Digital Chemistry, Problem set 4

Due April 2, 2025

1. Derive the expression for the partition function, Q, for a two-state system alike to that of Problem set 3, as a function of temperature. Assume that the ground state has energy $\epsilon_0 = 0$ and degeneracy g_0 and the excited state has energy ϵ_1 and degeneracy g_1.

2. Write the expression for the free energy of the system as a function of temperature.

3. Derive the expressions for the populations of the ground and the excited state, respectively, as functions of temperature.

4. Derive the expression for the average energy in two ways: first, from the definition of the mean and second, by taking the partial derivative of $\ln Q$ in temperature. Both way must give the same result.

5. Based on the solutions of Problems 2 and 4 and making use of the relationship between free energy, energy, and entropy, derive the expression for the entropy of the system as a function of temperature.

6. Using the value of the relative energy of 1-bromopropane (product II of propane photobromination), which is defined relative to that of 2-bromopropane (product I of propane photobromiation) obtained by solving Problem 1 of Problem set 3, plot the following quantities as functions of temperature (from $T = 0$ K to $T = 500$ K):

   (a) The populations of product I and product II (in one graph).

   (b) The average energy and the free energy of the system (in one graph).

   (c) The entropy of the system.