Chem340
Physical Chemistry for Biochemists
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Homework 7
Due Date Mar. 9, 2011


**P6.2)** Calculate $\Delta A$ for the isothermal compression of 2.00 mol of an ideal gas at 298 K from an initial volume of 35.0 L to a final volume of 12.0 L. Does it matter whether the path is reversible or irreversible?

$dA = -SdT - PdV$

At constant $T$, we consider the reversible process. Because $A$ is a state function, any path whether reversible or irreversible, between the same initial and final states will give the same result.

$$\Delta A = -\int_{V_i}^{V_f} PdV = -nRT \ln \frac{V_f}{V_i} = -2.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln \frac{12.0 \text{ L}}{35.0 \text{ L}} = 5.30 \times 10^3 \text{ J}$$

**P6.3)** Calculate $\Delta G$ for the isothermal expansion of 2.50 mol of an ideal gas at 350 K from an initial pressure of 10.5 bar to a final pressure of 0.500 bar.

$dG = -SdT + VdP$

At constant $T$, we consider the reversible process. Because $G$ is a state function, any path between the same initial and final states will give the same result.

$$\Delta G = \int_{P_i}^{P_f} VdP = nRT \ln \frac{P_f}{P_i} = 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 350 \text{ K} \times \ln \frac{0.500 \text{ bar}}{10.5 \text{ bar}} = -22.1 \times 10^3 \text{ J}$$
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.

a) for the isothermal reversible path

$$\Delta G = \int_{V_i}^{V_f} VdP = nRT \ln \frac{P_f}{P_i} = nRT \ln \frac{V_f}{V_i}$$

$$= 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln \frac{10.0 \text{ L}}{50.0 \text{ L}} = -9.97 \times 10^3 \text{ J}$$

$$\Delta A = -\int_{V_i}^{V_f} PdV = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln \frac{50.0 \text{ L}}{10.0 \text{ L}} = -9.97 \times 10^3 \text{ J}$$

b) Because $A$ and $G$ are state functions, the answers are the same as to part a) because the systems go between the same initial and final states, $T,V_i \rightarrow T,V_f$.

$$\Delta G - \Delta A = \Delta H - \Delta U = \Delta (PV) = \Delta (nRT).$$

Therefore, $\Delta G = \Delta A$ for an ideal gas if $T$ is constant.

P6.5) The pressure dependence of $G$ is quite different for gases and condensed phases. Calculate $G_m(C, \text{ solid, graphite}, 100 \text{ bar, } 298.15 \text{ K})$ and $G_m(\text{He, g, } 100 \text{ bar, } 298.15 \text{ K})$ relative to their standard state values. By what factor is the change in $G_m$ greater for He than for graphite?
For a solid or liquid,
\[ \Delta G = \int_{P_i}^{P_f} VdP = V(P_f - P_i) \]
\[ G_m(C, s, 100 \text{ bar}) = G_m(C, s, 1 \text{ bar}) + V_m(P_f - P_i) = G_m(C, s, 1 \text{ bar}) + \frac{M}{\rho}(P_f - P_i) \]
\[ = 0 + \frac{12.011 \times 10^{-3} \text{ kg}}{2250 \text{ kg m}^{-3}} \times 99.0 \times 10^5 \text{ Pa} = 52.8 \text{ J} \]

Treating He as an ideal gas,
\[ G_m(\text{He}, g, 100 \text{ bar}) = G_m(\text{He}, g, 1 \text{ bar}) + \int_{P_i}^{P_f} VdP \]
\[ = 0 + RT \ln \frac{P_f}{P_i} = 1 \text{ mole} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298.15 \text{ K} \times \ln \frac{100 \text{ bar}}{1 \text{ bar}} = 11.4 \times 10^3 \text{ J} \]

This result is a factor of 216 greater than that for graphite.

**P6.6** Assuming that \( \Delta H_f^\circ \) is constant in the interval from 275 to 600 K, calculate \( \Delta G \) for the process \((\text{H}_2\text{O}, \text{g}, 298 \text{ K}) \rightarrow (\text{H}_2\text{O}, \text{g}, 525 \text{ K})\).

\[ \Delta G_f^\circ (\text{H}_2\text{O}, \text{g}, 525 \text{ K}). \]

\[ \Delta G_f^\circ (T_2) = T_2 \left[ \frac{\Delta G_f^\circ (T_1)}{T_1} + \Delta H_f^\circ (T_1) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \]
\[ = 525 \text{ K} \times \left[ \frac{-228.6 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 241.8 \times 10^3 \text{ J mol}^{-1} \times \left( \frac{1}{525 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \]
\[ \Delta G_f^\circ (525 \text{ K}) = -218.5 \times 10^3 \text{ J mol}^{-1} \]

