Problem 2

\[ B(x) = \frac{2S+1}{2s} \coth \left( \frac{2S+1}{2s} x \right) - \frac{1}{2s} \coth \left( \frac{1}{2s} x \right) \]

\[ \coth_n(x) = \frac{1}{x} + \frac{x^3}{3} + \frac{x^5}{45} + \ldots \]

So: \[ B(x) \approx \frac{2S+1}{2s} \left[ \frac{2S}{(2S+1)x} + \frac{2S+1}{6s} x - \frac{1}{45} \left( \frac{2S+1}{2s} \right)^3 x^3 \right] \]

\[ - \frac{1}{2s} \left[ \frac{2S}{x} + \frac{x}{6s} - \frac{1}{45} \cdot \frac{x^3}{8s^3} \right] \]

\[ = \frac{1}{x} + \frac{(2S+1)^2}{12s^2} - \frac{1}{45} \cdot \frac{(2S+1)^4}{(2s)^4} x - \frac{1}{x} - \frac{x}{12s^2} + \frac{1}{45} \cdot \frac{x^3}{(2s)^4} \]

\[ = \frac{(2S+1)^2 - 1}{12s^2} x - \frac{1}{45} \frac{(2S+1)^4 - 1}{(2s)^4} x^3 \]

\[ = \frac{(S+1)}{3s} x - \frac{1}{45} \frac{(2S+1)^4 - 1}{(2s)^4} x^3 \]

\[ (2S+1)^4 - 1 = (4S^2 + 4S + 1)^2 - 1 = [4S(S+1) + 1]^2 - 1 \]

\[ = 16S^2(S+1)^2 + 8S(S+1) + 1 - 1 = 8S(S+1)[2S(S+1) + 1] \]

\[ = 8S(S+1)[2S^2 + 2S + 1] = 8S(S+1)[(S+1)^2 + S^2] \]

\[ = \frac{(S+1)}{3s} x - \frac{1}{45} \frac{8S(S+1)[(S+1)^2 + S^2]}{(2s)^4} x^3 \]

Now, we know that:

\[ m = B\left(\frac{3s}{S+1}, \frac{m}{c}\right) \]
So:

\[
m = B \left( \frac{3s}{s+1}, \frac{m}{c} \right) - \frac{1}{3s} \cdot \frac{8s(s+1)[(s+1)^2 + s^2]}{2s^4} \cdot \left( \frac{3s}{s+1} \frac{m}{c} \right)^3
\]

\[
= \frac{m}{c} - \frac{1}{45} \cdot \frac{8s(s+1)[(s+1)^2 + s^2]}{2s^4} \cdot \frac{27}{(s+1)^3} \left( \frac{m}{c} \right)^3
\]

\[
= \frac{m}{c} - \frac{1}{5} \cdot \frac{([s+1]^2 + s^2) \cdot 3}{2(s+1)^2} \left( \frac{m}{c} \right)^3
\]

\[
\frac{1}{\gamma} - 1 = \frac{3}{10} \frac{(s+1)^2 + s^2}{(s+1)^2} \frac{m^2}{c^3}
\]

\[
m^2 = (\gamma^2 - 1^3) \frac{10}{3} \frac{(s+1)^2}{(s+1)^2 + s^2}
\]

Now, \( \gamma = \frac{T}{T_c} = \frac{T_c - T}{T_c} = 1 - \frac{T_c - T}{T_c} \)

Close to \( T_c \), \( \frac{T_c - T}{T} \ll 1 \)

Denote \( \frac{T_c - T}{T} \equiv \Delta \)

\[
\gamma^2 - 1^3 = (1 - \Delta)^2 - (1 - \Delta)^3 = 1 - 2\Delta + \Delta^2 - 1 + 3\Delta - 3\Delta^2 + \Delta^3 = \Delta - 2\Delta^2 + \Delta^3 \propto \Delta
\]

\( \text{ignoring higher order terms} \)

So:

\[
m^2 = \frac{10}{3} \frac{(s+1)^2}{(s+1)^2 + s^2} \frac{T_c - T}{T_c} \Rightarrow m \propto (T_c - T)^{\frac{1}{2}}
\]
In the limit of low temperatures, we have

\[
\left( \frac{1}{\varepsilon} \right) \left( \frac{1}{\varepsilon^2 \theta} \right) \int dx (1 + \varepsilon) = \infty
\]

Thus, \( \gamma = (1) \).

