# CHEM 26200 (Thermodynamics) Problem Sets

Steven Labalme

March 1, 2022

# Contents

# 1   The Boltzmann Factor and Partition Functions

1/25:   1. Derive the value of $PV$ for a gas of photons in terms of the total internal energy. Use $E = h\nu$ and $p = h\nu/c$ for the photon energy and momentum, respectively, and follow a similar method to that used for an ideal gas in class.

*Proof.* We first seek to derive an expression for the number of collisions per second per area (of the wall of the container). Consider the number $N(v_x)$ of photons with speed $v_x$ in the $x$ direction. Assuming that such photons are equally distributed throughout the container, their density in any region is $N(v_x)/V$. Thus, their "flux" at the wall of the container is this density $N(v_x)/V$, times the area $A$ of the wall, times the $x$-velocity $v_x$ of the photons. Additionally, assuming elastic collisions, a single photon colliding with the wall transfers $2p_x = 2h\nu/v_x$ of momentum. It follows that the change in momentum per second of an area $A$ of the wall (i.e., the force $F$ at the wall) is $\frac{N(v_x)}{V}Av_x \cdot 2p_x$. But, of course, we must sum over all possible $v_x$; note that since all photons travel at the speed of light $c = v_x^2 + v_y^2 + v_z^2$, we must integrate from $0$ to $c$ (photons with $v_x \leq 0$ don't collide with the wall in question and no photon has $v_x > c$). It follows that

$$F = \int_0^c 2p_x \cdot \frac{N(v_x)}{V}Av_x \,\mathrm{d}v_x$$
$$= \int_0^c 2\frac{h\nu}{v_x} \cdot \frac{N(v_x)}{V}Av_x \,\mathrm{d}v_x$$
$$= \int_0^c 2h\nu \cdot \frac{N(v_x)}{V}A \,\mathrm{d}v_x$$
$$= \frac{2h\nu A}{V} \int_0^c N(v_x) \,\mathrm{d}v_x$$
$$\frac{F}{A} = \frac{2h\nu}{V}\frac{N}{2}$$
$$PV = Nh\nu$$
$$= NE$$
$$\boxed{PV = U}$$

$\square$

2. Apply the Boltzmann factor.

(a) For $N_2$ at $300\,\mathrm{K}$, give the ratio of molecules in $J = 5$ over $J = 4$. Indicate also if the transition from $J = 4$ to $J = 5$ is observable by microwave absorption spectroscopy. Data on $N_2$ are in Table 18.2 on McQuarrie and Simon (1997, p. 739).

*Proof.* From Table 18.2, we have that $\Theta_{\mathrm{rot}} = 2.88\,\mathrm{K}$ for $N_2$. Therefore, we have that

$$\frac{p_5}{p_4} = \frac{(2(5)+1)\mathrm{e}^{-(2.88)(5)((5)+1)/300}}{(2(4)+1)\mathrm{e}^{-(2.88)(4)((4)+1)/300}}$$
$$\boxed{\frac{p_5}{p_4} = 1.11}$$

Also, the transition from $J = 4$ to $J = 5$ is $\boxed{\text{not observable}}$ by microwave absorption spectroscopy since $N_2$ does not have a permanent dipole moment.  $\square$

(b) Also, for $N_2$ at $300\,\mathrm{K}$, give the ratio of molecules in $n = 1$ over $n = 0$ for the vibrational states.

*Proof.* From Table 18.2, we have that $\Theta_{\text{vib}} = 3374\,\text{K}$ for $N_2$. Therefore, we have that

$$\frac{p_1}{p_0} = \frac{e^{-(3374)(1)/300}}{e^{-(3374)(0)/300}}$$

$$\boxed{\frac{p_5}{p_4} = 1.305 \times 10^{-5}}$$

$\square$

(c) Problem 18-28 (calculating a moment of inertia based on masses and distances).

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 $^{14}N^{14}N^{16}O$. Compare your answer with the value obtained from $\Theta_{\text{rot}}$ in Table 18.4.

*Proof.* Take the middle nitrogen atom to be the center of the coordinate system and the molecular axis to be the $x$-axis. Let $x_1 = 109.8$ pm and $x_3 = 121.8$ pm. Then the center of mass is at

$$x_{\text{CM}} = \frac{\sum_{i=1}^{3} m_i x_i}{\sum_{i=1}^{3} m_i}$$

$$\boxed{x_{\text{CM}} = 9.355\,\text{pm}}$$

It follows that the moment of inertia about an axis perpendicular to the bond axis is

$$I_B = \sum_{i=1}^{3} m_i x_i^2$$

$$= m_1(x_1 + x_{\text{CM}})^2 + m_2 x_{\text{CM}}^2 + m_3(x_3 - x_{\text{CM}})^2$$

$$\boxed{I_B = 6.727 \times 10^{-46}\,\text{kg m}^2}$$

Thus, our calculated rotational temperature is

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2 I_B k_B} = 0.5985\,\text{K}$$

which has percent error of $0.829\%$ from $0.603\,\text{K}$, the value from Table 18.4.     $\square$

(d) Calculate the fraction of protons in the two spin orientations for a magnetic field of 10 T at 300 K. Follow Example 17-1 and Problem 17-8.

*Proof.* Let $B_z = 10$ T, $T = 300$ K, and $\gamma = 26.7522 \times 10^7\,\text{rad}\,\text{T}^{-1}\,\text{s}^{-1}$ be the magnetogyric ratio for a proton. If $N_w$ is the number of protons aligned with a magnetic field and $N_o$ is the number of protons opposed to the field, then

$$\frac{N_o}{N_w} = e^{-\hbar \gamma B_z / k_B T}$$

$$\boxed{\frac{N_o}{N_w} = 1.0}$$

$\square$

(e) Problem 17-41.

The lowest electronic states of $Na_{(g)}$ are tabulated below.

| Term symbol | Energy/cm$^{-1}$ | Degeneracy |
|---|---|---|
| $^2S_{1/2}$ | 0.000 | 2 |
| $^2P_{1/2}$ | 16 956.183 | 2 |
| $^2P_{3/2}$ | 16 973.379 | 4 |
| $^2S_{1/2}$ | 25 739.86 | 2 |

Calculate the fraction of the atoms in each of these electronic states in a sample of $Na_{(g)}$ at $1000\,K$. Repeat this calculation for a temperature of $2500\,K$.