**P6.7** Calculate \( \Delta G_{\text{reaction}}^\circ \) for the reaction \( \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \) at 298.15 K. Calculate \( \Delta G_{\text{reaction}}^\circ \) at 650 K assuming that \( \Delta H_{\text{reaction}}^\circ \) is constant in the temperature interval of interest.

\[ \Delta G_{\text{reaction}}^\circ (298.15 \text{ K}) = \Delta G_f^\circ (\text{CO}_2, g) - \Delta G_f^\circ (\text{CO}, g) - \frac{1}{2} \Delta G_f^\circ (\text{O}_2, g) \]
\[ = -394.4 \times 10^3 \text{ J mol}^{-1} + 137.2 \times 10^3 \text{ J mol}^{-1} - 0 \]
\[ = -257.2 \times 10^3 \text{ J mol}^{-1} \]
\[ \Delta H_{\text{reaction}}^{\circ} (298.15K) = \Delta H_f^{\circ} (\text{CO}_2, g) - \Delta H_f^{\circ} (\text{CO}, g) - \frac{1}{2} \Delta H_f^{\circ} (\text{O}_2, g) \]
\[ = -393.5 \times 10^3 \text{J mol}^{-1} + 110.5 \times 10^3 \text{J mol}^{-1} - 0 \]
\[ = -283.0 \times 10^3 \text{J mol}^{-1} \]

\[ \Delta G_{\text{reaction}}^{\circ} (T_2) = T_2 \left[ \frac{\Delta G_{\text{reaction}}^{\circ} (T_1)}{T_1} + \Delta H_{\text{reaction}}^{\circ} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \]

\[ \Delta G_{\text{reaction}}^{\circ} (650 \text{ K}) = 650 \text{ K} \times \left[ \frac{-257.2 \times 10^3 \text{J mol}^{-1}}{298.15 \text{ K}} - 283.0 \times 10^3 \text{J mol}^{-1} \times \left( \frac{1}{650 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \]
\[ = -226.8 \times 10^3 \text{J mol}^{-1} \]

**P6.8)** Calculate \( \Delta A_{\text{reaction}}^{\circ} \) and \( \Delta G_{\text{reaction}}^{\circ} \) for the reaction \( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O(l)} \) at 298 K from the combustion enthalpy of methane and the entropies of the reactants and products.

All reactants and products are treated as ideal gases

\[ \Delta G_{\text{combustion}}^{\circ} = \Delta H_{\text{combustion}}^{\circ} - T \Delta S_{\text{combustion}}^{\circ} \]
\[ \Delta S_{\text{combustion}}^{\circ} = S^{\circ} (\text{CO}_2, g) + 2S^{\circ} (\text{H}_2\text{O}, l) - S^{\circ} (\text{CH}_4, g) - 2S^{\circ} (\text{O}_2, g) \]
\[ = 213.8 \text{ J mol}^{-1} \text{K}^{-1} + 2 \times 70.0 \text{ J mol}^{-1} \text{K}^{-1} - 186.3 \text{ J mol}^{-1} \text{K}^{-1} - 2 \times 205.2 \text{ J mol}^{-1} \text{K}^{-1} \]
\[ = -242.9 \text{ J mol}^{-1} \text{K}^{-1} \]
\[ \Delta G_{\text{combustion}}^{\circ} = -890.3 \times 10^3 \text{J mol}^{-1} - 298.15 \text{ K} \times \left( -242.7 \text{ J mol}^{-1} \text{K}^{-1} \right) = -817.9 \times 10^3 \text{J mol}^{-1} \]

\[ \Delta A_{\text{combustion}}^{\circ} = \Delta U_{\text{combustion}}^{\circ} - T \Delta S_{\text{combustion}}^{\circ} \]
\[ = \Delta H_{\text{combustion}}^{\circ} - \Delta (PV)_{\text{combustion}} - T \Delta S_{\text{combustion}}^{\circ} \]
\[ = \Delta G_{\text{combustion}}^{\circ} + T \Delta S_{\text{combustion}}^{\circ} - \Delta (PV) - T \Delta S_{\text{combustion}}^{\circ} \]
\[ = \Delta G_{\text{combustion}}^{\circ} - \Delta nRT \]

where \( \Delta n \) is the change in the number of moles of gas phase species in the reaction
\[ = -817.9 \times 10^3 \text{J mol}^{-1} - (-2) \times 8.314 \text{J mol}^{-1} \text{K}^{-1} \times 298.15 \text{ K} \]
\[ \Delta A_{\text{combustion}}^{\circ} = -812.9 \times 10^3 \text{J mol}^{-1} \]

