Physical Chemistry of Materials 2

Due date: October 5, 2012

Homework #2

1. Evaluate the translational partition function for H_2 confined to a volume of 100 cm^3 at 298 K. Perform the same calculation for N_2 under identical conditions.

2. Calculate the rotational partition function for SO_2 at 298 K where B_A=2.03 cm^{-1}, B_B=0.344 cm^{-1}, and B_C=0.293 cm^{-1}.

3. Evaluate the vibrational partition function for SO_2 at 298 K where the vibrational frequencies are 519, 1151, and 1361 cm^{-1}.

4. (a) We have made the assumption that the harmonic oscillator model is valid such that anharmonicity can be neglected. However, anharmonicity can be included in the expression for vibrational energies. The energy levels for an anharmonic oscillator are given by

$$\varepsilon_n = hc\tilde{\nu}\left(n+\frac{1}{2}\right) - hc\tilde{\chi}\tilde{\nu}\left(n+\frac{1}{2}\right)^2 + \cdots$$

Neglecting zero point energy, the energy levels become $\varepsilon_n = hc\tilde{\nu}n - hc\tilde{\chi}\tilde{\nu}n^2 + \cdots$. Using the preceding expression, demonstrate that the vibrational partition function for the anharmonic oscillator is

$$q_{v,anharmonic} = q_{v,harm}\left(1+\beta hc\tilde{\chi}\tilde{\nu}q_{v,harm}^2\left(e^{-2\beta\tilde{\nu}n} + e^{-\beta\tilde{\nu}n}\right)\right)$$

In deriving the preceding result, the following series relationship will prove useful:

$$\sum_{n=0}^{\infty} n^2 x^n = \frac{x^2+x}{(1-x)^3}$$

(b) For H_2, $\tilde{\nu} = 4401.2\,\text{cm}^{-1}$ and $\tilde{\chi}\tilde{\nu} = 121.3\,\text{cm}^{-1}$. Use the result from (a) to determine the percent error in q_v if anharmonicity is ignored.

5. Determine the total molecular partition function for gaseous H_2O at 100 K confined to a volume of 1 cm^3. The rotational constants for water are B_A=27.8 cm^{-1}, B_B=14.5 cm^{-1}, and B_C=9.95 cm^{-1}. The vibrational frequencies are 1615, 3694, and 3802 cm^{-1}. The ground electronic state is non-degenerate.

6. Derive the partition function for a monatomic van der Waals gas:

$$Q = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} (V - Nb)^N \, e^{aN^2/VkT}$$

where a and b are the van der Waals constants.

7. Solve the problems in Atkin's 9th edition: 15.14, 15.22, 16.18.