*Proof.* At $1000\,K$, we have

$$f_{^2S_{1/2}} = \frac{2e^{-0.000/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{1.000}$$

$$f_{^2P_{1/2}} = \frac{2e^{-16956.183/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{2.546 \times 10^{-11}}$$

$$f_{^2P_{3/2}} = \frac{4e^{-16973.379/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{4.968 \times 10^{-11}}$$

$$f_{^2S_{1/2}} = \frac{2e^{-25739.86/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{8.275 \times 10^{-17}}$$

At $1000\,K$, we have

$$f_{^2S_{1/2}} = \frac{2e^{-0.000/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{0.9998}$$

$$f_{^2P_{1/2}} = \frac{2e^{-16956.183/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{5.784 \times 10^{-5}}$$

$$f_{^2P_{3/2}} = \frac{4e^{-16973.379/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{1.145 \times 10^{-4}}$$

$$f_{^2S_{1/2}} = \frac{2e^{-25739.86/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{3.690 \times 10^{-7}}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ $\square$

3. **Problem 17-38.** In the second question, in addition to the ideal monoatomic gas, apply the formula also to the case of solid obeying the law of Dulong and Petit for the average internal energy.

   The following equation gives the ensemble average of $E$, which we assert is the same as the experimentally observed value. In this problem, we will explore the standard deviation about $\langle E \rangle$ (see MathChapter B). We will start with either the right or second from the right term below.

   $$\langle E \rangle = U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_BT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

   Differentiate again with respect to $\beta$ or $T$ to show that (MathChapter B)

   $$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = k_BT^2 C_V$$

   where $C_V$ is the heat capacity. To explore the relative magnitude of the spread about $\langle E \rangle$, consider

   $$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{k_BTC_V}}{\langle E \rangle}$$

   To get an idea of the sie of this ratio, use the values of $\langle E \rangle$ and $C_V$ for a (monoatomic) ideal gas, namely $\frac{3}{2}Nk_BT$ and $\frac{3}{2}Nk_B$, respectively, and show that $\sigma_E/\langle E \rangle$ goes as $1/\sqrt{N}$. What does this trend say about the likely observed deviations from the average macroscopic energy?

   *Proof.* We are given that
   $$-\frac{\partial \ln Q}{\partial \beta} = \langle E \rangle$$

   We can show that

   $$\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} = \frac{1}{Q}\frac{\partial^2}{\partial \beta^2}\left(\sum_j e^{-E_j\beta}\right) = \sum_j E_j^2 \frac{e^{-E_j\beta}}{Q} = \sum_j E_j^2 p_j = \langle E^2 \rangle$$

Therefore,

$$
\begin{aligned}
k_B T^2 C_V &= k_B T^2 \frac{\partial \langle E \rangle}{\partial T} \\
&= k_B T^2 \frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} \\
&= k_B T^2 \frac{\partial \langle E \rangle}{\partial \beta} \cdot -\frac{1}{k_B T^2} \\
&= -\frac{\partial \langle E \rangle}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta} \left( -\frac{\partial \ln Q}{\partial \beta} \right) \\
&= \frac{\partial}{\partial \beta} \left( \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right) \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} + \frac{\partial}{\partial \beta} \left( \frac{1}{Q} \right) \cdot \frac{\partial Q}{\partial \beta} \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} + \frac{\partial}{\partial Q} \left( \frac{1}{Q} \right) \frac{\partial Q}{\partial \beta} \cdot \frac{\partial Q}{\partial \beta} \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2} \left( \frac{\partial Q}{\partial \beta} \right)^2 \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left( \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2 \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left( \frac{\partial \ln Q}{\partial \beta} \right)^2 \\
&= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left( -\frac{\partial \ln Q}{\partial \beta} \right)^2 \\
&= \langle E^2 \rangle - \langle E \rangle^2 = \sigma_E^2
\end{aligned}
$$

as desired.

As to the second part of the question, plugging in the given values yields

$$
\begin{aligned}
\frac{\sigma_E}{\langle E \rangle} &= \frac{\sqrt{k_B T C_V}}{\langle E \rangle} \\
&= \frac{\sqrt{k_B T \cdot 3 N k_B / 2}}{3 N k_B T / 2} \\
&= \frac{1}{\sqrt{N}} \cdot \frac{1}{\sqrt{3T/2}}
\end{aligned}
$$

which will indeed behave like $1/\sqrt{N}$ as $N \to \infty$. This means that as the number of particles increase, the deviations from the average energy will grow smaller and smaller.

Performing the same analysis on a solid obeying the law of Dulong and Petit yields

$$
\begin{aligned}
\frac{\sigma_E}{\langle E \rangle} &= \frac{\sqrt{k_B T C_V}}{\langle E \rangle} \\
&= \frac{\sqrt{k_B T \cdot 3 N R}}{3 N R T} \\
&= \frac{1}{\sqrt{N}} \cdot \frac{\sqrt{k_B}}{\sqrt{3RT}}
\end{aligned}
$$

so $\sigma_E / \langle E \rangle$ will also behave like $1/\sqrt{N}$ as $N \to \infty$ for this type of solid. $\qquad \square$

4. (a) Problem 17-11 and also verify that the pressure derived from this partition function gives the van der Waals equation (16.5).

Although we will not do so in this book, it is possible to derive the partition function for a monoatomic van der Waals gas as

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N e^{aN^2/V k_B T}$$

where $a$ and $b$ are the van der Waals constants. Derive an expression for the energy of a monoatomic van der Waals gas.

