

Differentiate with respect to x and then multiply by x to obtain

$$s_1 = \sum_{v=0}^{\infty} vx^v = x \frac{ds_0}{dx} = x \frac{d}{dx} \left(\frac{1}{1-x} \right) = \frac{x}{(1-x)^2}$$

Using the same approach, show that

$$s_2 = \sum_{v=0}^{\infty} v^2 x^v = \frac{x + x^2}{(1-x)^3}$$

Following the procedure outlined in the problem, we find

$$\begin{aligned} s_0 &= \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \\ \frac{ds_0}{dx} &= \sum_{n=0}^{\infty} nx^{n-1} = \frac{1}{(1-x)^2} \\ x \frac{ds_0}{dx} &= \sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2} = s_1 \end{aligned}$$

Likewise,

$$\begin{aligned} s_1 &= \sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2} \\ \frac{ds_1}{dx} &= \sum_{n=0}^{\infty} n^2 x^{n-1} = \frac{1}{(1-x)^2} + \frac{2x}{(1-x)^3} \\ x \frac{ds_1}{dx} &= \sum_{n=0}^{\infty} n^2 x^n = x \left[\frac{1-x+2x}{(1-x)^3} \right] \\ &= \frac{x+x^2}{(1-x)^3} \end{aligned}$$

Partition Functions and Ideal Gases

PROBLEMS AND SOLUTIONS

- 18-1. Equation 18.7 shows that $\langle \varepsilon_{\text{trans}} \rangle = \frac{3}{2} k_B T$ in three dimensions, and Problem 18-3 shows that $\langle \varepsilon_{\text{trans}} \rangle = \frac{1}{2} k_B T$ in one dimension and $\frac{2}{2} k_B T$ in two dimensions. Show that typical values of translational quantum numbers at room temperature are $O(10^9)$ for $m = 10^{-26}$ kg, $a = 1$ dm, and $T = 300$ K.

The average translational energy at 300 K is on the order of $k_B T = 4.142 \times 10^{-21}$ J. Recall that

$$\langle \varepsilon \rangle = \frac{h^2 n^2}{8ma^2}$$

So

$$\begin{aligned} n^2 &\approx \frac{8ma^2}{h^2} k_B T = \frac{8(10^{-26} \text{ kg})(0.1 \text{ m})^2}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2} (4.142 \times 10^{-21} \text{ J}) \\ n &\approx 2.75 \times 10^9 \end{aligned}$$

In two and three dimensions, $\langle \varepsilon_{\text{trans}} \rangle$ depends on the sum of the squares of the respective quantum numbers. So for comparable values of a for each dimension, n will be of $O(10^9)$.

- 18-2. Show that the difference between the successive terms in the summation in Equation 18.4 is very small for $m = 10^{-26}$ kg, $a = 1$ dm, and $T = 300$ K. Recall from Problem 18-1 that typical values of n are $O(10^9)$.

Equation 18.4 gives

$$q_{\text{trans}}(V, T) = \left[\sum_{n=1}^{\infty} \exp \left(\frac{-\beta h^2 n^2}{8ma^2} \right) \right]^3$$

The difference between terms in $q_{\text{trans}}(V, T)$ is then

$$e^{-A(n+1)^2} - e^{-An^2} = e^{-An^2} [e^{-A(2n+1)} - 1]$$

where $A = \beta h^2 / 8ma^2 \sim 10^{-19}$. Therefore,

$$e^{-A(2n+1)} - 1 \approx 10^{-10}$$

18-3. Show that

$$q_{\text{trans}}(a, T) = \left(\frac{2\pi mk_{\text{B}}T}{h^2} \right)^{1/2} a$$

in one dimension and that

$$q_{\text{trans}}(a, T) = \left(\frac{2\pi mk_{\text{B}}T}{h^2} \right) a^2$$

in two dimensions. Use these results to show that $\langle \epsilon_{\text{trans}} \rangle$ has a contribution of $k_{\text{B}}T/2$ to its total value for each dimension.

Remember that $\int_0^\infty e^{-\alpha n^2} dn = \left(\frac{\pi}{4\alpha} \right)^{1/2}$. Then, for one dimension,

$$q_{\text{trans}}(a, T) = \int_0^\infty e^{-\beta h^2 n^2 / 8ma^2} dn = \left(\frac{2\pi mk_{\text{B}}T}{h^2} \right)^{1/2} a$$

And for two dimensions,

$$q_{\text{trans}}(a, T) = \left(\int_0^\infty e^{-\beta h^2 n^2 / 8ma^2} dn \right)^2 = \left(\frac{2\pi mk_{\text{B}}T}{h^2} \right) a^2$$

Now

$$\langle \epsilon_{\text{trans}} \rangle = k_{\text{B}}T^2 \left(\frac{\partial \ln q_{\text{trans}}}{\partial T} \right)_V$$

The partition function is proportional to $T^{n/2}$, where n is the dimension. So

$$\left(\frac{\partial \ln q_{\text{trans}}}{\partial T} \right)_V = \frac{n}{2T}$$

and

$$\langle \epsilon_{\text{trans}} \rangle = k_{\text{B}}T^2 \frac{n}{2T} = \frac{nk_{\text{B}}T}{2}$$

18-4. Using the data in Table 8.6, calculate the fraction of sodium atoms in the first excited state at 300 K, 1000 K, and 2000 K.

We can use the second line of Equation 18.10 to calculate the fraction of sodium atoms in the first excited state, with $g_{e1} = 2$, $g_{e2} = 2$, $g_{e3} = 4$, and $g_{e4} = 2$:

$$f_2 = \frac{2e^{-\beta\epsilon_{e2}}}{2 + 2e^{-\beta\epsilon_{e2}} + 4e^{-\beta\epsilon_{e3}} + 2e^{-\beta\epsilon_{e4}} + \dots}$$

Using the data in Table 8.6, we find that the numerator of this fraction is

$$2 \exp \left[-\frac{16\,956.183 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right]$$

and the denominator is

$$2 + 2 \exp \left[-\frac{16\,956.183 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] + 4 \exp \left[-\frac{16\,973.379 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] \\ + 2 \exp \left[-\frac{25\,739.86 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] + \dots$$

Using these values, we find that the values of f_2 for the various temperatures are

$$f_2(T = 300 \text{ K}) = 4.8 \times 10^{-36}$$

$$f_2(T = 1000 \text{ K}) = 2.5 \times 10^{-11}$$

$$f_2(T = 2000 \text{ K}) = 5.0 \times 10^{-6}$$

18-5. Using the data in Table 18.1, evaluate the fraction of lithium atoms in the first excited state at 300 K, 1000 K, and 2000 K.

We can use the second line of Equation 18.10 to calculate the fraction of lithium atoms in the first excited state, with $g_{e1} = 2$, $g_{e2} = 2$, $g_{e3} = 4$, and $g_{e4} = 2$:

$$f_2 = \frac{2e^{-\beta\epsilon_{e2}}}{2 + 2e^{-\beta\epsilon_{e2}} + 4e^{-\beta\epsilon_{e3}} + 2e^{-\beta\epsilon_{e4}} + \dots}$$

Using the data in Table 8.6, we find that the numerator of this fraction is

$$2 \exp \left[-\frac{14\,903.66 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right]$$

and the denominator is

$$2 + 2 \exp \left[-\frac{14\,903.66 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] + 4 \exp \left[-\frac{14\,904.00 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] \\ + 2 \exp \left[-\frac{27\,206.12 \text{ cm}^{-1}}{(0.6950 \text{ cm}^{-1} \cdot \text{K}^{-1})T} \right] + \dots$$

Using these values, we find that the values of f_2 for the various temperatures are

$$f_2(T = 300 \text{ K}) = 9.0 \times 10^{-32}$$

$$f_2(T = 1000 \text{ K}) = 4.9 \times 10^{-10}$$

$$f_2(T = 2000 \text{ K}) = 2.2 \times 10^{-5}$$

18-6. Show that each dimension contributes $R/2$ to the molar translational heat capacity.

In Problem 18.3, we showed that $\langle \epsilon_{\text{trans}} \rangle$ has a contribution of $k_{\text{B}}T/2$ from each dimension. From Chapter 17,

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = N \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_{N,V}$$

Because

$$\left(\frac{\partial \epsilon}{\partial T}\right)_{N,V} = \left[\frac{\partial(k_B T/2)}{\partial T}\right]_{N,V} = \frac{k_B}{2}$$

each dimension contributes $Nk_B/2 = R/2$ to the molar translational heat capacity.

18-7. Using the values of Θ_{vib} and D_0 in Table 18.2, calculate the values of D_e for CO, NO, and K_2 .

We can use the definitions $D_e = D_0 + h\nu/2$ and $\Theta_{\text{vib}} = h\nu/k_B$ to write

$$D_e = D_0 + \frac{k_B \Theta_{\text{vib}}}{2} = D_0 + \frac{R \Theta_{\text{vib}}}{2}$$

$$D_e(\text{CO}) = 1070 \text{ kJ}\cdot\text{mol}^{-1} + \frac{(8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(3103 \text{ K})}{2} \\ = 1083 \text{ kJ}\cdot\text{mol}^{-1}$$

$$D_e(\text{NO}) = 626.8 \text{ kJ}\cdot\text{mol}^{-1} + \frac{(8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(2719 \text{ K})}{2} \\ = 638.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$D_e(\text{K}_2) = 53.5 \text{ kJ}\cdot\text{mol}^{-1} + \frac{(8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(133 \text{ K})}{2} \\ = 54.1 \text{ kJ}\cdot\text{mol}^{-1}$$

18-8. Calculate the characteristic vibrational temperature Θ_{vib} for $\text{H}_2(\text{g})$ and $\text{D}_2(\text{g})$ ($\tilde{\nu}_{\text{H}_2} = 4401 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{D}_2} = 3112 \text{ cm}^{-1}$).

