Digital Chemistry, Problem set 4

Due March 31, 2026

1. Derive the expression for the partition function, Q, for a two-state system. Label the ground and the excited states as "g" and "e", respectively. Shift the energy scale to the energy of the ground state so that $E_g = 0$ and $E_e = \epsilon$ and assume that the degeneracies of the ground and of the excited state are ω_g and ω_e, respectively; note that $\omega_g \geq 1$ and $\omega_e \geq 1$.

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 ways 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 *o*-nitrophenol with respect to that of *p*-nitrophenol given in Problem 1 of Problem set 3, plot the following quantities as functions of temperature (from $T = 0$ K to $T = 500$ K) assuming that the two species are at equilibrium:

   (a) The populations of *p*-nitrophenol and *o*-nitrophenol (in one graph).

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

   (c) The entropy of the system.