Chemistry 410B **Exam 1** **Spring 2012**

Solutions

1. **40 points.**

   (a) Calculate the probability of finding $^{1}H^{127}I$ in the $J = 5$ rotational state at 298 K, given that $B_e = 3.2535\,\mathrm{cm}^{-1}$ and $q_{\mathrm{rot}}(298\,\mathrm{K}) = 63.7$. **Solution:**

$$\mathcal{P}(J) = \frac{g_{\mathrm{rot}} e^{-\epsilon_{\mathrm{rot}}/(k_B T)}}{q_{\mathrm{rot}}(T)} = \frac{(2J+1)e^{-B_e J(J+1)/(k_B T)}}{q_{\mathrm{rot}}(T)}$$

$$\mathcal{P}(J=5) = \frac{(11)\exp\left\{-30(3.2535\,\mathrm{cm}^{-1})/\left[(0.6950\,\mathrm{cm}^{-1}/\,\mathrm{K})(298\,\mathrm{K})\right]\right\}}{63.7} = \boxed{0.108.}$$

   (b) Write the integral necessary to calculate the number of atoms in a 1.00 mol sample of helium at 273 K that have speeds greater than $200\,\mathrm{m\,s}^{-1}$. Include any necessary numerical values and unit conversions. **Solution:**

$$N(v > v_0) = N_{\mathrm{total}} \int_{v_0}^{\infty} \mathcal{P}_v(v)\,dv$$

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

$$\frac{m}{2k_B T} = \frac{(4.003\,\mathrm{amu})(1.661\cdot 10^{-24}\,\mathrm{g\,amu}^{-1})}{2(1.381\cdot 10^{-23}\,\mathrm{J\,K}^{-1})(273\,\mathrm{K})} \equiv C$$

$$N(v > 200\,\mathrm{m\,s}^{-1}) = 4\pi(6.022\cdot 10^{23})\left(\frac{C}{\pi}\right)^{3/2}\int_{200\,\mathrm{m\,s}^{-1}}^{\infty} v^2\, e^{-Cv^2}\,dv$$

   (c) Calculate the average speed of gas-phase UF_6 at 298 K. **Solution:** The molar mass of UF_6 is $352.02\,\mathrm{g\,mol}^{-1}$, so we convert grams to kilograms and plug the number into the formula for $\langle v\rangle$:

$$\langle v\rangle = \sqrt{\frac{8RT}{\pi\mathcal{M}}} = \sqrt{\frac{8(8.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1})(298\,\mathrm{K})}{\pi(0.35202\,\mathrm{kg\,mol}^{-1})}} = \boxed{134\,\mathrm{m\,s}^{-1}.}$$

   (d) Simplify

$$\mathcal{I}(T) = 4\pi\int_0^{\infty}\left(e^{-u(R)/(k_B T)} - 1\right)R^2 dR$$

   in the limit of the ideal gas. **Solution:** In the ideal gas limit, $u(R) = 0$, so the integral becomes

$$\mathcal{I}(T) = 4\pi\int_0^{\infty}\left(e^0 - 1\right)R^2 dR = 4\pi\int_0^{\infty}(1-1)\,R^2 dR = \boxed{0.}$$

2. The entropy of helium gas at 298 K and a pressure of 1.00 bar is tabulated as $126.04\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$.

   (a) If entropy behaves rigorously like an extensive parameter, find the entropy of a *single* He atom under these conditions. **Solution:** If entropy is extensive, then the value is proportional to the size of the sample. If we divide all the extensive parameters (including V and N) by Avogadro's number, then we should arrive at the entropy of a single He atom at this pressure and temperature (to the extent those are definable for a single molecule):

$$S_{N=1} = \frac{S}{\mathcal{N}_A} = \frac{126.04\,\mathrm{J\,K^{-1}\,mol^{-1}}}{6.022 \cdot 10^{23}\,\mathrm{mol^{-1}}} = \boxed{2.093 \cdot 10^{-22}\,\mathrm{J\,K^{-1}}.}$$

(b) Use the ideal gas law to determine the volume that this single atom would occupy under these conditions. **Solution:** One way to do this is to rewrite the ideal gas law, $PV = nRT$, in terms of molecular (rather than molar) units, $PV = Nk_BT$, and then solve for V when $N = 1$. Remember to use the right units for P in that case:

$$V_{N=1} = \frac{Nk_BT}{P} = \frac{(1)(1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}{1.00 \cdot 10^5\,\mathrm{Pa}} = \boxed{4.12 \cdot 10^{-26}\,\mathrm{m^3}}$$

or $41{,}200\,\mathrm{\AA}^3$. Alternatively, we could use $PV = nRT$ but set $n = 1/\mathcal{N}_A$.

