12.1 Ideal solutions

Solutions are among the most important kinds of systems in the chemical and biochemical sciences and technologies, spanning an enormous range of different phenomena and scales. The simplest model of a solution is the so-called ideal one.

An ideal solution is defined by the following properties.

- Components are non-interacting. In other words, there are no explicit energetic interactions between molecules of different species.
- (2) At constant temperature and pressure, an ideal entropy of mixing contributes to the total entropy due to the presence of different species.
- (3) Ideal solutions are usually excellent approximations to real ones in the near-pure limit, in which there is one major component (e.g., a solvent) and the concentrations of all other species (solutes) are very small.

To develop a thermodynamic model of ideal solutions, we first evaluate the entropy of mixing using a simple model. Figure 12.1 illustrates a lattice mixing model for a binary system. Though the lattice certainly does not represent molecular-structural features of actual liquids, the final behavior of the mixing entropy is surprisingly insensitive to its use. Prior to mixing the particles are completely separated into different regions of the system volume. One configuration exists for this state, and thus the entropy is zero. If the particles are then allowed to mix randomly, the number of arrangements of N_A A particles and N_B B particles in the $N=N_A+N_B$ sites is given by the combinations formula

$$\begin{split} &\Omega_{\text{mix}}(N_{\text{A}}, N_{\text{B}}) = \frac{(N_{\text{A}} + N_{\text{B}})!}{N_{\text{A}}! N_{\text{B}}!} \approx \frac{(N_{\text{A}} + N_{\text{B}})^{N_{\text{A}} + N_{\text{B}}}}{N_{\text{A}}^{N_{\text{A}}} N_{\text{B}}^{N_{\text{B}}}} \\ &= \left(\frac{N_{\text{A}}}{N_{\text{A}} + N_{\text{B}}}\right)^{-N_{\text{A}}} \left(\frac{N_{\text{B}}}{N_{\text{A}} + N_{\text{B}}}\right)^{-N_{\text{B}}} \end{split} \tag{12.1}$$

In the second line, we applied Stirling's approximation. By taking the logarithm to obtain the entropy, we find

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