

## ENTROPY OF MIXING IN A SMALL SYSTEM

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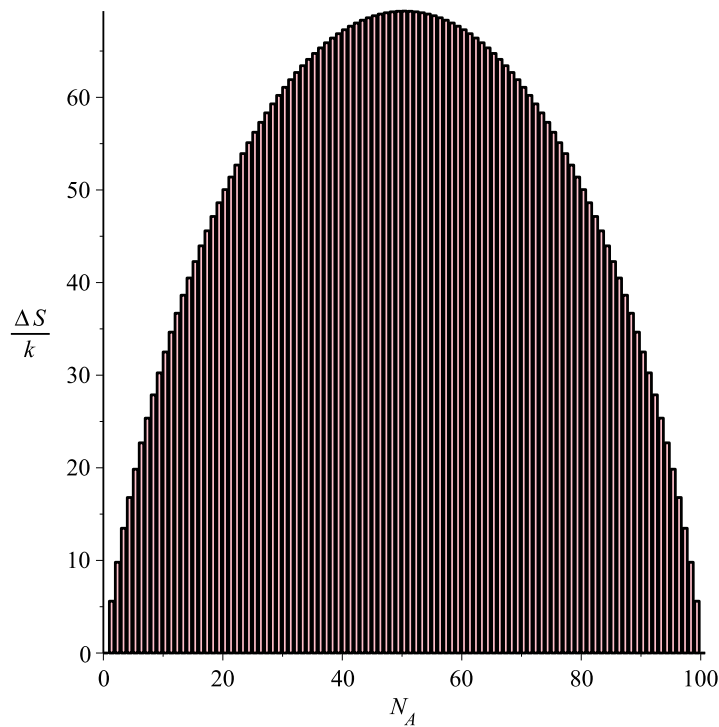
Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.57.

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

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

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  $\Delta S_{\text{mixing}}/k$  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.