

PHY306: Homework#10 Solutions, Spring 10

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1 Problem 6.5(10pts)

(a) At 300K, $kT=0.026\text{eV}$, as computed on page 13 of textbook. 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

$$P_1 = \frac{6.84}{7.99} = 0.86; P_2 = \frac{1}{7.99} = 0.13; P_3 = \frac{0.15}{7.99} = 0.02$$

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

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

And the probabilities are

$$P_1 = \frac{1}{1.17} = 0.86; P_2 = \frac{0.15}{1.17} = 0.13; P_3 = \frac{0.02}{1.17} = 0.02$$

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

2 Problem 6.12(5pts)

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

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

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

3 Problem 6.41(10pts)

In a two-dimensional "flatland", the probability of a molecule having velocity vector \vec{v} is still proportional to the Boltzmann factor, $e^{-mv^2/2kT}$. But the velocity vectors now live in a two-dimensional plane, and those with magnitude v have their tips on a circle with radius v . So the number of velocity vectors corresponding to speed v is now proportional to the circumference of a circle, $2\pi v$. With this new geometrical factor, we can write,

$$P(v) = C \cdot 2\pi v \cdot e^{-mv^2/2kT}$$

To find the normalization constant, set the integral over all v equal to 1:

$$1 = \int_0^{\infty} 2\pi C v e^{-mv^2/2kT} dv = 2\pi C \left(\frac{2kT}{m}\right) \int_0^{\infty} x e^{-x^2} dx = 2\pi C \left(\frac{2kT}{m}\right) \cdot \frac{1}{2}.$$

So $C = m/2\pi kT$ and the final result for the speed distribution is

$$P(v) = \left(\frac{m}{2\pi kT}\right) 2\pi v e^{-mv^2/2kT}.$$

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. 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 $v_{max} = \sqrt{kT/m}$.

4 Problem 6.44(5pts)

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

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

5 Problem 6.47(5pts)

A degree of freedom freezes out when kT is less than or comparable to the spacing between the lowest energy levels. In a one-dimensional box, the energy levels are $E_n = h^2 n^2 / 8mL^2$, so for nitrogen in a 1-cm box, the spacing between the two lowest levels is

$$E_2 - E_1 = \frac{3}{8} \frac{(6.63 \times 10^{-34} J \cdot s)^2}{(28)(1.66 \times 10^{-27} kg)(0.01m)^2} = 3.5 \times 10^{-38} J = 2.2 \times 10^{-19} eV.$$

The freeze-out temperature would therefore be approximately

$$T = \frac{E_2 - E_1}{k} = \frac{2 \times 10^{-19} eV}{8.6 \times 10^{-5} eV/K} = 2.6 \times 10^{-15} K,$$

or less than 3 femtokelvins. And in all realistic situations we assume that the translational motion of molecules in macroscopic boxes is nowhere near freezing out and therefore can be treated "classically" by converting the partition sum into an integral.

6 Problem 6.49(10pts)

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

$$U = \frac{3}{2} NkT + NkT = \frac{5}{2} NkT = \frac{5}{2} nRT = \frac{5}{2} (1mol)(8.314 J/mol \cdot K)(298K) = 6190J.$$

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

$$nRT = (1mol)(8.314 J/mol \cdot K)(298K) = 2480J, \text{ that is, } H = 8670J.$$

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

$$Z_{int} = Z_{rot} = \frac{kT}{2\epsilon} = \frac{(8.617 \times 10^{-5} eV/K)(298K)}{2(0.00025 eV)} = 51.$$

We also need the quantum volume,

$$\begin{aligned} v_Q &= \left(\frac{h}{\sqrt{2\pi m kT}} \right)^3 = \left(\frac{6.63 \times 10^{-34} J \cdot s}{\sqrt{2\pi(38)(1.66 \times 10^{-27} kg)(1.38 \times 10^{23} J/K)(298K)}} \right)^3 \\ &= (1.91 \times 10^{-11} m)^3 = 6.98 \times 10^{-33} m^3. \end{aligned}$$

and the average volume per particle,

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

From these numbers we can compute the logarithm,

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

The Helmholtz free energy is therefore

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

while the Gibbs free energy is

$$G = F + PV = -50.8kJ + 2480J = -48.3kJ$$

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

$$S = \frac{U - F}{T} = \frac{(6190J) - (-50800J)}{298K} = 191J/K.$$

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

$$\mu = \frac{G}{N} = \frac{-48.3kJ}{6.02 \times 10^{23}} = 8.03 \times 10^{-20} J = -0.501eV.$$