*Proof.* We have that

$$\ln Q = -\ln N! + \frac{3N}{2} \ln \left( \frac{2\pi m k_B}{h^2} \right) + \frac{3N}{2} \ln T + N \ln(V - Nb) + \frac{aN^2}{V k_B T}$$

$$= \frac{3N}{2} \ln T + \frac{aN^2}{V k_B T} + \text{terms not involving } T$$

Therefore,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

$$= k_B T^2 \frac{\partial}{\partial T} \left( \frac{3N}{2} \ln T + \frac{aN^2}{V k_B T} \right)$$

$$= k_B T^2 \left( \frac{3N}{2T} - \frac{aN^2}{V k_B T^2} \right)$$

$$\boxed{\langle E \rangle = \frac{3}{2} N k_B T - \frac{aN^2}{V}}$$

As to the second part of the question, we have that

$$\ln Q = \ln \left( \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} \right) + N \ln(V - Nb) + \frac{aN^2}{V k_B T}$$

$$= N \ln(V - Nb) + \frac{aN^2}{V k_B T} + \text{terms not involving } V$$

Therefore,

$$\langle P \rangle = k_B T \frac{\partial \ln Q}{\partial V}$$

$$= k_B T \frac{\partial}{\partial V} \left( N \ln(V - Nb) + \frac{aN^2}{V k_B T} \right)$$

$$= k_B T \left[ \frac{N}{V - Nb} - \frac{a}{k_B T} \left( \frac{N}{V} \right)^2 \right]$$

$$= \frac{N k_B T}{V - Nb} - a \left( \frac{N}{V} \right)^2$$

$$\left( P + \frac{aN^2}{V^2} \right) (V - Nb) = N k_B T$$

as desired. $\square$

(b) Then do Problem 17-12.

An approximate partition function for a gas of hard spheres can be obtained from the partition function of a monoatomic gas by replacing $V$ in

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!} \qquad\qquad q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V$$

with $V - b$, where $b$ is related to the volume of the $N$ hard spheres. Derive expressions for the energy and the pressure of this system.

*Proof.* We have that

$$\ln Q = N \ln q - \ln N!$$

$$= N \left( \ln \left(\frac{2\pi m}{h^2}\right)^{3/2} (V - b) - \frac{3}{2} \ln \beta \right) - \ln N!$$

$$= -\frac{3N}{2} \ln \beta + \text{terms not involving } \beta$$

Therefore,

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta}\left(-\frac{3N}{2} \ln \beta\right)$$

$$= \frac{3N}{2\beta}$$

$$\boxed{\langle E \rangle = \frac{3}{2} N k_B T}$$

We also have that

$$\ln Q = N \ln q - \ln N!$$

$$= N \left( \ln \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} + \ln(V - b) \right) - \ln N!$$

$$= N \ln(V - b) + \text{terms not involving } V$$

Therefore,

$$\langle P \rangle = k_B T \frac{\partial \ln Q}{\partial V}$$

$$= k_B T \frac{\partial}{\partial V} (N \ln(V - b))$$

$$\boxed{\langle P \rangle = \frac{N k_B T}{V - b}}$$

$\square$

5. Problem 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.

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

Apply this formula to

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

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 the second equation herein by an integral for $N_{2(g)}$ at $300\,\text{K}$ and $H_{2(g)}$ at $300\,\text{K}$ (being so light, $H_2$ is an extreme example).

*Proof.* We will calculate the constituent results in the Euler-Maclaurin summation formula separately before assembling them into the final sum. Thus, we have

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

$$\begin{aligned}
\frac{\mathrm{d}f}{\mathrm{d}J} &= 2e^{-\Theta_{\text{rot}}J(J+1)/T} + (2J+1)\frac{\mathrm{d}}{\mathrm{d}J}\left(e^{-\Theta_{\text{rot}}J(J+1)/T}\right)\\
&= 2e^{-\Theta_{\text{rot}}J(J+1)/T} + (2J+1)\frac{\mathrm{d}}{\mathrm{d}u}\left(e^{-\Theta_{\text{rot}}u/T}\right)\frac{\mathrm{d}u}{\mathrm{d}J}\\
&= 2e^{-\Theta_{\text{rot}}J(J+1)/T} + (2J+1)\cdot-\frac{\Theta_{\text{rot}}}{T}e^{-\Theta_{\text{rot}}J(J+1)/T}\cdot(2J+1)\\
&= \left(2 - \frac{\Theta_{\text{rot}}}{T}(2J+1)^2\right)e^{-\Theta_{\text{rot}}J(J+1)/T}
\end{aligned}$$

$$\begin{aligned}
\frac{\mathrm{d}^2f}{\mathrm{d}J^2} &= \frac{\mathrm{d}}{\mathrm{d}J}\left(2 - \frac{\Theta_{\text{rot}}}{T}(2J+1)^2\right)e^{-\Theta_{\text{rot}}J(J+1)/T} + \left(2 - \frac{\Theta_{\text{rot}}}{T}(2J+1)^2\right)\frac{\mathrm{d}}{\mathrm{d}J}\left(e^{-\Theta_{\text{rot}}J(J+1)/T}\right)\\
&= -\frac{\Theta_{\text{rot}}}{T}\cdot 2(2J+1)\cdot 2\cdot e^{-\Theta_{\text{rot}}J(J+1)/T} + \left(2 - \frac{\Theta_{\text{rot}}}{T}(2J+1)^2\right)\cdot-\frac{\Theta_{\text{rot}}}{T}e^{-\Theta_{\text{rot}}J(J+1)/T}\cdot(2J+1)\\
&= \left(\frac{\Theta_{\text{rot}}}{T}(2J+1)^2 - 6\right)\frac{\Theta_{\text{rot}}}{T}(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial^3 f}{\partial J^3} &= \frac{\mathrm{d}}{\mathrm{d}J}\left(\frac{\Theta_{\text{rot}}^2}{T^2}(2J+1)^2 - 6\frac{\Theta_{\text{rot}}}{T}\right)(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T} + \left(\frac{\Theta_{\text{rot}}}{T}(2J+1)^2 - 6\right)\frac{\Theta_{\text{rot}}}{T}\frac{\mathrm{d}}{\mathrm{d}J}\left((2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}\right)\\
&= \frac{4\Theta_{\text{rot}}^2}{T^2}(2J+1)^2e^{-\Theta_{\text{rot}}J(J+1)/T} + \left(\frac{\Theta_{\text{rot}}}{T}(2J+1)^2 - 6\right)\frac{\Theta_{\text{rot}}}{T}\left(2 - \frac{\Theta_{\text{rot}}}{T}(2J+1)^2\right)e^{-\Theta_{\text{rot}}J(J+1)/T}\\
&= \frac{4\Theta_{\text{rot}}^2}{T^2}(2J+1)^2e^{-\Theta_{\text{rot}}J(J+1)/T} + \left(-\frac{\Theta_{\text{rot}}^2}{T^2}(2J+1)^4 + 8\frac{\Theta_{\text{rot}}}{T}(2J+1)^2 - 12\right)\frac{\Theta_{\text{rot}}}{T}e^{-\Theta_{\text{rot}}J(J+1)/T}\\
&= \left(-\frac{\Theta_{\text{rot}}^2}{T^2}(2J+1)^4 + 12\frac{\Theta_{\text{rot}}}{T}(2J+1)^2 - 12\right)\frac{\Theta_{\text{rot}}}{T}e^{-\Theta_{\text{rot}}J(J+1)/T}
\end{aligned}$$

