

# CHEMICAL THERMODYNAMICS AND KINETICS

## PROBLEM SET #2

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September 29, 2020

**Exploring partition functions for diatomic molecules.** This problem set continues the work that we began on the class worksheet. The energy of diatomic molecules can be written as the sum of the electronic, translational, rotational, and vibrational energy. Assume ideal gas behavior throughout the problem set, such that the molecular energies are additive.

**Part I: Electronic Energy.** The molecular partition function of the electronic energy is similar to that of the monatomic gas:  $q_{\text{elec}} = \sum_i g_{e,i} \exp(-\beta \varepsilon_{e,i})$ . For monatomic gases, the ground state energy is taken to be “0.” For a diatomic molecule, some references will set the ground state energy level to  $-D_e$ , where  $D_e$  is the dissociation energy.

While the numeric value of  $\langle E \rangle$  depends upon our choice of the “zero” (see above), the fraction of population in the excited state does **not** depend on our choice of zero. Suppose diatomic gas  $A$  absorbs light at 300 nm. What is the fraction of sample  $A$  that is in the excited state at 100°C? Assume that the ground and excited states are nondegenerate.

**Solution.** The energy difference between our two energy levels is equal to the energy of the photon,  $E_p = h\nu = h\frac{c}{\lambda}$ , where we have  $c$  as the speed of light and  $h$  equal to Planck’s constant. Thus, our two energy levels possess energies

$$\varepsilon_{e,0} = -D_e; \quad \varepsilon_{e,1} = E_p - D_e.$$

Seeing as these are the only two levels in question, and dividing their exponential by the partition function gets messy, let’s instead consider the ratio of their partition function components (note nondegeneracy cancels the  $g$  coefficient):

$$\begin{aligned} \frac{q_{\text{ground}}}{q_{\text{excited}}} &= \frac{\exp(-\beta(-D_e))}{\exp(-\beta(E_p - D_e))} = \exp(\beta D_e + \beta(E_p - D_e)) \\ &= \exp(\beta D_e + \beta E_p - \beta D_e) = \exp(\beta E_p) \\ &= \exp\left(\frac{h\frac{c}{\lambda}}{k_B T}\right) \\ &= \exp\left(\frac{6.63 \times 10^{-34} \text{ J s } \frac{3 \times 10^{17} \text{ nm/s}}{300 \text{ nm}}}{(1.38 \times 10^{-23} \text{ J/K})(373 \text{ K})}\right) = 8.7 \times 10^{55} \\ q_{\text{ground}} &= q_{\text{excited}} \cdot 8.7 \times 10^{55}. \end{aligned}$$

With this relationship, we find

$$\begin{aligned}
 \frac{q_{\text{excited}}}{q_{\text{tot}}} &= \frac{q_{\text{excited}}}{q_{\text{excited}} + q_{\text{ground}}} \\
 &= \frac{q_{\text{excited}}}{q_{\text{excited}} + (q_{\text{excited}} \cdot 8.7 \times 10^{55})} \\
 &= \frac{1}{1 + 8.7 \times 10^{55}} \\
 &= \boxed{1.15 \times 10^{-56}} \approx 0.
 \end{aligned}$$

**Part II: Translational Motion.** The molecular partition function of the translational energy in 3-dimensions ( $x, y, z$ ) is identical to that of the monatomic gas:

$$q_{\text{trans}}(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V.$$

Thus, we can ask, what is the value of  $\langle \varepsilon_{\text{trans}} \rangle$  if we restrict ourselves to 1-dimension?

**Sanity Check.** Well, according to the Equipartition Theorem, we'd have  $\langle \varepsilon_{\text{trans}} \rangle = \frac{1}{2} k_B T$  for one molecule. However, let's see if we can get there with the given expression. By equivalent logic as the given expression (and by the same derivation — without the second and third dimensions — as we did on the worksheet), we find

$$q_{\text{trans}}(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{1/2} L, \quad (1)$$

when we restrict ourselves to one degree of freedom (hence length, as opposed to volume). We'll need two more equations from class, namely

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

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}. \quad (3)$$

By combining equations (1) and (3) to find the partial differential, we find

$$\begin{aligned}
 \frac{\partial \ln Q(N, V, T)}{\partial T} &= \frac{\partial}{\partial T} \left( \ln \frac{\left( \frac{2\pi m k_B T}{h^2} \right)^{N/2} L^N}{N!} \right) \\
 &= \frac{\partial}{\partial T} \left( \frac{N}{2} [\ln(2\pi m k_B T) - \ln(h^2)] + \ln(L^N) - \ln(N!) \right) \\
 &= \frac{\partial}{\partial T} \left( \frac{N}{2} \ln(T) + \frac{N}{2} \ln(2\pi m k_B) \right) \\
 &= \frac{N}{2T}.
 \end{aligned}$$

Now, we can substitute into (2):

$$\langle E \rangle = k_B T^2 \left( \frac{N}{2T} \right) = \frac{N}{2} k_B T.$$

Although, when we realize that we're only describing a single molecule, that  $N$  becomes 1, yielding the same result as the Equipartition Theorem.