From the definition of Θ_{vib} , we can write $\Theta_{\text{vib}} = hc\tilde{\nu}/k_B$. Then

$$\Theta_{\text{vib}}(\text{H}_2) = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.9979 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(4401 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 6332 \text{ K}$$

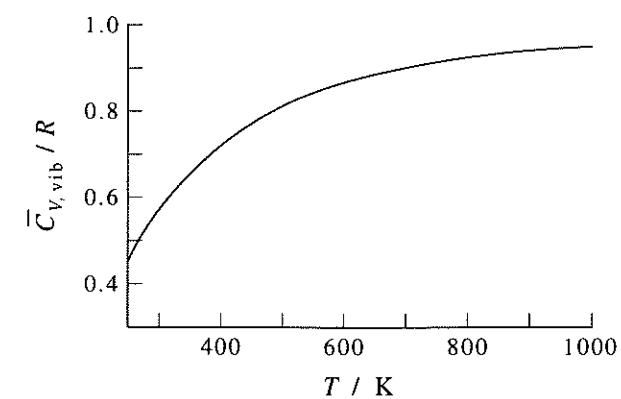
$$\Theta_{\text{vib}}(\text{D}_2) = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.9979 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(3112 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 4478 \text{ K}$$

18-9. Plot the vibrational contribution to the molar heat capacity of $\text{Cl}_2(\text{g})$ from 250 K to 1000 K.

Use Equation 18.26 to write $\bar{C}_{V,\text{vib}}$ as a function of T :

$$\bar{C}_{V,\text{vib}} = R \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

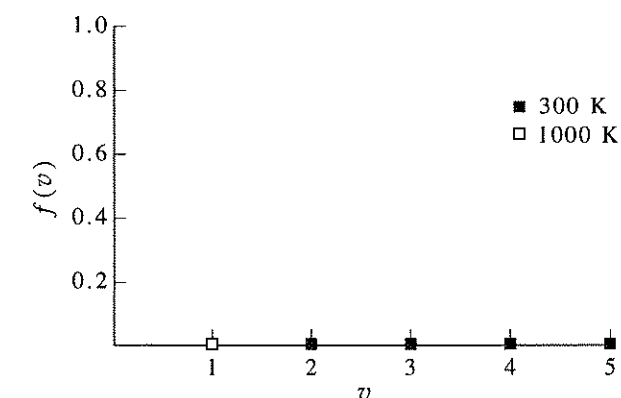
For Cl_2 , we use $\Theta_{\text{vib}} = 805 \text{ K}$ (Table 18.2) in the above equation and plot $\bar{C}_{V,\text{vib}}$ versus T .



18-10. Plot the fraction of $\text{HCl}(\text{g})$ molecules in the first few vibrational states at 300 K and 1000 K.

Use Equation 18.28, substituting $\Theta_{\text{vib}} = 4227 \text{ K}$ (Table 18.2), to write f_v as a function of v , and plot. At 300 K $f_{v>0} = 7.6 \times 10^{-7}$ and at 1000 K $f_{v>0} = 1.46 \times 10^{-2}$.

$$f_v = (1 - e^{-\Theta_{\text{vib}}/T}) e^{-v\Theta_{\text{vib}}/T}$$



18-11. Calculate the fraction of molecules in the ground vibrational state and in all the excited states at 300 K for each of the molecules in Table 18.2.

The fraction of molecules in the ground vibrational state is given by (Equation 18.27)

$$f_0 = 1 - e^{-\Theta_{\text{vib}}/T}$$

and the fraction in all the excited states is $1 - f_0$, or $e^{-\Theta_{\text{vib}}/T}$. We can use the Θ_{vib} for the molecules given in Table 18.2 to find f_0 and $f_{v>0}$.

molecule	f_0	$f_{v>0}$
H ₂	1.0000	1.0066×10^{-9}
D ₂	1.0000	4.3555×10^{-7}
Cl ₂	0.93167	6.8335×10^{-2}
Br ₂	0.78633	0.21367
I ₂	0.064180	0.35820
O ₂	0.99946	5.4213×10^{-4}
N ₂	0.99999	1.3051×10^{-5}
CO	0.99997	3.2207×10^{-5}
NO	0.99988	1.1584×10^{-4}
HCl	1.0000	7.5996×10^{-7}
HBr	1.0000	3.2942×10^{-6}
HI	0.99998	1.8706×10^{-5}
Na ₂	0.053389	0.46611
K ₂	0.35811	0.64189

18-12. Calculate the value of the characteristic rotational temperature Θ_{rot} for H₂(g) and D₂(g). (The bond lengths of H₂ and D₂ are 74.16 pm.) The atomic mass of deuterium is 2.014.

The reduced masses of hydrogen and deuterium, respectively, are

$$\mu(\text{H}_2) = \frac{(1.674 \times 10^{-27} \text{ kg})^2}{2(1.674 \times 10^{-27} \text{ kg})} = 8.370 \times 10^{-28} \text{ kg}$$

and

$$\mu(\text{D}_2) = \frac{(3.344 \times 10^{-27} \text{ kg})^2}{2(3.344 \times 10^{-27} \text{ kg})} = 1.672 \times 10^{-27} \text{ kg}$$

Now use the formula $\Theta_{\text{rot}} = \hbar^2/2\mu R^2 k_B$ (Equation 18.32) to find the value of Θ_{rot} for hydrogen and deuterium:

$$\Theta_{\text{rot}}(\text{H}_2) = \frac{(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{2(8.370 \times 10^{-28} \text{ kg})(74.16 \times 10^{-12} \text{ m})^2(1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})} = 87.56 \text{ K}$$

$$\Theta_{\text{rot}}(\text{D}_2) = \frac{(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{2(1.674 \times 10^{-27} \text{ kg})(74.16 \times 10^{-12} \text{ m})^2(1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})} = 43.78 \text{ K}$$

18-13. The average molar rotational energy of a diatomic molecule is RT . Show that typical values of J are given by $J(J+1) = T/\Theta_{\text{rot}}$. What are typical values of J for N₂(g) at 300 K?

If $\langle E \rangle = RT$, then $\epsilon = k_B T$. From Equation 18.30a,

$$J(J+1) = \frac{2Ik_B T}{\hbar^2} = \frac{T}{\Theta_{\text{rot}}}$$

For N₂ at 300 K,

$$J(J+1) \approx 104$$

and $J \approx 9$ or 10.

18-14. There is a mathematical procedure to calculate the error in replacing a summation by an integral as we do for the translational and rotational partition functions. The formula is called the Euler-Maclaurin summation formula and goes as follows:

$$\sum_{n=a}^b f(n) = \int_a^b f(n)dn + \frac{1}{2}\{f(b) + f(a)\} - \frac{1}{12} \left\{ \left. \frac{df}{dn} \right|_{n=a} - \left. \frac{df}{dn} \right|_{n=b} \right\} + \frac{1}{720} \left\{ \left. \frac{d^3 f}{dn^3} \right|_{n=a} - \left. \frac{d^3 f}{dn^3} \right|_{n=b} \right\} + \dots$$

Apply this formula to Equation 18.33 to obtain

$$q_{\text{rot}}(T) = \frac{T}{\Theta_{\text{rot}}} \left\{ 1 + \frac{1}{3} \left(\frac{\Theta_{\text{rot}}}{T} \right) + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right] \right\}$$

Calculate the correction to replacing Equation 18.33 by an integral for N₂(g) at 300 K; H₂(g) at 300 K (being so light, H₂ is an extreme example).

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} = \int_0^{\infty} dJ(2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} + \frac{1}{2}(f(\infty) + f(0)) - \frac{1}{12} \left[\left. \frac{df}{dJ} \right|_{J=0} - \left. \frac{df}{dJ} \right|_{J=\infty} \right] + \frac{1}{720} \left[\left. \frac{d^3 f}{dJ^3} \right|_{J=0} - \left. \frac{d^3 f}{dJ^3} \right|_{J=\infty} \right] + \dots$$

Let $u = J(J+1)$ and $du = (2J+1)dJ$. Then at $J=0$, $u=0$, and at $J=\infty$, $u=\infty$. Also, find the first and third derivatives of $f(J)$:

$$\begin{aligned} f(J) &= (2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} \\ \frac{df}{dJ} &= \frac{-\Theta_{\text{rot}}}{T}(2J+1)^2 e^{-\Theta_{\text{rot}} J(J+1)/T} + 2e^{-\Theta_{\text{rot}} J(J+1)/T} \\ \frac{d^2 f}{dJ^2} &= 4 \left(\frac{-\Theta_{\text{rot}}}{T} \right) (2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} + \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 (2J+1)^3 e^{-\Theta_{\text{rot}} J(J+1)/T} \\ &\quad + 2 \left(\frac{-\Theta_{\text{rot}}}{T} \right) (2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} \\ \frac{d^3 f}{dJ^3} &= 8 \left(\frac{-\Theta_{\text{rot}}}{T} \right) e^{-\Theta_{\text{rot}} J(J+1)/T} + 4 \left(\frac{\Theta_{\text{rot}}}{T} \right) e^{-\Theta_{\text{rot}} J(J+1)/T} + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^2 \right] \end{aligned}$$

$$q_{\text{rot}} = \int_0^{\infty} (2J+1)e^{-\Theta_{\text{rot}} J(J+1)/T} + \frac{1}{2}(1) - \frac{1}{12} \left(\frac{-\Theta_{\text{rot}}}{T} + 2 \right)$$

$$\begin{aligned}
 & + \frac{1}{720} \left(-8 \frac{\Theta_{\text{rot}}}{T} - 4 \frac{\Theta_{\text{rot}}}{T} \right) + O \left\{ \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 \right\} \\
 & = \frac{T}{\Theta_{\text{rot}}} \left\{ 1 + \frac{1}{3} \left(\frac{\Theta_{\text{rot}}}{T} \right) + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^2 \right] \right\}
 \end{aligned}$$

For N_2 the correction factor to q_{rot} at 300 K is 0.32%; for H_2 , the correction factor is 9.45%.