Since

\[
\left( \frac{1}{\varepsilon^2 \theta} \right) \int dx \varepsilon + 1 = (1)
\]

we have

\[
\left( \frac{1}{\varepsilon^2 \theta} \right) \int dx \varepsilon + 1 = \gamma
\]

Thus, the first two terms \( f = 0 \) and \( g = 1 \) are important. Therefore

\[
\gamma = (1)
\]
THE CLASSICAL ROTATIONAL PARTITION FUNCTION

4.3 (a) For most polyatomic molecules at temperatures above the normal boiling point of the fluid, the rotational energy levels are so closely spaced that they approximate to a continuum, and rotational energy may be calculated accurately on the basis that the molecule is a rigid body obeying the laws of classical mechanics.

Show that the rotational kinetic energy of a heteronuclear diatomic molecule about its centre of mass is given by

\[ \varepsilon = \frac{1}{2I} \left( P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta} \right), \]

where \( I \) is the moment of inertia, and \( P_\theta \) and \( P_\phi \) are the moments conjugate to \( \theta \) and \( \phi \).

(b) Obtain the rotational partition function for the rotation of a heteronuclear diatomic molecule by evaluating the phase integral introduced in Problem 3.4.

\[ Z_{\text{rot}} = \frac{1}{h^3} \int_0^{2\pi} d\phi \int_0^\infty dP_\phi \int_0^{\pi} \sin^2 \theta d\theta \exp \left[ -\frac{1}{2kT} \left( \frac{P_\theta^2}{2} + \frac{P_\phi^2}{\sin^2 \theta} \right) \right]. \]

(c) The general quantum mechanical solution for the rotational coordinates of a rigid body with three degrees of rotational freedom is complicated but, since the moments of inertia of all but the very lightest of molecules are large, and as the quantum levels are closely spaced compared with \( kT \) at temperatures above the normal boiling point of the substance, the classical partition function may be safely used.

Evaluation of the classical phase integral yields

\[ Z_{\text{rot}} = \frac{\sqrt{\pi \alpha}}{\alpha h^3} (8\pi^2 kT)^{\frac{3}{2}} (I_a I_b I_c)^{\frac{1}{2}}, \]

where \( \alpha \) is the symmetry number of the molecule and is defined as the number of values of the rotational coordinates which all correspond to one orientation of the molecule. The quantity \( I_a I_b I_c \) is the product of the three principal moments of inertia of the molecule.

Obtain expressions for the rotational energy, heat capacity, free energy, and entropy from the above partition function.

Solution

(a) The molecule rotates about the centre of gravity \( c \). The total energy is the sum of the precessional energy, in which the atoms of mass \( m_A \) and \( m_B \) follow the circular orbits shown in Figure 4.3.1 with velocity \( \omega \) and the energy of end-over-end rotation with velocity \( d\theta / dt \). The moment of inertia is

\[ I = m_A r_A^2 + m_B r_B^2 = \frac{m_A m_B}{m_A + m_B} (r_A - r_B)^2 \]
Chapter 4

4.4 Ideal classical gases of polyatomic molecules

The precessional inertia is

\[ I_\alpha = m_A (A \dot{a})^2 + m_B (B \dot{b})^2 \]

so that

\[ \int_0^\infty \exp \left(-\frac{P_\theta^2}{2kT} \right) dP_\theta = (2\pi/kT)^{\frac{1}{2}}. \]

Using the same standard integral again we have

3. \[ Z_{\text{rot}} = \frac{2\pi}{h^4} (2\pi/kT)^{\frac{1}{2}} \int_0^\infty \exp \left(-\frac{P_\theta^2}{2kT \sin^2 \theta} \right) dP_\theta \frac{d \theta}{\sin^2 \theta}. \]

4. \[ Z_{\text{rot}} = \frac{2\pi}{h^4} (2\pi/kT)^{\frac{1}{2}} \int_0^\pi \sin \theta \ d \theta = \frac{8\pi^2 k T}{h^2}. \]

The total energy \( e \) is therefore

\[ e = E_\alpha + E_\beta = \frac{1}{2} I(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta). \]

Differentiating with respect to \( \theta \) and \( \phi \) we obtain the angular momenta \( P_\theta \) and \( P_\phi \).

\[ P_\theta = \frac{\partial e}{\partial \theta} = I \dot{\theta}, \quad P_\phi = \frac{\partial e}{\partial \phi} = I \dot{\phi} \sin^2 \theta \]

so that

\[ e = \frac{i}{2I} \left(P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta} \right). \]

(b) The fourfold integration is straightforward.