**P6.10)** The standard Gibbs energy of formation \( \Delta G_f^{\circ} \) for carbon dioxide gas is \(-394.4 \text{ kJ mol}^{-1} \). Calculate the Gibbs energy of formation of carbon dioxide at its normal sea level partial pressure of 0.00031 atm.
The Gibbs energy of formation is given by:

\[ \Delta G_f (p) = \Delta G_f^0 (p^0) + n R T \ln \left( \frac{p}{p^0} \right) \]

\[ = \left( -394.4 \text{ kJ mol}^{-1} \right) + (1 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln \left( \frac{0.00031 \text{ atm}}{0.99969 \text{ atm}} \right) \]

\[ = -414.4 \text{ kJ mol}^{-1} \]

**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 \( \text{NH}_3 \). 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 \( \Delta G_f^0 (\text{NH}_3, \text{aq}) = -80.3 \text{ kJ mol}^{-1} \).

\[
\Delta G_{\text{reaction}}^0 = \sum_i v_i^0 \Delta G_i^0 = (1) \times \left( \Delta G_{\text{NH}_3(aq)}^0 \right) + \left( -\frac{3}{2} \right) \times \left( \Delta G_{\text{H}_2\text{O}(l)}^0 \right)
\]

\[ = (1) \times (-80.3 \text{ kJ mol}^{-1}) + \left( -\frac{3}{2} \right) \times (-237.1 \text{ kJ mol}^{-1}) = 275.35 \text{ kJ mol}^{-1} \]

The equilibrium constant is then:

\[
K_p = \exp \left[ -\frac{\Delta G_{\text{reaction}}^0}{R T} \right] = \exp \left[ -\frac{(275.35 \text{ kJ mol}^{-1}) \text{ kJ mol}^{-1}}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right] = 5.45 \times 10^{-49}
\]
P6.14) Consider the equilibrium

\[ \text{NO}_2 \ (g) \rightleftharpoons \text{NO} \ (g) + \frac{1}{2} \text{O}_2 \]

One mole of \( \text{NO}_2 \) is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the contents of the vessel gives the following results:

<table>
<thead>
<tr>
<th>T</th>
<th>700K</th>
<th>800K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(NO)/P(NO(_2))</td>
<td>0.872</td>
<td>2.50</td>
</tr>
</tbody>
</table>

a. Calculate \( K_P \) at 700 and 800 K.

\[
K_P(700K) = \frac{[\text{NO}][O_2]^{\frac{1}{2}}}{[\text{NO}_2]} = \frac{[P_{\text{NO}}][P_{O_2}]^{\frac{1}{2}}}{[P_{\text{NO}_2}]} = \frac{[0.872][0.872]^{\frac{1}{2}}}{[1]} = 0.934
\]

\[
K_P(800K) = \frac{[\text{NO}][O_2]^{\frac{1}{2}}}{[\text{NO}_2]} = \frac{[P_{\text{NO}}][P_{O_2}]^{\frac{1}{2}}}{[P_{\text{NO}_2}]} = \frac{[2.5][2.5]^{\frac{1}{2}}}{[1]} = 3.952
\]

b. Calculate \( \Delta G_{\text{reaction}}^0 \) at 298.15K assuming that \( \Delta H_{\text{reaction}}^0 \) is independent of temperature.

\[
\Delta G_{700}^0 = -RT \ln K_P(700K) = -0.397 \text{ kJ mol}^{-1}
\]

\[
\Delta G_{800}^0 = -RT \ln K_P(800K) = -9.140 \text{ kJ mol}^{-1}
\]

P6.16) Consider the reaction \( \text{FeO(s)} + \text{CO(g)} \rightleftharpoons \text{Fe(s)} + \text{CO}_2(g) \) for which \( K_P \) is found to have the following values:

<table>
<thead>
<tr>
<th>T</th>
<th>600°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_P )</td>
<td>0.9</td>
<td>0.396</td>
</tr>
</tbody>
</table>

a. Calculate \( \Delta G_{\text{reaction}}^0 \), \( \Delta S_{\text{reaction}}^0 \), and \( \Delta H_{\text{reaction}}^0 \) for this reaction at 600°C. Assume
that $\Delta H^0_{\text{reaction}}$ is independent of temperature.

\[
\Delta G^0_{873} = -RT \ln K_p(873K) = -0.764 \text{ kJ mol}^{-1}
\]

\[
\Delta G^0_{1273} = -RT \ln K_p(1273K) = -9.804 \text{ kJ mol}^{-1}
\]

