

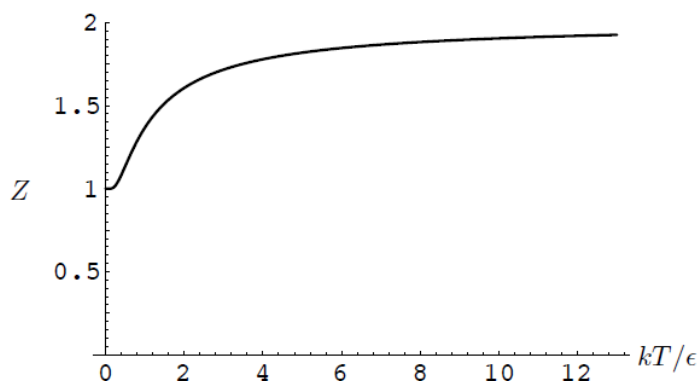
HW-Solution-set7

6.3, 6.5, 6.10, 6.12, 6.13, 6.16, 6.25, 6.29, 6.31, 6.33, 6.37, 6.44, 6.48, 6.49, 6.52.

Problem 6.3. For this two-state system,

$$Z = e^0 + e^{-\epsilon/kT} = 1 + e^{-\epsilon/kT},$$

where $\epsilon = 2$ eV is the energy of the excited state. Thus Z varies between 1 (in the limit $T \rightarrow 0$) and 2 (in the limit $T \rightarrow \infty$). To plot the partition function vs. temperature it's convenient to define the dimensionless variable $t = kT/\epsilon$, so $Z = 1 + e^{-1/t}$. The value of t at $T = 300$ K is about $1/80 = .013$, while the value of t at $T = 300,000$ K is about 13. (Recall that at 300 K, $kT = .026$ eV $\approx 1/40$ eV.) Here, then, is a plot of Z vs. t for values of t up to 13:



Plugging in the particular temperatures given yields the following values:

$$\begin{aligned} T = 300 \text{ K} : \quad Z &= 1 + e^{-1/.013} = 1 + 2.2 \times 10^{-34} \\ T = 3000 \text{ K} : \quad Z &= 1 + e^{-1/.13} = 1.00043 \\ T = 30,000 \text{ K} : \quad Z &= 1 + e^{-1/1.3} = 1.46 \\ T = 300,000 \text{ K} : \quad Z &= 1 + e^{-1/13} = 1.93 \end{aligned}$$

Notice that the approach to 1 at low temperature is much more dramatic than the approach to 2 at high temperature.

Problem 6.5. (A three-state toy model.)

- (a) At 300 K, $kT = 0.026$ eV, as computed on page 13. Therefore the partition function for this system is

$$Z = e^{-(-0.05/0.026)} + e^0 + e^{-(0.05/0.026)} = 6.84 + 1 + 0.15 = 7.99.$$

- (b) Numbering the states 1, 2, and 3 in the order listed, the probabilities are

$$\mathcal{P}_1 = \frac{6.84}{7.99} = 0.86; \quad \mathcal{P}_2 = \frac{1}{7.99} = 0.13; \quad \mathcal{P}_3 = \frac{0.15}{7.99} = 0.02.$$

(c) Measuring the energies now relative to the ground state, we have

$$Z = e^0 + e^{-(0.05/0.026)} + e^{-(0.10/0.026)} = 1 + 0.15 + 0.02 = 1.17.$$

And the probabilities are

$$\mathcal{P}_1 = \frac{1}{1.17} = 0.86; \quad \mathcal{P}_2 = \frac{0.15}{1.17} = 0.13; \quad \mathcal{P}_3 = \frac{0.02}{1.17} = 0.02.$$

So even though the partition function changes, the probabilities are unchanged, as they must be because nature can't possibly care what we use as our zero-point for measuring energy.

Problem 6.10. (Vibrational excitations of H₂O.)