These terms evaluate under the conditions $a = 0$ and $b = \infty$ to

$$\int_0^{\infty} f(J)\,\mathrm{d}J = \frac{T}{\Theta_{\text{rot}}}$$

$$f(0) = 1 \qquad\qquad\qquad\qquad f(\infty) = 0$$

$$\left.\frac{\mathrm{d}f}{\mathrm{d}J}\right|_{J=0} = 2 - \frac{\Theta_{\text{rot}}}{T} \qquad\qquad\qquad\qquad \left.\frac{\mathrm{d}f}{\mathrm{d}J}\right|_{J=\infty} = 0$$

$$\left.\frac{\mathrm{d}^3 f}{\mathrm{d}J^3}\right|_{J=0} = \frac{\Theta_{\mathrm{rot}}}{T}\left(-\frac{\Theta_{\mathrm{rot}}^2}{T^2} + 12\frac{\Theta_{\mathrm{rot}}}{T} - 12\right) \qquad\qquad \left.\frac{\mathrm{d}^3 f}{\mathrm{d}J^3}\right|_{J=\infty} = 0$$

It follows by applying the full Euler-Maclaurin formula that

$$q_{\mathrm{rot}}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\Theta_{\mathrm{rot}}J(J+1)/T}$$

$$= \int_0^{\infty} f(J)\,\mathrm{d}J + \frac{1}{2}(f(\infty)+f(0)) - \frac{1}{12}\left(\left.\frac{\mathrm{d}f}{\mathrm{d}J}\right|_{J=0} - \frac{\mathrm{d}f}{\mathrm{d}J}_{J=\infty}\right) + \frac{1}{720}\left(\left.\frac{\mathrm{d}^3 f}{\mathrm{d}J^3}\right|_{J=0} - \frac{\mathrm{d}^3 f}{\mathrm{d}J^3}_{J=\infty}\right) + \cdots$$

$$= \frac{T}{\Theta_{\mathrm{rot}}} + \frac{1}{2}(0+1) - \frac{1}{12}\left[\left(2-\frac{\Theta_{\mathrm{rot}}}{T}\right)-0\right] + \frac{1}{720}\left[\frac{\Theta_{\mathrm{rot}}}{T}\left(-\frac{\Theta_{\mathrm{rot}}^2}{T^2}+12\frac{\Theta_{\mathrm{rot}}}{T}-12\right)-0\right] + \cdots$$

$$= \frac{T}{\Theta_{\mathrm{rot}}} + \frac{1}{2} - \frac{1}{6} + \frac{1}{12}\frac{\Theta_{\mathrm{rot}}}{T} - \frac{1}{720}\frac{\Theta_{\mathrm{rot}}^3}{T^3} + \frac{1}{60}\frac{\Theta_{\mathrm{rot}}^2}{T^2} - \frac{1}{60}\frac{\Theta_{\mathrm{rot}}}{T} + \cdots$$

$$= \frac{T}{\Theta_{\mathrm{rot}}} + \frac{1}{3} + \frac{1}{15}\frac{\Theta_{\mathrm{rot}}}{T} + \frac{1}{60}\frac{\Theta_{\mathrm{rot}}^2}{T^2} - \frac{1}{720}\frac{\Theta_{\mathrm{rot}}^3}{T^3} + \cdots$$

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

Now since our approximation for $q_{\mathrm{rot}}(T)$ by an integral yields $T/\Theta_{\mathrm{rot}}$ as a result, we know that the correction factor to second order is

$$\text{correction factor} = \frac{1}{3}\left(\frac{\Theta_{\mathrm{rot}}}{T}\right) + \frac{1}{15}\left(\frac{\Theta_{\mathrm{rot}}}{T}\right)^2$$

Therefore, for $N_2$ ($\Theta_{\mathrm{rot}} = 2.88\,\mathrm{K}$) at $T = 300\,\mathrm{K}$, we have that

$$\boxed{\text{correction factor} = 0.321\,\%}$$

while for $H_2$ ($\Theta_{\mathrm{rot}} = 85.3\,\mathrm{K}$) at $T = 300\,\mathrm{K}$, we have that

$$\boxed{\text{correction factor} = 10.0\,\%}$$

$\square$

6. Problem 17-33. Discuss at which temperatures the heat capacity deviates from the result given.

   We will learn in Chapter 18 that the rotational partition function of an asymmetric top molecule is given by

   $$q_{\mathrm{rot}}(T) = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B T}{h^2}}$$

   where $\sigma$ is a constant and $I_A, I_B, I_C$ are the three (distinct) moments of inertia. Show that the rotational contribution to the molar heat capacity is $\overline{C}_{V,\mathrm{rot}} = 3R/2$.

