Feb. 12, 2007

Chem. 1480

Problem Set 4, due Feb. 19, 2007

Do the following problems from Atkins (8th Ed.). These are *not* to be handed in for grading; solutions will be distributed via .pdf:

Chapt. 17: Exercises 17.1a, 17.8a, 17.13a; Numerical problem: 17.1; Theoretical Problem 17.22

The following two problems are to be handing in for grading:

(1) In class we calculated the equilibrium constant for the gas phase dissociation reaction:

$$Na_2(g) \rightarrow 2Na(g)$$

using statistical mechanics. We found the "activity" coefficient equilibrium constant K_a [such that $K_a = (p_{Na} / p^o)^2 / (p_{Na_2} / p^o)$] at 1000 K, specifically $K_a = 2.4$. Repeat this calculation at the two temperatures *T=800, 1200K*. [Molecular constants relevant to the problem are given in Atkins (8th Ed.) Ex. 17.6.]

(2) Consider the gas phase reaction:

$$H(g) + HCl(g) \rightarrow Cl(g) + H_2(g)$$

(a) According to the law of mass action,

$$\frac{[Cl][H_2]}{[H][HCl]} = K_c$$

where $[H_2]$ is the concentration of H_2, etc., and K_c is the appropriate equilibrium constant. If concentrations are measured in numbers of atoms or molecules per unit volume, write an expression for K_c in terms of the molecular partition functions q_{H_2}, q_{HCl}, and the atomic partition functions q_H and q_{Cl}.

(b) The molecular partition function q_{H_2} can be written as a product

$$q_{H_2} = q_{H_2}^{rot} q_{H_2}^{vib} q_{H_2}^{trans} q_{H_2}^{elect},$$

where the factors on the right hand side account for the contributions from rotation, vibration, translation, and electronic motion. Evaluate the rotational partition function $q_{H_2}^{rot}$ at T = 1000 K, given that the rotational constant of H_2 is 59.3 cm^{-1}.

(c) Evaluate the ratio of translational partition functions for *H* and *Cl* atoms, i.e. $q_H^{trans} / q_{Cl}^{trans}$. [Hint: The answer should be independent of temperature.]