**Chemistry 410B** **Exam 1** **Spring 2008**

**Solutions**

1. Estimate the degeneracy of two argon atoms in a container of volume $1.00 \cdot 10^{-9}$ m$^3$ with a total energy of $2.00 \cdot 10^{-20}$ J. **Solution:** This is applying our approximation that the 2-particle degeneracy $g_2$ is roughly $g_1^2$. We start from the one-particle degeneracy in the three-dimensional box, but use $\varepsilon$ equal to one half the total energy:

$$\begin{aligned}
g_1(\varepsilon) &= \frac{32\pi V(2m^3\varepsilon)^{1/2}d\varepsilon}{h^3} \\
&= \frac{32\pi(1.00 \cdot 10^{-9}\ \text{m}^3)[2(39.9\ \text{amu})^3(1.661 \cdot 10^{-27}\ \text{kg amu}^{-1})^3(1.00 \cdot 10^{-20}\ \text{J})]^{1/2}(2.5 \cdot 10^{-26}\ \text{J})}{(6.626 \cdot 10^{-34}\ \text{J s})^3} \\
&= 2.08 \cdot 10^{19} \\
g_2 \approx g_1^2 &= \boxed{4.35 \cdot 10^{38}}
\end{aligned}$$

2. A sample and reservoir are in contact with each other. The degeneracy of the sample obeys the equation $g = AE^2$, while for the reservoir, $g_r = A_r E_r^{20}$. If the sample has an energy of 1.00 J, what is the energy of the reservoir $E_r$ when the sample and reservoir are at the same temperature? **Solution:** Our rigorous definition for temperature relates the derivatives of the E and $\ln g$, so if we know $g$ in terms of $E$, we can obtain an analytical expression for $T$:

$$\begin{aligned}
\ln g &= \ln A \ + \ 2\ln E \\
\left(\frac{\partial \ln g}{\partial E}\right)_{V,N} &= \frac{2}{E} = \frac{1}{k_B T} \\
\ln g_r &= \ln A_r \ + \ 20\ln E_r \\
\left(\frac{\partial \ln g_r}{\partial E_r}\right)_{V,N} &= \frac{20}{E_r} = \frac{1}{k_B T}
\end{aligned}$$

The temperature is the same for both reservoir and sample:

$$\frac{2}{E} = \frac{20}{E_r} \qquad E_r = 10E = \boxed{10.0\,\text{J}}.$$

3. Our sample consists of $N$ gas-phase ions of mass $m$ at temperature $T$, confined in a chamber that measures from $-a/2$ to $+a/2$ along each of the $X$, $Y$, and $Z$ axes. The potential energy seen by each ion is $u_i = \mathcal{E}_0\, Z_i^2$. Neglect interactions between the ions.

   (a) Write an expression for the *total* potential energy.

$$U(X_1, \ldots, Z_N) = \sum_{i=1}^{N} u_i = \sum_{i=1}^{N} \mathcal{E}_0\, Z_i^2$$

(b) Find the *total* translational partition function.

$$
\begin{aligned}
Q_{\rm trans}(\beta,V) &= \frac{1}{N!}\left(\frac{8\pi m}{h^2\beta}\right)^{3N/2} Q'_U(\beta,V) = \frac{1}{N!}\left(\frac{8\pi m}{h^2\beta}\right)^{3N/2} \int_{-a/2}^{a/2}\cdots\int_{-a/2}^{a/2} e^{-U(X_1,\ldots,Z_N)/(k_BT)}dX_1\ldots dZ_N \\
&= \frac{1}{N!}\left(\frac{8\pi m k_BT}{h^2}\right)^{3N/2} \int_{-a/2}^{a/2}\cdots\int_{-a/2}^{a/2} e^{-\sum_i \mathcal{E}_0\, Z_i^2}dX_1\ldots dZ_N \\
&= \frac{1}{N!}\left(\frac{8\pi m k_BT}{h^2}\right)^{3N/2} \left[\int_{-a/2}^{a/2} dX_1\right]\left[\int_{-a/2}^{a/2} dY_1\right]\left[\int_{-a/2}^{a/2} dX_2\right]\ldots\left[\int_{-a/2}^{a/2} dY_N\right] \\
&\times \left[\int_{-a/2}^{a/2} e^{-\mathcal{E}_0\, Z_1^2}dZ_1\right]\ldots\left[\int_{-a/2}^{a/2} e^{-\mathcal{E}_0\, Z_N^2}dZ_N\right] \\
&= \frac{1}{N!}\left(\frac{8\pi m k_BT}{h^2}\right)^{3N/2} [a]\,[a]\,[a]\ldots[a] \left[\int_{-a/2}^{a/2}\left(1-\mathcal{E}_0\, Z_1^2\right)dZ_1\right]\ldots\left[\int_{-a/2}^{a/2}\left(1-\mathcal{E}_0\, Z_N^2\right)dZ_N\right] \\
&= \frac{1}{N!}\left(\frac{8\pi m k_BT}{h^2}\right)^{3N/2} a^{2N}\left[Z_1-\tfrac{1}{3}\mathcal{E}_0\, Z_1^3\right]_{-a/2}^{a/2}\ldots\left[Z_1-\tfrac{1}{3}\mathcal{E}_0\, Z_N^3\right]_{-a/2}^{a/2} \\
&= \frac{1}{N!}\left(\frac{8\pi m k_BT}{h^2}\right)^{3N/2} a^{2N}\left[a-\tfrac{1}{12}\mathcal{E}_0\, a^3\right]^N
\end{aligned}
$$

4. If the vibrational partition function of an $O_2$ sample is 1.045, what percentage of the molecules is in the state $v=0$? **Solution:** This is asking for the probability function $\mathcal{P}(v=0)$, which we can calculate in one step if we already know $q_{\rm vib}$, because the energy of the $v=0$ ground state we have set to zero:

$$\mathcal{P}(v=0) = \frac{e^{E(v=0)/(k_BT)}}{q_{\rm vib}} = \frac{1}{1.045} = 0.957.$$

   The percentage in the $v=0$ state is therefore $\boxed{95.7\%}$.

5. Begin with a sample of 1.00 mol $N_2$ gas at 300 K. Indicate the factor by which the energy $E_0$ of the original sample changes. **Solution:** We're working from $E=\frac{1}{2}N_{\rm ep}Nk_BT$. The change is proportional to the number of moles $n$ and the temperature $T$, andf to the number of equipartition degrees of freedom $N_{\rm ep}$. For $N_2$ and $CO_2$ at low $T$, $N_{\rm ep}=5$, because we count only the three translational and two rotational degrees of freedom. At high $T$, we add 2 to get 7 for $N_2$ (for the kinetic and potential terms in the stretch) and 8 to get 13 for $CO_2$ (which has four vibrational modes).

| **changing original sample by** | **multiplies $E_0$ by factor of** |
|---|---|
| raising temperature by 300 K | $T/T_0 = 2$ |
| raising temperature by 900 K | $(T/T_0)(N_{\rm ep}/N_{\rm ep,0}) = 4(7/5) = 28/5$ |
| removing 0.50 mol $N_2$ at 300 K | $N/N_0 = 1/2$ |
| adding 3.00 mol $CO_2$ at 300 K | $N/N_0 = 4$ |
| adding 3.00 mol $CO_2$ and raising temperature by 900 K | $T(N_{N_2}N_{\rm ep,N_2} + N_{CO_2}N_{\rm ep,CO_2})/(T_0N_0N_{\rm ep,0})$ $= 184/5$ |