Using the Gibbs-Helmholtz equation:

\[
\frac{\Delta G^0_{T_1}}{T_1} = \frac{\Delta G^0_{T_2}}{T_2} + \Delta H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\Delta H = \left( \frac{\Delta G^0_{T_1}}{T_1} - \frac{\Delta G^0_{T_2}}{T_2} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1} = \left( \frac{\Delta G^0_{1273}}{1273} - \frac{\Delta G^0_{873}}{873} \right) \left( \frac{1}{1273} - \frac{1}{873} \right)^{-1} = -29.53 \text{ kJ / mol}
\]

\[
\Delta G = \Delta H - T \Delta S
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]

\[
\Delta S_{1273} = \frac{\Delta H - \Delta G_{1273}}{1273} = -22.6 \text{ J / K}
\]

\[
\Delta S_{873} = \frac{\Delta H - \Delta G_{873}}{873} = -22.6 \text{ J / K}
\]

b. Calculate the mole fraction of CO$_2$(g) present in the gas phase at 600°C.

\[
K_p(873K) = \frac{[P_{CO_2}]}{[P_{CO}]} = \frac{[CO_2]}{[CO]} = \frac{0.9}{1.0} = 0.900
\]

\[
X_{CO_2} = \frac{n_{CO_2}}{n_{\text{total}}} = \frac{[0.9]}{[0.9 + 1.0]} = 0.47
\]

P6.17) If the reaction \[ \text{Fe}_2\text{N} (s) + \frac{3}{2} \text{H}_2 (g) \rightleftharpoons 2 \text{Fe} (s) + \text{NH}_3 (g) \] comes to equilibrium at a total pressure of 1 bar, analysis of the gas shows that at 700 and 800 K, $P_{NH_3}/P_{H_2} = 2.165$ and 1.083, respectively, if only H$_2$(g) was initially present in the gas phase and Fe$_2$N(s) was in excess.

a. Calculate $K_P$ at 700 and 800 K.
b. Calculate $\Delta S_{\text{reaction}}^\circ$ at 700 and 800 K and $\Delta H_{\text{reaction}}^\circ$ assuming that it is independent of temperature.

c. Calculate $\Delta G_{\text{reaction}}^\circ$ for this reaction at 298.15 K.

a) $\text{FeN}_2(s) + \frac{3}{2} \text{H}_2(g) \rightarrow 2\text{Fe}(s) + \text{NH}_3(g)$

$$K_p = \frac{P_{\text{NH}_3} / P^\circ}{(P_{\text{H}_2} / P^\circ)^{3/2}}$$

$P_{\text{total}} = 1 \text{ atm} = P_{\text{NH}_3} + P_{\text{H}_2}$

At 700 K,

1 atm = 2.165 $P_{\text{H}_2} + P_{\text{H}_2} = 3.165 P_{\text{H}_2}$

$P_{\text{H}_2} = 0.316 \text{ atm, } P_{\text{NH}_3} = 0.684 \text{ atm}$

$$K_p(700 \text{ K}) = \frac{0.684}{(0.316)^{3/2}} = 3.85$$

At 800 K

1 atm = 1.083 $P_{\text{H}_2} + P_{\text{H}_2} = 2.083 P_{\text{H}_2}$

$P_{\text{H}_2} = 0.480 \text{ atm, } P_{\text{NH}_3} = 0.520 \text{ atm}$

$$K_p(800 \text{ K}) = \frac{0.520}{(0.480)^{3/2}} = 1.56$$

b) Assume that $\Delta H_{\text{reaction}}^\circ$ is independent of temperature

$$\ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} = -\frac{\Delta H_{\text{reaction}}^\circ}{R} \left( \frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)$$

$$-R \ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} = \Delta H_{\text{reaction}}^\circ$$

$$\Delta H_{\text{reaction}}^\circ = \left( \frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right) = -42.1 \text{ kJ mol}^{-1}$$
\[ \Delta G_{\text{reaction}} (700 \text{ K}) = -RT \ln K_p (700 \text{ K}) = -7.81 \text{ kJ mol}^{-1} \]
\[ \Delta G_{\text{reaction}} (800 \text{ K}) = -RT \ln K_p (800 \text{ K}) = -2.91 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{reaction}} (700 \text{ K}) = \frac{\Delta H_{\text{reaction}} - \Delta G_{\text{reaction}} (700 \text{ K})}{700 \text{ K}} = 48.9 \text{ J mol}^{-1} \text{ K}^{-1} \]
\[ \Delta S_{\text{reaction}} (800 \text{ K}) = 48.9 \text{ J mol}^{-1} \text{ K}^{-1} \]

The values of \( \Delta S_{\text{reaction}} \) at 700 K and 800 K are nearly the same because

\[ |\Delta G_{\text{reaction}}| \ll |\Delta H_{\text{reaction}}| \]

c) \[ \ln K_p (298.15 \text{ K}) = \ln K_p (700 \text{ K}) - \frac{\Delta H_{\text{reaction}}}{R} \left( \frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) \]
\[ = \ln 3.85 + \frac{42.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left( \frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) = 11.1 \]
\[ \Delta G_{\text{reaction}} (298.15 \text{ K}) = -RT \ln K_p (298.15 \text{ K}) \]
\[ = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times 11.1 = -27.5 \text{ kJ mol}^{-1} \]

P6.18) Many biological macromolecules undergo a transition called denaturation.