18-15. Apply the Euler-Maclaurin summation formula (Problem 18-14) to the one-dimensional version of Equation 18.4 to obtain

$$q_{\text{trans}}(a, T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} a + \left[\frac{1}{2} + \frac{h^2}{48ma^2 k_B T} \right] e^{-h^2/8ma^2 k_B T}$$

Show that the correction amounts to about $10^{-8}\%$ for $m = 10^{-26}$ kg, $a = 1$ dm, and $T = 300$ K.

The one-dimensional version of Equation 18.4 is

$$q = \sum_{n=1}^{\infty} \exp \left(-\frac{\beta h^2 n^2}{8ma^2} \right) = \sum_{n=1}^{\infty} e^{-bn^2}$$

where we let $b = \beta h^2/8ma^2$. The pertinent derivatives of q are

$$\begin{aligned}
 \frac{dq}{dn} &= -2bne^{-bn^2} \\
 \frac{d^2q}{dn^2} &= -2be^{-bn^2} + 4b^2n^2e^{-bn^2} \\
 \frac{d^3q}{dn^3} &= 4b^2ne^{-bn^2} - 8b^3n^3e^{-bn^2}
 \end{aligned}$$

We can approximate

$$\int_1^{\infty} e^{-bn^2} dn \approx \int_0^{\infty} e^{-bn^2} dn$$

and use the Euler-Maclaurin summation formula from Problem 18-14 to find

$$\begin{aligned}
 q &= \int_0^{\infty} e^{-bn^2} dn + \frac{1}{2} (e^{-b} - 0) - \frac{1}{12} (-2be^{-b}) + \frac{1}{720} (4b^2e^{-b} - 8b^3e^{-b}) \\
 &= \left(\frac{2\pi m a^2 k_B T}{h^2} \right)^{1/2} + \left(\frac{1}{2} + \frac{1}{6}b + \frac{1}{180}b^2 - \frac{1}{90}b^3 \right) e^{-b} \\
 &= \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} a + \left[\frac{1}{2} + \frac{h^2}{48ma^2 k_B T} + O(b^2) \right] e^{-h^2/8ma^2 k_B T}
 \end{aligned}$$

For $m = 10^{-26}$ kg, $a = 1$ dm, and $T = 300$ K, simply replacing the sum by an integral gives a value of 2.43×10^9 . The correction term is 0.5, which is $2 \times 10^{-8}\%$ of the value of the sum.

18-16. We were able to evaluate the vibrational partition function for a harmonic oscillator exactly by recognizing the summation as a geometric series. Apply the Euler-Maclaurin summation formula (Problem 18-14) to this case and show that

$$\begin{aligned}
 \sum_{v=0}^{\infty} e^{-\beta(v+\frac{1}{2})h\nu} &= e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} e^{-v\Theta_{\text{vib}}/T} \\
 &= e^{-\Theta_{\text{vib}}/2T} \left[\frac{T}{\Theta_{\text{vib}}} + \frac{1}{2} + \frac{\Theta_{\text{vib}}}{12T} + \dots \right]
 \end{aligned}$$

Show that the corrections to replacing the summation by an integration are very large for $\text{O}_2(\text{g})$ at 300 K. Fortunately, we don't need to replace the summation by an integration in this case.

Recall that $\Theta_{\text{vib}} = h\nu/k_B$, so

$$\sum_{v=0}^{\infty} e^{-\beta(v+\frac{1}{2})h\nu} = e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} e^{-v\Theta_{\text{vib}}/T}$$

Then

$$f(v) = e^{-v\Theta_{\text{vib}}/T} \quad f'(v) = -\frac{\Theta_{\text{vib}}}{T} e^{-v\Theta_{\text{vib}}/T} \quad f'''(v) = -\left(\frac{\Theta_{\text{vib}}}{T} \right)^3 e^{-v\Theta_{\text{vib}}/T}$$

and applying the Euler-Maclaurin summation formula yields

$$\begin{aligned}
 \sum_{v=0}^{\infty} e^{-v\Theta_{\text{vib}}/T} &= \int_0^{\infty} e^{-v\Theta_{\text{vib}}/T} dv + \frac{1}{2}(1) - \frac{1}{12} \left(-\frac{\Theta_{\text{vib}}}{T} \right) + \frac{1}{720} \left(-\frac{\Theta_{\text{vib}}}{T} \right)^3 + O(T^{-3}) \\
 &= \frac{T}{\Theta_{\text{vib}}} + \frac{1}{2} + \frac{\Theta_{\text{vib}}}{12T} + O(T^{-3})
 \end{aligned}$$

Then

$$\sum_{v=0}^{\infty} e^{-\beta(v+\frac{1}{2})h\nu} = e^{-\Theta_{\text{vib}}/2T} \left[\frac{T}{\Theta_{\text{vib}}} + \frac{1}{2} + \frac{\Theta_{\text{vib}}}{12T} + O(T^{-3}) \right]$$

For O_2 , $\Theta_{\text{vib}} = 2256$ K. Using Equation 18.23, we find that

$$q_{\text{vib}}(T) = \frac{e^{-2256 \text{ K}/600 \text{ K}}}{1 - e^{-2256 \text{ K}/600 \text{ K}}} = 0.0238$$

and using the correction, we have

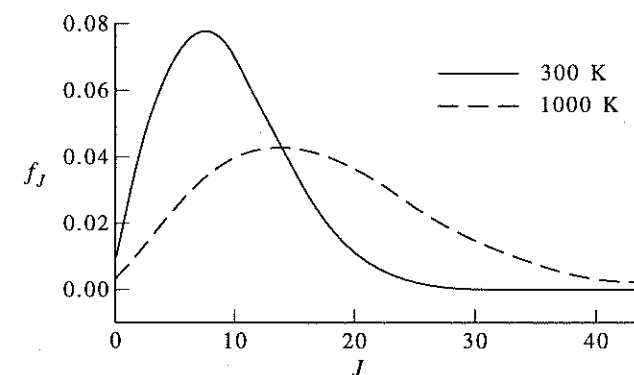
$$q_{\text{vib}}(T) = e^{-2256 \text{ K}/600 \text{ K}} \left(\frac{300 \text{ K}}{2256 \text{ K}} + \frac{1}{2} + \frac{2256 \text{ K}}{3600 \text{ K}} \right) = 0.0293$$

which is about a 20% difference.

18-17. Plot the fraction of $\text{NO}(\text{g})$ molecules in the various rotational levels at 300 K and at 1000 K.

Use Equation 18.35, substituting $\Theta_{\text{rot}} = 2.39$ K (Table 18.2), to write f_J as a function of J , and plot.

$$f_J = (2J+1) \left(\frac{\Theta_{\text{rot}}}{T} \right) e^{-\Theta_{\text{rot}} J(J+1)/T}$$



18-18. Show that the values of J at the maximum of a plot of f_J versus J (Equation 18.35) is given by

$$J_{\max} \approx \left(\frac{T}{2\Theta_{\text{rot}}} \right)^{1/2} - \frac{1}{2}$$

Hint: Treat J as a continuous variable. Use this result to verify the values of J at the maxima in the plots in Problem 18-17.

$$f_J = (2J+1) \frac{\Theta_{\text{rot}}}{T} e^{-\Theta_{\text{rot}} J(J+1)/T}$$

At the maximum of a plot of f_J versus J , the slope is zero, so

$$\frac{df}{dJ} = \frac{2\Theta_{\text{rot}}}{T} e^{-\Theta_{\text{rot}} J_{\max}(J_{\max}+1)/T} - (2J_{\max}+1)^2 \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 e^{-\Theta_{\text{rot}} J_{\max}(J_{\max}+1)/T} = 0$$

We can solve this equation for J_{\max} :

$$\begin{aligned} (2J_{\max}+1)^2 \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 e^{-\Theta_{\text{rot}} J_{\max}(J_{\max}+1)/T} &= \frac{2\Theta_{\text{rot}}}{T} e^{-\Theta_{\text{rot}} J_{\max}(J_{\max}+1)/T} \\ (2J_{\max}+1)^2 &= \frac{2T}{\Theta_{\text{rot}}} \\ J_{\max} &= \left(\frac{T}{2\Theta_{\text{rot}}} \right)^{1/2} - \frac{1}{2} \end{aligned}$$

For NO(g) at 300 K and 1000 K, $\Theta_{\text{rot}} = 2.39$ K, so the values of J_{\max} given by the above equation are $J_{\max} \approx 7$ and $J_{\max} \approx 14$, respectively, in agreement with the plot in Problem 18-17.

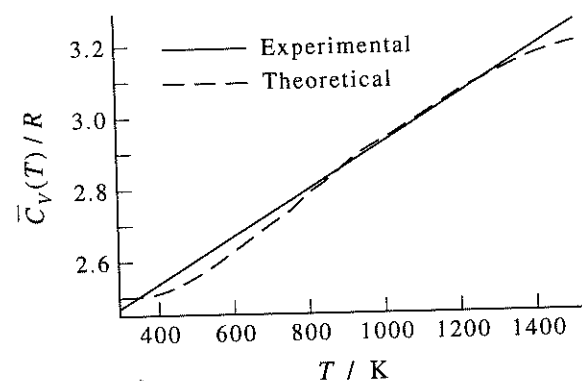
18-19. The experimental heat capacity of N₂(g) can be fit to the empirical formula

$$\bar{C}_V(T)/R = 2.283 + (6.291 \times 10^{-4} \text{ K}^{-1})T - (5.0 \times 10^{-10} \text{ K}^{-2})T^2$$

over the temperature range 300 K < T < 1500 K. Plot $\bar{C}_V(T)/R$ versus T over this range using Equation 18.41, and compare your results with the experimental curve.

