{universe}} = -\frac{\Delta H^0_{\text{Rxn}}}{T} \\
   \Delta S^0_{\text{Rxn}} = \left\{ (1)(183.74) + (2)(69.91) \right\} = \left\{ (1)(186.264) + (2)(205.138) \right\} \text{ J mol}^{-1} \text{ K}^{-1} \\
   \Delta S^0_{\text{Rxn}} = -242.98 \text{ J K}^{-1}
   \]

   Next calculate \( \Delta S^0_{\text{surroundings}} \) using \( \Delta H^0_{\text{Rxn}} \)

   Next page.
7. CONTINUED  NOTE $\Delta H^0$ is in kJ not J!

$\Delta H^0_{\text{rexn}} = \frac{3}{2}(1)(-393.509) + (2)(-285.830) + (1)(-14.81) \frac{3}{2} \text{ kJ mol}^{-1}$

$\Delta H^0 = -890.359 \text{ kJ mol}^{-1}$

$\nu = 890.359 \text{ J mol}^{-1}$

$\Delta S^0_{\text{surr}} = \frac{-890.359 \text{ J mol}^{-1}}{298.15 \text{ K}}$

$\Delta S^0_{\text{surr}} = -2986.28 \text{ J K}^{-1} \text{ (for 1 mole CH4 reacted)}$

$\Delta S^0_{\text{universe}} = \Delta S^0_{\text{rexn}} + \Delta S^0_{\text{surr}}$

$\Delta S^0_{\text{universe}} = \Delta S^0_{\text{rexn}} + \left( \frac{-\Delta H^0_{\text{rexn}}}{T} \right)$

$\Delta S^0_{\text{universe}} = -242.98 \text{ JK}^{-1} + \left\{ -(-2986.28 \text{ JK}^{-1}) \right\}$

$\Delta S^0_{\text{universe}} = +2743.30 \text{ JK}^{-1} = +2743.33 \text{ kJ K}^{-1}$

($\text{for the reaction of 1 mole of CH}_4$)
8. How is $\Delta G^\circ_{sys}$ related to $\Delta S^\circ_{universe}$? What is the connection between $\Delta G^\circ_{sys}$ and spontaneity?

$$\Delta G^\circ_{sys} = -T \Delta S^\circ_{universe}$$

$$\Delta S^\circ_{universe}$$ is positive for spontaneous processes

$$\Rightarrow -T \Delta S^\circ_{universe} = +$$

$$\Rightarrow$$

$$\Delta G^\circ_{sys}$$ is negative

$$\Delta G^\circ < 0 =$$ Spontaneous

$$\Delta G^\circ > 0 =$$ Non-Spontaneous; Spontaneous in reverse

$$\Delta G^\circ = 0 =$$ Equilibrium

9. Given that $\Delta G = \Delta H - T \Delta S$, predict the sign of $\Delta G$ under the following conditions:

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Sign of $\Delta G$ at low temperature</th>
<th>Sign of $\Delta G$ at high temperature</th>
<th>Spontaneous? (high temperature, low temperature or all temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>@ low T</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>@ high T</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>@ all T</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>Non spontaneous @ all T</td>
</tr>
</tbody>
</table>

10. Using the information of question #7, predict the sign of $\Delta G$ for the following reactions: (no need to do any calculations to solve this exercise)

This is an elaboration of Prob. #9

a. $\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{CO}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$

1 mole(s) + 6 mole(g) -> 6 mole(g) + 6 mole(l)

$\Delta S_{sys} = +$<br>$\Rightarrow$ (Prob. #9)

$\Delta G = (-)$

b. $\text{COCl}_2(g) \rightarrow \text{CO}(g) + \text{Cl}_2(g)$ $\Delta H = +110.4\text{kJ}$

1 mole(g) -> 2 mole(g) $\Delta S_{sys} = +$

$\Rightarrow$ (Prob. #2)

$\Delta G = +$, low T

$\Delta H = +$

$c. \text{Cl}_2(g) \rightarrow 2\text{Cl}(g)$ $\text{R-xn is simply breaking a Cl-Cl bond}$ $\text{Bond breaking takes energy - is endothermic}$

$\Rightarrow$ $\Delta H = +$

$\Rightarrow$ $\Delta G = +$, low T

1 mole(g) -> 2 mole(g) $\Delta S_{sys} = +$

$\Rightarrow$ $\Delta G = -$, high T
11. Calculate $\Delta G^0$ at 298K for the reaction

$$4\text{HCl}(g) + \text{O}_2(g) \rightarrow 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{rxn}} = -114.4\text{kJ}$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S^0\left(\frac{\text{J}}{\text{mol} \cdot \text{K}}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl(g)</td>
<td>186.8</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>205.0</td>
</tr>
<tr>
<td>Cl$_2$(g)</td>
<td>223.0</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>188.7</td>
</tr>
</tbody>
</table>

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

$$\Delta S^\circ_{\text{rxn}} = \left\{\begin{align*}
\text{[2(23.0) + 2(188.7)]} - \text{[2(185.8) + 2(205.0)]} & = -128.8 \text{ J} \cdot \text{K}^{-1} \quad \text{(For 1 mole of O}_2\text{ reacted)} \\
& = -128.8 \text{ kJ} \cdot \text{K}^{-1}
\end{align*}\right\}$$

$$\Delta G^\circ_{\text{rxn}} = -114.4 \text{ kJ} - (298 \text{K})(-128.8 \text{ kJ} \cdot \text{K}^{-1}) = -76.02 \text{ kJ}$$

12. Calculate the standard free energy change for the combustion of 1 mole of methane from the standard free energies of formation of the products and reactants.

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\circ_{\text{rxn}} (\frac{\text{kJ}}{\text{mol}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$(g)</td>
<td>-50.8</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-394.4</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>-228.6</td>
</tr>
</tbody>
</table>

$$\Delta G^\circ_{\text{rxn}} = \left\{\begin{align*}
(3)(-228.6) + (1)(-394.4) & = -851.6 \text{ kJ} \\
(1)(-50.8) + (2)(0) & = -101.6 \text{ kJ}
\end{align*}\right\}$$

$$\Delta G^\circ_{\text{rxn}} = -800.8 \text{ kJ}$$