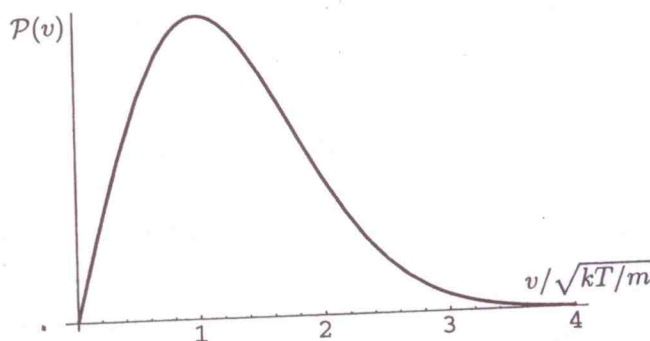


This distribution function dies exponentially as $v \rightarrow \infty$, just as in three dimensions; as $v \rightarrow 0$, however, it is linear rather than parabolic. Here's a plot:



The most likely velocity *vector* is zero, just as in three dimensions, because its Boltzmann factor is the largest ($e^0 = 1$). But the most likely speed is nonzero. To find it, set $dP/dv = 0$:

$$0 = \frac{dP}{dv} \propto e^{-mv^2/2kT} - (v) \left(\frac{mv}{kT} \right) e^{-mv^2/2kT} = \left(1 - \frac{mv^2}{kT} \right) e^{-mv^2/2kT}.$$

The solution is $v_{\max} = \sqrt{kT/m}$, which looks right from the plot.

Problem 6.42. (F and S for a harmonic oscillator.)

(a) The Helmholtz free energy of a single harmonic oscillator is

$$F_1 = -kT \ln Z_1 = -kT \ln(1 - e^{-\beta\epsilon})^{-1} = kT \ln(1 - e^{-\beta\epsilon}),$$

so since F is an extensive quantity, the Helmholtz free energy for N oscillators is

$$F = NkT \ln(1 - e^{-\beta\epsilon}).$$

(b) To find the entropy just differentiate with respect to T :

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_N = -Nk \ln(1 - e^{-\beta\epsilon}) - NkT(1 - e^{-\beta\epsilon})^{-1} \epsilon e^{-\beta\epsilon} \left(\frac{d\beta}{dT} \right) \\ &= -Nk \ln(1 - e^{-\beta\epsilon}) + Nk \frac{\epsilon/kT}{e^{\beta\epsilon} - 1}. \end{aligned}$$

Problem 6.43. (Alternative definition of entropy.)

(a) For an isolated system, $P(s) = 0$ unless s is an accessible state, so we can restrict the sum to accessible states which gives

$$S = -k \sum_s \frac{1}{\Omega} \ln \frac{1}{\Omega} = \frac{k \ln \Omega}{\Omega} \sum_s (1).$$

The number of terms in the sum is just Ω , so this expression reduces to the familiar one, $S = k \ln \Omega$.

(b) For a system in thermal contact with a reservoir at temperature T , we can write

$$\ln \mathcal{P}(s) = \ln(e^{-\beta E(s)}/Z) = -\beta E(s) - \ln Z = \frac{1}{kT}(-E(s) + F),$$

by equation 6.56. Therefore the alternative definition of entropy reduces to

$$S = -k \sum_s \frac{e^{-\beta E(s)}}{Z} \frac{1}{kT} (-E(s) + F) = \frac{1}{T} \sum_s E(s) \frac{e^{-\beta E(s)}}{Z} - \frac{F}{T} \sum_s \frac{e^{-\beta E(s)}}{Z} = \frac{\bar{E}}{T} - \frac{F}{T},$$

which is equivalent to the original definition of F , that is, $F = \bar{E} - TS$.

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 6.45. The free energy is given by equation 6.90,

$$F = -NkT [\ln V - \ln N - \ln v_Q + 1] + F_{\text{int}}.$$

Before differentiating with respect to T to get the entropy, note that $v_Q = (h^2/2\pi mkT)^{3/2}$, so $-\ln v_Q = \frac{3}{2} \ln T$ plus a temperature-independent constant. Therefore the entropy is

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk [\ln(V/Nv_Q) + 1] + NkT \cdot \frac{3}{2} \frac{1}{T} - \frac{\partial F_{\text{int}}}{\partial T} \\ &= Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{\text{int}}}{\partial T}. \end{aligned}$$

The chemical potential is

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT [\ln(V/Nv_Q) + 1] + NkT \cdot \frac{1}{N} + \frac{\partial F_{\text{int}}}{\partial N} \\ &= -kT \ln(V/Nv_Q) - kT \ln Z_{\text{int}} = -kT \ln \left(\frac{V Z_{\text{int}}}{Nv_Q} \right), \end{aligned}$$

where in the second line I've used the definition $F_{\text{int}} = -NkT \ln Z_{\text{int}}$.

