**Chemistry 410B** **Exam 2** **Spring 2008**

**Solutions**

1. (a) Find the value of $z = PV_m/(RT)$ for the ideal gas. **Solution:** For the ideal gas, $PV = nRT$, $V_m = V/n = RT/P$, so

$$z = \frac{PV_m}{RT} = \frac{P(RT/P)}{RT} = \boxed{1}.$$

(b) Put an X next to the name of the molecule that will have the *greatest* value of $z$ at a pressure of 1.00 bar and 298 K. **Solution:** We want the molecule which, at given observed pressure and temperature, has the highest molar volume. Solving the van der Waals equation for $V_m$, we find

$$V_m = \frac{RT}{P + \frac{a}{RT}} + b.$$

Therefore, we want the molecule with the *smallest* value of $a$ and *largest* value of $b$, which is $\boxed{\text{HCN}}$.

2. Assuming the integral approximation is valid for the rotational partition function, and that the harmonic approximation is valid for vibrations, write an expression for the fraction of the sample of a gas-phase, diatomic molecule that will be in the rotational *and* vibrational ground state ($J = 0$, $v = 0$), in terms of the temperature $T$ and the constants $B$ and $\omega_e$. **Solution:** We know that the numerator will be 1, because we measure the energy from the ground state (so $E = 0$ for the ground state) and the degeneracy of the ground state is 1. Then we use the approximate forms of the partition functions:

$$\begin{aligned}\mathcal{P}(v, J) = \mathcal{P}(J = 0)\mathcal{P}(v = 0) &= \frac{g(J)e^{E_{\text{rot}}/(k_BT)}g(J)e^{E_{\text{vib}}/(k_BT)}}{q_{\text{rot}}q_{\text{vib}}} \\ &= \frac{(1)e^0(1)e^0}{(k_BT/B)(1 - e^{-\omega_e/(k_BT)})^{-1}} = \frac{B(1 - e^{-\omega_e/(k_BT)})}{k_BT}\end{aligned}$$

3. An isotopically enhanced sample has $n_{\text{DI}}$ moles of deuterated hydrogen iodide and $n_{\text{HI}}$ moles of common HI at 398 K. Comparison of the infrared intensities of the $v = 1 \rightarrow 2$ transition finds a ratio of 0.100 for DI molecules ($\omega_e = 1640$ cm$^{-1}$) in the $v = 1$ state to HI molecules ($\omega_e = 2310$ cm$^{-1}$) in the $v = 1$ state. What is the ratio $n_{\text{DI}}/n_{\text{HI}}$ in the entire sample? **Solution:** The number of molecules in each state is the total number of molecules times the probability for that state. Converting the vibrational constants to temperature units gives $\omega_{\text{DI}}/k_B = 2360$ cm$^{-1}$ and $\omega_{\text{HI}}/k_B = 3324$ cm$^{-1}$.

$$\begin{aligned}0.100 &= \frac{N_{\text{DI}}e^{-\omega_{\text{DI}}/(k_BT)}(1 - e^{-\omega_{\text{DI}}/(k_BT)})}{N_{\text{HI}}e^{-\omega_{\text{HI}}/(k_BT)}(1 - e^{-\omega_{\text{HI}}/(k_BT)})} \\ &= \left(\frac{N_{\text{DI}}}{N_{\text{HI}}}\right)\frac{e^{-2360/398}(1 - e^{-2360/398})}{e^{-3324/398}(1 - e^{-3324/398})} = \left(\frac{N_{\text{DI}}}{N_{\text{HI}}}\right)(11.24)\end{aligned}$$

$$\left(\frac{n_{\rm DI}}{n_{\rm HI}}\right) = \frac{0.100}{11.24} = \boxed{0.0089}.$$

By the way, you could also just assume $q_{\rm vib} \approx 1$, after seeing that $\omega_e \gg k_B T$ for both molecules.

4. The possible spin states for one $^{14}$N nucleus, which has spin $I = 1$, are $m_I = 1$ ($\alpha$), $m_I = 0$ ($\beta$), and $m_I = -1$ ($\gamma$).
   (a) List all the distinct *two-particle* nuclear spin states for $^{14}N_2$.
   (b) Put an "**e**" next to each of these nuclear spin states that will be associated with even $J$ rotational levels of the $N_2$ molecule. **Solution:** There should be nine states altogether, since there are three possible $m_I$ values for each nucleus. Because the $^{14}$N nucleus has integer spin, it is a boson, and the even $J$ values (symmetric roatational wavefunction) must have a symmetric nuclear wavefunction:

$$\begin{array}{ccc} (\alpha\alpha)\mathbf{e} & (\beta\beta)\mathbf{e} & (\gamma\gamma)\mathbf{e} \\ (\alpha\beta+\beta\alpha)\mathbf{e} & (\alpha\gamma+\gamma\alpha)\mathbf{e} & (\beta\gamma+\gamma\beta)\mathbf{e} \\ (\alpha\beta-\beta\alpha) & (\alpha\gamma-\gamma\alpha) & (\beta\gamma-\gamma\beta) \end{array}$$

Whereas a diatomic with $I = 0$ indistinguishable nuclei has no odd $J$ states, and with $I = 1/2$ has a weight of 1:3 for even $J$ to odd $J$, here the weight is 6:3 for even $J$ to odd $J$. As the nuclear spin rises, the difference between odd and even $J$ spin weights approaches 1.

5. The derivation of $C_{Vm}$ for a fluid arrives at

$$C_{Vm} = \frac{3R}{2} + 2\pi\mathcal{N}_A^2\left(\frac{\rho_m}{\mathcal{M}}\right)\int_0^\infty u(R)\, e^{-u(R)/(k_BT)}\left(\frac{u(R)}{k_BT^2}\right) R^2 dR$$

Assume instead a potential $u(R) = -\epsilon$ if $R_{\rm LJ} < R < 2R_{\rm LJ}$ and $u(R) = \infty$ everywhere else. **Solution:** The $e^{-u(R)/(k_BT)}$ term makes the integrand vanish outside the range $R_{\rm LJ} < R < 2R_{\rm LJ}$, so we just plug in and integrate over this region:

$$\begin{aligned} C_{Vm} &= \frac{3R}{2} + 2\pi\mathcal{N}_A^2\left(\frac{\rho_m}{\mathcal{M}}\right)\int_{R_{\rm LJ}}^{2R_{\rm LJ}} u(R)\, e^{-u(R)/(k_BT)}\left(\frac{u(R)}{k_BT^2}\right) R^2 dR \\ &= \frac{3R}{2} + 2\pi\mathcal{N}_A^2\left(\frac{\rho_m}{\mathcal{M}}\right)\int_{R_{\rm LJ}}^{2R_{\rm LJ}}\left(\frac{\epsilon^2}{k_BT^2}\right) e^{-\epsilon/(k_BT)} R^2 dR \\ &= \frac{3R}{2} + 2\pi\mathcal{N}_A^2\left(\frac{\rho_m}{\mathcal{M}}\right)\left(\frac{\epsilon^2}{k_BT^2}\right) e^{-\epsilon/(k_BT)} \left.\frac{R^3}{3}\right|_{R_{\rm LJ}}^{2R_{\rm LJ}} \\ &= \frac{3R}{2} + 2\pi\mathcal{N}_A^2\left(\frac{\rho_m}{\mathcal{M}}\right)\left(\frac{\epsilon^2}{k_BT^2}\right) e^{-\epsilon/(k_BT)}\left(\frac{7R_{\rm LJ}^3}{3}\right) \end{aligned}$$

This will generally be smaller than the liquid value, in agreement with observation.