For N₂, $\Theta_{\text{vib}} = 3374$ K, so we plot the experimental equation given in the problem text and the theoretical equation

$$\frac{\bar{C}_V(T)}{R} = \frac{5}{2} + \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$



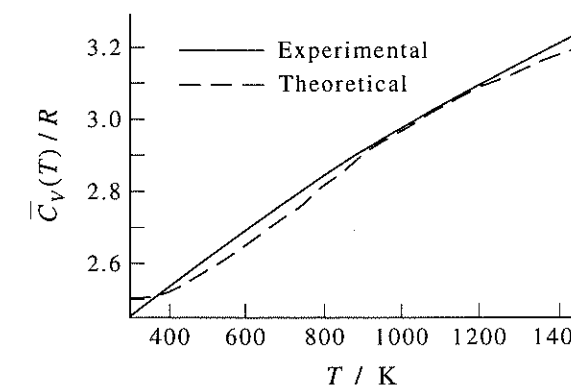
18-20. The experimental heat capacity of CO(g) can be fit to the empirical formula

$$\bar{C}_V(T)/R = 2.192 + (9.240 \times 10^{-4} \text{ K}^{-1})T - (1.41 \times 10^{-7} \text{ K}^{-2})T^2$$

over the temperature range 300 K < T < 1500 K. Plot $\bar{C}_V(T)/R$ versus T over this range using Equation 18.41, and compare your results with the experimental curve.

For CO, $\Theta_{\text{vib}} = 3103$ K, so we plot the experimental equation given in the problem text and the theoretical equation

$$\frac{\bar{C}_V(T)}{R} = \frac{5}{2} + \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$



18-21. Calculate the contribution of each normal mode to the molar vibrational heat capacity of H₂O(g) at 600 K.

For H₂O, the values of Θ_{vib} for the three normal modes are 2290 K, 5160 K, and 5360 K. For $\Theta_{\text{vib},j} = 5360$ K,

$$\frac{\bar{C}_{V,j}}{R} = \left(\frac{5360}{600} \right)^2 \frac{e^{-5360/600}}{(1 - e^{-5360/600})^2} = 1.05 \times 10^{-2}$$

For $\Theta_{\text{vib},j} = 5160$ K,

$$\frac{\bar{C}_{V,j}}{R} = \left(\frac{5160}{600} \right)^2 \frac{e^{-5160/600}}{(1 - e^{-5160/600})^2} = 1.36 \times 10^{-2}$$

For $\Theta_{\text{vib},j} = 2290$ K,

$$\frac{\bar{C}_{V,j}}{R} = \left(\frac{2290}{600} \right)^2 \frac{e^{-2290/600}}{(1 - e^{-2290/600})^2} = 0.335$$

18-22. In analogy to the characteristic vibrational temperature, we can define a characteristic electronic temperature by

$$\Theta_{\text{elec},j} = \frac{\epsilon_{ej}}{k_B}$$

where ϵ_{ej} is the energy of the j th excited electronic state relative to the ground state. Show that if we define the ground state to be the zero of energy, then

$$q_{\text{elec}} = g_0 + g_1 e^{-\Theta_{\text{elec},1}/T} + g_2 e^{-\Theta_{\text{elec},2}/T} + \dots$$

The first and second excited electronic states of O(g) lie 158.2 cm^{-1} and 226.5 cm^{-1} above the ground electronic state. Given $g_0 = 5$, $g_1 = 3$, and $g_2 = 1$, calculate the values of $\Theta_{\text{elec},1}$, $\Theta_{\text{elec},2}$, and q_{elec} (ignoring any higher states) for O(g) at 5000 K.

Substituting the values given in the problem into the definition of $\Theta_{\text{elec},j}$ gives

$$\Theta_{\text{elec},1} = \frac{158.2 \text{ cm}^{-1}}{0.69509 \text{ cm}^{-1} \cdot \text{K}^{-1}} = 227.6 \text{ K}$$

$$\Theta_{\text{elec},2} = \frac{226.5 \text{ cm}^{-1}}{0.69509 \text{ cm}^{-1} \cdot \text{K}^{-1}} = 325.8 \text{ K}$$

We can write q_{elec} as (Equation 18.8)

$$\begin{aligned} q_{\text{elec}} &= \sum g_{ej} e^{\epsilon_{ej}/k_B T} \\ &= g_0 + g_1 e^{-\Theta_{\text{elec},1}/T} + g_2 e^{-\Theta_{\text{elec},2}/T} + \dots \\ q_{\text{elec}} &= 5 + 3e^{-227.6/5000} + 1e^{-325.8/5000} = 8.803 \end{aligned}$$

18-23. Determine the symmetry numbers for H_2O , HOD , CH_4 , SF_6 , C_2H_2 , and C_2H_4 .

Symmetry numbers of selected molecules

Molecule	Symmetry Number
H_2O	2
HOD	1
CH_4	12
SF_6	24
C_2H_2	2
C_2H_4	4

18-24. The $\text{HCN}(\text{g})$ molecule is a linear molecule, and the following constants determined spectroscopically are $I = 18.816 \times 10^{-47} \text{ kg} \cdot \text{m}^2$, $\tilde{\nu}_1 = 2096.7 \text{ cm}^{-1}$ (HC-N stretch), $\tilde{\nu}_2 = 713.46 \text{ cm}^{-1}$ (H-C-N bend, two-fold degeneracy), and $\tilde{\nu}_3 = 3311.47 \text{ cm}^{-1}$ (H-C stretch). Calculate the values of Θ_{rot} and Θ_{vib} and \bar{C}_V at 3000 K.

We can use the definitions of Θ_{rot} and Θ_{vib} to write

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = 2.1405 \text{ K}$$

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k_B}$$

$$\Theta_{\text{vib},1} = 3017 \text{ K (HC-N stretch)}$$

$$\Theta_{\text{vib},2} = 1026 \text{ K (H-C-N bend)}$$

$$\Theta_{\text{vib},3} = 4764 \text{ K (H-C stretch)}$$

For linear polyatomic molecules, Equation 18.59 holds, and so

$$\begin{aligned} \frac{\bar{C}_V}{R} &= \frac{5}{2} + \sum_{j=1}^4 \bar{C}_{\text{vib},j} \\ &= \frac{5}{2} + \left(\frac{3017}{3000}\right)^2 \frac{e^{-3017/3000}}{(1 - e^{-3017/3000})^2} + 2 \left(\frac{1026}{3000}\right)^2 \frac{e^{-1026/3000}}{(1 - e^{-1026/3000})^2} \\ &\quad + \left(\frac{4764}{3000}\right)^2 \frac{e^{-4764/3000}}{(1 - e^{-4764/3000})^2} \\ &= 2.5 + 0.92 + 1.98 + 0.81 = 6.21 \end{aligned}$$

18-25. The acetylene molecule is linear, the $\text{C}\equiv\text{C}$ bond length is 120.3 pm , and the C-H bond length is 106.0 pm . What is the symmetry number of acetylene? Determine the moment of inertia (Section 13-8) of acetylene and calculate the value of Θ_{rot} . The fundamental frequencies of the normal modes are $\tilde{\nu}_1 = 1975 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 3370 \text{ cm}^{-1}$, $\tilde{\nu}_3 = 3277 \text{ cm}^{-1}$, $\tilde{\nu}_4 = 729 \text{ cm}^{-1}$, and $\tilde{\nu}_5 = 600 \text{ cm}^{-1}$. The normal modes $\tilde{\nu}_4$ and $\tilde{\nu}_5$ are doubly degenerate. All the other modes are nondegenerate. Calculate $\Theta_{\text{vib},j}$ and \bar{C}_V at 300 K.

The symmetry number of acetylene is 2 (Problem 18.24). Choose the coordinate axis to bisect the center of the triple bond. Then

$$\begin{aligned} I &= \sum_i m_i z_i^2 = 2 \left(\frac{120.3 \times 10^{-12} \text{ m}}{2} \right)^2 (1.995 \times 10^{-26} \text{ kg}) \\ &\quad + 2 \left(\frac{120.3 \times 10^{-12} \text{ m}}{2} + 106.0 \times 10^{-12} \text{ m} \right)^2 (1.67 \times 10^{-27} \text{ kg}) \\ &= 2.368 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

We can use the definitions of Θ_{rot} and Θ_{vib} to write

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = 1.701 \text{ K}$$

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k_B}$$

$$\Theta_{\text{vib},2} = 2841 \text{ K}$$

$$\Theta_{\text{vib},3} = 4849 \text{ K}$$

$$\Theta_{\text{vib},4} = 4715 \text{ K}$$

$$\Theta_{\text{vib},5} = 1049 \text{ K}$$

$$\Theta_{\text{vib},6} = 863.3 \text{ K}$$

The vibrational molar heat capacities are given by (Equation 18.26)

$$\bar{C}_{V,\text{vib}} = R \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

Because acetylene is a linear polyatomic molecule, we can use Equation 18.59 to find the molar heat capacity at 300 K:

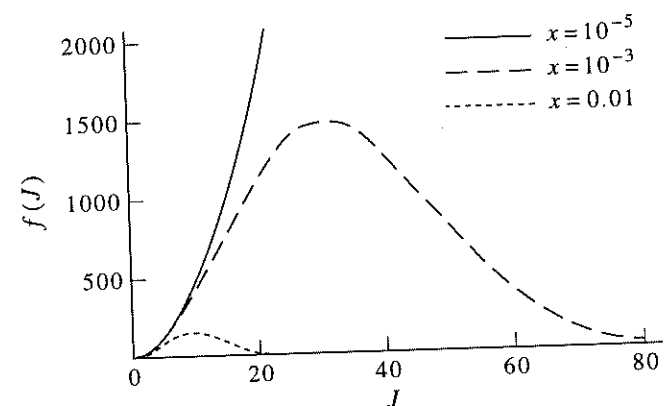
$$\begin{aligned}\frac{\bar{C}_V}{R} &= \frac{5}{2} + \sum_{j=1}^7 \bar{C}_{\text{vib},j} \\ &= \frac{5}{2} + \bar{C}_{\text{vib},1} + \bar{C}_{\text{vib},2} + \bar{C}_{\text{vib},3} + 2\bar{C}_{\text{vib},4} + 2\bar{C}_{\text{vib},5} \\ &= \frac{5}{2} + 6.92 \times 10^{-3} + 2.50 \times 10^{-5} + 3.69 \times 10^{-5} + 2(0.394) + 2(0.523) \\ &= 4.34\end{aligned}$$

18-26. Plot the summand in Equation 18.53 versus J , and show that the most important values of J are large for $T \gg \Theta_{\text{rot}}$. We use this fact in going from Equation 18.53 to Equation 18.54.

