5.2: The Ensemble Entropy and the Value of ß

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 $\hat{W}_{\text{max}}$ occurs for the equilibrium population set, $\left\{\hat{N}^{\bullet}_1,\ \hat{N}^{\bullet}_2,\dots,\ \hat{N}^{\bullet}_i,\dots\right\}$, we have

$$\hat{W}_{\text{max}} = \hat{N}! \prod^{\infty}_{i=1} \frac{\Omega^{\hat{N}^{\bullet}_i}_i}{\hat{N}^{\bullet}_i!}$$

so that

$$S_{\text{ensemble}} = \hat{N}S = k \ln \hat{N}! + k \sum^{\infty}_{i=1} \hat{N}^{\bullet}_i \ln \Omega_i - k \sum^{\infty}_{i=1} \ln \left(\hat{N}^{\bullet}_i!\right)$$

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

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

Substituting, and introducing Stirling's approximation, we find

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

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

$$\sum^{\infty}_{i=1} \hat{N}^{\bullet}_i E_i = E_{\text{ensemble}} = \hat{N}E$$

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

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

(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)