(a) The partition function for this vibrating atom is

$$Z = e^{-hf/2kT} + e^{-3hf/2kT} + e^{-5hf/2kT} + \dots$$

At 300 K,

$$\frac{hf}{kT} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(4.8 \times 10^{13} \text{ s}^{-1})}{(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 7.68,$$

so the partition function is approximately

$$\begin{aligned} Z &= e^{-3.84} + e^{-11.52} + e^{-19.20} + \dots \\ &= 0.0215 + (9.9 \times 10^{-6}) + (4.6 \times 10^{-9}) + \dots \\ &= 0.0215. \end{aligned}$$

The probabilities of the lowest two excited states are therefore

$$\mathcal{P}_1 = \frac{9.9 \times 10^{-6}}{0.0215} = 0.00046, \quad \mathcal{P}_2 = \frac{4.6 \times 10^{-9}}{0.0215} = 2.1 \times 10^{-7}.$$

The probability of the ground state is very nearly 1; more precisely,

$$\mathcal{P}_0 = 1 - 0.00046 = 0.99954.$$

(b) At 700 K, the ratio hf/kT is smaller by a factor of 3/7, so $hf/kT = 3.25$ and the partition function is

$$\begin{aligned} Z &= e^{-1.624} + e^{-4.873} + e^{-8.121} + e^{-11.37} + \dots \\ &= 0.1971 + 0.0077 + 0.0003 + 0.00001 + \dots \\ &= 0.2051. \end{aligned}$$

The probabilities are therefore

$$\mathcal{P}_0 = \frac{0.1971}{0.2051} = 0.961, \quad \mathcal{P}_1 = \frac{0.0077}{0.2051} = 0.038, \quad \mathcal{P}_2 = \frac{0.0003}{0.2051} = 0.001.$$

Problem 6.12. If the molecules are in equilibrium with a reservoir of temperature T , then the probability of a molecule being in any one of the excited states, relative to the ground state, should be

$$\frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-(E_1-E_0)/kT}.$$

We are given that this relative probability is approximately 1/10. Therefore,

$$-\frac{E_1 - E_0}{kT} = \ln \frac{1}{10} = -2.303,$$

or

$$T = \frac{4.7 \times 10^{-4} \text{ eV}}{(2.303)(8.62 \times 10^{-5} \text{ eV/K})} = 2.4 \text{ K}.$$

The uncertainty in the data, however, is somewhat large. We now know that the temperature is closer to 2.7 K, and that the “reservoir” is the cosmic background radiation, a gas of photons that fills the entire observable universe (see Section 7.4).

Problem 6.13. The ratio of probabilities under these conditions should be

$$\frac{\mathcal{P}(n)}{\mathcal{P}(p)} = \frac{e^{-m_n c^2/kT}}{e^{-m_p c^2/kT}} = e^{-(\Delta m)c^2/kT} = \exp\left(-\frac{(2.3 \times 10^{-30} \text{ kg})(3 \times 10^8 \text{ m/s})^2}{(1.38 \times 10^{-23} \text{ J/K})(10^{11} \text{ K})}\right) = 0.86.$$

In other words, there should be 86 neutrons for every 100 protons. That makes 186 particles total, so the fraction of protons should be $100/186 = 0.54$, and the fraction of neutrons should be $86/186 = 0.46$.

Problem 6.16. Starting from the definition of Z ,

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_s e^{-\beta E(s)} = \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} = \sum_s (-E(s)) e^{-\beta E(s)}.$$

Now just multiply by $-1/Z$, cancel the minus signs, and move the Z inside the sum:

$$-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \sum_s (-E(s)) e^{-\beta E(s)} = \sum_s E(s) \frac{e^{-\beta E(s)}}{Z} = \sum_s E(s) \mathcal{P}(s) = \overline{E}.$$

Problem 6.25. Because of the symmetry of the CO_2 molecule, a 180° rotation has no effect on its state, and therefore we should divide its rotational partition function by 2 just as for a diatomic molecule with identical atoms:

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{0.026 \text{ eV}}{2(0.000049 \text{ eV})} = 265.$$

Problem 6.29. From the graph plotted in the previous problem, we see that the rotational heat capacity falls off steeply when kT/ϵ is between about 0.3 and 0.6; the heat capacity is at about half its asymptotic value when $kT/\epsilon \approx 0.4$. For HD, that translates to a temperature of

$$T = \frac{0.4 \epsilon}{k} = \frac{(0.4)(0.0057 \text{ eV})}{8.62 \times 10^{-5} \text{ eV/K}} = 26 \text{ K}.$$

Problem 6.31. If state q has energy $c|q|$, then the Boltzmann factor for this state is $e^{-\beta c|q|}$ and the partition function is the sum of all these Boltzmann factors:

$$Z = \sum_q e^{-\beta c|q|} = \frac{1}{\Delta q} \sum_q e^{-\beta c|q|} \Delta q.$$