The summand in Equation 18.53 is

$$(2J+1)^2 e^{-\hbar^2 J(J+1)/2Ik_B T} = (2J+1)^2 e^{-J(J+1)\Theta_{\text{rot}}/T}$$

Let $x = \Theta_{\text{rot}}/T$, so that for $\Theta_{\text{rot}} \ll T$ x is small, and then plot the summand versus J for different values of x .



We can see that for $\Theta_{\text{rot}} \ll T$, the most important values of J (as far as contributions to the summand are concerned) are large, so Equation 18.54 holds quite well when this condition is met.

18-27. Use the Euler-Maclaurin summation formula (Problem 18-14) to show that

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}} \right)^{3/2} + \frac{1}{6} + O\left(\frac{\Theta_{\text{rot}}}{T}\right)$$

for a spherical top molecule. Show that the correction to replacing Equation 18.53 by an integral is about 1% for CH_4 and 0.001% for CCl_4 at 300 K.

For a spherical top molecule,

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\hbar^2 J(J+1)/2Ik_B T} \quad (18.53)$$

The pertinent derivatives are

$$\begin{aligned}f(J) &= (2J+1)^2 e^{-\Theta_{\text{rot}} J(J+1)/T} \\ \frac{df}{dJ} &= 4(2J+1)e^{-\Theta_{\text{rot}}(J^2+J)/T} - \frac{\Theta_{\text{rot}}}{T}(2J+1)^3 e^{-\Theta_{\text{rot}}(J^2+J)/T} \\ \frac{d^2 f}{dJ^2} &= 8e^{-\Theta_{\text{rot}}(J^2+J)/T} - \frac{10\Theta_{\text{rot}}}{T}(2J+1)^2 e^{-\Theta_{\text{rot}}(J^2+J)/T} \\ &\quad + \left(\frac{\Theta_{\text{rot}}}{T}\right)^2 (2J+1)^4 e^{-\Theta_{\text{rot}}(J^2+J)/T}\end{aligned}$$

Applying the Euler-Maclaurin summation formula gives

$$\begin{aligned}q_{\text{rot}}(T) &= \frac{1}{\sigma} \int_0^{\infty} e^{-\Theta_{\text{rot}}(J^2+J)/T} + \frac{1}{2}(1) - \frac{1}{12} \left[4 + O\left(\frac{\Theta_{\text{rot}}}{T}\right) \right] + O\left(\frac{\Theta_{\text{rot}}}{T}\right) \\ &= \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}} \right)^{3/2} + \frac{1}{6} + O\left(\frac{\Theta_{\text{rot}}}{T}\right)\end{aligned}$$

where we have included the symmetry number σ in the integral, as was done in the text. For CH_4 at 300 K the integral has a value of 37.07, and the correction term is about 1% of that; for CCl_4 at 300 K the integral has a value of about 32 500, and the correction term is about 0.001% of that.

18-28. The N-N and N-O bond lengths in the (linear) molecule N_2O are 109.8 pm and 121.8 pm, respectively. Calculate the center of mass and the moment of inertia of $^{14}\text{N}^{14}\text{N}^{16}\text{O}$. Compare your answer with the value obtained from Θ_{rot} in Table 18.4.

Choose the coordinate axis to bisect the central nitrogen atom. Then the moment of inertia (using the isotopic masses from the *CRC Handbook*) is

$$\begin{aligned}I &= \sum_i m_i z_i^2 = (109.8 \times 10^{-12} \text{ m})^2 (2.325 \times 10^{-26} \text{ kg}) \\ &\quad + (121.8 \times 10^{-12} \text{ m})^2 (2.656 \times 10^{-26} \text{ kg}) \\ &= 6.744 \times 10^{-46} \text{ kg}\cdot\text{m}^2\end{aligned}$$

and the center of mass of the molecule (relative to the central nitrogen atom) is

$$\begin{aligned}X &= 0 + \frac{14.003}{44.001} (109.8 \times 10^{-12} \text{ m}) + \frac{15.995}{44.013} (121.8 \times 10^{-12} \text{ m}) \\ &= 7.922 \times 10^{-11} \text{ m}\end{aligned}$$

The center of mass of the molecule is 79.22 pm away from the central nitrogen atom, along the N-O bond. The value of Θ_{rot} calculated from the above values is

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = 0.597 \text{ K}$$

This value is within 1% of that in Table 18.4.

18-29. $\text{NO}_2(\text{g})$ is a bent triatomic molecule. The following data determined from spectroscopic measurements are $\tilde{\nu}_1 = 1319.7 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 749.8 \text{ cm}^{-1}$, $\tilde{\nu}_3 = 1617.75 \text{ cm}^{-1}$, $\tilde{A}_0 = 8.0012 \text{ cm}^{-1}$, $\tilde{B}_0 = 0.43304 \text{ cm}^{-1}$, and $\tilde{C}_0 = 0.41040 \text{ cm}^{-1}$. Determine the three characteristic vibrational temperatures and the characteristic rotational temperatures for each of the principle axes of $\text{NO}_2(\text{g})$ at 1000 K. Calculate the value of \bar{C}_V at 1000 K.

We can use Equation 18.49 to find $\Theta_{\text{vib},j}$:

$$\Theta_{\text{vib},j} = \frac{h\nu_j}{k_B} = \frac{hc\tilde{\nu}_j}{k_B}$$

$$\Theta_{\text{vib},1} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(1319.7 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 1899 \text{ K}$$

$$\Theta_{\text{vib},2} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(749.8 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 1079 \text{ K}$$

$$\Theta_{\text{vib},3} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(1617.75 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 2328 \text{ K}$$

and Equation 18.32 for Θ_{rot} :

$$\Theta_{\text{rot},A} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(8.0012 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 11.51 \text{ K}$$

$$\Theta_{\text{rot},B} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(0.43304 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 0.6230 \text{ K}$$

$$\Theta_{\text{rot},C} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(0.41040 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}} = 0.5905 \text{ K}$$

Finally, we use Equation 18.59 to determine the value of \bar{C}_V at 1000 K.

$$\frac{\bar{C}_V}{R} = 2 \left(\frac{3}{2} \right) + (1.899)^2 \frac{e^{-1.899}}{(1 - e^{-1.899})^2} + (1.079)^2 \frac{e^{-1.079}}{(1 - e^{-1.079})^2} + (2.328)^2 \frac{e^{-2.328}}{(1 - e^{-2.328})^2}$$

$$= 5.304$$

18-30. The experimental heat capacity of $\text{NH}_3(\text{g})$ can be fit to the empirical formula

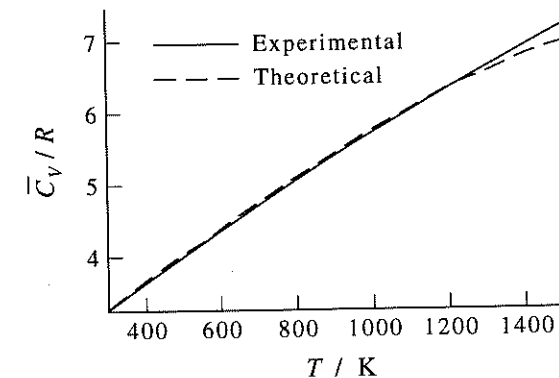
$$\bar{C}_V(T)/R = 2.115 + (3.919 \times 10^{-3} \text{ K}^{-1})T - (3.66 \times 10^{-7} \text{ K}^{-2})T^2$$

over the temperature range $300 \text{ K} < T < 1500 \text{ K}$. Plot $\bar{C}_V(T)/R$ versus T over this range using Equation 18.62 and the molecular parameters in Table 18.4, and compare your results with the experimental curve.

For NH_3 , we plot the experimental equation given in the problem text and the theoretical equation

$$\frac{\bar{C}_V(T)}{R} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^6 \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}T}}{(1 - e^{-\Theta_{\text{vib},j}T})^2} \quad (18.62)$$

where $\Theta_{\text{vib},1} = 4800 \text{ K}$, $\Theta_{\text{vib},2} = 1360 \text{ K}$, $\Theta_{\text{vib},3} = \Theta_{\text{vib},4} = 4880 \text{ K}$, and $\Theta_{\text{vib},5} = \Theta_{\text{vib},6} = 2330 \text{ K}$ (Table 18.4).



18-31. The experimental heat capacity of $\text{SO}_2(\text{g})$ can be fit to the empirical formula

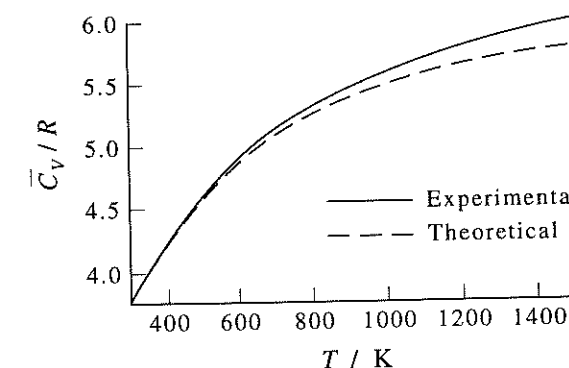
$$\bar{C}_V(T)/R = 6.8711 - \frac{1454.62 \text{ K}}{T} + \frac{160351 \text{ K}^2}{T^2}$$

over the temperature range $300 \text{ K} < T < 1500 \text{ K}$. Plot $\bar{C}_V(T)/R$ versus T over this range using Equation 18.62 and the molecular parameters in Table 18.4, and compare your results with the experimental curve.