**Application.** For a more specific application, consider the value of the translational quantum number for molecular nitrogen at room temperature and dimension  $L = 1$  dm that would correspond to the average translational energy above. To this end, suppose we have an  $\varepsilon_{\text{trans}} = \langle E \rangle$ . We also know,

$$\langle E \rangle = \frac{1}{2}k_B T, \quad \varepsilon_{\text{trans}} = \frac{h^2}{8mL^2}(n_x)^2.$$

Thus, by substitution we find,

$$\begin{aligned} \frac{1}{2}k_B T &= \frac{h^2}{8mL^2}(n_x)^2 \\ \sqrt{\frac{4k_B T m L^2}{h^2}} &= n_x \\ \sqrt{\frac{4(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})(2.32 \times 10^{-26} \text{ kg})(.1 \text{ m})^2}{(6.63 \times 10^{-34} \text{ Js})^2}} &= n_x \\ \boxed{7.6 \times 10^9 = n_x}, \end{aligned}$$

noting that the units cancel. This tells us that the spacing between energy levels is very small because the partition function is so ridiculously large. This matches with our intuition — the discrete energy levels are so close together that they behave continuously!

### Part III: Rotational Motion.

Claim: For a diatomic molecule,

$$\begin{aligned} q_{\text{rot}}(T) &= \frac{8\pi^2 I k_B T}{h^2} = \frac{T}{\theta_{\text{rot}}}, \quad \text{where} \\ \theta_{\text{rot}} &= \frac{h^2}{8\pi^2 I k_B} \ll T. \end{aligned}$$

**Derivation:** Consider our partition function and our quantum definition of rotational energy (based on a rotor),

$$\begin{aligned} q_{\text{rot}} &= \sum_{\forall J} g_{r,J} \exp(-\beta \varepsilon_{r,J}), \\ \varepsilon_J &= \frac{\hbar^2}{2I} J(J+1), \quad g_J = 2J+1, \end{aligned}$$

where  $J \in 0 \cup \mathbb{N}$ , and  $\beta = 1/k_B T$ . Combining these ideas, we have

$$\begin{aligned} q_{\text{rot}} &= \sum_{J=0}^{\infty} (2J+1) \exp\left(-\beta \frac{\hbar^2}{2I} J(J+1)\right) \\ &\approx \int_0^{\infty} \exp(-\alpha J(J+1))(2J+1) dJ, \end{aligned}$$

where  $\alpha = \beta \frac{\hbar^2}{2I}$ . Let's now employ the following substitution. Let,

$$u = J(J+1) = J^2 + J$$

$$\frac{du}{dJ} = 2J + 1 \implies du = (2J + 1)dJ$$

$$\frac{J}{u} \left| \begin{array}{l} 0 \rightarrow \infty \\ 0 \rightarrow \infty \end{array} \right.$$

Thus, we have

$$q_{\text{rot}} \approx \int_0^\infty \exp(-\alpha u) du = -\alpha [e^{-\alpha u}]_0^\infty$$

$$= -\frac{1}{\alpha} [0 - 1]$$

$$= \frac{2Ik_B T}{\hbar^2}.$$

Recalling that  $\hbar = h/2\pi$ , we yield the claim:

$$q_{\text{rot}} = \frac{8\pi^2 Ik_B T}{h^2}.$$

**Getting Graphical.** Now, what if we have the bond length of  $\text{N}_2$  ( $R_e = 109.8$  pm)? Well, then we can find  $\theta_{\text{rot}}$ . We find

$$\theta_{\text{rot}} = \frac{h^2}{8\pi^2 Ik_B} = \frac{h^2}{8\pi^2 \frac{m_1 m_2}{m_1 + m_2} R_e^2 k_B}$$