Denaturation is a process whereby a structured, biological active molecule, called the native form, unfolds or becomes unstructured and biologically inactive. The equilibrium is

\[ \text{n native (folded) \leftrightarrow \text{denatured (unfolded)} } \]

For a protein at pH = 2, the enthalpy change associated with denaturation is \( \Delta H^\circ = 418.0 \text{ kJ mol}^{-1} \) and the entropy change is \( \Delta S^\circ = 1.3 \text{ kJ K}^{-1} \text{ mol}^{-1} \).

a. Calculate the Gibbs energy change for the denaturation of the protein at pH = 2 and \( T = 303 \text{ K} \). Assume the enthalpy and entropy are temperature independent between 298.15 and 303 K.

b. Calculate the equilibrium constant for the denaturation of protein at pH = 2 and \( T \)
= 303 K.

c. Based on your answers for parts (a) and (b), is protein structurally stable at pH = 2 and $T = 303$ K?

a) We first need to calculate $\Delta G_{\text{den}}$ at 298 K:

$$\Delta G_{\text{den}} (298 \text{ K}) = \Delta H_{\text{den}} (298 \text{ K}) - T \Delta S_{\text{den}} = (418000 \text{ J mol}^{-1}) - (1300 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$$

$$= 30600 \text{ J mol}^{-1}$$

Then $\Delta G_{\text{reaction}} (303 \text{ K})$ can be calculated using:

$$\Delta G_{\text{reaction}} (T_2) = T_2 \times \left[ \frac{\Delta G_{\text{reaction}} (T_1)}{T_1} + \Delta H_{\text{reaction}} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

$$\Delta G_{\text{reaction}} (303 \text{ K}) = (303 \text{ K}) \times \left[ \frac{30600 \text{ J mol}^{-1}}{(298 \text{ K})} + (418.00 \text{ kJ mol}^{-1}) \left( \frac{1}{303 \text{ K}} - \frac{1}{298 \text{ K}} \right) \right]$$

$$= 24098.97 \text{ J mol}^{-1}$$

b) The equilibrium constant at 303 K is:

$$K_p (303 \text{ K}) = \exp \left[ - \frac{\Delta G_{\text{den}}}{R \cdot T} \right]$$

$$= \exp \left[ - \frac{(24098.97 \text{ J mol}^{-1} \text{ J mol}^{-1})}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right] = 5.97 \times 10^{-5}$$

c) The large positive $\Delta G_{\text{den}}$ and the small equilibrium constant indicate that the protein is stable.

**P6.19)** The melting temperature of a protein is defined as the temperature at which the equilibrium constant for denaturation has the value $K = 1$. Assuming that the enthalpy of denaturation is temperature independent, use the information in Problem P6.18 to calculate the melting temperature of the protein at pH = 2.
We first calculate the equilibrium constant at 298 K:

\[
K_p(298 \text{ K}) = \exp \left[ -\frac{\Delta G_{\text{reaction}}^0(298 \text{ K})}{R T} \right] \\
= \exp \left[ -\frac{(30600 \text{ J mol}^{-1})}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right] = 4.329 \times 10^{-6}
\]

We then solve for \( T_m \), with \( \ln(K_p(T_m)) = \ln(1) = 0 \):

\[
\ln(K_p(T_m)) = \ln(K_p(298)) - \frac{\Delta H_{\text{reaction}}^0}{R} \left( \frac{1}{T_m} - \frac{1}{(298.15 \text{ K})} \right)
\]

\[
T_m = \frac{1}{\left( \frac{1}{(298.15 \text{ K})} - \frac{R \ln(K_p(T_m)) - \ln(K_p(298))}{\Delta H_{\text{reaction}}^0} \right)} = \frac{1}{\left( \frac{1}{(298.15 \text{ K})} + \frac{8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (0 - \ln(4.329 \times 10^{-6}))}{(-418000 \text{ J mol}^{-1})} \right)} = 321.5 \text{ K}
\]

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

From P5.45 we have:

- \( \Delta S_{\text{den}}(310 \text{ K}) = 1109.4 \text{ J K}^{-1} \text{ mol}^{-1} \)
- \( \Delta H_{\text{den}}(310 \text{ K}) = 343.9 \text{ kJ K}^{-1} \text{ mol}^{-1} \)
- \( \Delta H_{\text{den}}(340 \text{ K}) = 640.1 \text{ kJ K}^{-1} \text{ mol}^{-1} \)

\( \Delta G_{\text{den}}(310 \text{ K}) \) is then:

\[
\Delta G_{\text{den}}(310 \text{ K}) = \Delta H_{\text{den}}(310 \text{ K}) - T \Delta S_{\text{den}}(310 \text{ K}) \\
= (343.9 \text{ kJ mol}^{-1}) - (310 \text{ K}) \times (1109.4 \text{ J K}^{-1} \text{ mol}^{-1}) = 0 \text{ kJ mol}^{-1}
\]