In the limit $\Delta q \rightarrow 0$ the sum becomes an integral:

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c|q|} dq = 2 \cdot \frac{1}{\Delta q} \int_0^{\infty} e^{-\beta c q} dq = \frac{2}{\Delta q} \left(-\frac{1}{\beta c} \right) e^{-\beta c q} \Big|_0^{\infty} = \frac{2}{\beta c \Delta q} \equiv C \beta^{-1}.$$

(Since the integral is symmetric under $q \rightarrow -q$, I've written it as twice the integral over only positive q values. This trick gets rid of the absolute value bars.) The average energy is therefore

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\beta}{C} (-C \beta^{-2}) = \frac{1}{\beta} = kT.$$

Problem 6.33. The mass of an oxygen molecule is 32 u, so for oxygen at 300 K,

$$\sqrt{\frac{kT}{m}} = \sqrt{\frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{32(1.66 \times 10^{-27} \text{ kg})}} = 279 \text{ m/s}.$$

The most likely speed, v_{\max} , is just this times $\sqrt{2}$, or 395 m/s. To get the rms speed, we instead multiply by $\sqrt{3}$ to get 484 m/s. And to get the average speed, we multiply by $\sqrt{8/\pi}$ to get 446 m/s.

Problem 6.37. In analogy with equation 6.51, imagine first that the v values are discretely spaced, then take the continuum limit:

$$\begin{aligned} \overline{v^2} &= \sum_v v^2 \mathcal{D}(v) dv \rightarrow \int_0^{\infty} v^2 \mathcal{D}(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} \int_0^{\infty} v^4 e^{-mv^2/2kT} dv \\ &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} \left(\frac{2kT}{m} \right)^{5/2} \int_0^{\infty} x^4 e^{-x^2} dx = \frac{8kT}{\sqrt{\pi} m} \int_0^{\infty} x^4 e^{-x^2} dx. \end{aligned}$$

The integral over x is worked out in Appendix B, Problem B.2; or you can look it up in a table or ask a computer. The answer is $3\sqrt{\pi}/8$, so finally we have

$$\overline{v^2} = \frac{8kT}{\sqrt{\pi}m} \cdot \frac{3\sqrt{\pi}}{8} = \frac{3kT}{m},$$

in agreement with equation 6.41 and the equipartition theorem.

Problem 6.44. For N indistinguishable, noninteracting molecules that can exchange places with each other,

$$Z = \frac{1}{N!} Z_1^N,$$

so

$$\begin{aligned} F &= -kT \ln Z = -kT [N \ln Z_1 - \ln N!] \\ &= -kT [N \ln Z_1 - N \ln N + N] = -NkT \left[\ln \frac{Z_1}{N} + 1 \right]. \end{aligned}$$

Therefore the chemical potential is

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT \left[\ln \frac{Z_1}{N} + 1 \right] - NkT \frac{\partial}{\partial N} (-\ln N) = -kT \ln \frac{Z_1}{N}.$$

Problem 6.48. (S and μ for a diatomic gas.)

- (a) For a collection of N rotating diatomic molecules, the internal contribution to the free energy is

$$F_{\text{int}} = -NkT \ln(Z_e Z_{\text{rot}}),$$

where (at ordinary temperatures) Z_{rot} is kT/ϵ for a molecule composed of two different atoms, or $kT/2\epsilon$ for a molecule composed of identical atoms. Either way, Z_{rot} is simply a constant times T , so

$$\frac{\partial F_{\text{int}}}{\partial T} = -Nk \ln(Z_e Z_{\text{rot}}) - NkT \frac{1}{T} = -Nk [\ln(Z_e Z_{\text{rot}}) + 1].$$

Therefore, according to equation 6.92,

$$S = Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] + Nk [\ln(Z_e Z_{\text{rot}}) + 1] = Nk \left[\ln \left(\frac{V Z_e Z_{\text{rot}}}{Nv_Q} \right) + \frac{7}{2} \right].$$

