Chemistry 60641 | Spring 2025
Professor J. Daniel Gezelter | Due Wednesday, April 2, 2025

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. Problem 9.1 in McQuarrie's Statistical Mechanics: Consider the reaction A $\longleftrightarrow$ 2 B. The canonical ensemble partition function for an ideal binary mixture is

$$Q(N_A, N_B, V, T) = \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

Minimize the Helmholtz free energy with the stoichiometric constraint $2N_A + N_B = \mathrm{constant}$ to show that

$$\frac{N_B^{*2}}{N_A^*} = \frac{q_B^2}{q_A}$$

where N_A^* and N_B^* are the equilibrium numbers of A and B. Can you generalize this approach to the reaction aA + bB $\longleftrightarrow$ cC + dD?

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

4. Consider the reaction given by:

$$H_2(g) + D_2(g) \longleftrightarrow 2\,HD(g)$$

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

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

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.