1. Consider the reaction \(6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow 6\text{O}_2(g) + \text{C}_6\text{H}_{12}\text{O}_6(s)\), corresponding to the synthesis of glucose. If each of the reagents is present at a pressure of 1 atm:
(a) What are the values of \(\Delta S, \Delta S_{\text{surr}},\) and \(\Delta S_{\text{surr}}\), per mole of glucose formed, when the reaction is carried out at room temperature?
(b) What about at 350K?
(c) How much do \(\Delta H^o_{\text{rxn}}\) and \(\Delta S^o_{\text{rxn}}\) vary with temperature over this range?
(d) What are the partial pressures of each of the gases when the reaction comes to equilibrium at 298K and under a total pressure of 1 atm?

\[\begin{align*}
\Delta S &= 6\Sigma S_{\text{gas}} + 6\Sigma S_{\text{water}} - 6\Sigma S_{\text{gas}} - 6\Sigma S_{\text{water}} = 6(205.2 \text{ J/mol} \cdot \text{K}) + 6(213.8 \text{ J/mol} \cdot \text{K}) - 6(70.0 \text{ J/mol} \cdot \text{K}) \\
\Delta S &= 238.4 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{mix}} &= 0.26 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{surr}} &= -9.41 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{mix}} &= (-0.26 \text{ J/mol} \cdot \text{K}) - (-9.41 \text{ J/mol} \cdot \text{K}) \\
\Delta S_{\text{mix}} &= -9.67 \text{ J/mol} \cdot \text{K} < 0 \quad \text{reaction is not spontaneous, proceeds from right to left}
\end{align*}\]

b) At \(T = 350K\):
\[\begin{align*}
\Delta S &= 6\Sigma S_{\text{gas}} + 6\Sigma S_{\text{water}} - 6\Sigma S_{\text{gas}} - 6\Sigma S_{\text{water}} = 6(205.2 \text{ J/mol} \cdot \text{K}) + 6(213.8 \text{ J/mol} \cdot \text{K}) - 6(70.0 \text{ J/mol} \cdot \text{K}) \\
\Delta S &= 238.4 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{mix}} &= -307.3 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{surr}} &= -0.307 \text{ J/mol} \cdot \text{K} \\
\Delta S_{\text{mix}} &= -9.97 \text{ J/mol} \cdot \text{K} < 0 \quad \text{reaction is not spontaneous, proceeds from right to left}
\end{align*}\]

c) \[\begin{align*}
\Delta S_{\text{rxn}} &= \Delta H_{\text{rxn}} / \Delta T \\
\Delta S_{\text{rxn}} &= 17.1 \text{ J/mol} \cdot \text{K} \\
\Delta H_{\text{rxn}} &= -280.8 \text{ J/mol} \\
\Delta S_{\text{rxn}} &= -8.28 \text{ J/mol} \cdot \text{K}
\end{align*}\]

d) \[\begin{align*}
\Delta H_{\text{rxn}} &= \Delta H_{\text{gas}} + \Delta H_{\text{water}} \\
\Delta H_{\text{rxn}} &= 249.4 \text{ J/mol} - 238.8 \text{ J/mol} \\
\Delta H_{\text{rxn}} &= 0.5 \text{ J/mol}
\end{align*}\]

2. (a) In a gaseous sample of oxygen atoms and diatomic oxygen in equilibrium at 298K and under a pressure of 1 atm, what fraction of it is dissociated?
(b) At what temperature is the sample 1% dissociated?
(c) At 298K and under a pressure of 10,000 atm, what fraction is dissociated?
\[ \Delta S_{fus} = \tilde{S}_{fus} - 2 \tilde{S}_{m} + 2 \left( 161.1 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \right) = -117.0 \frac{\text{cal}}{\text{mol} \cdot \text{K}} = -0.117 \text{ cal/K} \]
\[ \Delta G_{fus} = \Delta H_{fus} - T \Delta S = \left( -494.4 \frac{\text{cal}}{\text{mol}} \right) - (298 K) \left( -0.117 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \right) = -463.5 \text{ kcal} \]

a) At equilibrium
\[ K = \frac{P_{fus}}{P_{Hg}^2} = e^{\frac{\Delta G}{RT}} \]
\[ e^{\frac{\Delta G}{RT}} = 1.39 \times 10^8 \Rightarrow x \approx 1 \text{ and } (1-x)^{m} \ll 1 \]
\[ \left( \frac{1}{1+x} \right)^{m} = 2.36 \times 10^{-11} \]
\[ P_{fus} = 1 \text{ atm and } P_{Hg} = 2.36 \times 10^{-11} \text{ atm} \]

b) Fraction dissociated
\[ \frac{n_{fus}}{n_{Hg}} = \frac{P_{fus}}{P_{Hg}} = (2.36 \times 10^{-11}) \approx 2.36 \times 10^{-11} \]

c) \[ A + T = 298 K \text{ and } P = 10,000 \text{ atm} \]
\[ \Delta K = (10^{10} - x) = 1.79 \times 10^{-8} \ll 1 \]
\[ (10^{10} - x) = \left( 1.79 \times 10^{-8} \right) \]

3. (a) What is the standard molar entropy \( \tilde{S}_{\circ} \) of solid mercury at its normal (P = 1 atm) melting temperature, \( T_{fus}^\circ \) (Hg)? What is \( \tilde{S}_{\circ} \) for liquid mercury at this temperature? (b) What is the heat of fusion, \( \Delta H_{sol-liq} \), at \( T_{sol-liq}^\circ \) (Hg) \( \equiv T_{fus}^\circ \) (Hg), 1 atm? (c) What is the entropy change \( \Delta S_{sol-liq} \), at \( T_{fus}^\circ \) (Hg), 1 atm? (d) What is \( \Delta G_{sol-liq} \), at \( T_{fus}^\circ \) (Hg), 1 atm?