At 340 K we obtain:
\[
\frac{\Delta G^0}{T_2} = \frac{\Delta G^0}{T_1} + \Delta H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
\[
\Delta G^0_{340} = (340) \left( \frac{0}{310} \right) + (340)(640.1) \left( \frac{1}{340} - \frac{1}{310} \right) = -61.945 \text{kJ/mol}
\]

**P6.24** At \( T = 298 \text{ K} \) and pH=3 chymotrypsinogen denatures with \( \Delta G^0 = 30.5 \text{ kJ/mol} \), \( \Delta H^p = 163 \text{ kJ mol}^{-1} \), and \( \Delta C_{p,m} = 8.36 \text{ kJ K}^{-1} \text{ mol}^{-1} \). Determine \( \Delta G^0 \) for the denaturation of chymotrypsinogen at \( T = 320. \text{ K} \) and pH=3. Assume \( \Delta C_{p,m} \) is constant between \( T = 298 \text{ K} \) and \( T = 320. \text{ K} \).

First, we calculate \( \Delta S_0 \) at \( T = 298 \text{ K} \):

\[
\Delta S(298 \text{ K}) = -\left( \frac{\Delta G(298 \text{ K}) - \Delta H(298 \text{ K})}{T} \right)
= -\left( \frac{(30.5 \text{ kJ mol}^{-1}) - (163 \text{ kJ mol}^{-1})}{(298 \text{ K})} \right) = 0.445 \text{ kJ K}^{-1} \text{ mol}^{-1}
\]

To calculate \( \Delta G^0 \) at \( T = 320 \text{ K} \) we need to calculate \( \Delta H \) and \( \Delta S \) at \( T = 320 \text{ K} \) with a constant \( \Delta C_{p,m} \):

\[
\Delta H(320 \text{ K}) = \Delta H(298 \text{ K}) + \Delta C_{p,m} \Delta T
= (163 \text{ kJ mol}^{-1}) + (8.36 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (22 \text{ K}) = 346.92 \text{ kJ mol}^{-1}
\]

\[
\Delta S(320 \text{ K}) = \Delta S(298 \text{ K}) + n \Delta C_{p,m} \ln \left( \frac{T_{320}}{T_{298}} \right)
= (445 \text{ J K}^{-1} \text{ mol}^{-1}) + (8.36 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times \ln \left( \frac{320 \text{ K}}{298 \text{ K}} \right)
= 1040.46 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\( \Delta G^0 \) at \( T = 320 \text{ K} \) is then:

\[
\Delta G(320 \text{ K}) = \Delta H(320 \text{ K}) - T \Delta S(320 \text{ K})
= (346.92 \text{ kJ mol}^{-1}) - (320 \text{ K}) \times (1040.46 \text{ J K}^{-1} \text{ mol}^{-1}) = 13.97 \text{ kJ mol}^{-1}
\]
P6.28) Calculate $H_{O_2}^{mixture}$ (298.15 K, 1 bar) for oxygen in air, assuming that the mole fraction of O$_2$ in air is 0.200.

For pure O$_2$:
$$\mu_{O_2}^{(pure)} = \Delta G_m^{\circ}(O_2) = -T \Delta S_m^{\circ}(O_2) = -(298.15 K) \times (205.2 \text{ J mol}^{-1} \text{ K}^{-1}) = -61180.38 \text{ J mol}^{-1}$$

For O$_2$ in air:
$$\mu_{O_2}^{(mix)} = \mu_{O_2}^{(pure)} + R T \ln x_{O_2}$$
$$= (-61180.38 \text{ J mol}^{-1}) + (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times \ln(0.200) = -65.2 \text{ kJ mol}^{-1}$$

P6.30) You have containers of pure H$_2$ and He at 298 K and 1 atm pressure.

Calculate $\Delta G_{mixing}$ relative to the unmixed gases of

a. a mixture of 10 mol of H$_2$ and 10 mol of He.

b. a mixture of 10 mol of H$_2$ and 20 mol of He.

c. Calculate $\Delta G_{mixing}$ if 10 mol of pure He are added to the mixture of 10 mol of H$_2$ and 10 mol of He.

a) $\Delta G_{mixing} = 20 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2}\right) = -34.4 \text{ kJ}$

b) $\Delta G_{mixing} = 30 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{3} \ln \frac{1}{3} + \frac{2}{3} \ln \frac{2}{3}\right) = -47.3 \text{ kJ}$

c) $\Delta G_{mixing} = \Delta G_{mixing}^{(pure \ gases)} - \Delta G_{mixing}^{(10 \text{ mol A} + 10 \text{ mol B})}$
$$= -47.3 + 34.4 = -12.9 \text{ kJ}$$

