Statistical Thermodynamics

Statistical thermodynamics aims to describe the properties of thermodynamic systems simply by looking at the most probable state of a system of *N* molecules. The most probable state can be found by considering all arrangements of the molecules, and looking at the arrangement with the highest *weight*.

The *weight* of a system of molecules is the total number of arrangements of a particular distribution, and is defined as $W = \frac{N!}{n_1!n_2!\cdots n_k!}$ where $n_1, n_2, \dots, n_k$ are the number of molecules in each respective state. Using methods from mathematics, one can approximate that $\ln W = N \ln N - \sum_i n_i \ln n_i$.

Additionally, the molecules are subject to two additional constraints: conservation of energy and conservation of mass. These imply that $\sum_i n_i \varepsilon_i = E_{tot}$ and $\sum_i n_i = N$, where ε_i is the energy of the *i*th state.

Finally, one can show that the population of each state is given by the Boltzmann distribution:

$$n_i = N \cdot \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

where the energy levels are in ascending order, and $\beta = \frac{1}{k_B T}$. We call the denominator $\sum_i e^{-\beta\varepsilon_i}$ the *partition function* and denote it *q*.

1. Consider a two-state system, with one state at zero energy and the other at an energy of ε. Find the proportion of molecules at each state at arbitrary temperature.

2. What are the proportions of molecules in each state when temperature approaches 0 or infinity?

$T \to 0$:

$T \to \infty$:

3. Find the total energy of the two-state system at arbitrary temperature. What is its maximum and at what temperature is this maximum achieved?

E =

Max energy = Achieved at T =

The electronic energy levels in a hydrogen atom are given by $E_n = -\frac{R_H}{n^2}$ where $R_H = 2.178 \cdot 10^{-1}\ \ J$.

4. Calculate the theoretical number of hydrogen atoms at the $n = 2$ energy state in one mol of hydrogen atoms at $T = 4000\ K$.
Hint: It is reasonable to assume that there are essentially no hydrogen atoms at higher energy states.

The vibrational energy levels of a molecule are given by $E_n = h\left(n + \frac{1}{2}\right)\nu$ where ν is the vibrational wavenumber.

5. Find the vibrational partition function for a molecule with vibrational wavenumber ν.
Hint: $\sum_{i \geq 0} x^i = \frac{1}{1-x}$.

The previous problems have shown how to manipulate and calculate q. Our next goals will be to use statistical thermodynamics express fundamental thermodynamic aspects, in terms of q.

6. Show that the total energy of the system is given by $E = -\frac{N}{q} \cdot \frac{dq}{d\beta}$.

Hint: $\frac{d}{d\beta}\left(e^{-\beta\varepsilon}\right) = -\varepsilon e^{-\beta\varepsilon}$.

7. Show that the entropy of the system is given by $S = \frac{E}{T} + Nk \ln q$.

Hint: $S = k \ln W$.

Finally, we will try to understand a theoretical negative temperature scale.

8. Find the ratio of populations in a two-state system. In terms of the ratio of populations, when would temperature theoretically be negative?

9. Consider the energy of a general system. Does a system have more energy as $T \to 0$ from a negative temperature or a positive temperature? Justify your answer.