For SO_2 , we plot the experimental equation given in the problem text and the theoretical equation

$$\frac{\bar{C}_V(T)}{R} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^3 \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}T}}{(1 - e^{-\Theta_{\text{vib},j}T})^2} \quad (18.62)$$

where $\Theta_{\text{vib},1} = 1660 \text{ K}$, $\Theta_{\text{vib},2} = 750 \text{ K}$, and $\Theta_{\text{vib},3} = 1960 \text{ K}$ (Table 18.4).



18-32. The experimental heat capacity of $\text{CH}_4(\text{g})$ can be fit to the empirical formula

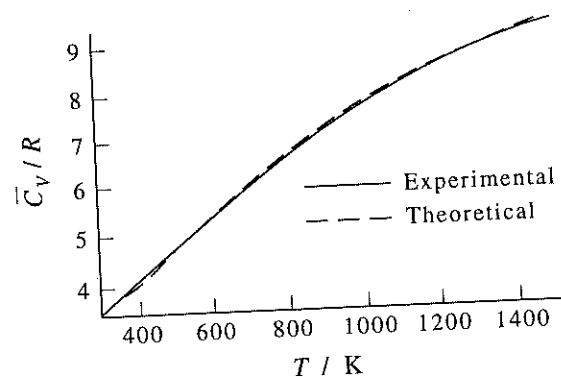
$$\bar{C}_V(T)/R = 1.099 + (7.27 \times 10^{-3} \text{ K}^{-1})T + (1.34 \times 10^{-7} \text{ K}^{-2})T^2 - (8.67 \times 10^{-10} \text{ K}^{-3})T^3$$

over the temperature range $300 \text{ K} < T < 1500 \text{ K}$. Plot $\bar{C}_V(T)/R$ versus T over this range using Equation 18.62 and the molecular parameters in Table 18.4, and compare your results with the experimental curve.

For CH_4 , we plot the experimental equation given in the problem text and the theoretical equation

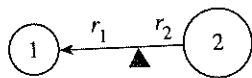
$$\frac{\bar{C}_V(T)}{R} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^9 \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}T}}{(1 - e^{-\Theta_{\text{vib},j}T})^2} \quad (18.62)$$

where $\Theta_{\text{vib},1} = 4170 \text{ K}$, $\Theta_{\text{vib},2} = \Theta_{\text{vib},3} = 2180 \text{ K}$, $\Theta_{\text{vib},4} = \Theta_{\text{vib},5} = \Theta_{\text{vib},6} = 4320 \text{ K}$, and $\Theta_{\text{vib},7} = \Theta_{\text{vib},8} = \Theta_{\text{vib},9} = 1870 \text{ K}$ (Table 18.4).



18-33. Show that the moment of inertia of a diatomic molecule is μR_e^2 , where μ is the reduced mass, and R_e is the equilibrium bond length.

Let the point labelled in the figure be the center of mass of the molecule. r_1 and r_2 are the distances from the center of mass to masses 1 and 2 (with masses m_1 and m_2), respectively; R_0 is the bond length and M is the total mass of the molecule.



We can then write (by the definition of the center of mass)

$$r_1 = \frac{m_2 r_2}{m_1}$$

Now, because $R_0 = r_1 + r_2$ and $M = m_1 + m_2$,

$$R_0 = \left(\frac{m_2}{m_1} + 1 \right) r_2 = \frac{M}{m_1} r_2$$

Finally, because $I = \sum_j m_j r_j^2$ and $\mu = m_1 m_2 / M$,

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 = \left[m_1 \left(\frac{m_2}{m_1} \right)^2 + m_2 \right] r_2^2 \\ &= \left(\frac{m_2^2}{m_1} + m_2 \right) \frac{m_1^2 R_0^2}{M^2} = \left(\frac{m_2 M}{m_1} \right) \frac{m_1^2 R_0^2}{M^2} \\ &= \frac{m_1 m_2}{M} R_0^2 = \mu R_0^2 \end{aligned}$$

18-34. Given that the values of Θ_{rot} and Θ_{vib} for H_2 are 85.3 K and 6332 K, respectively, calculate these quantities for HD and D_2 . *Hint:* Use the Born-Oppenheimer approximation.

In the Born-Oppenheimer approximation, the potential curve of a diatomic molecule is independent of the isotopes of the constituent atoms. Then, in the formula $I = \mu R_0^2$, R_0 is the same for D_2 , H_2 , and HD. Therefore, in the harmonic oscillator-rigid rotator approximation,

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B} \sim \mu^{-1/2} \quad \text{and} \quad \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} \sim \mu^{-1}$$

We can calculate the reduced masses of H_2 , D_2 , and HD in atomic masses:

$$\mu_{\text{H}_2} = \frac{1.008 \text{ amu}}{2} = 0.504 \text{ amu} \quad \mu_{\text{D}_2} = \frac{2.014 \text{ amu}}{2} = 1.007 \text{ amu}$$

$$\mu_{\text{DH}} = \frac{(2.014 \text{ amu})(1.008 \text{ amu})}{3.022 \text{ amu}} = 0.672 \text{ amu}$$

Now we can use the relationships between μ and Θ_{vib} and μ and Θ_{rot} to find rotational and vibrational temperatures of D_2 :

$$\begin{aligned} \frac{\Theta_{\text{vib},\text{D}_2}}{\Theta_{\text{vib},\text{H}_2}} &= \left(\frac{\mu_{\text{H}_2}}{\mu_{\text{D}_2}} \right)^{1/2} \\ \Theta_{\text{vib},\text{D}_2} &= \left(\frac{0.504 \text{ amu}}{1.007 \text{ amu}} \right)^{1/2} (6332 \text{ K}) = 4480 \text{ K} \\ \frac{\Theta_{\text{rot},\text{D}_2}}{\Theta_{\text{rot},\text{H}_2}} &= \frac{\mu_{\text{H}_2}}{\mu_{\text{D}_2}} \\ \Theta_{\text{rot},\text{D}_2} &= \frac{0.504 \text{ amu}}{1.007 \text{ amu}} (85.3 \text{ K}) = 42.7 \text{ K} \end{aligned}$$

Similarly, for HD

$$\begin{aligned} \frac{\Theta_{\text{vib},\text{DH}}}{\Theta_{\text{vib},\text{H}_2}} &= \left(\frac{\mu_{\text{H}_2}}{\mu_{\text{DH}}} \right)^{1/2} \\ \Theta_{\text{vib},\text{DH}} &= \left(\frac{0.504 \text{ amu}}{0.672 \text{ amu}} \right)^{1/2} (6332 \text{ K}) = 5484 \text{ K} \\ \frac{\Theta_{\text{rot},\text{DH}}}{\Theta_{\text{rot},\text{H}_2}} &= \frac{\mu_{\text{H}_2}}{\mu_{\text{DH}}} \\ \Theta_{\text{rot},\text{DH}} &= \frac{0.504 \text{ amu}}{0.672 \text{ amu}} (85.3 \text{ K}) = 64.0 \text{ K} \end{aligned}$$

18-35. Using the result for $q_{\text{rot}}(T)$ obtained in Problem 18-14, derive corrections to the expressions $\langle E_{\text{rot}} \rangle = RT$ and $C_{V,\text{rot}} = R$ given in Section 18-5. Express your result in terms of powers of Θ_{rot}/T .

From Problem 18-14, we write q_{rot} as

$$q_{\text{rot}}(T) = \frac{T}{\Theta_{\text{rot}}} \left\{ 1 + \frac{1}{3} \left(\frac{\Theta_{\text{rot}}}{T} \right) + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right] \right\}$$

$$\ln q_{\text{rot}} = \ln \frac{T}{\Theta_{\text{rot}}} + \ln \left\{ 1 + \frac{1}{3} \frac{\Theta_{\text{rot}}}{T} + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right] \right\}$$

We use the expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - O(x^4) \quad (I.12)$$

to write $\ln q_{\text{rot}}$ as

$$\ln q_{\text{rot}} = \ln \frac{T}{\Theta_{\text{rot}}} + \left[\frac{1}{3} \frac{\Theta_{\text{rot}}}{T} + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 \right] - \frac{1}{2} \left(\frac{1}{3} \frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right]$$

$$= \ln \frac{T}{\Theta_{\text{rot}}} + \frac{1}{3} \frac{\Theta_{\text{rot}}}{T} + \frac{1}{90} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right]$$

Now we use Equation 17.21 to write $\langle E \rangle$ as

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_{N,V}$$

$$= R T^2 \left[\frac{1}{T} - \frac{1}{3} \frac{\Theta_{\text{rot}}}{T^2} - \frac{1}{45} \frac{\Theta_{\text{rot}}^2}{T^3} + O(T^{-4}) \right]$$

$$= R T - \frac{R \Theta_{\text{rot}}}{3} - \frac{R \Theta_{\text{rot}}^2}{45 T} + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^2 \right]$$

Finally, use the definition of constant-volume heat capacity (Equation 17.25) to write

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}$$

$$= R + \frac{R}{45} \left(\frac{\Theta_{\text{rot}}}{T} \right)^2 + O \left[\left(\frac{\Theta_{\text{rot}}}{T} \right)^3 \right]$$

18-36. Show that the thermodynamic quantities P and C_V are independent of the choice of a zero of energy.

