We now make use of the method of Lagrange multipliers. (See Appendix I for a description of this technique.) We multiply the constraint equations by Lagrange multipliers λ_1, λ_2, and λ_3 respectively:

$$\lambda_1 \sum_{i=0}^{\infty} dN_{a,i} = 0, \tag{2.17a}$$

$$\lambda_2 \sum_{j=0}^{\infty} dN_{b,j} = 0, \tag{2.17b}$$

$$\lambda_3 \sum_{i=0}^{\infty} \varepsilon_i dN_{a,i} + \lambda_3 \sum_{j=0}^{\infty} \varepsilon_j dN_{b,j} = 0. \tag{2.17c}$$

We then add these equations and subtract Eq. (2.15) to get

$$\lambda_1 \sum_{i=0}^{\infty} dN_{a,i} + \lambda_3 \sum_{i=0}^{\infty} \varepsilon_i dN_{a,i} - \sum_{i=0}^{\infty} dN_{a,i} \ln g_i + \sum_{i=0}^{\infty} dN_{a,i} \ln N_{a,i}$$
$$+ \lambda_2 \sum_{j=0}^{\infty} dN_{b,j} + \lambda_3 \sum_{j=0}^{\infty} \varepsilon_j dN_{b,j} - \sum_{j=0}^{\infty} dN_{b,j} \ln g_j + \sum_{j=0}^{\infty} dN_{b,j} \ln N_{b,j} = 0,$$

which reduces to

$$\sum_{i=0}^{\infty} (\lambda_1 + \lambda_3 \varepsilon_i - \ln g_i + \ln N_{a,i})\, dN_{a,i} + \sum_{j=0}^{\infty} (\lambda_2 + \lambda_3 \varepsilon_j - \ln g_j + \ln N_{b,j})\, dN_{b,j} = 0. \tag{2.18}$$

At the maximum, this relation must hold for arbitrary choices of $dN_{a,i}$ and $dN_{b,j}$, which implies that the coefficients of the differential terms must all be zero:

$$\lambda_1 + \lambda_3 \varepsilon_i - \ln g_i + \ln N_{a,i} = 0, \tag{2.19a}$$

$$\lambda_2 + \lambda_3 \varepsilon_j - \ln g_j + \ln N_{b,i} = 0. \tag{2.19b}$$

Solving these relations for $N_{a,i}$ and $N_{b,j}$, we obtain

$$N_{a,i} = g_i e^{-\lambda_1} e^{-\lambda_3 \varepsilon_i}, \tag{2.20a}$$

$$N_{b,j} = g_j e^{-\lambda_2} e^{-\lambda_3 \varepsilon_j}. \tag{2.20b}$$

Using the constraint relations (2.1) and (2.2) together with Eq. (2.20) yields

$$N_a = \sum_{i=0}^{\infty} N_{a,i} = \sum_{i=0}^{\infty} g_i e^{-\lambda_1} e^{-\lambda_3 \varepsilon_i} = e^{-\lambda_1} \sum_{i=0}^{\infty} g_i e^{-\lambda_3 \varepsilon_i}, \tag{2.21a}$$

$$N_b = \sum_{j=0}^{\infty} N_{b,j} = \sum_{j=0}^{\infty} g_j e^{-\lambda_2} e^{-\lambda_3 \varepsilon_j} = e^{-\lambda_2} \sum_{j=0}^{\infty} g_j e^{-\lambda_3 \varepsilon_j}. \tag{2.21b}$$

Combining Eqs. (2.20) and (2.21), we find that

$$\frac{N_{a,i}}{N_a} = \frac{g_i e^{-\lambda_1} e^{-\lambda_3 \varepsilon_i}}{e^{-\lambda_1} \sum_{i=0}^{\infty} g_i e^{-\lambda_3 \varepsilon_i}} = \frac{g_i e^{-\lambda_3 \varepsilon_i}}{\sum_{i=0}^{\infty} g_i e^{-\lambda_3 \varepsilon_i}}, \tag{2.22a}$$

$$\frac{N_{b,j}}{N_b} = \frac{g_j e^{-\lambda_2} e^{-\lambda_3 \varepsilon_j}}{e^{-\lambda_2} \sum_{j=0}^{\infty} g_j e^{-\lambda_3 \varepsilon_j}} = \frac{g_j e^{-\lambda_3 \varepsilon_j}}{\sum_{j=0}^{\infty} g_j e^{-\lambda_3 \varepsilon_j}}. \tag{2.22b}$$

The distributions above are generally written in the forms

$$\frac{N_{a,i}}{N_a} = \frac{g_i e^{-\lambda_3 \varepsilon_i}}{Z_a} \tag{2.23a}$$

and

$$\frac{N_{b,j}}{N_b} = \frac{g_j e^{-\lambda_3 \varepsilon_j}}{Z_b}, \tag{2.23b}$$

where

$$Z_a = \sum_{i=0}^{\infty} g_i e^{-\lambda_3 \varepsilon_i}, \tag{2.24a}$$

$$Z_b = \sum_{j=0}^{\infty} g_j e^{-\lambda_3 \varepsilon_j}. \tag{2.24b}$$

Equations (2.23a) and (2.23b) above are the distributions that maximize $\ln W$ subject to the imposed constraints. They are generalized *Boltzmann distributions* in terms of the as yet undefined constant λ_3. The parameters Z_a and Z_b are termed *partition functions*. In a single-component system only one partition function would be defined, usually just designated as Z. We will see that a partition function is itself a thermodynamic property because it is a unique function of the macrostate of the system.