   *Proof.* We have that

   $$\ln q_{\mathrm{rot}} = \frac{3}{2}\ln T + \ln\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B}{h^2}}$$

   $$= \frac{3}{2}\ln T + \text{terms not involving } T$$

It follows that

$$\langle E \rangle = k_B T^2 \frac{\partial \ln q_{\text{rot}}}{\partial T}$$
$$= k_B T^2 \frac{\partial}{\partial T} \left( \frac{3}{2} \ln T \right)$$
$$= k_B T^2 \cdot \frac{3}{2T}$$
$$= \frac{3}{2} k_B T$$

so that

$$C_{V,\text{rot}} = \frac{\partial \langle E \rangle}{\partial T}$$
$$= \frac{\partial}{\partial T} \left( \frac{3}{2} k_B T \right)$$
$$= \frac{3}{2} k_B$$
$$\boxed{\overline{C}_{V,\text{rot}} = \frac{3}{2} R}$$

Note that at temperatures for which $\boxed{\Theta_{\text{rot}} \ll T \text{ is not satisfied}}$ the above result will not hold since our derivation of the partition function relies on using this result to approximate an infinite sum as an indefinite integral.                                                                   $\square$

# 2   The First and Second Laws of Thermodynamics

2/8:    1. Consider the following experiment with an ideal gas, and derive the relation between $\gamma$, $h$, and $h'$.

Let the system sit at $P_0, T_0$ where $h = 0$. Pump a little gas in (add $\Delta n$) and wait so that $T$ is back to $T_0$; measure $h$. Open the valve to air quickly to $P_0$ and close again. Justify why this can be considered a reversible adiabatic expansion. Wait so that $T$ is back to $T_0$; measure $h'$.
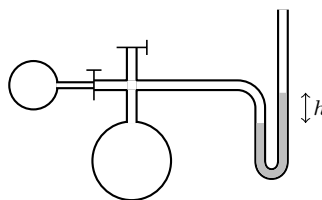


*Answer.* State 1 is $P_0 V_0 = nRT_0$, state 2 is $(P_0 + h)V_0 = (n + \Delta n_1)RT_0$, and state 3 is $(P_0 + h')V_0 = (n + \Delta n_1 + \Delta n_2)RT_0$. It follows that

$$(P_0 + h)V_0 = (n + \Delta n_1)RT_0$$
$$P_0 V_0 + hV_0 = nRT_0 + \Delta n_1 RT_0$$
$$hV_0 = \Delta n_1 RT_0$$
$$hV_0 = \Delta n_1 \cdot \frac{P_0 V_0}{n}$$
$$\frac{h}{P_0} = \frac{\Delta n_1}{n}$$

$$(P_0 + h')V_0 = (n + \Delta n_1 - \Delta n_2)RT_0$$
$$P_0 V_0 + h'V_0 = nRT_0 + \Delta n_1 RT_0 - \Delta n_2 RT_0$$
$$h'V_0 = \Delta n_1 RT_0 - \Delta n_2 RT_0$$
$$h'V_0 = \frac{nh}{P_0} \cdot RT_0 - \Delta n_2 RT_0$$
$$h'V_0 = \frac{nh}{P_0} \cdot \frac{P_0 V_0}{n} - \Delta n_2 \cdot \frac{P_0 V_0}{n}$$
$$h' = h - \frac{P_0 \Delta n_2}{n}$$
$$\frac{\Delta n_2}{n} = \frac{h - h'}{P_0} = \frac{C_P}{C_V} \frac{h}{P_0}$$

$$h - h' = \frac{hC_P}{C_V}$$
$$C_V(h - h') = hC_P$$
$$h(C_V - C_P) = h'C_V$$
$$\frac{h'}{h} = \frac{C_V - C_P}{C_V}$$
$$= 1 - \gamma$$

$\square$

2. (a) $n$ moles of an ideal gas with a given $\gamma$ undergo an adiabatic expansion from $V_a$ to $V_b$. Calculate the work done and the total energy change.

*Answer.* Let the initial pressure of the gas be $P_a$. Then

$$w = -\int_{V_a}^{V_b} P \, dV$$

$$= -\int_{V_a}^{V_b} \frac{P_a V_a^\gamma}{V^\gamma} \, dV$$

$$\boxed{w = \frac{P_a V_a^\gamma}{\gamma - 1}(V_b^{1-\gamma} - V_a^{1-\gamma})}$$

Additionally, since the process is adiabatic (i.e., $\delta q = 0$), we know that $\Delta U = w$. Thus,

$$\boxed{\Delta U = \frac{P_a V_a^\gamma}{\gamma - 1}(V_b^{1-\gamma} - V_a^{1-\gamma})}$$

□

(b) $n$ moles of an ideal gas with a given $\gamma$ undergo an isobaric expansion from $V_a$ to $V_b$. Calculate the work done and the total energy change.

*Answer.* Let the constant pressure throughout the expansion be $P$. Then

$$\boxed{w = P(V_b - V_a)}$$

Additionally, since $PV_a = nRT_a$ and $PV_b = nRT_b$, we have that

$$\Delta U = \int_{T_a}^{T_b} C_V \, dT$$

$$= C_V(T_b - T_a)$$

$$\boxed{\Delta U = \frac{C_V P}{nR}(V_b - V_a)}$$

□

3. (a) Consider a Carnot cycle for an ideal gas. Derive the relation $Q_1/T_1 + Q_2/T_2 = 0$ where $Q_1, Q_2$ are the heat transferred to the system along the isotherms at $T_1, T_2$.

*Answer.* The Carnot cycle is a four step process. The four steps are isothermal expansion (at $T_1$; we let $Q_1$ be the heat absorbed during this process), adiabatic expansion (the amount $Q$ of heat absorbed or released is zero), isothermal compression ($Q_2$ at $T_2$), and adiabatic compression ($Q = 0$). During each of these reversible processes, there is a change in entropy $dS = \delta q_{\text{rev}}/T$. Thus, the total change in entropy $\Delta S$ is given by

$$\Delta S = \int_{T_1}^{T_1} \frac{Q_1}{T_1} \, dT + \int_{T_1}^{T_2} \frac{0}{T} \, dT + \int_{T_2}^{T_2} \frac{Q_2}{T_2} \, dT + \int_{T_2}^{T_1} \frac{0}{T} \, dT$$

$$= \frac{Q_1}{T_1} + \frac{Q_2}{T_2}$$

But since $\Delta S = 0$ around a closed loop (such as the Carnot cycle), we have that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

as desired.                                                                                          □

(b) Consider an ideal gas going from $V_1, T_1$ to $V_2, T_2$. Calculate the entropy change in terms of $V_1, V_2, T_2, T_2$.