Begin with Equation 17.14,

$$Q = \sum_j e^{-\beta E_j}$$

Now choose E_0 to be the zero of energy and define

$$Q_0 = \sum_j e^{-\beta(E_j - E_0)}$$

such that

$$Q = e^{-\beta E_0} Q_0$$

Now use Equation 17.32 to write

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = k_B T \left[\frac{\partial}{\partial V} (-\beta E_0 + \ln Q_0) \right]_{N,\beta} = k_B T \left(\frac{\partial \ln Q_0}{\partial V} \right)_{N,\beta}$$

and use Equation 17.21 to write

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = k_B T^2 \left[\frac{\partial}{\partial T} (-\beta E_0 + \ln Q_0) \right]_{N,V} = E_0 + k_B T^2 \left(\frac{\partial \ln Q_0}{\partial T} \right)_{N,V}$$

Because $\bar{C}_V = (\partial \langle E \rangle / \partial T)_{N,V}$ (Equation 17.25), we can write

$$\bar{C}_V = \left\{ \frac{\partial}{\partial T} \left[E_0 + k_B T^2 \left(\frac{\partial \ln Q_0}{\partial T} \right)_{N,V} \right] \right\}_{N,V} = \left\{ \frac{\partial}{\partial T} \left[k_B T^2 \left(\frac{\partial \ln Q_0}{\partial T} \right)_{N,V} \right] \right\}_{N,V}$$

Therefore, the values of P and \bar{C}_V are independent of the choice of a zero of energy, as they must be.

18-37. Molecular nitrogen is heated in an electric arc. The spectroscopically determined relative populations of excited vibrational levels are listed below.

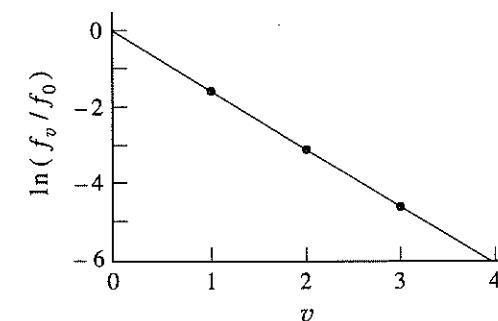
v	0	1	2	3	4	...
$\frac{f_v}{f_0}$	1.000	0.200	0.040	0.008	0.002	...

Is the nitrogen in thermodynamic equilibrium with respect to vibrational energy? What is the vibrational temperature of the gas? Is this value necessarily the same as the translational temperature? Why or why not?

At thermal equilibrium,

$$\frac{f_v}{f_0} = \frac{e^{-\beta h \nu (v+1/2)}}{q_{\text{vib}}} \left(\frac{e^{-\beta h \nu / 2}}{q_{\text{vib}}} \right)^{-1} = e^{\beta h \nu v}$$

Thus, if nitrogen is in thermodynamic equilibrium with respect to vibrational energy, the graph of $\ln(f_v/f_0)$ vs. v will be a straight line with slope $-\beta h \nu$. The following figure shows the plot of $\ln(f_v/f_0)$ versus v .



The slope of the line of best fit is -1.5648 , which, using $\tilde{\nu}_{N_2} = 2330 \text{ cm}^{-1}$ (Table 5.1), corresponds to a vibrational temperature of 2140 K. The vibrational and translational temperatures need not be equal, because the time scale of the energy transfer between vibrational states and between

translational states can be quite different (the energy transfer between vibrational states is usually orders of magnitude slower than that between translational states).

- 18-38. Consider a system of independent diatomic molecules constrained to move in a plane, that is, a two-dimensional ideal diatomic gas. How many degrees of freedom does a two-dimensional diatomic molecule have? Given that the energy eigenvalues of a two-dimensional rigid rotator are

$$\epsilon_J = \frac{\hbar^2 J^2}{2I} \quad J = 0, 1, 2, \dots$$

(where I is the moment of inertia of the molecule) with a degeneracy $g_J = 2$ for all J except $J = 0$, derive an expression for the rotational partition function. The vibrational partition function is the same as for a three-dimensional diatomic gas. Write out

$$q(T) = q_{\text{trans}}(T)q_{\text{rot}}(T)q_{\text{vib}}(T)$$

and derive an expression for the average energy of this two-dimensional ideal diatomic gas.

A two-dimensional diatomic molecule has two translational degrees of freedom, one vibrational degree of freedom, and one rotational degree of freedom. We know that

$$\epsilon_J = \frac{\hbar^2 J^2}{2I} = \Theta_{\text{rot}} k_B J^2 \quad J = 0, 1, 2, \dots$$

So

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^\infty dJ g_J e^{-\epsilon_J/k_B T}$$

$$q_{\text{rot}} = 1 + 2 \int_0^\infty dJ e^{-J^2 \Theta_{\text{rot}}/T} \approx \left(\frac{\pi T}{\Theta_{\text{rot}}} \right)^{1/2}$$

We are told that q_{vib} is the same for a two-dimensional gas as it is for a three-dimensional gas, and we know q_{trans} for an ideal two-dimensional gas from Problem 18.3. We can now obtain an expression for the average energy of this gas:

$$q(T) = q_{\text{trans}}(T)q_{\text{rot}}(T)q_{\text{vib}}(T)$$

$$= \left(\frac{2a^2 \pi m k_B T}{h^2} \right) \left(\frac{\pi T}{\Theta_{\text{rot}}} \right)^{1/2} \left(\frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \right)$$

We now wish to find the temperature-dependent terms of $\ln q$:

$$\ln q = \ln T + \frac{1}{2} \ln T - \frac{\Theta_{\text{vib}}}{2T} - \ln(1 - e^{-\Theta_{\text{vib}}/2T}) + \text{terms not containing } T$$

Now, as in Example 18.5, we can take

$$\langle E \rangle = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

$$= RT^2 \left(\frac{1}{T} + \frac{1}{2T} + \frac{\Theta_{\text{vib}}}{2T^2} + \frac{\Theta_{\text{vib}}}{T^2} \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/2T}} \right)$$

$$= \frac{3RT}{2} + \frac{R\Theta_{\text{vib}}}{2} + R\Theta_{\text{vib}} \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/2T}}$$

- 18-39. What molar constant-volume heat capacities would you expect under classical conditions for the following gases: (a) Ne, (b) O₂, (c) H₂O, (d) CO₂, and (e) CHCl₃?

Each of the gases has a contribution of $3R/2$ to its heat capacity from the translational partition function. In addition, there is a contribution of $R/2$ for each rotational degree of freedom and R for each vibrational degree of freedom. Therefore, the molar heat capacities are

- a. $\frac{3}{2}R + 0R + 0R = \frac{3}{2}R$
 b. $\frac{3}{2}R + \frac{2}{2}R + R = \frac{7}{2}R$
 c. $\frac{3}{2}R + \frac{3}{2}R + 3R = 6R$
 d. $\frac{3}{2}R + \frac{2}{2}R + 4R = \frac{13}{2}R$
 e. $\frac{3}{2}R + \frac{3}{2}R + 9R = 12R$

- 18-40. In Chapter 13, we learned that the harmonic-oscillator model can be corrected to include anharmonicity. The energy of an anharmonic oscillator was given as (Equation 13.21)

$$\tilde{\epsilon}_v = \left(v + \frac{1}{2} \right) \tilde{\nu}_e - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 + \dots$$

where the frequency $\tilde{\nu}_e$ is expressed in cm^{-1} . Substitute this expression for $\tilde{\epsilon}_v$ into the summation for the vibrational partition function to obtain

$$q_{\text{vib}}(T) = \sum_{v=0}^{\infty} e^{-\beta \tilde{\epsilon}_v} = \sum_{v=0}^{\infty} e^{-\beta \tilde{\nu}_e (v + \frac{1}{2})} e^{\beta \tilde{x}_e \tilde{\nu}_e (v + \frac{1}{2})^2}$$

Now expand the second factor in the summand, keeping only the linear term in $\tilde{x}_e \tilde{\nu}_e$, to obtain

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} + \beta \tilde{x}_e \tilde{\nu}_e e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} \left(v + \frac{1}{2} \right)^2 e^{-\Theta_{\text{vib}}v/T} + \dots$$

where $\Theta_{\text{vib}}/T = \beta \tilde{\nu}_e$. Given that (Problem I-15)

$$\sum_{v=0}^{\infty} v x^v = \frac{x}{(1-x)^2}$$

and

$$\sum_{v=0}^{\infty} v^2 x^v = \frac{x^2 + x}{(1-x)^3}$$

show that

$$q_{\text{vib}}(T) = q_{\text{vib,ho}}(T) \left[1 + \beta \tilde{x}_e \tilde{\nu}_e \left(\frac{1}{4} + 2q_{\text{vib,ho}}^2(T) \right) + \dots \right]$$

where $q_{\text{vib,ho}}(T)$ is the harmonic-oscillator partition function. Estimate the magnitude of the correction for Cl₂(g) at 300 K, for which $\Theta_{\text{vib}} = 805$ K and $\tilde{x}_e \tilde{\nu}_e = 2.675 \text{ cm}^{-1}$.

