20.13: The Degeneracy of an Isolated System and its Entropy

In Section 20.10, we observe that the entropy of an isolated equilibrium system can be defined as $S = k \ln W_{max}$. In Section 20.12, we see that the system-energy degeneracy is a sum of terms, one of which is $W_{max} = W \left(N_i^{\bullet}, g_i \right)$. That is, we have

$$\Omega_E = W_{max} + \sum_{\{N_i\} \neq \left\{N_i^{\bullet}\right\}, E_{total}} W\left(N_i, g_i\right)$$

where the last sum is taken over all energy-qualifying population sets other than the most-probable population set.

Let us now consider the relative magnitude of Ω_E and W_{max}. Clearly, $\Omega_E \geq W_{max}$. If only one population set is consistent with the total-molecule and total-energy constraints of the isolated system, then $\Omega_E = W_{max}$. In general, however, we must expect that there will be many, possibly an enormous number, of other population sets that meet the constraints. Ultimately, the relative magnitude of Ω_E and W_{max} depends on the energy levels available to the molecules and the number of molecules in the system and so could be almost anything. However, rather simple considerations lead us to expect that, for most macroscopic collections of molecules, the ratio $\alpha = \Omega_E / W_{max}$ will be much less than W_{max}. That is, although the value of α may be very large, for macroscopic systems we expect to find $\alpha \ll W_{max}$. If $\Omega_E = W_{max}$, then $\alpha = 1$, and $\ln \alpha = 0$.

Because W for any population set that contributes to Ω_E must be less than or equal to W_{max}, the maximum value of α must be less than the number of population sets which satisfy the system constraints. For macroscopic systems whose molecules have even a modest number of accessible energy levels, calculations show that W_{max} is a very large number indeed. Calculation of α for even a small collection of molecules is intractable unless the number of accessible molecular energy levels is small. Numerical experimentation on small systems, with small numbers of energy levels, shows that the number of qualifying population sets increases much less rapidly than W_{max} as the total number of molecules increases. Moreover, the contribution that most qualifying population sets make to Ω_E is much less than W_{max}.

For macroscopic systems, we can be confident that W_{max} is enormously greater than α. Hence Ω_E is enormously greater than α. When we substitute for W_{max} in the isolated-system entropy equation, we find

$$\begin{aligned} S &= k \ln W_{max} \\ &= k \ln(\Omega_E / \alpha) \\ &= k \ln \Omega_E - k \ln \alpha \\ &\approx k \ln \Omega_E \end{aligned}$$

where the last approximation is usually very good.

In many developments, the entropy of an isolated system is defined by the equation $S = k \ln \Omega_E$ rather than the equation we introduced first, $S = k \ln W_{max}$. From the considerations above, we expect the practical consequences to be the same. In Section 20.14, we see that the approximate equality of $\ln W_{max}$ and $\ln \Omega_E$ is a mathematical consequence of our other assumptions and approximations.