Chemistry 410B **Exam 1** **Spring 2009**

Solutions (revised)

1. **40 points.**

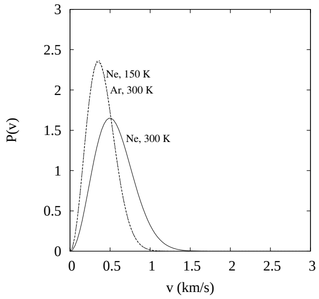
   (a) Fig. 13.4 shows a sample with 3 particles and a degeneracy of $1.3 \cdot 10^{10}$ at an energy of $50\varepsilon_0$. What is the entropy for this sample? **Solution:**

$$S = k_B \ln \Omega = (1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}) \ln(1.3 \cdot 10^{10}) = \boxed{3.2 \cdot 10^{-22}\,\mathrm{J\,K^{-1}}}.$$

   (b) Sodium dimer (Na_2) has a vibrational constant of $159.13\,\mathrm{cm^{-1}}$. Calculate the vibrational partition function of Na_2 to three significant figures at $300.0\,\mathrm{K}$. **Solution:** We may start by calculating $\omega_e/k_B = 228.96\,\mathrm{K}$.

$$\begin{aligned} q_{\mathrm{vib}} &= \sum_{v=0}^{\infty} e^{-E_{\mathrm{vib}}/(k_B T)} = \sum_{v=0}^{\infty} e^{-v\omega_e/(k_B T)} \\ &= e^{0/(k_B T)} + e^{-\omega_e/(k_B T)} + e^{-2\omega_e/(k_B T)} + \ldots \\ &= 1 + e^{-228.96/300.0} + e^{-2\cdot 228.96/300.0)} + e^{-3\cdot 228.96/300.0)} + \ldots \\ &= 1 + 0.47 + 0.22 + 0.10 + 0.05 + 0.02 + 0.01 = \boxed{1.87}. \end{aligned}$$

   (c) Sketch in $\mathcal{P}(v)$ for Ar gas at 300 K, and for Ne gas at 150 K.



   (d) How many equipartition degrees of freedom N_{ep} are present in H_2CO (i) when vibrations are *not* included? (ii) when vibrations *are* included? **Solution:**

$$N_{\mathrm{ep}} = 3\,(\text{trans}) \;+ 3\,(\text{rot}) \;= \boxed{6} \text{ without vib} \quad + (3 \cdot 4 - 6)\,(\text{vib}) \times 2 \;= \boxed{18} \text{ with vib}$$

2. The two-particle sample A has four states, all equally likely. Sample B with two particles has four states: two have probability x and two have probability $2x$. Calculate the Gibbs entropy for A and for B. **Solution:** For A, we have four equal probabilities. To be normalized, they must add up to 1, so each probability is 0.25. For B, we have $x + x + 2x + 2x = 6x = 1$, so $x = 1/6$ and the probabilities are 1/6, 1/6, 1/3, and 1/3. The Gibbs entropies are:

$$S_{\mathrm{A}} = -N k_B \sum_{i=1}^{4} \mathcal{P}(i) \ln \mathcal{P}(i) = -2k_B \left[4\left(\frac{1}{4}\ln\frac{1}{4}\right)\right] = 2.77k_B = \boxed{3.83 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}}$$

$$S_{\mathrm{B}} = -2k_B \left[2\left(\frac{1}{3}\ln\frac{1}{3}\right) + 2\left(\frac{1}{6}\ln\frac{1}{6}\right)\right] = 2.66k_B = \boxed{3.67 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}}$$

The maximum Gibbs entropy corresponds to all states equally likely, so $S_{\mathrm{A}} > S_{\mathrm{B}}$.

3. Write the integral expression that should be solved to find the fraction of molecules in a sample of helium traveling between $10^2\,\mathrm{m\,s^{-1}}$ and $10^3\,\mathrm{m\,s^{-1}}$ at 298 K. **Solution:** We want the probability distribution for speed, $\mathcal{P}(v)$, integrated only between the limits given.

$$\int_{10^2}^{10^3} \mathcal{P}(v)\,dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{10^2}^{10^3} v^2 e^{-mv^2/(2k_BT)}\,dv.$$

Plugging in the mass, temperature, and k_B, we find that

$$\frac{m}{2k_BT} = \frac{(4.00\,\mathrm{amu})(1.661\cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})}{2(1.381\cdot 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})} = 8.07\cdot 10^{-7}\,\mathrm{s^2\,m^{-2}}.$$

So the final expression can be written

$$(1.64\cdot 10^{-9})\int_{10^2}^{10^3} v^2\,\exp(-8.07\cdot 10^{-7} v^2)\,dv.$$

4. If 0.100% of the OCS molecules in a sample can be found in the $v_2 = 2$ vibrational level, find the temperature T, where $g_2 = v_2$ and $\omega_2 = 520\,\mathrm{cm^{-1}}$. **Solution:** The probability depends on the energy, degeneracy, partitiion function, and temperature. We have everything except q_{vib} and T. Normally we would expect q_{vib} to be close to one, and the fact that only 0.100% of the molecules are in this excited state suggests that may be a good approximation. Then we can solve for T:

$$\begin{aligned}
\mathcal{P}(v_2 = 2) &= \frac{g e^{-E_{\mathrm{vib}}/(k_BT)}}{q_{\mathrm{vib}}} \\
T &= \frac{-E_{\mathrm{vib}}}{k_B \ln\left(\frac{q_{\mathrm{vib}}\mathcal{P}(v_2=2)}{g}\right)} \\
&\approx -\frac{2(520\,\mathrm{cm^{-1}})}{(0.695\,\mathrm{cm^{-1}/\,K})\ln\left(\frac{(1)(0.00100)}{3}\right)} = 187\,K.
\end{aligned}$$

We can improve this value by correcting our original assumption that $q_{\mathrm{vib}} \approx 1$. We find the contribution from a molecules in the state $v_2 = 1$: $2e^{-\omega_2/(k_BT)} = 0.04$, so our q_{vib} is better approximated by $1 + 0.04 = 1.04$. Replacing $q_{\mathrm{vib}} \approx 1$ by $q_{\mathrm{vib}} \approx 1.14$ in the equation for T above, we get a final value of $T = \boxed{188\,\mathrm{K}}$.