ENTROPY OF MIXING IN A SMALL SYSTEM

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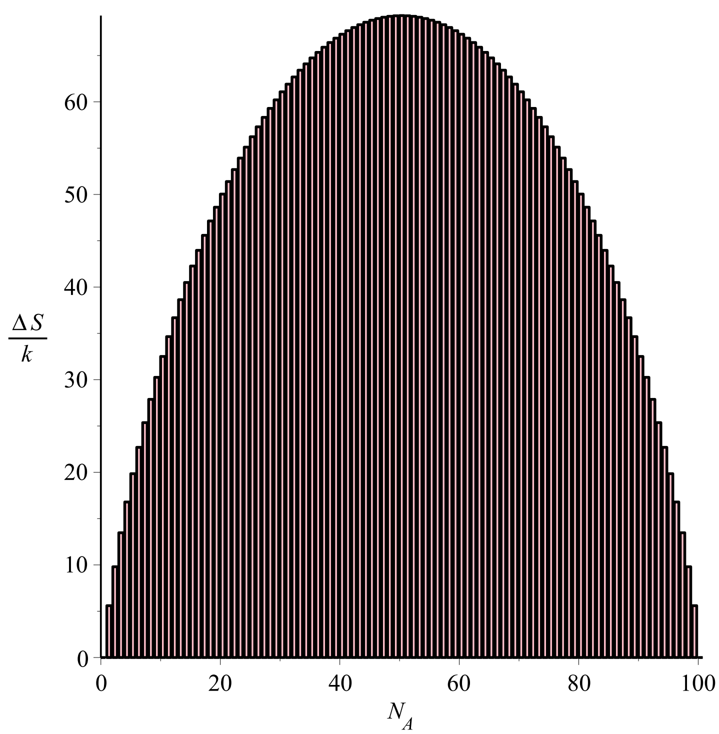
Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.57.

As an example of the entropy changes when two pure substances are mixed, consider a system of 100 molecules, which may vary in composition from 100% of species A through a mixture of A and B to 100% pure B. The entropy of mixing is given by

$$\Delta S_{mixing}=-Nk\left[x\ln x+(1-x)\ln(1-x)\right]$$

where $N=N_A+N_B$ is the fixed total number of molecules (100 here) and $x=N_A/N$.

For a small system such as this, we can generate an array of $\Delta S_{mixing}/k$ values for each value of N_A from 0 to 100. Plotting this as a bar chart, we get



Starting from $N_A = 0$ where $\Delta S/k = 0$ (since there is only one species at this point, there is no mixing), we see that the entropy increase per molecule as we convert successive molecules from A to B decreases. The changes in $\Delta S/k$ for the first few steps are:

add molecule number	change in $\frac{\Delta S}{k}$
1	5.60
2	4.20
3	3.67
4	3.32
5	3.06

The rate at which the entropy increases declines as we convert more molecules from A to B. If we add a slight impurity into an initially pure mixture of 100% B, this generates a larger increase in entropy than if we add a bit more impurity to an already mixed system.