

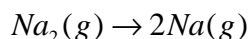
Feb. 12, 2007  
**Chem. 1480**  
**Problem Set 4**, due Feb. 19, 2007

Do the following problems from Atkins (8<sup>th</sup> 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

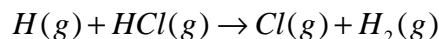
The following two problems are to be handing in for grading:

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



using statistical mechanics. We found the “activity” coefficient equilibrium constant  $K_a$  [such that  $K_a = (p_{\text{Na}} / p^\circ)^2 / (p_{\text{Na}_2} / p^\circ)$ ] at 1000 K, specifically  $K_a = 2.4$ . Repeat this calculation at the two temperatures  $T=800, 1200\text{K}$ . [Molecular constants relevant to the problem are given in Atkins (8<sup>th</sup> Ed.) Ex. 17.6.]

(2) Consider the gas phase reaction:



(a) According to the law of mass action,

$$\frac{[\text{Cl}][\text{H}_2]}{[\text{H}][\text{HCl}]} = K_c$$

where  $[\text{H}_2]$  is the concentration of  $\text{H}_2$ , 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  $q_{\text{H}_2}, q_{\text{HCl}}$ , and the atomic partition functions  $q_{\text{H}}$  and  $q_{\text{Cl}}$ .

(b) The molecular partition function  $q_{\text{H}_2}$  can be written as a product

$$q_{\text{H}_2} = q_{\text{H}_2}^{\text{rot}} q_{\text{H}_2}^{\text{vib}} q_{\text{H}_2}^{\text{trans}} q_{\text{H}_2}^{\text{elect}},$$

where the factors on the right hand side account for the contributions from rotation, vibration, translation, and electronic motion. Evaluate the rotational partition function  $q_{\text{H}_2}^{\text{rot}}$  at  $T = 1000\text{ K}$ , given that the rotational constant of  $\text{H}_2$  is  $59.3\text{ cm}^{-1}$ .

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