P6.38) Consider the equilibrium in the reaction $3\text{O}_2(g) \leftrightharpoons 2\text{O}_3(g)$ with $\Delta H_{reaction}^{\circ} = 285.4 \times 10^3 \text{ J mol}^{-1}$ at 298 K. Assume that $\Delta H_{reaction}^{\circ}$ is independent of temperature.
a. Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the pressure is increased.

b. Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the temperature is increased.

c. Calculate $K_P$ at 550 K.

d. Calculate $K_x$ at 550 K and 0.500 bar.

a) Since the number of moles on the product side (2) is smaller than on the reactant side (3), increasing the pressure would shift the equilibrium towards the product side.

b) Since the reaction is endothermic ($\Delta H > 0$), increasing the temperature would shift the equilibrium towards the products.

c) To obtain $K_p$ at 550 K, first $K_p$ at 298.15 has to be calculated. This requires the calculation of $\Delta S_{\text{reaction}}^o$, and subsequently $\Delta G_{\text{reaction}}^o$ at 298.15 K:

$$\Delta S_{\text{reaction}}^o (298.15 \text{ K}) = \sum_i v_i S_{f,i}^o = 2 \times (238.9 \text{ J K}^{-1} \text{ mol}^{-1}) - 3 \times (205.2 \text{ J K}^{-1} \text{ mol}^{-1}) = -137.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_p (298.15 \text{ K}) = \text{Exp} \left[ - \frac{\Delta G (298.15 \text{ K})}{R T} \right]$$

$$= \text{Exp} \left[ - \frac{(285.4 \times 10^3 \text{ J mol}^{-1}) + (298.15K) \times (-137.8 \text{ J K}^{-1} \text{ mol}^{-1})}{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \times (550 \text{ K})} \right] = 5.9865 \times 10^{-58}$$

Then:

$$K_p (550 \text{ K}) = \text{Exp} \left[ \ln(298.15 \text{ K}) - \frac{285.4 \times 10^3}{8.314472 \times 298.15} \left( \frac{1}{550} - \frac{1}{298.15} \right) \right] = 4.98 \times 10^{-35}$$

d) $K_x$ at 550 K and 0.500 bar with $\Delta v = 1$ is given by:

$$K_x = K_p \left( \frac{p}{p^\Delta v} \right)^{-\Delta v} = K_p \left( \frac{0.5 \text{ bar}}{1.0 \text{ bar}} \right)^{-1} = 2 K_p = 2 \times (4.98 \times 10^{-35}) = 9.96 \times 10^{-35}$$

Q1. Prove that $\left\{ \frac{\partial (\Delta A / T)}{\partial (1 / T)} \right\}_V = -\Delta U / T^2$ and $\left\{ \frac{\partial (\Delta A / T)}{\partial (T)} \right\}_V = \Delta U$. They are also known as Gibbs-Helmholtz equations. Write an expression analogous to Eq. (6.37) to relate $\Delta A$ at two temperatures. (Modified from P6.27).
\[
\frac{\partial (\Delta A/T)}{\partial (T)} = \frac{1}{T} \frac{\partial \Delta A}{\partial T} \bigg|_V - \frac{\Delta S}{T} - \frac{\Delta A}{T^2} = -\frac{\Delta A + T \Delta S}{T^2} = -\Delta U/T^2
\]

\[
\frac{\partial (\Delta A/T)}{\partial (1/T)} = \left(\frac{\partial (\Delta A/T)}{\partial T}\right)_V \left(\frac{\partial T}{\partial (1/T)}\right)_V = -T^2 \left(\frac{\partial (\Delta A/T)}{\partial (1/T)}\right)_V = \Delta U
\]

At constant \( V \),

\[
\int_{T_1}^{T_2} d\left(\frac{\Delta A}{T}\right) = \int_{T_1}^{T_2} d\left(\frac{\Delta U}{T}\right)
\]

\[
\frac{\Delta A(T_2)}{T_2} \approx \frac{\Delta A(T_1)}{T_1} + \Delta U(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]
Q2. Figure 6.8 in p126 depicts the total Gibbs energy for a mixture of NO\textsubscript{2}(g) and N\textsubscript{2}O\textsubscript{4}(g) at a different ratio in its equilibrium between (2 - 2\(\xi\)) mole of NO\textsubscript{2} and \(\xi\) mole of N\textsubscript{2}O\textsubscript{4}(g) at a constant pressure and temperature at 1 bar and 298 K. (a) Reproduce the plots for \(G_{\text{pure}}\) and \(G_{\text{mixture}}\) assuming that \(G_{\text{m}}^{0}(\text{NO}_2, \text{g}) = -38.45 \text{ kJ mol}^{-1}\) and \(G_{\text{m}}^{0}(\text{N}_2\text{O}_4, \text{g}) = -79.60 \text{ kJ mol}^{-1}\). (b) Explain how you obtained the equations to calculate \(G_{\text{pure}}\) and \(G_{\text{mixture}}\). (c) How much is \(\xi\) in the equilibrium state.
(Modified from P6.41)