$$= \frac{(6.63 \times 10^{-34} \text{ Js})^2}{8\pi^2 \frac{(2.32 \times 10^{-26} \text{ kg})^2}{2(2.32 \times 10^{-26} \text{ kg})} (1.089 \times 10^{-10} \text{ m})^2 (1.38 \times 10^{-23} \text{ J/K})}$$

$$= \boxed{2.9 \text{ K}},$$

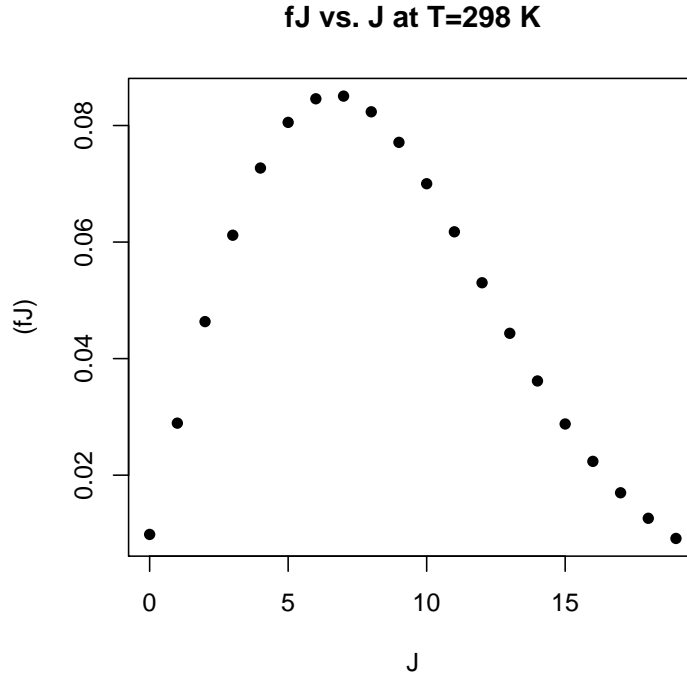
recalling that  $I = \mu R_e^2$  and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ . Notice, this is *far smaller* than  $T$ , as per our claim. Next, let's consider  $f_J$ , the fraction of molecules in the  $J^{\text{th}}$  energy level,

$$f_J = \frac{q_{r,J}}{q_{\text{rot}}} = \frac{(2J+1) \exp\left(-\frac{1}{k_B T} \cdot \frac{\hbar^2}{2I} J(J+1)\right)}{\frac{T}{\theta_{\text{rot}}}}$$

$$f_J = \frac{\theta_{\text{rot}} (2J+1) \exp\left(-\frac{\hbar^2}{8\pi^2 I k_B T} J(J+1)\right)}{T}$$

$$\boxed{f_J = \frac{\theta_{\text{rot}} (2J+1) \exp\left(-\frac{\theta_{\text{rot}}}{T} J(J+1)\right)}{T}}.$$

Now, let's plot  $f_J$  vs  $J$  for  $J < 19$  at room temperature. Turning to our trusty friend, the R statistical software, we can throw together a splendid little plot:



Whoa! Check out that center mode! Most molecules seem to occupy those middle energy levels. Also, note how the consecutive spacing decreases as the levels progress.

**Part IV: Vibrational Motion.**

A diatomic gas can be modeled using a single harmonic oscillator. Let's derive it! Let's begin by letting  $\theta_{\text{vib}} = \frac{h\nu}{k_B}$ . Then, recall the following two definitions from class,

$$q_{\text{vib}} = \sum_{n=0}^{\infty} g_{v,n} \exp(-\beta \varepsilon_{v,n})$$

$$\varepsilon_{v,n} = h\nu \left( n + \frac{1}{2} \right).$$

Note that there is only one energy level per energy state. Next, by substitution, we find

$$\begin{aligned}
q_{\text{vib}} &= \sum_{n=0}^{\infty} (1) \exp \left( - \left( \frac{1}{k_B T} \right) \left[ h\nu \left( n + \frac{1}{2} \right) \right] \right) \\
&= \sum_{n=0}^{\infty} \exp \left( - \frac{\theta_{\text{vib}}(n + 1/2)}{T} \right) \\
&= \sum_{n=0}^{\infty} \frac{\exp(-\theta_{\text{vib}}n/T)}{\exp(\theta_{\text{vib}}/2T)} \\
&= \exp(-\theta_{\text{vib}}/2T) \sum_{n=0}^{\infty} \underbrace{\left[ \underbrace{\left( \frac{1}{e} \right)^{\theta_{\text{vib}}/T}}_{x < 1} \right]^n}_{(1-x)^{-1}} \\
&= \exp(-\theta_{\text{vib}}/2T) \cdot \left( \frac{1}{1-x} \right) \\
&= \exp(-\theta_{\text{vib}}/2T) \cdot \left( \frac{1}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \\
\boxed{q_{\text{vib}} = \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)}}
\end{aligned}$$