The rotational partition function for oxygen at room temperature is

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{(8.617 \times 10^{-5} \text{ eV/K})(298 \text{ K})}{2(0.00018 \text{ eV})} = 71,$$

while the quantum volume is

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k T}} \right)^3 = \left(\frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2\pi(32)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}} \right)^3$$

$$= (1.79 \times 10^{-11} \text{ m})^3 = 5.73 \times 10^{-33} \text{ m}^3$$

and the average volume per particle (at atmospheric pressure) is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3.$$

From these numbers we can compute the logarithm

$$\ln\left(\frac{V Z_e Z_{\text{rot}}}{N v_Q}\right) = \ln\left(\frac{(4.07 \times 10^{-26} \text{ m}^3)(3)(71)}{5.73 \times 10^{-33} \text{ m}^3}\right) = 21.14.$$

Thus the entropy under these conditions is

$$S = Nk[21.14 + 3.50] = (24.6)nR = 205 \text{ J/K},$$

precisely in agreement with the measured value (to the number of significant figures used in the calculation).

(b) The chemical potential is $-kT$ times the same logarithm:

$$\mu = -(8.62 \times 10^{-5} \text{ eV/K})(298 \text{ K})(21.1) = -0.54 \text{ eV}.$$

Problem 6.49. As shown in Section 6.2, the rotational energy of a diatomic molecule at room temperature is kT , corresponding to two degrees of freedom. Therefore the total thermal energy of a mole of N_2 is

$$U = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT = \frac{5}{2}nRT = \frac{5}{2}(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K}) = 6190 \text{ J}.$$

The enthalpy is just $U + PV = U + nRT$, so it's larger by

$$nRT = (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K}) = 2480 \text{ J}, \quad \text{that is,} \quad H = 8670 \text{ J}.$$

To compute the remaining quantities we need the internal partition function, which in this case is purely rotational:

$$Z_{\text{int}} = Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{(8.617 \times 10^{-5} \text{ eV/K})(298 \text{ K})}{2(.00025 \text{ eV})} = 51.$$

We also need the quantum volume,

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k T}} \right)^3 = \left(\frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2\pi(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}} \right)^3$$

$$= (1.91 \times 10^{-11} \text{ m})^3 = 6.98 \times 10^{-33} \text{ m}^3,$$

and the average volume per particle,

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3.$$

From these numbers we can compute the logarithm

$$\ln \left(\frac{V Z_{\text{int}}}{N v_Q} \right) = \ln \left(\frac{(4.07 \times 10^{-26} \text{ m}^3)(51)}{6.98 \times 10^{-33} \text{ m}^3} \right) = 19.5.$$

The Helmholtz free energy is therefore

$$F = -nRT \left[\ln \left(\frac{V Z_{\text{int}}}{N v_Q} \right) + 1 \right] = -(2480 \text{ J})[19.5 + 1] = -50.8 \text{ kJ},$$

while the Gibbs free energy is

$$G = F + PV = -50.8 \text{ kJ} + 2480 \text{ J} = -48.3 \text{ kJ}.$$

The easiest way to get the entropy is from the definition $F = U - TS$:

$$S = \frac{U - F}{T} = \frac{(6190 \text{ J}) - (-50,800 \text{ J})}{298 \text{ K}} = 191 \text{ J/K}$$

(in agreement with the measured value tabulated on page 405). And the easiest way to get the chemical potential is from $G = N\mu$:

$$\mu = \frac{G}{N} = \frac{-48.3 \text{ kJ}}{6.02 \times 10^{23}} = 8.03 \times 10^{-20} \text{ J} = -.501 \text{ eV}.$$

Problem 6.52. As in the nonrelativistic case, the allowed wavelengths (in one dimension) are $\lambda_n = 2L/n$, and therefore the allowed momenta are $p_n = h/\lambda_n = hn/2L$. Now, however, the relation between energy and momentum is $E = pc$, so the allowed energies are $E_n = hcn/2L$. Therefore the single-particle partition function is

$$Z_{1d} = \sum_n e^{-E_n/kT} = \sum_n e^{-hcn/2LkT}.$$

When L is macroscopic the number of terms in the sum that are significant is very large, so we can convert the sum to an integral to obtain

$$Z_{1d} = \int_0^\infty e^{-hcn/2LkT} dn = -\frac{2LkT}{hc} e^{-hcn/2LkT} \Big|_0^\infty = \frac{2LkT}{hc}.$$

As expected, the partition function is directly proportional to L and increases with increasing temperature.