# 20.8: The Probabilities of Microstates that Have the Same Energy

In Section 20.2, we introduce the assumption that, for a molecule in a constant-N-V-T system, for which the $g_i$ and $\epsilon_i$ are fixed, the probability of a quantum state, $\rho\left(\epsilon_i\right)$, depends only on its energy. It follows that two or more quantum states that have the same energy must have equal probabilities. We accept the idea that the probability depends only on energy primarily because we cannot see any reason for a molecule to prefer one state to another if both states have the same energy.

We extend this thinking to multi-molecule systems. If two microstates have the same energy, we cannot see any reason for the system to prefer one rather than the other. In a constant-N-V-T system, in which the total energy is not otherwise restricted, each microstate of $\{N_1,\ N_2,\dots,N_i,\dots.\}$ occurs with probability $\rho\left(\epsilon_1\right)^{N_1}\rho\left(\epsilon_2\right)^{N_2}\dots\rho\left(\epsilon_i\right)^{N_i}\dots.$, and each microstate of $\{N^{\#}_1,N^{\#}_2,\ \dots,N^{\#}_I,\dots\ \}$ occurs with probability $\rho\left(\epsilon_1\right)^{N^{\#}_1}\rho\left(\epsilon_2\right)^{N^{\#}_2}\dots\rho\left(\epsilon_i\right)^{N^{\#}_i}\ \dots.$ When the energies of these population sets are equal, we infer that these probabilities are equal, and their value is a constant of the system. That is,

$$\begin{aligned} &\rho\left(\epsilon_1\right)^{N_1}\rho\left(\epsilon_2\right)^{N_2}\dots\rho\left(\epsilon_i\right)^{N_i}\dots. \\ &=\rho\left(\epsilon_1\right)^{N^{\#}_1}\rho\left(\epsilon_2\right)^{N^{\#}_2}\dots\rho\left(\epsilon_i\right)^{N^{\#}_i}\ \dots. \quad =\rho_{MS,N,E}=\text{constant} \end{aligned}$$

where we introduce $\rho_{MS,N,E}$ to represent the probability of a microstate of a system of $N$ molecules that has total energy $E$. If $E=E^{\#}$, then $\rho_{MS,N,E}=\rho_{MS,N,E^{\#}}$.

When we think about it critically, the logical basis for this equal-probability idea is not very impressive. While the idea is plausible, it is not securely rooted in any particular empirical observation or prior postulate. The equal-probability idea is useful only if it leads us to theoretical models that successfully mirror the behavior of real macroscopic systems. This it does. Accordingly, we recognize that the equal-probability idea is really a fundamental postulate about the behavior of quantum-mechanical systems. It is often called the *principle of equal a priori probabilities***:**

**Definition: principle of equal *a priori* probabilities**

For a particular system, all microstates that have the same energy have the same probability.

Our development of statistical thermodynamics relies on the principle of equal *a priori* probabilities. For now, let us summarize the important relationships that the principle of equal *a priori* probabilities imposes on our microscopic model for the probabilities of two population sets of a constant-N-V-T system that have the same energy:

- A given population set $\left\{N_1,\ N_2,\dots,N_i,\dots.\right\}$ gives rise to $W\left(N_i,g_i\right)$ microstates, and each of these microstates has energy

$$E=\sum^{\infty}_{i=1}{N_i{\epsilon }_i}$$

- A second population set, $\{N^{\#}_1,N^{\#}_2,\ \dots,N^{\#}_I,\dots\ \}$, that has the same energy need not—and usually will not—give rise to the same number of microstates. In general, for two such population sets,

$$W\left(N_i,g_i\right)\neq W\left(N^{\#}_i,g_i\right)$$

  However, because each microstate of either population set has the same energy, we have

$$E=\sum^{\infty}_{i=1}{N_i{\epsilon }_i}=\sum^{\infty}_{i=1}{N^{\#}_i{\epsilon }_i}$$

- The probability of a microstate of a given population set $\left\{N_1,\ N_2,\dots,N_i,\dots.\right\}$ depends only on its energy:

$$\rho\left(\epsilon_1\right)^{N_1}\rho\left(\epsilon_2\right)^{N_2}\dots\rho\left(\epsilon_i\right)^{N_i}\dots.=\rho_{MS,N,E}=\text{constant}$$