1. \[ \int_0^{2\pi} d \phi = 2\pi \]

2. \[ \int_0^\infty \exp \left(-\frac{P_\theta^2}{2kT} \right) dP_\theta. \]

This has the form of the Gaussian error integral

\[ \int_0^\infty \exp(-ax^2)dx = \frac{1}{\sqrt{\pi a}}. \]

4.4 Polyatomic molecules in the gaseous phase are free to rotate about the centre of mass of the molecule. This rotational motion is strictly independent of the translational motion, and at moderate temperatures in which the vibrational modes of the molecule are excited only to a negligible extent, it can be assumed to be independent of vibrational motion within the molecule.

A heteronuclear diatomic molecule has two degrees of rotational freedom, and the rotational energy is quantized such that the energy \( \epsilon_j \) in the \( j \)th rotational state is given by

\[ \epsilon_j = j(j+1) \frac{\hbar^2}{8\pi^2 I} = j(j+1) \hbar \theta_r, \]

where \( \theta_r = \hbar^2/8\pi^2 I k \) and has the dimensions of temperature. Each rotational state except the first \( (J = 0) \) is doubly degenerate, as the
The rotational entropy is given by:

\[
\gamma_0 N = 10^3 g
\]

so that

\[
\mathcal{L}_0 N = \left( \frac{v^4}{L^4 U^8} \right) \mathcal{L}_0 \gamma_0 N = \left( \frac{v^4}{L^4 U^8} \right) \mathcal{L}_0 \gamma_0 N = 10^3 g
\]

From the rotational partition function we obtain

\[
\frac{v^4}{L^4 U^8} = 10^3 Z
\]

and so that

\[
\frac{v^4}{L^4 U^8} = 10^3 Z
\]

The rotational entropy is given by:

\[
\gamma_0 N = 10^3 g
\]

so that

\[
\mathcal{L}_0 N = \left( \frac{v^4}{L^4 U^8} \right) \mathcal{L}_0 \gamma_0 N = \left( \frac{v^4}{L^4 U^8} \right) \mathcal{L}_0 \gamma_0 N = 10^3 g
\]

From the rotational partition function we obtain

\[
\frac{v^4}{L^4 U^8} = 10^3 Z
\]

and so that

\[
\frac{v^4}{L^4 U^8} = 10^3 Z
\]

We have the integral in the form

\[
\int_0^\infty \left[ \frac{J}{\theta f(1+f)} \right] \mathcal{L}_0 \gamma_0 N = 10^3 Z
\]

and

\[
\int_0^\infty \left[ \frac{J}{\theta f(1+f)} \right] \mathcal{L}_0 \gamma_0 N = 10^3 Z
\]

When we can replace the sum by an integral

\[
\left( \frac{J}{\theta f(1+f)} \right) \mathcal{L}_0 \gamma_0 N = 10^3 Z
\]

Hence

\[
(1+f) = \gamma_0 N \frac{L^4 U^8}{v^4} = f_0
\]

The rotational energy and the defects are given by:

\[
(4) \text{ The rotational energy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(5) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(6) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(7) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(8) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(9) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]

\[
(10) \text{ The rotational entropy } \gamma_0 N \text{ and the defects } f_0 \text{ are given by}
\]
As we know that the high temperature limits are $E_{\text{rot}} = N_0 k T$ and $C_{\text{rot}} = N_0 k$, we can sketch the rotational energy and heat capacity curves (see Figure 4.4.1). The point of inflection in the energy curve results in a maximum in the corresponding heat capacity curve.

A CONVENIENT FORMULA FOR THE HIGH TEMPERATURE ROTATIONAL PARTITION FUNCTION

4.5 The partition function for a molecule in which two degrees of rotational freedom are possible is given by the equation

$$ Z_{\text{rot}} = \sum_{J=0}^{\infty} \frac{(2J+1) \exp \left[ -\frac{J(J+1)\theta_r}{T} \right]}{\theta_r} . $$

If $\theta_r/T$ is large, $Z_{\text{rot}}$ can be evaluated only by direct summation. If $\theta_r/T < 1$, it is possible to construct a simple and convenient expression for $Z_{\text{rot}}$ which does not contain a summation of exponential terms. Mulholland (2) used the Euler-Maclaurin expansion, which expresses the difference between the (unknown) sum and the corresponding (known) integral in polynomial form, to obtain a simple expression for $Z_{\text{rot}}$.

