Pathria & Beale, Chapter 1

Problem 1.4

We consider a gas of \( N \) hard spheres, each with
radius \( r_o \) and volume \( V_o = \frac{4}{3} \pi r_o^3 \), confined to a
region of volume \( V \).

The factor in \( \Omega = e^S \) that depends on \( V \)
is the product of \( N \) factors, one for each of
the successive particles inserted into the volume.

The center-of-mass of a hard sphere must be a
distance \( r_o \) away from the boundary of the
container. The volume for the first particle is
therefore \( V - A r_o \), where \( A \) is the area of the
container.

The center-of-mass of the second hard sphere must
be a distance \( r_o \) away from the boundary and
also a distance \( 2r_o \) away from the center of mass
of the first hard sphere. The volume factor for
the second particle is therefore \( V - A r_o - \frac{4}{3} \pi (2r_o)^3 \).

The volume factor for each successive hard sphere
is smaller by the same term. The complete
volume factor in \( \Omega = e^S \) is therefore
\[
\prod_{n=1}^{N} \left( V - A_r - (n-1) \frac{S V_0}{V - A_r} \right) \\
= \left( V - A_r \right)^N \prod_{n=1}^{N} \left( 1 - (n-1) \frac{S V_0}{V - A_r} \right) \\
= \left( V - A_r \right)^N \exp \left( \sum_{n=1}^{N} \log \left( 1 - (n-1) \frac{S V_0}{V - A_r} \right) \right)
\]

If \( N V_0 < V \), the logarithm can be approximated by the first term in its expansion in powers of \( V_0/V - A_r \).

\[
\log \left( 1 - (n-1) \frac{S V_0}{V - A_r} \right) \approx -(n-1) \frac{S V_0}{V - A_r}
\]

The sum then reduces to

\[
\sum_{n=1}^{N} \left( -(n-1) \frac{S V_0}{V - A_r} \right)
= - \frac{S V_0}{V - A_r} \sum_{n=1}^{N} (n-1)
= - \frac{S V_0}{V - A_r} \frac{(N-1)N}{2}
\]

\[
\approx - \frac{4N_0 N^2}{V - A_r}
\]

The volume factor \( \Omega = e^S \) reduces to

\[
\left( V - A_r \right)^N \exp \left( - \frac{4N_0 N^2}{V - A_r} \right)
= \left[ \left( V - A_r \right) \exp \left( - \frac{4N_0 N}{V - A_r} \right) \right]^N
\]
If \( Nv_0 \ll V \), the exponential can be expanded to first order in \( \frac{Nv_0}{V-Ar_0} \). The volume factor reduces to

\[
\left[ (V-Ar_0) \left( 1 - \frac{4Nv_0}{V-Ar_0} \right) \right]^N
\]

\[
= (V-Ar_0 - 4Nv_0)^N
\]

If the length scale for the container is \( L \), the volume scales as \( L^3 \) and the area scales as \( L^2 \). In the thermodynamic limit, the term \( Ar_0 \) is negligible compared to \( V \). The volume factor therefore reduces to

\[
(V - 4Nv_0)^N
\]

The volume \( V \) is decreased by 4 times the total volume of the \( N \) hard spheres.
Problem 1.6

The thermodynamic variables of a monatomic gas satisfy

\[ PV = NkT \quad \text{and} \quad E = \frac{3}{2} NkT \]

The initial temperature, pressure, and volume are

\[ kT = (1.38 \times 10^{-23} \text{ J/K}) (300 \text{K}) = 4.14 \times 10^{-21} \text{ J} \]

\[ P = 1 \text{ atm} = 1.01 \times 10^5 \frac{\text{J}}{\text{m}^3} \]

\[ V = (1 \text{ m}) \pi (0.1 \text{ m}/2)^2 = 7.85 \times 10^{-3} \text{ m}^3 \]

The number of atoms is

\[ N = \frac{PV}{kT} \]

\[ = \frac{(1.01 \times 10^5 \text{ J/m}^3)(7.85 \times 10^{-3} \text{ m}^3)}{4.14 \times 10^{-21} \text{ J}} \]

\[ = 1.92 \times 10^{23} \]