Problem 6.51. Because the translational kinetic energy does not depend on position, the integrand is independent of r and therefore the d^3r integral simply gives a factor of V , the volume of the box. The momentum integrals can be evaluated either in rectangular or spherical coordinates. I'll use rectangular coordinates; then

$$E_{\text{tr}} = \frac{|\vec{p}|^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m},$$

and the exponential of $-E_{\text{tr}}/kT$ can be factored to give

$$Z_{\text{tr}} = \frac{V}{h^3} \int dp_x \int dp_y \int dp_z e^{-p_x^2/2mkT} e^{-p_y^2/2mkT} e^{-p_z^2/2mkT}.$$

But these are just ordinary Gaussian integrals, for which the general formula is

$$\int e^{-\alpha p^2} dp = \sqrt{\frac{\pi}{\alpha}}.$$

In our case each integral gives $\sqrt{\pi \cdot 2mkT}$, so

$$Z_{\text{tr}} = \frac{V}{h^3} (2\pi mkT)^{3/2} = \frac{V}{v_Q},$$

in agreement with equation 6.82.

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.

Problem 6.53. As shown in Section 5.6, the equilibrium condition for a chemical reaction is the same as the reaction equation, with the name of each species replaced by its chemical potential and \leftrightarrow replaced by $=$. Therefore, if the dissociation of hydrogen is at equilibrium, we must have $\mu_{\text{H}_2} = 2\mu_{\text{H}}$. Treating each species as an ideal gas, the chemical potentials are given by equation 6.93, almost. This formula assumes that each molecule has energy zero when it is at rest, whereas the energy of an H_2 molecule at rest is actually less than that of

two H atoms at rest, the difference being the dissociation energy calculated in Problem 1.53, $\epsilon_d = 4.49$ eV. I'll take the energy of an H atom at rest to be zero; then the energy of an H_2 molecule at rest is $-\epsilon_d$, and the chemical potential is shifted accordingly. Thus, the equilibrium condition for the dissociation reaction is

$$-kT \ln \left(\frac{V Z_{\text{int}, H_2}}{N_{H_2} v_{Q, H_2}} \right) - \epsilon_d = -2kT \ln \left(\frac{V Z_{\text{int}, H}}{N_H v_{Q, H}} \right).$$

Dividing through by $-kT$ and exponentiating both sides gives

$$\frac{V Z_{\text{int}, H_2}}{N_{H_2} v_{Q, H_2}} e^{\epsilon_d/kT} = \left(\frac{V Z_{\text{int}, H}}{N_H v_{Q, H}} \right)^2.$$

To simplify this expression, consider first the internal partition functions. For H_2 , the internal partition function is a product of rotational and vibrational contributions. There is no electronic spin degeneracy, and electronic excited states are unimportant at the temperatures of interest. There is also a nuclear spin degeneracy of 4, 2 for each spin-1/2 proton. Meanwhile, the internal partition function for atomic hydrogen consists of a nuclear spin degeneracy factor of 2, multiplied by an electronic spin degeneracy factor of 2. Excited electronic states again contribute negligibly. When this partition function is squared, we see that the nuclear degeneracy factor of 4 cancels between the two sides, leaving us with only the electronic degeneracy factor of $2^2 = 4$. The equilibrium condition is therefore

$$\frac{V Z_{\text{rot}} Z_{\text{vib}}}{N_{H_2} v_{Q, H_2}} e^{\epsilon_d/kT} = \frac{4V^2}{N_H^2 v_{Q, H}^2}.$$

Next, recall that the quantum volume of a particle is proportional to its mass to the $-3/2$ power. Since the mass of H_2 is twice the mass of H, we can write $v_{Q, H_2} = v_{Q, H}/2^{3/2}$ and cancel a factor of $v_{Q, H}$ to obtain

$$\frac{V Z_{\text{rot}} Z_{\text{vib}}}{N_{H_2}} e^{\epsilon_d/kT} = \frac{\sqrt{2} V^2}{N_H^2 v_{Q, H}}.$$

