Problem set 5

Due April 14, 2026

1. Assign the appropriate statistical ensembles to the following systems:

   (a) Wine in an old-fashioned wine-skin (check Wikipedia or another reference if you are not sure what a wine-skin is).

   (b) Liquid dinitrogen tetraoxide at equilibrium with gaseous N_2O_4 and gaseous NO_2 (the product of its dissociation) in a sealed and thermally-insulated flask.

   (c) A sealed bottle of soda.

   (d) A glass of water.

2. Using the probability-based formula for entropy learned on today's lecture

$$S = -k_B \sum_{i=1}^{Z} P_i \ln P_i$$

   where P_i is the Boltzmann probability of microstate i, derive the formula for the entropy of the two-state system considered in Problem 1 of Problem Set 3 as a function of temperature and demonstrate that the result is the same as that obtained from the formula

$$S = \frac{E - F}{T}$$

   implemented when solving problem 5 of Problem set 4.

   Note that a "microstate" literally means a "microstate" and not a group of degenerate states. Also note that k_B becomes R when the "per mol" quantities are considered.

3. Using the probability-based formula for entropy demonstrate that, for a system with Z microstates whose energies are $\epsilon_1,\ \epsilon_2, \ldots, \epsilon_Z$, the entropy reaches maximum when the populations of all microstates obey the Boltzmann distribution.

Hint: Apply the Lagrange multiplier method, the two constraints being (1) the normalization of probabilities to 1 and (2) the constraint on the weighted energy average, the weights being microstate probabilities. The latter can be compared to an honestly conducted game with "zero" sum of gains and losses.