Entropy of Mixing: A Statistical View

Chemistry CHEM 213W

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As was mentioned in class, it is possible to give a simple quantitative microscopic derivation of the expression for the entropy of mixing for an ideal solution. To begin, consider the following simple lattice model for a solution:

![Lattice Diagram]

Fig. 1

The volume occupied by the solution has been divided into $M$ equivalent cells, and each is randomly occupied by a single molecule of a given type in the solution. Let $N_i$ be the number of molecules of the $i$'th species (the "solvent" counts as a species).

How many states are available for the solution in this model? Specifically, how many ways can the molecules occupy the cells? Consider species 1: The first molecule can choose $M$ cells, the second $M-1$, etc. Finally, the last species 1 molecule can choose $M-N_1-1$ different cells to occupy. Thus the number of ways of assigning the species 1 molecules to the cells is

$$M(M-1)\cdots(M-N_1-1) \equiv \frac{M!}{(M-N_1)!},$$

(1)

where $N! = N(N-1)(N-2)\cdots1$ is called the factorial function.

The other species must still be added to the lattice. Consider species 2. Now there are only $M-N_1$ cells to choose from; by repeating the preceding argument, it is easy to show that the number of ways of adding species 2 is
The total number of ways of adding both species 1 and species 2 to the lattice is the product of the ways of adding each; i.e.,

$$\frac{M!}{(M-N_1-N_2)!}.$$  

(2)

Finally, we can repeat the argument until the entire lattice is filled. The total number of ways of adding the molecules to the solution is

$$M!.$$  

(3)

Does each of these ways correspond to a state of the system? The answer is no, not because we have made an error in our calculation, but because we have ignored a basic property of nature; namely, the Heisenberg Uncertainty Principle. Equation (4) would be correct if we could distinguish the different molecules of each species. The uncertainty principle makes this impossible, and thus each state of the system cannot depend on which of the equivalent molecules are in the specific cells -- it is impossible to tell.

Thus Eq. (4) overcounts the number of different states available to the system. By how much? Again consider species 1. After the $N_1$ cells are chosen one still has the freedom to permute species 1 molecules between the different chosen cells; there are $N_1!$ ways of permuting the species 1 molecules, and these permutations are included in Eq. (2). However, as we have just argued, quantum mechanics makes these permutations irrelevant to the calculation of the number of inequivalent states available to the system, and hence, Eq. (2) should be divided by the number of ways of rearranging the equivalent molecules on the same set of lattice cells. By repeating this argument for all species, it follows that the number of inequivalent states of the solution are:

$$\frac{M!}{N_1!N_2!\cdots}.$$  

(5)

The calculation of the entropy of mixing now follows by using the statistical (Boltzmann) expression for the entropy:

$$S = k_B \ln(\text{number of states}),$$  

where $k_B$ is Boltzmann’s constant ($k_B = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$). By using Eq. (5) in Eq. (6), we obtain

$$\Delta S_{\text{mixing}} = k_B \left[ \ln(M!) - \sum_i \ln(N_i!) \right].$$  

(7)

This still doesn’t look like the expression we obtained in class. Note, however, that the factorials which appear in Eq. (7) are factorials of huge numbers ($\approx 10^{23}$). There is an accurate approximation for the natural logarithm of a large factorial known as Sterling’s formula; it is:

$$\ln(N!) \approx N[\ln(N) - 1]$$  

(8)

(try it for N=50). If Eq. (8) is used in Eq. (7) and we remember that $M = \sum_i N_i$, a little algebra shows that
\[ S_{\text{mixing}} = -k_B \sum_i N_i \ln \left( \frac{N_i}{M} \right) \quad (8) \]

Since, \( x_i \), the mole fraction of species \( i \) is \( \frac{N_i}{M} \).

Eq. (8) is equivalent to the expression we obtained by examining solutions that obey Raoult’s Law. (Recall that the gas constant \( R = k_B N_A \), where \( N_A \) is Avogadro’s number).