

23.2: The Ensemble Entropy and the Value of β

At equilibrium, the entropy of the \hat{N} -system ensemble, S_{ensemble} , must be a maximum. By arguments that parallel those in [Chapter 20](#), \hat{W} is a maximum for the ensemble population set that characterizes this equilibrium state. Applying the Boltzmann definition to the ensemble, the ensemble entropy is $S_{\text{ensemble}} = k \ln \hat{W}_{\text{max}}$. Since all \hat{N} systems in the ensemble have effectively the same entropy, S , we have $S_{\text{ensemble}} = \hat{N}S$. When we assume that \hat{W}_{max} occurs for the equilibrium population set, $\{\hat{N}_1^*, \hat{N}_2^*, \dots, \hat{N}_i^*, \dots\}$, we have

$$\hat{W}_{\text{max}} = \hat{N}! \prod_{i=1}^{\infty} \frac{\Omega_i^{\hat{N}_i^*}}{\hat{N}_i^*!}$$

so that

$$S_{\text{ensemble}} = \hat{N}S = k \ln \hat{N}! + k \sum_{i=1}^{\infty} \hat{N}_i^* \ln \Omega_i - k \sum_{i=1}^{\infty} \ln(\hat{N}_i^*!)$$

From the Boltzmann distribution function, $\hat{N}_i^*/\hat{N} = Z^{-1} \Omega_i \exp(-\beta E_i)$, we have

$$\ln \Omega_i = \ln Z + \ln \hat{N}_i^* + \beta E_i - \ln \hat{N}$$

Substituting, and introducing [Stirling's approximation](#), we find

$$\begin{aligned} \hat{N}S &= k \hat{N} \ln \hat{N} - k \hat{N} + k \sum_{i=1}^{\infty} \hat{N}_i^* \left(\ln Z + \ln \hat{N}_i^* + \beta E_i - \ln \hat{N} \right) - k \sum_{i=1}^{\infty} \left(\hat{N}_i^* \ln \hat{N}_i^* - \hat{N}_i^* \right) \\ &= \hat{N} k \ln Z + k \beta \sum_{i=1}^{\infty} \hat{N}_i^* E_i \end{aligned}$$

Since $\sum_{i=1}^{\infty} \hat{N}_i^* E_i$ is the energy of the \hat{N} -system ensemble and the energy of each system is the same, we have

$$\sum_{i=1}^{\infty} \hat{N}_i^* E_i = E_{\text{ensemble}} = \hat{N}E$$

Substituting, we find

$$S = k \beta E + k \ln Z$$

where S , E , and Z are the entropy, energy, and partition function for the N -molecule system. From the fundamental equation, we have

$$\left(\frac{\partial E}{\partial S} \right)_V = T$$

Differentiating $S = k \beta E + k \ln Z$ with respect to entropy at constant volume, we find

$$1 = k \beta \left(\frac{\partial E}{\partial S} \right)_V$$

and it follows that

$$\beta = \frac{1}{kT}$$

We have, for the N -molecule system

$$Z = \sum_{i=1}^{\infty} \Omega_i \exp \left(\frac{-E_i}{kT} \right)$$

(System partition function)

$$\hat{P}_i = Z^{-1} \Omega_i \exp\left(\frac{-E_i}{kT}\right)$$

(Boltzmann's equation)

$$S = \frac{E}{T} + k \ln Z$$

(Entropy of the N-molecule system)

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