*Answer.* We will calculate the entropy change along two separate paths (reversible processes) that together move an ideal gas from $V_1, T_1$ to $V_2, T_2$. In particular, we go from $V_1, T_1$ to $V_2, T_1$ isothermally and then from $V_2, T_1$ to $V_2, T_2$ isochorically. If we call these processes $A$ and $B$, it follows that

$$\Delta S = \Delta S_A + \Delta S_B$$

$$= nR \ln \frac{V_2}{V_1} + \int_{T_1}^{T_2} \frac{C_V}{T} \, dT$$

$$\boxed{\Delta S = nR \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1}}$$

□

4. Practicing with partial derivatives.

By expressing the internal energy state function $U$ in terms of $V$ and $T$ variables and alternatively with $P$ and $T$ variables, show that

$$\left( \frac{\partial U}{\partial P} \right)_T = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \qquad \left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial U}{\partial V} \right)_T$$

Then derive that

$$C_P - C_V = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

Show that

$$\left( \frac{\partial U}{\partial V} \right)_T = 0$$

for an ideal gas. And then show that

$$C_P - C_V = nR$$

*Answer.* The total differential for $U(P,T)$ is

$$dU = \left( \frac{\partial U}{\partial P} \right)_T dP + \left( \frac{\partial U}{\partial T} \right)_P dT$$

It contains the two partial derivatives for which we want to find expressions. Thus, we need only manipulate an analogous equation into the above form. To do so, we use the total differential for $U(V,T)$

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT$$

This is close, but we need $dP$, not $dV$. Thus, we substitute the total differential for $V(P,T)$

$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

into the above expression to get

$$dU = \left( \frac{\partial U}{\partial V} \right)_T \left[ \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT \right] + \left( \frac{\partial U}{\partial T} \right)_V dT$$

$$= \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial T} \right)_V dT$$

$$= \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T dP + \left[ \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial U}{\partial T} \right)_V \right] dT$$

The first two equations follow by comparing the above with the total differential for $U(P,T)$.

It follows from the second equation and the definition of enthalpy that

$$\left(\frac{\partial}{\partial T}(H - PV)\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial P}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

Noting that $\partial P/\partial T = 0$ for $P$ a constant function (the derivative is taken at constant pressure) and employing the definitions of $C_P, C_V$ gives us

$$C_P - P\left(\frac{\partial V}{\partial T}\right)_P - V \cdot 0 = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

as desired.

Since the internal energy $U$ of an ideal gas is solely a function of temperature $T$, taking the partial derivative of $U$ with respect to $V$ is equivalent to taking the derivative of a constant function, and thus we clearly have

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

It follows since $V = nRT/P$ by the ideal gas law that

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= [P + 0]\frac{nR}{P}$$

$$= nR$$

as desired. □

5. Write that $dU = T\,dS - P\,dV$ and derive the following two relations.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

*Answer.* The total differential of $U(T,V)$ is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Thus, we have that

$$T\,dS - P\,dV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

$$= \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

The two equations follow by comparing the above with the total differential for $S(T, V)$, given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

□

6. Problem 21-10. Show your work.

It has been found experimentally that $\Delta_{\text{vap}}\overline{S} \approx 88\,\text{J K}^{-1}\,\text{mol}^{-1}$ for many nonassociated liquids. This rough rule of thumb is called **Trouton's rule**. Use the following data to test the validity of Trouton's rule.

| Substance | $t_{\text{fus}}/°\text{C}$ | $t_{\text{vap}}/°\text{C}$ | $\Delta_{\text{fus}}\overline{H}/\text{kJ mol}^{-1}$ | $\Delta_{\text{vap}}\overline{H}/\text{kJ mol}^{-1}$ |
|---|---|---|---|---|
| Pentane | -129.7 | 36.06 | 8.42 | 25.79 |
| Hexane | -95.3 | 68.73 | 13.08 | 28.85 |
| Heptane | -90.6 | 98.5 | 14.16 | 31.77 |
| Ethylene oxide | -111.7 | 10.6 | 5.17 | 25.52 |
| Benzene | 5.53 | 80.09 | 9.95 | 30.72 |
| Diethyl ether | -116.3 | 34.5 | 7.27 | 26.52 |
| Tetrachloromethane | -23 | 76.8 | 3.28 | 29.82 |
| Mercury | -38.83 | 356.7 | 2.29 | 59.11 |
| Bromine | -7.2 | 58.8 | 10.57 | 29.96 |

*Answer.* We know that

$$\Delta_{\text{vap}}\overline{S} = \frac{\Delta_{\text{vap}}\overline{H}}{t_{\text{vap}}}$$

Thus, for pentane (for example), we have that

$$\Delta_{\text{vap}}\overline{S}(\text{pentane}) = \frac{25.79\,\text{kJ mol}^{-1}}{36.06\,°\text{C}} = \frac{2.579 \times 10^4\,\text{J mol}^{-1}}{309.21\,\text{K}} = 83.41\,\text{J K}^{-1}\,\text{mol}^{-1}$$

We can run the same calculation for all of the other values to learn that

$$\Delta_{\text{vap}}\overline{S}(\text{hexane}) = 84.39\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{heptane}) = 85.47\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{ethylene oxide}) = 89.92\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{benzene}) = 86.97\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{diethyl ether}) = 86.19\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{tetrachloromethane}) = 85.20\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{mercury}) = 93.84\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$\Delta_{\text{vap}}\overline{S}(\text{bromine}) = 90.24\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Since the mean of this set of values of $\Delta_{\text{vap}}\overline{S}$ is $87.29 \approx 88$ and the standard deviation is relatively small, the given data supports Trouton's rule.                                        □

7. Problem 21-37. Show your reasoning.

Given that $\tilde{\nu}_1 = 1321.3\,\text{cm}^{-1}$, $\tilde{\nu}_2 = 750.8\,\text{cm}^{-1}$, $\tilde{\nu}_3 = 1620.3\,\text{cm}^{-1}$, $\tilde{A}_0 = 7.9971\,\text{cm}^{-1}$, $\tilde{B}_0 = 0.4339\,\text{cm}^{-1}$, and $\tilde{C}_0 = 0.4103\,\text{cm}^{-1}$, calculate the standard molar entropy of $NO_{2(g)}$ at 298.15 K. (Note that $NO_{2(g)}$ is a bent triatomic molecule.) How does your value compare with that in Table 21.2?