(a) Obtain an expression for the rotational partition function of a homonuclear diatomic molecule as a polynomial in $\theta_r/T$ using the Euler-Maclaurin summation formula in the form

$$ Z_{\text{rot}} = \frac{T}{\theta_r} \exp \left( \frac{\theta_r}{4T} \right) \left[ 1 + \sum_{n=0}^{\infty} a_n \left( \frac{\theta_r}{T} \right)^{n+1} \right] , $$

where

$$ a_n = -\frac{1}{(n+1)!} \frac{\Gamma(n+1) - \Gamma(n+2)}{n+1} , $$

and where $B_{2n}$ are the Bernoulli numbers

$$ B_2 = \frac{1}{6} , \quad B_4 = -\frac{1}{30} , \quad B_6 = \frac{1}{42} , \quad B_8 = -\frac{1}{30} , \quad B_{10} = \frac{5}{66} . $$

(b) Show that the polynomial obtained in part (a) is given by the general formula

$$ Z_{\text{rot}} = \frac{T}{\theta_r} \exp \left( \frac{\theta_r}{4T} \right) \left[ 1 + \frac{\Gamma(1) - \Gamma(2)}{1!} \left( \frac{\theta_r}{T} \right)^2 + \frac{\Gamma(3) - \Gamma(4)}{2!} \left( \frac{\theta_r}{T} \right)^4 + \ldots \right] , $$

where $\Gamma(n)$ is the Gamma function with $J = 0$.

The higher derivatives are readily obtained

$$ f^0(0) = 1 + \frac{1}{12} \left( \frac{\theta_r}{T} \right)^2 + \frac{1}{315} \left( \frac{\theta_r}{T} \right)^3 + \ldots $$

and when $J = 0$, $f^0(0) = 1$.

$4.5$ The general formula gives

$$ Z_{\text{rot}} = \frac{T}{\theta_r} \exp \left( \frac{\theta_r}{4T} \right) \left[ 1 + \frac{\Gamma(1) - \Gamma(2)}{1!} \left( \frac{\theta_r}{T} \right)^2 + \frac{\Gamma(3) - \Gamma(4)}{2!} \left( \frac{\theta_r}{T} \right)^4 + \frac{\Gamma(5) - \Gamma(6)}{3!} \left( \frac{\theta_r}{T} \right)^6 + \ldots \right] , $$

On multiplying out and collecting terms we obtain the formula derived in part (a).

(c) To obtain the heat capacity we make use of the results

$$ F = -N k T \ln Z_{\text{rot}} , \quad E = -T^2 \frac{d(F/T)}{dT} , \quad C_v = \frac{3E}{\partial T} . $$

Thus

$$ \ln Z(T) = -\ln \frac{\theta_r}{T} - \ln \left( 1 - x \right) = -\left( \frac{\theta_r}{T} + \frac{1}{2} x^2 + \frac{1}{3} x^3 + \frac{1}{4} x^4 + \ldots \right) , $$

where

$$ x = -\left[ \frac{1}{3} + \frac{1}{15} \left( \frac{\theta_r}{T} \right)^2 + \frac{1}{315} \left( \frac{\theta_r}{T} \right)^3 + \ldots \right] . $$

Multiplying out and collecting terms, we find
\[
\ln Z(T) = -\left[ \ln \frac{\theta_v}{T} - \frac{1}{2} - \frac{\theta_v}{90 \frac{\theta_v}{T}} - \frac{8}{2835} \left( \frac{\theta_v}{T} \right)^3 + \ldots \right]
\]
from which we obtain
\[
E = NkT \left[ 1 - \frac{1}{3} \frac{\theta_v}{T} - \frac{1}{45} \left( \frac{\theta_v}{T} \right)^2 - \frac{8}{945} \left( \frac{\theta_v}{T} \right)^3 + \ldots \right].
\]
Note that as \( T \to \infty \) the energy approaches the limiting value of \( Nk(T - \frac{1}{2} \theta_v) \) rather than the classical value \( NkT \). Terms in \( \frac{1}{2} \theta_v \) do not occur in either the entropy or the heat capacity:
\[
C_v = Nk \left[ 1 + \frac{1}{45} \left( \frac{\theta_v}{T} \right)^2 + \frac{16}{945} \left( \frac{\theta_v}{T} \right)^3 + \ldots \right].
\]
Using \( S = E/T + Nk \ln Z \) we obtain
\[
S = Nk \left[ 1 - \frac{1}{3} \frac{\theta_v}{T} - \frac{1}{45} \left( \frac{\theta_v}{T} \right)^2 - \frac{8}{945} \left( \frac{\theta_v}{T} \right)^3 \right] - Nk \left[ \ln \frac{\theta_v}{T} - \frac{1}{3} \frac{\theta_v}{T} - \frac{1}{90} \frac{\theta_v}{T} - \frac{8}{2835} \left( \frac{\theta_v}{T} \right)^3 \right]
\]
\[
= Nk \left[ 1 - \ln \frac{\theta_v}{T} - \frac{1}{90} \frac{\theta_v}{T} - \frac{16}{2835} \left( \frac{\theta_v}{T} \right)^3 + \ldots \right].
\]
The limiting value \( Nk \) of the heat capacity as \( T \to \infty \) is approached from above. This is in accordance with the ideas of Problem 4.4.

