Entropy of an Ideal Mixture

This derivation is based off a question from the textbook Introduction to Thermal Physics by D. Schroeder (2000). Consider two substances which interact with each other in the same way as they do with themselves (an ideal mixture). Let N_A, Ω_A be the number of particles in and multiplicity of substance A, and let N_B, Ω_B be those same quantities for substance B. If two boxes, one filled with each substance, are in thermal contact then at thermal equilibrium the total multiplicity of the combined system is given by

$$\Omega_{tot} = \Omega_A \Omega_B$$

Now, say we remove the barrier between the boxes and allow the two substances to mix. If the two substances were truly identical, then the multiplicity of the system would remain constant. This is because any new states, where if we replaced the wall the boxes would not be in equilibrium, would be exceedingly unlikely and vastly outnumbered by Ω_{tot}.

If the substances are instead different, but interact in the same way as all identical particles, then the same states are accessible. However, for each accessible state we can choose which particles in it will be of type A (which implies which ones will be of type B). Since A and B are distinguishable, each possible choice would constitute a new microstate for the system. So the new multiplicity of the system would be

$$\Omega'_{tot} = \Omega_{tot} \binom{N}{N_A}$$

So since $S = k \ln \Omega$, the entropy change from mixing would be

$$\begin{aligned}
\Delta S &= k \ln \Omega'_{tot} - k \ln \Omega_{tot} \\
\Delta S &= k \ln \left(\Omega_{tot} \binom{N}{N_A} \right) - k \ln \Omega_{tot} \\
\Delta S &= k \ln \binom{N}{N_A}
\end{aligned}$$

which given that

$$\binom{N}{N_A} = \frac{N!}{N_A!(N - N_A)!}$$

can be approximated to

$$\Delta S = k(\ln N! - \ln N_A! - \ln (N - N_A)!)$$

(using the Stirling approximation). Thus,

$$\begin{aligned}\Delta S \approx& k(N \ln N - N - N_A \ln N_A + N_A - (N - N_A) \ln (N - N_A) + (N - N_A)) \\ =& k(N \ln N - N_A \ln N_A - (N - N_A) \ln (N - N_A))\end{aligned}$$

Defining $x = \frac{N_B}{N}$ (although we could achieve the same result with $x = \frac{N_A}{N}$), we can see that $N_A = N(1 - x)$ and $N - N_A = Nx$. Plugging this into the entropy expression:

$$\begin{aligned}\Delta S \approx& k(N \ln N - N(1 - x) \ln N(1 - x) - Nx \ln Nx) \\ =& - Nk[- \ln N + \ln N + \ln (1 - x) \\ & - x \ln N - x \ln (1 - x) + x \ln N + x \ln x] \\ =& - nR[x \ln x + (1 - x)x \ln (1 - x)]\end{aligned}$$

Thus, the entropy of mixing of an ideal mixture is

$$\Delta S = -nR[x \ln x + (1 - x)x \ln (1 - x)]$$