**Application.** Now, given the force constant  $k = 2,287 \text{ N m}^{-1}$  for  $\text{N}_2$ , we can calculate the fraction of nitrogen molecules in the  $n = 0$  and  $n = 1$  vibrational states at 298 K. What does this tell us about the spacing of the vibrational levels? First, let's calculate  $\theta_{\text{vib}}$ :

$$\begin{aligned}
\theta_{\text{vib}} &= \frac{h\nu}{k_B} = \frac{h\sqrt{k}}{k_B 2\pi\sqrt{\mu}} = \frac{h\sqrt{k}}{k_B 2\pi\sqrt{\frac{m_1 m_2}{m_1 + m_2}}} \\
&= \frac{(6.63 \times 10^{-34} \text{ Js})\sqrt{(2,287 \text{ N m}^{-1})}}{2\pi(1.38 \times 10^{-23} \text{ J/K})\sqrt{\frac{(2.32 \times 10^{-26} \text{ kg})^2}{2(2.32 \times 10^{-26} \text{ kg})}}} \\
\theta_{\text{vib}} &= 3390 \text{ K},
\end{aligned}$$

remembering  $\nu = (\sqrt{k/\mu})(1/2\pi)$ , with our  $\mu$  unchanged from above. Now, we can consider the fraction of molecules in a given energy level:

$$\frac{q_n}{q_{\text{vib}}} = \frac{\exp\left(\frac{-\theta_{\text{vib}}(n + \frac{1}{2})}{T}\right)}{\frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)}} = \dots = \frac{\exp(\theta_{\text{vib}}(1-n)/T) - \exp(-\theta_{\text{vib}}n/T)}{\exp(2\theta_{\text{vib}}/T)}.$$

After copious algebraic manipulation, we can now easily plug this into a calculator to find the actual numeric values; in that case, we can simply substitute  $T = 298 \text{ K}$  and  $\theta_{\text{vib}} = 3390 \text{ K}$ , and take our pick of  $n$ . Indeed, we find that the ratio yields zero for  $n = 1$ , and an undefined (infinite) value for  $n = 0$ . So, we're pretty clearly stuck at ground state. The energy levels must be infinitely far apart!

### Part V: Combining the Degrees of Freedom.

Now, we can write the molecular partition function of a diatomic molecule including all possible degrees of freedom. (Let's assume that the molecule is in the ground state, simplifying our electronic energy contribution). Then, we can scale it up to represent the partition function for a system of  $N$  diatomic molecules at constant  $N$ ,  $V$ , and  $T$ .

$$\begin{aligned}
q_{\text{mol}} &= q_{\text{elec}} \cdot q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \\
&= (1) \cdot \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \cdot \left( \frac{T}{\theta_{\text{rot}}} \right) \cdot \left( \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \\
q_{\text{mol}} &= T^{5/2} \cdot \left[ \frac{2\pi m k_B}{h^2} \right]^{3/2} \cdot \frac{V}{\theta_{\text{rot}}} \cdot \left( \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \\
Q(N, V, T) &= \left( T^{5/2} \cdot \left[ \frac{2\pi m k_B}{h^2} \right]^{3/2} \cdot \frac{V}{\theta_{\text{rot}}} \cdot \left( \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \right)^N / N! \\
\frac{\partial}{\partial T} \ln Q &= \frac{\partial}{\partial T} \left[ N \ln \left( T^{5/2} \cdot \left[ \frac{2\pi m k_B}{h^2} \right]^{3/2} \cdot \frac{V}{\theta_{\text{rot}}} \cdot \left( \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \right) - \ln(N!) \right] \\
&= N \frac{\partial}{\partial T} \left[ \ln(T^{5/2}) + \ln \exp(-\theta_{\text{vib}}/2T) - \ln(1 - \exp(-\theta_{\text{vib}}/T)) \right] \\
&= N \left( \frac{5}{2T} + \frac{\theta_{\text{vib}}}{2T^2} - \frac{\partial}{\partial T} \ln [1 - \exp(-\theta_{\text{vib}}/T)] \right).
\end{aligned}$$