THERMODYNAMIC PROPERTIES ARISING FROM SIMPLE HARMONIC MODES OF VIBRATION

4.6 (a) In Problem 3.9 it was shown that the partition function for a \([1]\)-oscillator of angular frequency \( \omega = 2\pi \nu \) is given by
\[
Z_{vib} = \exp \left( -\frac{1}{2} \frac{\hbar \omega}{kT} \right) / \left( 1 - \exp \left( -\frac{\hbar \omega}{kT} \right) \right).
\]
Show that the heat capacity and entropy of a \([1]\)-oscillator are independent of the amount of energy which may be possessed by the oscillator in its lowest vibrational state.

(b) The vibrational partition function for a polyatomic molecule with \( n \) vibrational modes may be written as the product of the partition functions of \( n \) distinguishable \([1]\)-oscillators [see Problem 3.9(d)].
\[
Z_{vib} = \prod \left[ \frac{1}{1 - \exp \left( -\frac{\hbar \omega}{kT} \right)} \right].
\]
A non-linear polyatomic molecule has \( 3n - 5 \) vibrational modes, and a linear molecule has \( 3n - 5 \). Of the \( 3n - 5 \) modes \( n - 1 \) are stretching vibrations and these generally have frequencies \( >1000 \text{ cm}^{-1} \). The remaining \( 2n - 5 \) are bending modes, and generally have frequencies considerably lower. Vibrational modes are excited at high temperatures, and an error in the assignment of these modes does not usually introduce an appreciable error into the calculated thermodynamic quantities.

It was shown in Problem 3.9(c) that the heat capacity of \( N \) identical distinguishable \([1]\)-oscillators is \( C_{vib} = NkE(2x) \) where \( x = \hbar \omega/2kT \) and
\[
E(x) = \frac{y^2 e^y}{(e^y - 1)^2}
\]
by graphical interpolation of the Einstein function \( E(y) \) tabulated below. Calculated the molar vibrational heat capacity and entropy at \( 298.15^\circ \text{K} \) of \( \text{O}_2 \), \( \text{Cl}_2 \), and \( \text{Br}_2 \) for which the fundamental vibrational frequencies are \( 1580, 565, \) and \( 323 \text{ cm}^{-1} \) respectively.

(c) By expanding the exponential term in the vibrational partition function and retaining only terms up to \( (\theta_v/T)^2 \), obtain simple approximate formulas for the heat capacity and entropy of a \([1]\)-oscillator which are valid in the region of temperature for which \( (\theta_v/T) < 1 \).

Use these formulas to calculate the vibrational heat capacity of diatomic iodine vapour at \( 100^\circ \text{C} \) and compare with the values obtained using the Einstein functions. (The fundamental vibrational frequency of \( \text{I}_2 \) is \( 214.6 \text{ cm}^{-1} \).)

Solution

(a) Rather than rewrite the numerator of the partition function in the form \( \exp(\xi_{min}/kT) \), we will carry the calculation through using \( \xi_{min} = \hbar \nu \).

The energy of the \([1]\)-oscillator is given by
\[
E_{vib} = NkT^2 \left( \frac{\partial}{\partial T} \ln Z_{vib} \right)_x
\]
so that
\[
E_{vib} = NkT^2 \int \frac{d}{dT} \left( \frac{1}{1 - \exp(-\hbar \nu/kT)} + \ln(\exp(-\hbar \nu/kT)) \right)
\]
\[
= Nk \left( \frac{\hbar \nu}{k} \right) \frac{1}{\exp(\hbar \nu/kT) - 1} + \frac{1}{2} N \hbar \nu.
\]