Substituting the expression for ϵ_v given in the problem into the vibrational partition function summation gives the equation

$$q_{\text{vib}}(T) = \sum_{v=0}^{\infty} e^{-\beta \epsilon_v} = \sum_{v=0}^{\infty} e^{-\beta \tilde{\nu}_e (v + \frac{1}{2})} \exp \left[\beta \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 + \dots \right]$$

Expanding the second factor in the summand and keeping only the linear term in $\tilde{x}_e \tilde{v}_e$ gives

$$\begin{aligned} q_{\text{vib}}(T) &= \sum_{v=0}^{\infty} e^{-\beta \tilde{v}_e (v + \frac{1}{2})} \left[1 + \beta \tilde{x}_e \tilde{v}_e (v + \frac{1}{2}) + \dots \right] \\ &= e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} e^{-\Theta_{\text{vib}}v/T} + \beta \tilde{x}_e \tilde{v}_e e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} (v + \frac{1}{2})^2 e^{-\Theta_{\text{vib}}v/T} \end{aligned}$$

We can use the geometric series (Equation I.3) to write this as

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} + \beta \tilde{x}_e \tilde{v}_e e^{-\Theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} (v + \frac{1}{2})^2 e^{-\Theta_{\text{vib}}v/T}$$

Using the sums given in the problem, we find that the sum in the equation for q_{vib} becomes

$$\begin{aligned} \sum_{v=0}^{\infty} (v + \frac{1}{2})^2 e^{-\Theta_{\text{vib}}v/T} &= \frac{e^{-2\Theta_{\text{vib}}/T} + e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^3} + \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2} + \frac{1}{4(1 - e^{-\Theta_{\text{vib}}/T})} \\ &= \frac{2e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^3} + \frac{1}{4(1 - e^{-\Theta_{\text{vib}}/T})} \end{aligned}$$

and q_{vib} is then

$$\begin{aligned} q_{\text{vib}} &= \frac{e^{-\Theta_{\text{vib}}/2T}}{(1 - e^{-\Theta_{\text{vib}}/T})} \left\{ 1 + \beta \tilde{x}_e \tilde{v}_e \left[\frac{1}{4} + 2 \left(\frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \right)^2 \right] \right\} \\ &= q_{\text{vib,ho}} \left[1 + \beta \tilde{x}_e \tilde{v}_e \left(\frac{1}{4} + 2q_{\text{vib,ho}}^2 \right) \right] \end{aligned}$$

We can use the parameters given in the problem for Cl_2 at 300 K to find q_{vib} at this temperature.

$$\begin{aligned} \frac{q_{\text{vib}}}{q_{\text{vib,ho}}} &= 1 + \frac{2.675 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \cdot \text{K}^{-1})(300 \text{ K})} \left[\frac{1}{4} + 2 \left(\frac{e^{-1.34}}{1 - e^{-2.68}} \right)^2 \right] \\ &= 1 + (0.0128)(0.250 + 0.158) = 1 + 0.0052 \end{aligned}$$

The correction factor is 0.52% of q_{vib} for a harmonic oscillator.

18-41. Prove that

$$\int_0^{\infty} e^{-\alpha n^2} dn \approx \int_1^{\infty} e^{-\alpha n^2} dn$$

if α is very small. *Hint:* Prove that

$$\int_0^1 e^{-\alpha n^2} dn \ll \int_0^{\infty} e^{-\alpha n^2} dn$$

by expanding the exponential in the first integral.

Expanding the exponential in the first integral gives (Equation I.2)

$$e^{-\alpha n^2} = 1 + (-\alpha n^2) + O(\alpha^2)$$

Then the first integral becomes

$$\int_0^1 e^{-\alpha n^2} dn = \int_0^1 [1 - \alpha n^2 + O(\alpha^2)] dn = 1 - \frac{1}{3}\alpha + O(\alpha^2)$$

We know that

$$\int_0^{\infty} e^{-\alpha n^2} dn = \left(\frac{\pi}{4\alpha} \right)^{1/2}$$

As $\alpha \rightarrow 0$, $\int_0^{\infty} e^{-\alpha n^2} dn \rightarrow \infty$ and $\int_0^1 e^{-\alpha n^2} dn \rightarrow 1$. Thus, as $\alpha \rightarrow 0$,

$$\int_0^1 e^{-\alpha n^2} dn \ll \int_0^{\infty} e^{-\alpha n^2} dn$$

so

$$\int_0^{\infty} e^{-\alpha n^2} dn \approx \int_1^{\infty} e^{-\alpha n^2} dn$$

18-42. In this problem, we will derive an expression for the number of translational energy states with (translational) energy between ϵ and $\epsilon + d\epsilon$. This expression is essentially the degeneracy of the state whose energy is

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \dots \quad (1)$$

The degeneracy is given by the number of ways the integer $M = 8ma^2\epsilon/h^2$ can be written as the sum of the squares of three positive integers. In general, this is an erratic and discontinuous function of M (the number of ways will be zero for many values of M), but it becomes smooth for large M , and we can derive a simple expression for it. Consider a three-dimensional space spanned by n_x , n_y , and n_z . There is a one-to-one correspondence between energy states given by Equation 1 and the points in this n_x , n_y , n_z space with coordinates given by positive integers. Figure 18.8 shows a two-dimensional version of this space. Equation 1 is an equation for a sphere of radius $R = (8ma^2\epsilon/h^2)^{1/2}$ in this space

$$n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2\epsilon}{h^2} = R^2$$

We want to calculate the number of lattice points that lie at some fixed distance from the origin in this space. In general, this is very difficult, but for large R we can proceed as follows. We treat R , or ϵ , as a continuous variable and ask for the number of lattice points between ϵ and $\epsilon + \Delta\epsilon$. To calculate this quantity, it is convenient to first calculate the number of lattice points consistent with an energy $\leq \epsilon$. For large ϵ , an excellent approximation can be made by equating the number of lattice points consistent with an energy $\leq \epsilon$ with the volume of one octant of a sphere of radius R .

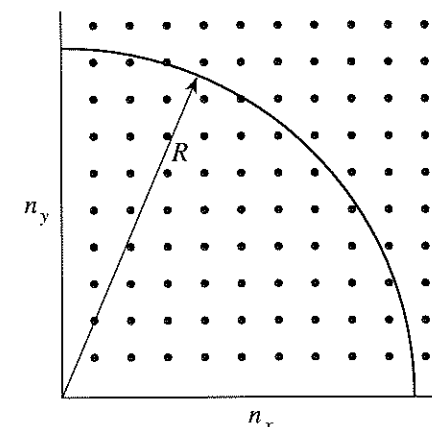


FIGURE 18.8

A two-dimensional version of the (n_x, n_y, n_z) space, the space with the quantum numbers n_x , n_y , and n_z as axes. Each point corresponds to an energy of a particle in a (two-dimensional) box.

We take only one octant because n_x , n_y , and n_z are restricted to be positive integers. If we denote the number of such states by $\Phi(\varepsilon)$, we can write

$$\Phi(\varepsilon) = \frac{1}{8} \left(\frac{4\pi R^3}{3} \right) = \frac{\pi}{6} \left(\frac{8ma^2\varepsilon}{h^2} \right)^{3/2}$$

The number of states with energy between ε and $\varepsilon + \Delta\varepsilon$ ($\Delta\varepsilon/\varepsilon \ll 1$) is

$$\omega(\varepsilon, \Delta\varepsilon) = \Phi(\varepsilon + \Delta\varepsilon) - \Phi(\varepsilon)$$

Show that

$$\omega(\varepsilon, \Delta\varepsilon) = \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon + O[(\Delta\varepsilon)^2]$$

Show that if we take $\varepsilon = 3k_B T/2$, $T = 300$ K, $m = 10^{-25}$ kg, $a = 1$ dm, and $\Delta\varepsilon$ to be 0.010ε (in other words 1% of ε), then $\omega(\varepsilon, \Delta\varepsilon)$ is $O(10^{28})$. So, even for a system as simple as a single particle in a box, the degeneracy can be very large at room temperature.

We can express $\Phi(\varepsilon)$ and $\Phi(\varepsilon + \Delta\varepsilon)$, by definition, as

$$\Phi(\varepsilon) = \frac{\pi}{6} \left(\frac{8ma^2\varepsilon}{h^2} \right)^{3/2} \quad \Phi(\varepsilon + \Delta\varepsilon) = \frac{\pi}{6} \left[\frac{8ma^2(\varepsilon + \Delta\varepsilon)}{h^2} \right]^{3/2}$$

Now we substitute these values into the expression given in the text for $\omega(\varepsilon, \Delta\varepsilon)$ and expand in $\Delta\varepsilon$:

$$\begin{aligned} \omega(\varepsilon, \Delta\varepsilon) &= \Phi(\varepsilon + \Delta\varepsilon) - \Phi(\varepsilon) \\ &= \frac{\pi}{6} \left(\frac{8ma^2}{h^2} \right)^{3/2} [(\varepsilon + \Delta\varepsilon)^{3/2} - \varepsilon^{3/2}] \\ &= \frac{\pi}{6} \left(\frac{8ma^2}{h^2} \right)^{3/2} \left\{ \varepsilon^{3/2} \left[\left(1 + \frac{\Delta\varepsilon}{\varepsilon} \right)^{3/2} - 1 \right] \right\} \\ &= \frac{\pi}{6} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{3/2} \left\{ 1 + \frac{3}{2} \frac{\Delta\varepsilon}{\varepsilon} + O\left[\left(\frac{\Delta\varepsilon}{\varepsilon} \right)^2 \right] - 1 \right\} \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{3/2} \frac{\Delta\varepsilon}{\varepsilon} + O[(\Delta\varepsilon)^2] \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon + O[(\Delta\varepsilon)^2] \end{aligned}$$

Substituting the desired values in the above equations gives $\omega(\varepsilon, 0.01\varepsilon) = 9.5 \times 10^{27} = O(10^{28})$.

18-43. The translational partition function can be written as a single integral over the energy ε if we include the degeneracy

$$q_{\text{trans}}(V, T) = \int_0^\infty \omega(\varepsilon) e^{-\varepsilon/k_B T} d\varepsilon$$

where $\omega(\varepsilon)d\varepsilon$ is the number of states with energy between ε and $\varepsilon + d\varepsilon$. Using the result from the previous problem, show that $q_{\text{trans}}(V, T)$ is the same as that given by Equation 18.6.

As $\Delta\varepsilon \rightarrow 0$, $\omega(\varepsilon, \Delta\varepsilon) \rightarrow \omega(\varepsilon)d\varepsilon$, so we can use (from the above problem)

$$\omega(\varepsilon)d\varepsilon = \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Substituting this into the expression given for q_{trans} gives

$$\begin{aligned} q_{\text{trans}} &= \int_0^\infty \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \int_0^\infty x e^{-x^2/k_B T} 2x dx \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \frac{k_B T}{2} (\pi k_B T)^{1/2} \\ &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} a^3 \end{aligned}$$

which is the same as Equation 18.6.