9.1 Distinguishable molecules. For the reaction given by Eq. (9.1), obtain the partition function assuming that all of the molecules are distinguishable. Then, show that minimizing the Helmholtz free energy leads to inconsistency.

If the molecules are distinguishable,

\[ Z = Z_{1A}^{N_A} Z_{1B}^{N_B} Z_{1AB}^{N_{AB}} \]

Then,

\[ F = -k_B T \ln Z = -k_B T (N_A \ln Z_{1A} + N_B \ln Z_{1B} + N_{AB} \ln Z_{1AB}) \]

Since \( \frac{\partial N_A}{\partial N_{AB}} = -1 \) and \( \frac{\partial N_B}{\partial N_{AB}} = -1 \),

\[
\frac{\partial}{\partial N_{AB}} \left( -\frac{F}{k_B T} \right) = \frac{\partial N_A}{\partial N_{AB}} \frac{\partial}{\partial N_A} N_A \ln Z_{1A} + \frac{\partial N_B}{\partial N_{AB}} \frac{\partial}{\partial N_B} N_B \ln Z_{1B} + \frac{\partial}{\partial N_{AB}} N_{AB} \ln Z_{1AB} \\
= -\ln Z_{1A} - \ln Z_{1B} + \ln Z_{1AB}
\]

Minimize \( F \) by changing \( N_{AB} \) leads to

\[ \ln Z_{1A} + \ln Z_{1B} = Z_{1AB} \]

which places an erroneous requirement on the relationship among the single-molecule partition functions and fails to provide a relationship among \( N_A, N_B, \) and \( N_{AB} \).

9.2 Sufficient condition for minimization of \( F \). Equation (9.7) gives a condition necessary for \( F \) to minimize, but it is not sufficient, since maximization of \( F \) satisfies the same Eq. (9.7). Show that \( F \) minimizes for Eq. (9.10).

If the second-order derivative of \( F \) by \( N_{AB} \) is positive, \( F \) will minimize at that value of \( N_{AB} \).

\[
\frac{\partial^2}{\partial N_{AB}^2} \left( -\frac{F}{k_B T} \right) = \frac{\partial N_A}{\partial N_{AB}} \frac{1}{N_A} + \frac{\partial N_B}{\partial N_{AB}} \frac{1}{N_B} - \frac{1}{N_{AB}} = -\frac{1}{N_A} - \frac{1}{N_B} - \frac{1}{N_{AB}}
\]

which is negative.

9.3 Decomposition of a diatomic molecule. Develop a discussion similar to the one in Section 9.1 to derive \( K_N \) given by Eq. (9.24).
\[ Z = \frac{Z_{1A}^N A^N}{N_{A_2}! N_A^!} \]

\[ \ln Z = N_{A_2} (\ln Z_{1A_2} - \ln N_{A_2} + 1) + N_A (\ln Z_{1A} - \ln N_A + 1) \]

\[ \frac{\partial}{\partial N_A} \left( -\frac{F}{k_B T} \right) = \frac{\partial N_{A_2}}{\partial N_A} \frac{\partial}{\partial N_{A_2}} N_{A_2} (\ln Z_{1A_2} - \ln N_{A_2} + 1) + \frac{\partial}{\partial N_A} N_A (\ln Z_{1A} - \ln N_A + 1) \]

\[ = -\frac{1}{2} (\ln Z_{1A_2} - \ln N_{A_2}) + (\ln Z_{1A} - \ln N_A) \]

When \( F \) minimizes,

\[ K_N = \frac{N_A^2}{N_{A_2}} = \frac{Z_{1A}^2}{Z_{1A_2}} \]

### 9.4 Variance.

Calculate the variance of \( N_A \) for the isomerization reaction in Section 9.3.

\[ \left\langle N_A^2 \right\rangle = \left\langle N_A (N_A - 1) \right\rangle + \left\langle N_A \right\rangle \]

where

\[ \left\langle N_A (N_A - 1) \right\rangle = \frac{1}{Z} \sum_{N_A=2}^{N} N_A (N_A - 1) \frac{Z_{1A}^{N_A} Z_{1B}^{N-N_A}}{N_A! (N-N_A)!} = \frac{1}{Z} \sum_{N_A=2}^{N} \frac{Z_{1A}^{N_A} Z_{1B}^{N-N_A}}{(N_A-2)! (N-N_A)!} \]

\[ = \frac{Z_{1A}^2}{Z} \sum_{N_A=2}^{N} \frac{Z_{1A}^{N-2} Z_{1B}^{(N-2)-(N_A-2)}}{(N_A-2)! [(N-2) - (N_A - 2)]!} = \frac{Z_{1A}^2}{Z} \frac{(Z_{1A} + Z_{1B})^{N-2}}{(N-2)!} \]

\[ = N(N-1) \frac{Z_{1A}^2}{(Z_{1A} + Z_{1B})^2} \]

