

Problem Set 4

1. Compute  $K_p$ , the pressure-based equilibrium constant for the dissociation 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  $A \longleftrightarrow 2B$ . The canonical ensemble partition function for an ideal binary mixture is

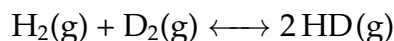
$$Q(N_A, N_B, V, T) = \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

Minimize the Helmholtz free energy with the stoichiometric constraint  $2N_A + N_B =$  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:



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  $T = 10^\circ C$  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.