(a)

\[
\begin{align*}
G_{\text{pure}} &= (2 - 2\xi) G_{\text{m}}^{0} (\text{NO}_2, \text{g}) + \xi G_{\text{m}}^{0} (\text{N}_2\text{O}_4, \text{g}) = (2 - 2\xi) \times (-38.45 \text{ kJ mol}^{-1}) \\
&\quad + \xi \times (-79.60 \text{ kJ mol}^{-1}) = -76.90 \text{ kJ mol}^{-1} - 2.70\xi \text{ kJ mol}^{-1} \\
G_{\text{mixture}} &= G_{\text{pure}} + \Delta G_{\text{mixing}} = G_{\text{pure}} + nRT(x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4}) \\
&= G_{\text{pure}} + (2 - \xi)RT \left( \frac{2 - 2\xi}{2 - \xi} \ln \frac{2 - 2\xi}{2 - \xi} + \frac{\xi}{2 - \xi} \ln \frac{\xi}{2 - \xi} \right) \\
&= -76.90 \text{ kJ mol}^{-1} - 2.70\xi \text{ kJ mol}^{-1} + 8.314472 \times 10^{-3} \times 298 \text{ kJ mol}^{-1} \\
&\quad \times (2 - 2\xi) \ln \frac{2 - 2\xi}{2 - \xi} + \xi \ln \frac{\xi}{2 - \xi}
\end{align*}
\]

(b) At the equilibrium state, \(G_{\text{mixture}}\) has a minimum is at \(\xi = 0.72\).
Q3. Plot $G_{\text{mixture}}(\xi)$ at 350K for the system described in Q2 (assume that the total pressure is 1 bar). Does $T$ affect $\xi$ in the equilibrium state? (Hint: first, obtain $G_m^0(\text{NO}_2, g)$ and $G_m^0(\text{N}_2\text{O}_4, g)$ at $T = 400K$.)

\[
G_m^0(\text{NO}_2, g, 350K) = \frac{350K}{298K} G_m^0(\text{NO}_2, g, 298K) + 350K \times \Delta H^o_T(\text{NO}_2, g)(\frac{1}{350K} - \frac{1}{298K}) \\
= \frac{350K}{298K} \times (-38.45 \text{ kJ mol}^{-1}) + 350K \times (33.2 \text{ kJ mol}^{-1})(\frac{1}{350K} - \frac{1}{298K}) \\
= -50.95 \text{ kJ mol}^{-1}
\]

\[
G_m^0(\text{N}_2\text{O}_4, g, 350K) = \frac{350K}{298K} G_m^0(\text{N}_2\text{O}_4, g, 298K) + 350K \times \Delta H^o_T(\text{N}_2\text{O}_4, g)(\frac{1}{350K} - \frac{1}{298K}) \\
= \frac{350K}{298K} \times (-50.95 \text{ kJ mol}^{-1}) + 350K \times (11.1 \text{ kJ mol}^{-1})(\frac{1}{350K} - \frac{1}{298K}) \\
= -95.43 \text{ kJ mol}^{-1}
\]

$G_{\text{mixture}} = G_{\text{pure}} + \Delta G_{\text{mixing}} = G_{\text{pure}} + nRT(x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4})$

\[
= (2 - 2\xi) G_m^0(\text{NO}_2, g, 350K) + \xi G_m^0(\text{N}_2\text{O}_4, g, 350K) + nRT(x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4}) \\
= (2 - 2\xi) \times (-50.95 \text{ kJ mol}^{-1}) + \xi \times (-95.43 \text{ kJ mol}^{-1}) + nRT(x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4}) \\
= -101.91 \text{ kJ mol}^{-1} + 6.49\xi \text{ kJ mol}^{-1} \\
+ (2 - \xi)RT(2 - 2\xi) \ln \frac{2 - 2\xi}{2 - \xi} + \xi \ln \frac{\xi}{2 - \xi} \\
= -125.94 \text{ kJ mol}^{-1} + 15.3\xi \text{ kJ mol}^{-1} + 8.314472 \times 10^{-3} \times 350 \text{ kJ mol}^{-1} \\
\times [(2 - 2\xi) \ln \frac{2 - 2\xi}{2 - \xi} + \xi \ln \frac{\xi}{2 - \xi}]
\]

$T$ affects $\xi$ of this reaction, $\xi_{\text{eq}}$ corresponds to $\xi \sim 0.16.$