*Answer.* Given molecular data, it will be easiest to calculate the standard molar entropy by means of the partition function $Q$. We can do this with the help of the equation

$$S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

To see if we can employ the $Q = q^N/N!$ approximation, we apply the following condition, where $P = 1\,\text{bar}$, $T = 298.15\,\text{K}$, $m = 46.01\,\text{g/mol} = 7.640 \times 10^{-26}\,\text{kg}$, and the rest of the terms are fundamental constants.

$$\frac{N}{V} \left( \frac{h^2}{8mk_B T} \right)^{3/2} \overset{?}{\ll} 1$$

$$\frac{P}{RT} \left( \frac{h^2}{8mk_B T} \right)^{3/2} \overset{?}{\ll} 1$$

$$5.596 \times 10^{-8} \overset{\checkmark}{\ll} 1$$

Indeed we can, so thus we write

$$S = k_B \ln \frac{q^N}{N!} + k_B T \left( \frac{\partial \ln q^N/N!}{\partial T} \right)_V$$

$$= Nk_B \ln q - k_B \ln N! + k_B T N \left( \frac{\partial \ln q}{\partial T} \right)_V - k_B T N \left( \frac{\partial \ln N!}{\partial T} \right)_V$$

$$= Nk_B \ln q - Nk_B \ln N + Nk_B + Nk_B T \left( \frac{\partial \ln q}{\partial T} \right)_V$$

$$= Nk_B + Nk_B \ln \frac{q}{N} + Nk_B T \left( \frac{\partial \ln q}{\partial T} \right)_V$$

Now for a nonlinear polyatomic molecule,

$$q(V,T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot g_{e1} e^{D_e/k_B T}$$

It follows that for $NO_2$ in particular,

$$q(V,T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{2} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^{3} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot e^{D_e/k_B T}$$

Then since

$$\ln q = \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{2} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^{3} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot e^{D_e/k_B T} \right]$$

$$= \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4 \Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}} + \sum_{j=1}^{3} \ln \left[ \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] + \frac{D_e}{k_B T}$$

$$= \frac{3}{2} \ln T + \frac{1}{2} \cdot 3 \ln T + \sum_{j=1}^{3} \left[ -\frac{\Theta_{\text{vib},j}}{2T} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] + \frac{D_e}{k_B T} + \text{terms not involving } T$$

$$= 3 \ln T + \sum_{j=1}^{3} \left[ -\frac{\Theta_{\text{vib},j}}{2T} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] + \frac{D_e}{k_B T} + \text{terms not involving } T$$

and

$$\left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{T} + \sum_{j=1}^{3}\left[\frac{\Theta_{\mathrm{vib},j}}{2T^2} + \frac{(\Theta_{\mathrm{vib},j}/T^2)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right] - \frac{D_e}{k_B T^2}$$

$$Nk_B T\left(\frac{\partial \ln q}{\partial T}\right)_V = 3Nk_B + Nk_B\sum_{j=1}^{3}\left[\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{(\Theta_{\mathrm{vib},j}/T)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right] - \frac{ND_e}{T}$$

we have that

$$S = Nk_B + Nk_B \ln q - Nk_B \ln N + Nk_B T\left(\frac{\partial \ln q}{\partial T}\right)_V$$

$$= Nk_B + Nk_B\left\{\ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}V\right] + \frac{1}{2}\ln\frac{T^3\pi}{4\Theta_{\mathrm{rot},A}\Theta_{\mathrm{rot},B}\Theta_{\mathrm{rot},C}}\right.$$

$$\left. + \sum_{j=1}^{3}\ln\left[\frac{\mathrm{e}^{-\Theta_{\mathrm{vib},j}/2T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right] + \frac{D_e}{k_B T}\right\}$$

$$- Nk_B \ln N + 3Nk_B + Nk_B\sum_{j=1}^{3}\left[\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{(\Theta_{\mathrm{vib},j}/T)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right] - \frac{ND_e}{T}$$

$$= 4Nk_B + Nk_B\left\{\ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}V\right] + \frac{1}{2}\ln\frac{T^3\pi}{4\Theta_{\mathrm{rot},A}\Theta_{\mathrm{rot},B}\Theta_{\mathrm{rot},C}}\right.$$

$$\left. + \sum_{j=1}^{3}\left[-\frac{\Theta_{\mathrm{vib},j}}{2T} - \ln\left(1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}\right)\right] + \frac{D_e}{k_B T}\right\}$$

$$- Nk_B \ln N + Nk_B\sum_{j=1}^{3}\left[\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{(\Theta_{\mathrm{vib},j}/T)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right] - \frac{ND_e}{T}$$

$$= Nk_B\left\{4 + \ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}\frac{V}{N}\right] + \frac{1}{2}\ln\frac{T^3\pi}{4\Theta_{\mathrm{rot},A}\Theta_{\mathrm{rot},B}\Theta_{\mathrm{rot},C}}\right.$$

$$+ \sum_{j=1}^{3}\left[-\ln\left(1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}\right)\right]$$

$$\left. + \sum_{j=1}^{3}\left[\frac{(\Theta_{\mathrm{vib},j}/T)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}\right]\right\}$$

$$\frac{\overline{S}}{R} = 4 + \ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}\frac{RT}{PN_A}\right] + \frac{1}{2}\ln\frac{T^3\pi}{4\Theta_{\mathrm{rot},A}\Theta_{\mathrm{rot},B}\Theta_{\mathrm{rot},C}}$$

$$+ \sum_{j=1}^{3}\left[\frac{(\Theta_{\mathrm{vib},j}/T)\mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}} - \ln\left(1 - \mathrm{e}^{-\Theta_{\mathrm{vib},j}/T}\right)\right]$$

