Chemistry 562 **Fall 2012**

Problem Set 11

Due beginning of class on Wednesday, May 2nd

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. (a) Write out the equation for the canonical partition function Q in terms of the molecular translational, rotational, and vibrational partition functions of an HCN gas.

   (b) Find the equation for E for the HCN gas in terms of molecular parameters. (recall E=U-U(0)). Use the equation for the rotational molecular partition function in the high temperature limit. (*Note: HCN has 4 normal modes: the CH stretch, the CN stretch, and a doubly degenerate bend.*)

   (c) Find the equation for the molar heat capacity C_p of HCN in terms of molecular parameters and calculate it at 298 K. The normal modes for HCN are at 3311 cm^{-1} (CH stretch), 712 cm^{-1} (doubly degenerate bend), and 2097 cm^{-1} (CN stretch). You may use $C_p = C_v + \text{R}$. How does your value of C_p compare to the experimental value of 35.9 J/(mole K)?

2. For the reaction:

$$A_2 + B_2 \Leftrightarrow 2AB$$

where A and B are different isotopes of the same atom:

(a) Find the ratio $\dfrac{\left(q_{AB}^{T}\right)^2}{q_{A_2}^{T} q_{B_2}^{T}}$ in terms of m_{A_2}, m_{B_2}, and m_{AB}. (T refers to the translational partition function.)

(b) Find the ratio $\dfrac{\left(q_{AB}^{R}\right)^2}{q_{A_2}^{R} q_{B_2}^{R}}$ in terms of m_{A_2}, m_{B_2}, and m_{AB}. Use the high temperature limit for the rotational partition functions. Don't forget to include the symmetry number.

(c) Using the results of parts (a) and (b), and assuming the vibrational and electronic partition functions are 1, show that the equilibrium constant is equal to: $4\dfrac{m_{AB}}{\sqrt{m_{A_2} m_{B_2}}} e^{-\beta(2\varepsilon_{AB}^0 - \varepsilon_{A_2}^0 - \varepsilon_{B_2}^0)}$.

($\varepsilon_{AB}^0, \varepsilon_{A_2}^0$, *and* $\varepsilon_{B_2}^0$ *are the zero point energies of AB,* A_2*, and* B_2 *respectively*)

(d) For $H_2 + D_2 \Leftrightarrow 2HD$ at 300 K:

(i) Calculate the vibrational partition function of D_2 for $\tilde{\nu}_{D_2}$ = 3113 cm^{-1}. Was setting it to 1 above a good approximation for this reaction? Why? Explain qualitatively if this approximation will be better or worse for H_2 and HD.

(ii) Numerically calculate $q_{H_2}^R$ and compare it to the high temperature limit. Is the high temperature limit a good approximation for H_2? Why or why not? (B_{H_2} = 60 cm^{-1})

(iii) In the equilibrium constant equation, calculate the partition function term ($4\frac{m_{HD}}{\sqrt{m_{H_2}m_{D_2}}}$), and the zero point energy exponential term ($e^{-\beta(2\varepsilon_{HD}^0 - \varepsilon_{H_2}^0 - \varepsilon_{D_2}^0)}$) for $\tilde{\nu}_{H_2}$ and $\tilde{\nu}_{HD}$ equal to 4401 cm^{-1} and 3813 cm^{-1} respectively. What is the value of *K*? For this reaction, the relatively significant difference in zero point energies makes the exponential term relevant because the difference in zero point energies is non-zero, resulting in an exponential term that deviates from 1.

(iv) Qualitatively, do you expect the exponential term to be important for the following reaction:

$$^{35}Cl_2 + ^{37}Cl_2 \Leftrightarrow 2\,^{35}Cl^{37}Cl$$

In other words, will the exponential term be close to 1? Why or why not?