Therefore,

\[ \left\langle N_A^2 \right\rangle = N(N-1) \frac{Z_{1A}^2}{(Z_{1A} + Z_{1B})^2} + N \frac{Z_{1A}}{Z_{1A} + Z_{1B}} \]

The variance is
\[ \langle \Delta N_A^2 \rangle \rangle = \langle N_A^2 \rangle - \langle N_A \rangle^2 \]
\[ = N(N-1) \frac{Z_{1A}^2}{(Z_{1A} + Z_{1B})^2} + N \frac{Z_{1A}}{Z_{1A} + Z_{1B}} \left( \frac{Z_{1A}}{Z_{1A} + Z_{1B}} \right)^2 = N \frac{Z_{1A}Z_{1B}}{(Z_{1A} + Z_{1B})^2} \]

9.5 Formation of HCl. The equilibrium constant \( K_N \) for the chemical reaction,
\[ \text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl} \]
is expressed by the single-molecule partition functions:
\[ K_N = \frac{N_{\text{HCl}}^2}{N_{\text{H}_2}N_{\text{Cl}_2}} = \frac{Z_{\text{HCl}}^2}{Z_{\text{H}_2}Z_{\text{Cl}_2}} \]

All of the three components are in a gas phase.

(1) Express the pressure equilibrium constant \( K_p \) using molecular parameters such as \( m_{\text{H}_2}, m_{\text{Cl}_2}, \Theta_{\text{rot,H}_2}, \Theta_{\text{rot,Cl}_2}, \Theta_{\text{rot,HCl}}, \Theta_{\text{vib,H}_2}, \Theta_{\text{vib,Cl}_2}, \Theta_{\text{vib,HCl}} \), and \( \epsilon_{\text{HCl}} \) (with reference to \( \text{H}_2 \) and \( \text{Cl}_2 \)).

(2) Use \( \Delta_f G^\circ_{298}(\text{HCl}) = -95.30 \text{ kJ/mol} \) and the data below to find \( \epsilon_{\text{HCl}} \).

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \Theta_{\text{rot}, \text{K}} )</th>
<th>( \Theta_{\text{vib}, \text{K}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>87.6</td>
<td>6331</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>0.351</td>
<td>805.5</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>15.2</td>
<td>4302</td>
</tr>
</tbody>
</table>

(1) Since the total number of moles does not change by the reaction,
\[ K_p = K_N = \frac{Z_{\text{HCl}}^2}{Z_{\text{H}_2}Z_{\text{Cl}_2}} \]
The single-molecule partition functions at temperatures higher than \( \Theta_{\text{rot}} \) of \( \text{H}_2 \) are approximated as
\[ Z_{\text{H}_2} = V \left[ \frac{2\pi(2m_{\text{H}_2})k_B T}{h^2} \right]^{3/2} \frac{T}{\Theta_{\text{rot,H}_2}} \frac{1}{2 \sinh \frac{\Theta_{\text{vib,H}_2}}{2T}} \]
Therefore,

$$Z_{\text{Cl}_2} = V \left[ \frac{2\pi(2m_{\text{Cl}})k_B T}{h^2} \right]^{3/2} \frac{T}{\Theta_{\text{rot,Cl}_2}} \frac{1}{2 \sinh \frac{\Theta_{\text{vib,Cl}_2}}{2T}}$$

$$Z_{\text{HCl}} = V \left[ \frac{2\pi(m_H + m_{\text{Cl}})k_B T}{h^2} \right]^{3/2} \frac{T}{\Theta_{\text{rot,HCl}}} \frac{1}{2 \sinh \frac{\Theta_{\text{vib,HCl}}}{2T}} \exp(-\beta \varepsilon_{\text{HCl}})$$

Therefore,

$$K_p = \left[ \frac{(m_H + m_{\text{Cl}})^2}{4m_H m_{\text{Cl}}} \right]^{3/2} \frac{\Theta_{\text{rot,H}_2}}{\Theta_{\text{rot,HCl}}} \frac{\Theta_{\text{rot,Cl}_2}}{2 \sinh \frac{\Theta_{\text{vib,H}_2}}{2T}} \sinh \frac{\Theta_{\text{vib,Cl}_2}}{2T} \frac{\sinh \frac{\Theta_{\text{vib,HCl}}}{2T}}{2 \sinh \frac{\Theta_{\text{vib,HCl}}}{2T}} \exp(-2\beta \varepsilon_{\text{HCl}})$$

(2)

$$\left[ \frac{(m_H + m_{\text{Cl}})^2}{4m_H m_{\text{Cl}}} \right]^{3/2} = 28.2$$

$$\frac{\Theta_{\text{rot,H}_2}}{\Theta_{\text{rot,Cl}_2}} \frac{\Theta_{\text{rot,Cl}_2}}{\Theta_{\text{rot,HCl}}} = 0.133$$