We now construct the needed values from the given data on $NO_2$. In particular, since $\Theta_{\mathrm{vib}} = h\nu/k_B = hc\tilde{\nu}/k_B$, we have that

$$\Theta_{\mathrm{vib},1} = \frac{hc\tilde{\nu}_1}{k_B} \qquad \Theta_{\mathrm{vib},2} = \frac{hc\tilde{\nu}_2}{k_B} \qquad \Theta_{\mathrm{vib},3} = \frac{hc\tilde{\nu}_3}{k_B}$$

$$= 1901\,\mathrm{K} \qquad\qquad = 1080\,\mathrm{K} \qquad\qquad = 2331\,\mathrm{K}$$

Additionally, since $\Theta_{\mathrm{rot}} = \hbar^2/2Ik_B$ and $\tilde{X}_0 = h/8\pi^2 cI$, we have that

$$\Theta_{\mathrm{rot}} = \frac{h^2}{8\pi^2 Ik_B} = \frac{hc}{k_B}\cdot\frac{h}{8\pi^2 cI} = \frac{hc\tilde{X}_0}{k_B}$$

Thus,

$$\Theta_{\mathrm{rot},A} = \frac{hc\tilde{A}_0}{k_B} \qquad \Theta_{\mathrm{rot},B} = \frac{hc\tilde{B}_0}{k_B} \qquad \Theta_{\mathrm{rot},C} = \frac{hc\tilde{C}_0}{k_B}$$
$$= 11.50\,\mathrm{K} \qquad\qquad = 0.6241\,\mathrm{K} \qquad\qquad = 0.5902\,\mathrm{K}$$

The value of $M$ was given above (as $m$ in the molecular partition function criterion), and everything else is a fundamental constant. The one exception is pressure, which we take to be standard (i.e., $1\,\mathrm{bar} = 1 \times 10^5\,\mathrm{Pa}$). Choosing values such that all units cancel gives us

$$\boxed{\overline{S} = 234.3\,\mathrm{J\,mol^{-1}\,K^{-1}}}$$

$\square$

8. Problem 19-55.

Use the rigid rotator-harmonic oscillator model and the data in Table 18.2 to plot $\overline{C}_P(T)$ for $CO_{(g)}$ from $300\,\mathrm{K}$ to $1000\,\mathrm{K}$. Compare your result with the expression given in Problem 19-43.

*Answer.* For a linear molecule,

$$\frac{C_V}{Nk_B} = \frac{5}{2} + \sum_{j=1}^{3n-5} \left(\frac{\Theta_{\mathrm{vib},j}}{T}\right)^2 \frac{e^{-\Theta_{\mathrm{vib},j}/T}}{(1 - e^{-\Theta_{\mathrm{vib},j}/T})^2}$$

In particular, for a linear diatomic molecule,

$$\frac{C_V}{Nk_B} = \frac{5}{2} + \left(\frac{\Theta_{\mathrm{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\mathrm{vib}}/T}}{(1 - e^{-\Theta_{\mathrm{vib}}/T})^2}$$

Thus, since $C_P - C_V = Nk_B$, we have that

$$C_P = \frac{7}{2}Nk_B + Nk_B \left(\frac{\Theta_{\mathrm{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\mathrm{vib}}/T}}{(1 - e^{-\Theta_{\mathrm{vib}}/T})^2}$$
$$\overline{C}_V(T) = \frac{7}{2}R + R \left(\frac{\Theta_{\mathrm{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\mathrm{vib}}/T}}{(1 - e^{-\Theta_{\mathrm{vib}}/T})^2}$$

where $\Theta_{\mathrm{vib}} = 3103\,\mathrm{K}$ by Table 18.2. This function is plotted below in red, and the expression given in Problem 19-43 is plotted below in blue. They clearly follow the same general trend but nevertheless display not insignificant differences in their trajectory.



$\square$
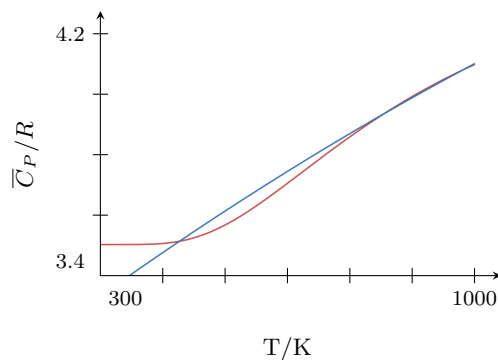
# 3   Deviations from Ideality

3/2:      1. An "ideal" rubber band is at $300\,\mathrm{K}$ and a mass of $200\,\mathrm{g}$ stretches its length by $10\,\mathrm{mm}$. Give the stretch length at $330\,\mathrm{K}$.

2. A pill of $0.1\,\mathrm{mol}$ of gadolinium (III) sulfate $(\mathrm{Gd_2(SO_4)_3})$ is used for adiabatic demagnetization.

   (a) Give the molar mass.

   (b) Assuming all electrons unpaired in the $f$ orbital, give the magnetic moment.

   (c) Calculate the heat transferred from the lattice to the spin degree of freedom as the field is varied from $1\,\mathrm{T}$ to $0\,\mathrm{T}$.

   (d) Estimate the heat capacity of the pill, and determine its lattice temperature if it starts at $4\,\mathrm{K}$.

3. A Joule-Thomson expansion is an adiabatic and reversible expansion from a pressure $P_1$ to a pressure $P_2$, made closer to reversible by having a porous section that slows down the gas.

   (a) Show that the Joule-Thomson expansion conserves enthalpy.

   (b) Show that an ideal gas's temperature is unchanged during a Joule-Thomson expansion.

   (c) Argue why a real gas can cool (or heat up) during a Joule-Thomson expansion.

   (d) Show that the temperature change is given by $(\partial T/\partial P)_H$.

   (e) Problem 22-48: Show that
   $$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$
   where $\alpha$ is the coefficient of thermal expansion.

   (f) Problem 22-49: Show that a gas with only excluded volume cools upon expansion.

   (g) Problem 22-51: Give the sign and estimate the magnitude of $(\partial T/\partial P)_H$ for $\mathrm{N_2}$ gas around $300\,\mathrm{K}$ from $100\,\mathrm{atm}$ to $1\,\mathrm{atm}$ based on van der Waals parameters.