(c) Find the number of ensemble states for the atom under these conditions. **Solution:**

$$\Omega = \exp\left(\frac{S}{k_B}\right) = \exp\left[(2.093 \cdot 10^{-22}\,\mathrm{J\,K^{-1}}/(1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}})\right] = \boxed{3.820 \cdot 10^6.}$$

3. Some reactions of organic molecules with iodine occur best at temperatures of up to 500 C (773 K), which just happens to be equal to $2.50\,\omega_e/k_B$. Approximate the vibrational energy as a continuous function of the quantum number v to estimate what fraction of I_2 molecules will be in vibrational states with $v \leq 4$. **Solution:** The probability of a molecule being vibrational levels with $v \leq 4$ is

$$\mathcal{P}(v \leq 4) = \frac{\sum_{v=0}^{4} e^{-\omega_e v/(k_BT)}}{q_{\mathrm{vib}}(T)}. = \frac{\sum_{v=0}^{4} e^{-\omega_e v/(k_BT)}}{\sum_{v=0}^{\infty} e^{-\omega_e v/(k_BT)}}.$$

We're told that we can treat v as a continuous parameter, which means we can replace the two sums by integrals, as we did for translational states:

$$\mathcal{P}(v \leq 4) \approx \frac{\int_0^4 e^{-\omega_e v/(k_BT)}\,dv}{\int_0^\infty e^{-\omega_e v/(k_BT)}\,dv} = \frac{-\left(\frac{k_BT}{\omega_e}\right) e^{-\omega_e v/(k_BT)}\Big|_0^4}{-\left(\frac{k_BT}{\omega_e}\right) e^{-\omega_e v/(k_BT)}\Big|_0^\infty}$$

$$= \frac{e^{-4\omega_e/(k_BT)} - 1}{0 - 1} = 1 - e^{-4\omega_e/(k_BT)} = 1 - e^{-4/2.50} = \boxed{0.798}$$

The actual fraction would be 0.864 (ignoring anharmonicity), so the integral approximation is good to within 10% in this case.

4. The disinfectant iodoform (CHI_3) has a vapor pressure of $4.5 \cdot 10^{-5}$ bar at 298 K. Assume that all the vibrational modes *except* those involving the H atom contribute to it energy

according to the equipartition principle. In a sample of air at 1.00 bar and 298 K containing iodoform at its vapor pressure, estimate the fraction of the total energy that is present in the iodoform. **Solution:** Iodoform will have $3 \cdot 5 - 6 = 9$ vibrational modes, but three of those will involve the H atom (because if you take away the H atom, there would only be 6 modes). Therefore, for the CHI_3 we would count $N_{\text{ep}} = 3 + 3 + (6 \times 2) = 18$ equipartition degrees of freedom, whereas for air we would count only $3+2 = 5$ for $N_{\text{ep,air}}$. We can use the ideal gas law to replace nRT in the equipartition energy by PV, where the P is the partial pressure of the gas. Because the vapor pressure of CHI_3 is so low compared to the total pressure, we can approximate the total pressure by the pressure of air. Therefore the fraction of energy in iodoform will be

$$\frac{E_{\text{CHI}_3}}{E_{\text{air}}} = \frac{\frac{1}{2} N_{\text{ep}} n_{\text{CHI}_3} RT}{\frac{1}{2} N_{\text{ep,air}} n_{\text{air}} RT} = \frac{N_{\text{ep}} P_{\text{CHI}_3} V}{N_{\text{ep,air}} P_{\text{air}} V} = \frac{(18)(4.5 \cdot 10^{-5}\,\text{bar})}{(5)(1.00\,\text{bar})} = \boxed{1.6 \cdot 10^{-4}.}$$

This exercise shows that a heavier gas can have a disproportionate effect on the properties of the air, in this case a contribution about three times greater than indicated by its relative concentration of $4.5 \cdot 10^{-5}$.