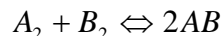


Problem Set 11

Due beginning of class on Wednesday, May 2nd

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

- 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.
 - 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.)
 - 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 $C_p = C_v + R$. How does your value of C_p compare to the experimental value of $35.9\text{ J}/(\text{mole K})$?
- For the reaction:



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

- Find the ratio $\frac{(q_{AB}^T)^2}{q_{A_2}^T q_{B_2}^T}$ in terms of m_{A_2} , m_{B_2} , and m_{AB} . (T refers to the translational partition function.)
- Find the ratio $\frac{(q_{AB}^R)^2}{q_{A_2}^R q_{B_2}^R}$ 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.
- 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:

$$4 \frac{m_{AB}}{\sqrt{m_{A_2} m_{B_2}}} e^{-\beta(2\varepsilon_{AB}^0 - \varepsilon_{A_2}^0 - \varepsilon_{B_2}^0)}$$
 (ε_{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 $H_2 + D_2 \rightleftharpoons 2HD$ at 300 K:

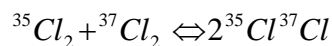
(i) Calculate the vibrational partition function of D_2 for $\tilde{\nu}_{D_2} = 3113 \text{ cm}^{-1}$. Was setting it to 1 above a good approximation for this reaction? Why? Explain qualitatively if this approximation will be better or worse for H_2 and HD .

(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? ($B_{H_2} = 60 \text{ cm}^{-1}$)

(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:



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