At 298.15 K,

$$\frac{\sinh \frac{\Theta_{\text{vib,H}_2}}{2T}}{\sinh \frac{\Theta_{\text{vib,HCl}}}{2T}} \frac{\sinh \frac{\Theta_{\text{vib,Cl}_2}}{2T}}{\sinh \frac{\Theta_{\text{vib,HCl}}}{2T}} = 0.0795$$

From $\Delta G_{298}^\circ(\text{HCl}) = -95.30 \text{ kJ/mol} = -1.583 \times 10^{-19} \text{ J}$, we get $K_p = 4.92 \times 10^{16}$ at 298.15 K. Then, $\exp(-2\beta \varepsilon_{\text{HCl}}) = 1.65 \times 10^{17}$, and $\varepsilon_{\text{HCl}} = -8.16 \times 10^{-20} \text{ J}$.

### 9.6 Haber process

We consider Haber process

$$3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$$

in a container of volume $V$ and temperature $T$. Let A, B, and C represent H$_2$, N$_2$, and NH$_3$, respectively. The system has $N_A$ molecules of H$_2$, $N_B$ molecules of N$_2$, and $N_C$ molecules of NH$_3$. The single-molecule partition functions are $Z_{1A}$, $Z_{1B}$, and $Z_{1C}$,
respectively.

(1) Express the equilibrium constant $K_N$ using $Z_{1A}$, $Z_{1B}$, and $Z_{1C}$.

(2) Express $K_N$ using microscopic parameters of the molecules. How does $K_N$ depend on $V$? Does it agree with Le Chatelier’s principle?

(3) Convert your answer in (1) into the pressure equilibrium constant $K_p$ for partial pressures, $p_A$, $p_B$, and $p_C$. How does $K_p$ depend on $V$?

(1)

$$Z = \frac{Z_{1A}^{N_A} Z_{1B}^{N_B} Z_{1C}^{N_C}}{N_A! N_B! N_C!}$$

$$\ln Z = N_A (\ln Z_{1A} - \ln N_A + 1) + N_B (\ln Z_{1B} - \ln N_B + 1) + N_C (\ln Z_{1C} - \ln N_C + 1)$$

Maximize $\ln Z$ (minimize $F$).

$$-\frac{3}{2} (\ln Z_{1A} - \ln N_A) - \frac{1}{2} (\ln Z_{1B} - \ln N_B) + (\ln Z_{1C} - \ln N_C) = 0$$

where

$$\frac{\partial N_A}{\partial N_C} = -\frac{3}{2}, \frac{\partial N_B}{\partial N_C} = -\frac{1}{2}$$

were used. Then,

$$K_N = \frac{N_C^2}{N_A^3 N_B} = \frac{Z_{1C}^2}{Z_{1A}^3 Z_{1B}}$$

(2)

$$Z_{1A} = V \left(\frac{2\pi m_A}{\beta h^2}\right)^{3/2} Z_{1A,\text{rot}} Z_{1A,\text{vib}},$$

$$Z_{1B} = V \left(\frac{2\pi m_B}{\beta h^2}\right)^{3/2} Z_{1B,\text{rot}} Z_{1B,\text{vib}},$$

$$Z_{1C} = V \left(\frac{2\pi m_C}{\beta h^2}\right)^{3/2} Z_{1C,\text{rot}} Z_{1C,\text{vib}} \exp(-\beta \varepsilon_C)$$
\[ K_N = \frac{1}{V^2} \left( \frac{2\pi}{\beta h^2} \right)^{-3} \left( \frac{m_C^2}{m_A^3 m_B} \right)^{3/2} \frac{(Z_{1C,\text{rot}} Z_{1C,\text{vib}})}{(Z_{1A,\text{rot}} Z_{1A,\text{vib}})^3 (Z_{1B,\text{rot}} Z_{1B,\text{vib}})} \exp(-2\beta \varepsilon_C) \]

\( K_N \) is proportional to \( 1/V^2 \).

Le Chatelier’s principle states that an increasing \( V \) shifts the equilibrium to left. Then, \( K_N \) decreases. There is an agreement.

(3)

\[ K_p = \frac{p_c^2}{p_A^3 p_B} = \left( \frac{V}{k_B T} \right)^2 \frac{N_C^3}{N_A^3 N_B} \]

\[ K_p = \beta^2 \left( \frac{2\pi}{\beta h^2} \right)^{-3} \left( \frac{m_C^2}{m_A^3 m_B} \right)^{3/2} \frac{(Z_{1C,\text{rot}} Z_{1C,\text{vib}})^2}{(Z_{1A,\text{rot}} Z_{1A,\text{vib}})^3 (Z_{1B,\text{rot}} Z_{1B,\text{vib}})} \exp(-2\beta \varepsilon_C) \]

\( K_p \) is independent of \( V \), a reasonable result.