Chemistry 60641 Fall 2014
Professor J. Daniel Gezelter Due Wednesday, November 5, 2014

Problem Set 4

1. Compute $K_p$, the pressure-based equilibrium constant for the dissocation reaction of $O_2$ at $T = 3000K$. The electronic ground-state degeneracy for oxygen atoms, $g_0(O) = 9$, while for oxygen molecules, $g_0(O_2) = 3$.

2. Do problem 9-1 in McQuarrie.

3. Using the translational partition function and the partition functions for harmonic oscillators and rigid rotators, do problem 9-9 in McQuarrie.

4. Consider the reaction given by:

$$H_2(g) + D_2(g) \leftrightarrow 2HD(g)$$

   Using molecular parameters (see table 6-1 in McQuarrie), show that the equilibrium constant for this reaction has a temperature dependence of roughly:

$$K(T) = 4.24e^{-77.7K/T}$$

5. Heat capacities of liquids

   a) $C_V$ for liquid argon (at $T = 100K$) is 18.7 J K$^{-1}$ mol$^{-1}$. How much of this heat capacity can you rationalize on the basis of your knowledge of gases?

   b) $C_V$ for liquid water at $T = 10°$C is about 75 J K$^{-1}$ mol$^{-1}$. Assuming water has three vibrations, how much of this heat capacity can you rationalize on the basis of gases? What is responsible for the rest?

6. For the nearest-neighbor Ising model,

$$\mathcal{H} = -H \sum_n \sigma_n - \frac{J}{2} \sum_{n,n'}^{N.N.} \sigma_n \sigma_{n'}$$

   with external magnetic field ($H \neq 0$), determine the zero-temperature states as a function of $J$ and $H$. Present the results on a H-J zero-temperature diagram marking clearly which states are favored in the various regions of the diagram.

7. For the one-dimensional Ising model, plot the average energy (actually $E/NJ$), the magnetic susceptibility, and the specific heat all against $kT/J$ between values of 0 and 5. Discuss the specific heat maximum at around $kT/J = 1$.

8. Extra credit: Maximum Entropy in Las Vegas

   You play a slot machine in Las Vegas. For every $1 coin you insert there are three outcomes:

   a) you lose $1.

   b) you win $1, so your profit is $0.

   c) you win $5, so your profit is $4.

   Suppose you find that your average expected profit over many trials is $0 (i.e. you play slots at a casino owned by someone exceedingly generous or stupid). Find the maximum entropy distribution for the probabilities $p_1$, $p_2$ and $p_3$ of observing each of these three outcomes.