Now let me use the ideal gas law to replace each V/N with kT/P , where P is the partial pressure of that species:

$$\frac{kT Z_{\text{rot}} Z_{\text{vib}}}{P_{H_2}} e^{\epsilon_d/kT} = \frac{\sqrt{2} (kT)^2}{P_H^2 v_{Q, H}}, \quad \text{or} \quad \frac{P_H^2}{P_{H_2}} = \frac{\sqrt{2} kT e^{-\epsilon_d/kT}}{Z_{\text{rot}} Z_{\text{vib}} v_{Q, H}}.$$

Dividing through by the reference pressure P° to make each side dimensionless, we finally obtain the law of mass action written in the conventional way:

$$\frac{P_H^2}{P^\circ P_{H_2}} = K, \quad \text{where} \quad K = \frac{\sqrt{2} kT e^{-\epsilon_d/kT}}{P^\circ v_{Q, H} Z_{\text{rot}} Z_{\text{vib}}}.$$

To facilitate numerical computations, let me define

$$K_0(T) \equiv \frac{\sqrt{2} kT}{P^\circ v_{Q, H}} = \frac{\sqrt{2} kT}{P^\circ} \left(\frac{2\pi m_H kT}{h^2} \right)^{3/2}.$$

At $T = 300$ K, this expression evaluates to 57,950. Since it is proportional to $T^{5/2}$, we can write

$$K_0(T) = (57,950)t^{5/2},$$

where $t = T/(300 \text{ K})$. To calculate the rotational partition function I'll use equation 6.33,

$$Z_{\text{rot}} \approx \frac{kT}{2\epsilon_r} = (1.70)t,$$

where I've used the value $\epsilon_r = 0.0076$ eV from Problem 6.30. (This formula really isn't very accurate until $Z_{\text{rot}} \gg 1$, but improving on it would be a lot of work and we'll see that the exact value of K at temperatures around 300 K isn't critical anyway.) The vibrational partition function was computed in Problem 6.20:

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\epsilon_v/kT}} = \frac{1}{1 - e^{-(17.0)/t}},$$

where I've used the value $\epsilon_v = 0.44$ eV estimated in Problem 3.26. Finally, let's write the exponential factor involving the dissociation energy as

$$e^{-\epsilon_d/kT} = e^{-(173.7)/t}.$$

Combining all these expressions, we have for the equilibrium constant

$$K = \frac{K_0(T) e^{-\epsilon_d/kT}}{Z_{\text{rot}} Z_{\text{vib}}} = \frac{(57,950)t^{5/2} \cdot e^{-(173.7)/t}}{(1.70)t \cdot (1 - e^{-(17.0)/t})^{-1}} = (34,090)t^{3/2}(1 - e^{-(17.0)/t})e^{-(173.7)/t}.$$

Rather than evaluating this whole expression at once, though, I entered the various pieces of it into a spreadsheet so I could see how each of them depends on temperature. Here are the results:

T (K)	K_0	Z_rot	Z_vib	e ^(-eps_d/kT)	K
300	57950	1.7	1.00	3.66E-76	1.2E-71
1000	1.18E+06	5.7	1.01	2.34E-23	4.8E-18
3000	1.83E+07	17.0	1.22	2.86E-08	0.025
6000	1.04E+08	34.0	1.75	1.69E-04	295
10000	3.72E+08	56.7	2.50	5.46E-03	14300

As you can see, the exponential factor of the dissociation energy is by far the most important contribution to K . At 300 K, this factor is so tiny that the equilibrium constant is utterly negligible, implying that H_2 is never dissociated (when in equilibrium). For example, even if the partial pressure of H_2 is only 10^{-10} bar, the partial pressure of atomic hydrogen would be negligible in comparison:

$$P_{\text{H}} = \sqrt{K \cdot P^\circ P_{\text{H}_2}} = 3.5 \times 10^{-31} \text{ bar}.$$

At higher total pressures, the ratio of H/H_2 would be even less. (This implies that cold interstellar clouds containing atomic hydrogen are not in thermodynamic equilibrium.) On the other hand, at the surface of the sun, where $T \approx 6000$ K, an H_2 partial pressure of 1 bar would imply an atomic hydrogen partial pressure of

$$P_{\text{H}} = \sqrt{K \cdot P^\circ P_{\text{H}_2}} = 17 \text{ bar},$$

so nearly 90% of the hydrogen would be ionized, and this percentage would be even higher at lower total pressures.