The initial energy is

\[ E = \frac{3}{2} NkT \]
\[ = \frac{3}{2} (1.92 \times 10^{23}) (4.14 \times 10^{-21} \text{ J}) \]

\[ = 1190 \text{ J} \]

The electrical discharge adds an energy of \(10^4 \text{ J}\). The resulting energy is \(E_1 = 11,190 \text{ J}\). The final temperature is

\[ T = \frac{E_1}{\frac{3}{2} N k} \]

\[ = \frac{11,190 \text{ J}}{\frac{3}{2} (1.92 \times 10^{23}) (1.38 \times 10^{-22} \text{ J/K})} \]

\[ = 2820 \text{ K} \]
Problem 1.9

Since \( N, V, E \) and the entropy \( S \) are all extensive quantities, the entropy satisfies

\[
S(2N, 2V, 2E) = 2S(N, V, E)
\]

Differentiating with respect to \( N \) and then setting \( \partial N = 1 \), we obtain

\[
\left( \frac{\partial S}{\partial N} \right)_{V,E} N + \left( \frac{\partial S}{\partial V} \right)_{N,E} V + \left( \frac{\partial S}{\partial E} \right)_{N,V} E = S
\]

The fundamental thermodynamic relation is

\[
dE = T dS - P dV + \mu dN
\]

The differential of \( S \) can be expressed as

\[
dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN
\]

We can now identify the partial derivatives of \( S \):

\[
\left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T} \quad \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{P}{T} \quad \left( \frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T}
\]

Inserting these into the extensivity relation, we get
\[-\frac{\mu}{T} N + \frac{P}{T} V + \frac{1}{T} E = S\]

This can be rewritten:

\[N'_{\mu} = E + PV - TS\]
Problem 1.11

At room temperature and pressure, nitrogen and oxygen are both diatomic gases. For separated gases consisting of $x_i$ moles of diatomic molecules with mass $m_i$, the ideal gas law is

$$PV = x_i N_A k T$$

The entropy is

$$S = x_i N_A k \left[ \log \frac{V}{x_i N_A} + \frac{3}{2} \log \frac{m_i k T}{2 \pi h^2} + f_i(T) \right]$$

where $f_i(T)$ takes into account vibration and rotations.

Separate gases of 1 mole of $O_2$ and 4 moles of $N_2$ at temperature $T$ and pressure $P$ will have volumes $V_{O_2} = N_A k T / P$ and $4V_{N_2}$ respectively. Their entropies are

$$S_{O_2} = N_A k \left[ \log \frac{V_{O_2}}{N_A} + \frac{3}{2} \log \frac{m_{O_2} k T}{2 \pi h^2} + f_{O_2}(T) \right]$$

$$S_{N_2} = 4N_A k \left[ \log \frac{4V_{N_2}}{4N_A} + \frac{3}{2} \log \frac{m_{N_2} k T}{2 \pi h^2} + f_{N_2}(T) \right]$$

If the two gases are allowed to mix, the resulting air will have volume $5V_{O_2}$. Its entropy will be
\[ S_{\text{air}} = N_A k_b \left[ \log \frac{5V_o}{N_A} + \frac{3}{2} \log \frac{m_g k_B}{2\pi \hbar^2} + f_{O_2}(T) \right] \]

\[ + 4N_A k_b \left[ \log \frac{5V_o}{4N_A} + \frac{3}{2} \log \frac{m_{N}_2 k_B}{2\pi \hbar^2} + f_{N}_2(T) \right] \]

The entropy of mixing is

\[ S_{\text{mixing}} = S_{\text{air}} - (S_{O_2} + S_{N}_2) \]

\[ = N_A k_b \log 5 + 4N_A k_b \log 2 \]

\[ = 2(\log 5 - \log 2)N_A k_b \]

The entropy of mixing per mole of the air is

\[ \frac{S_{\text{mixing}}}{5} = \frac{2}{5}(\log 5 - \log 2)R \]

where \( R = N_A k_b \) is the gas constant.