Consider the internal derivative:

$$\begin{aligned}
\frac{\partial}{\partial T} \ln [1 - \exp(-\theta_{\text{vib}}/T)] &= \left( \frac{\theta_{\text{vib}}}{T^2} \right) \cdot (-\exp(-\theta_{\text{vib}}/T)) \cdot \left( \frac{1}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \\
&= \left( \frac{\theta_{\text{vib}}}{T^2} \right) \frac{1}{1 - \exp(\theta_{\text{vib}}/T)}.
\end{aligned}$$

Thus, we have

$$\left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} = N \left( \frac{5}{2T} + \frac{\theta_{\text{vib}}}{2T^2} + \frac{\theta_{\text{vib}}}{T^2(\exp(\theta_{\text{vib}}/T) - 1)} \right),$$

which yields our energy term:

$$\begin{aligned}
\langle E \rangle &= k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} \\
&= k_B T^2 N \left( \frac{5}{2T} + \frac{\theta_{\text{vib}}}{2T^2} + \frac{\theta_{\text{vib}}}{T^2(\exp(\theta_{\text{vib}}/T) - 1)} \right) \\
\langle \bar{E} \rangle &= \frac{\langle E \rangle}{N} = k_B T^2 \left( \frac{5}{2T} + \frac{\theta_{\text{vib}}}{2T^2} + \frac{\theta_{\text{vib}}}{T^2(\exp(\theta_{\text{vib}}/T) - 1)} \right) \\
&= \boxed{\frac{5k_B T}{2} + \frac{k_B \theta_{\text{vib}}}{2} + \frac{k_B \theta_{\text{vib}}}{(\exp(\theta_{\text{vib}}/T) - 1)}}.
\end{aligned}$$

Notice, however, that the latter two terms are extremely small. So, we could simply say  $\langle \bar{E} \rangle = \frac{5k_B T}{2}$ . Notice, we have three degrees of translational freedom, and two of rotational freedom in this simplified term. (The vibrational freedom lives in those two insignificant terms.)

Next, we can find  $\overline{C_V}$ .

$$\begin{aligned}\overline{C_V} &= \left( \frac{\partial \langle \bar{E} \rangle}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} \left( \frac{5k_B T}{2} + \frac{k_B \theta_{\text{vib}}}{2} + \frac{k_B \theta_{\text{vib}}}{(\exp(\theta_{\text{vib}}/T) - 1)} \right) \\ &= \frac{5k_B}{2} + \underbrace{\frac{\theta_{\text{vib}}^2 k_B \exp(\theta_{\text{vib}}/T)}{T^2 (\exp(\theta_{\text{vib}}/T) - 1)^2}}_{\text{even tinier than before}} \\ \boxed{\overline{C_V} = \frac{5k_B}{2}}\end{aligned}$$

The pressure can also be calculated from the partition function:

$$\langle P \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta}$$

By rearranging this expression for a diatomic ideal gas, we can find the ideal gas law. Let's tackle that pesky partial first, employing our previous simplification strategy:

$$\begin{aligned}\left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta} &= \frac{\partial}{\partial V} \left[ N \ln \left( T^{5/2} \cdot \left[ \frac{2\pi m k_B}{h^2} \right]^{3/2} \cdot \frac{V}{\theta_{\text{rot}}} \cdot \left( \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} \right) \right) - \ln(N!) \right] \\ &= \frac{\partial}{\partial V} [N \ln V - N \ln \theta_{\text{rot}}] \\ &= \frac{N}{V}.\end{aligned}$$

Thus, we find

$$\begin{aligned}\langle P \rangle &= k_B T \frac{N}{V} \\ \langle P \rangle V &= T \underbrace{k_B (N_A \cdot n)}_R \\ \langle P \rangle V &= nRT,\end{aligned}$$

as desired.

Now, after all that work, we can reflect on how our calculated  $\langle \bar{E} \rangle$ ,  $\overline{C_V}$ , and  $\langle P \rangle$  would differ if we considered polyatomic gases. The only major difference would be an additional rotational degree of freedom; three points define a plane, which means we've introduced another axis of rotation. Note that this would not be the case for colinear molecules (such as azides, carbon dioxide, etc.; those would behave like diatomic molecules). As such, the coefficient of



5/2 would become 6/2, or 3. Hence, for polyatomic gases, we have,

$$\langle \overline{E} \rangle = 3k_B T$$

$$\overline{C_V} = 3k_B$$

$$\langle P \rangle = \frac{nRT}{V}.$$