4. Suppose we have a system consisting of 9 g of ice at 200K and y g of water at 330K, maintained at a pressure of 1 atm, and thermally-insulated (adiabatically-sealed). (a) What must y be to assure that the final state of the system, after it comes to equilibrium, is all liquid water at a uniform temperature of 273K (with no ice remaining)? (b) How much work is done on the system? (c) What change in energy, \( U \), does it undergo? (d) What is the change in enthalpy? (e) What are \( \Delta G \), and \( \Delta S \)?

\[ 9 \text{ g H}_{2}O \text{ at } 200 K \]
\[ y \text{ g H}_{2}O \text{ at } 330 K \]
\[ \frac{P}{1 \text{ atm}} \]

heat absorbed by \( 9 \text{ g ice (200 \text{K})} \) = equal and opposite heat absorbed by \( y \text{ g of water cooling (330 \text{K})} \)
5. Suppose we start with a mole of \( \text{NO}_2 (g) \) and allow the reaction \( \text{NO}_2 (g) = \text{NO}(g) + \frac{1}{2} \text{O}_2 (g) \) to come to equilibrium at 700K under a total pressure of 1 atm. Suppose further that we measure the equilibrium partial pressure of \( \text{NO} \) to be 0.872 times that of \( \text{NO}_2 \). When we equilibrate the reaction at 800K, on the other hand, we find that the ratio of \( p_{\text{NO}} \) to \( p_{\text{NO}_2} \) is 2.5 (instead of 0.872).

(a) What are the equilibrium constants for this reaction at 700K and at 800K?
(b) Calculate \( \Delta H^\circ_{\text{rxn}} \) (assuming it is temperature-independent), using only the information given above. How does this value for \( \Delta H^\circ_{\text{rxn}} \) compare with what you would calculate from tabulated heats of formation?

Know: \( \text{NO}_2 (g) \rightarrow \text{NO}(g) + \frac{1}{2} \text{O}_2 (g) \), at 700K \( P_{\text{NO}}^\circ = 0.872 \) \( P_{\text{NO}_2}^\circ \), and at 800K \( P_{\text{NO}}^\circ = 2.5 \) \( P_{\text{NO}_2}^\circ \)

Suppose we start initially with 1 mol of \( \text{NO}_2 (g) \), 0 of \( \text{O}_2 (g) \) and \( \text{NO}(g) \). Then we allow the reaction to come to equilibrium where we reacted \( x \) moles of \( \text{NO}_2 \), so we have \( y \) moles of \( \text{NO}(g) \) and \( \frac{1}{2} y \) moles of \( \text{O}_2 (g) \).

\[ \begin{align*}
\text{mol} & + (1-y) \text{mol} + y \text{mol} + \frac{1}{2} y \text{mol} = 1 + \frac{1}{2} y \text{mol} \\
\text{at} 700K \quad P_{\text{NO}_2}^\circ & = \frac{y}{1-y} = 0.872 \quad \text{(at 700K)}
\end{align*} \]
\[ y = 0.466 \quad \rightarrow \quad n_{\text{tot}} = 1 + \frac{1}{2} (0.466) = 1.233 \text{ mol} \]

Thus, \( P_{\text{H}_2} = \frac{0.466}{1.233} \text{ atm} = 0.378 \text{ atm} \)
\( P_{\text{O}_2} = \frac{1 - 0.466}{1.233} \text{ atm} = 0.433 \text{ atm} \)
\( P_{\text{N}_2} = \frac{1}{1.233} \text{ atm} = 0.819 \text{ atm} \)

\[ K(\text{780 K}) = \frac{P_{\text{N}_2}^{1/2}(P_{\text{H}_2})^{1/2}}{P_{\text{O}_2}} \approx \frac{(0.819)(0.466)}{0.433} \]

\[ K(\text{800 K}) = 0.38 \]

At 800 K,
\[ \frac{P_{\text{O}_2}}{P_{\text{N}_2}} = \frac{y}{1-y} = 2.5 \quad \rightarrow \quad y = 0.714 \quad \text{and} \quad n_{\text{tot}} = 1.357 \text{ mol} \]
\( P_{\text{N}_2} = \frac{0.714}{1.357} \text{ atm} = 0.526 \text{ atm} \)
\( P_{\text{N}_2} = \frac{1 - 0.714}{1.357} \text{ atm} = 0.211 \text{ atm} \)
\( P_{\text{O}_2} = \frac{1}{1.357} \text{ atm} = 0.738 \text{ atm} \)

\[ K(\text{800 K}) = \frac{P_{\text{N}_2}^{1/2}(P_{\text{H}_2})^{1/2}}{P_{\text{O}_2}} \approx \frac{(0.526)(0.466)}{0.738} \]

\[ K(\text{800 K}) = 1.28 \]

b) Assuming \( \Delta H_{\text{mn}} \) is independent of temperature

\[ \frac{\Delta H_{\text{mn}}^{\circ}}{K(T)} = - \Delta H_{\text{mn}}^{\circ} \left( \frac{1}{T} - \frac{1}{T} \right) \]

\[ \Delta H_{\text{mn}}^{\circ} = -R \ln \frac{K(T)}{K(T)} \left( \frac{1}{T} - \frac{1}{T} \right) \approx -(8.32 \text{ J/mol K}) \ln \frac{0.88}{1.28} \left( \frac{1}{800K} - \frac{1}{800K} \right) \]

\[ \Delta H_{\text{mn}}^{\circ} = 56.9 \text{ kJ/mol} \]