

# The lattice model of solutions

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## 1 Solubility and thermodynamics

Why do some substances dissolve in some solvents and not others? You probably have been exposed to a number of rules of thumb, but it's possible that you have never thought about this very important question in detail. We're going to apply a little thermodynamics here to help us think about the factors which are important in determining solubility (or miscibility, if we're talking about two liquids).

Recall that a process is thermodynamically favored at constant temperature and pressure if

$$\Delta G = \Delta H - T\Delta S < 0.$$

A mixture always has more microstates than two separated components, so the entropy of solution,  $\Delta_{\text{sol}}S$ , is always positive.<sup>1</sup> Accordingly, dissolving one substance in another is always entropically favored. Thus, the real question is whether  $\Delta_{\text{sol}}H$  is or is not too positive for  $\Delta_{\text{sol}}G$  to be negative, i.e. we will get a solution if

$$\Delta_{\text{sol}}H < T\Delta_{\text{sol}}S.$$

Of course, if  $\Delta_{\text{sol}}H$  is negative, then this inequality is automatically satisfied, and we will get a solution. If on the other hand  $\Delta_{\text{sol}}H > 0$ , then the inequality tells us that the enthalpy of solution can't be too large.

What we need to do then is to figure out how large the entropy and enthalpy of solution are likely to be, or at least what factors affect their magnitudes. We're going to start by looking at solutions involving small molecules to get our feet wet. Our eventual objective is to discuss polymer solutions.

## 2 The lattice model of solutions

The statistical mechanics of gases is easy because the molecules are typically far apart and randomly distributed in a volume. Conversely, solids are easy to treat because (at least for

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<sup>1</sup>Depending on the context,  $\Delta_{\text{sol}}S$  can also be called the **entropy of mixing**,  $\Delta_{\text{mix}}S$ .

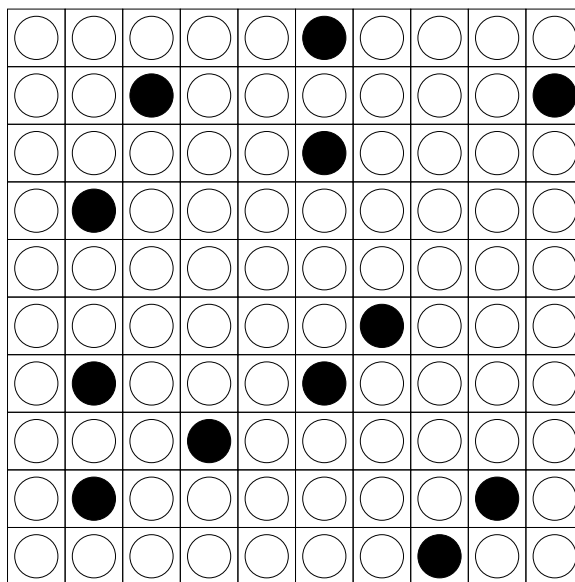


Figure 1: A two-dimensional square-lattice example of the lattice model of solutions. The open circles represent solvent molecules. The filled circles represent solute molecules.

crystalline solids, which includes many of the solids we are most interested in like metals) they are very regular. Solutions fall somewhere in between, which makes their statistical mechanical treatment difficult: They have short-range order due to the intermolecular forces between molecules, which are typically almost as close together in solutions as they are in solids, but they lack long-range order. One way to deal with this complexity is to use **models** which, hopefully, capture some aspects of the behavior of a solution. Provided we don't try to use a model for purposes which contradict in some way its basic assumptions, we can get a lot of qualitative and, sometimes, even quantitative insight into solution behavior this way.

Molecules occupy a certain amount of space. For now, let's consider a solvent/solute system in which the solvent and solute occupy similar volumes. Imagine that we put a little box around each solvent or solute molecule and pack them together in a regular lattice. Figure 1 illustrates this situation. This may sound like a model for a solid, but if we imagine that the molecules can move by swapping places with their neighbors, this is in fact a very crude model of the liquid state. For the purposes of illustration, we're going to picture this arrangement as a two-dimensional square lattice, although our treatment won't depend either on the number of spatial dimensions or on the geometry of the lattice. The lattice model will be a reasonable starting point for a theory of solutions provided we are not interested in properties which depend too sensitively on the details of relative molecular orientations.

## 2.1 Enthalpy of solution

In the crude model discussed here, there is no distinction between enthalpy and internal energy because the lattice does not change size when we introduce a solute molecule. Thus, there is no pressure-volume work, and  $\Delta U = \Delta H$ .

In solution thermodynamics, by convention solvent properties are labeled with the numerical subscript 1 and solute properties are labeled with 2, so  $N_1$  is the number of solvent molecules and  $N_2$  is the number of solute molecules, for instance. Let  $z$  be the **coordination number** of the lattice, i.e. the number of nearest-neighbor lattice sites. For the simple square lattice illustrated in figure 1,  $z = 4$ . We are going to imagine a lattice that contains  $N_0 = N_1 + N_2$  lattice sites, each occupied by a molecule. Initially, we imagine that the solute and solvent are spatially segregated (with, e.g., the solute molecules all at the surface). We will then randomly shuffle the molecules and ask ourselves what the effect is on the overall energy. One way to think about it is that we will randomly swap molecules from different parts of the lattice. If we do this enough times, then we will end up with a well-mixed solution.

First of all, let's dispense with a myth which many chemistry students carry with them: The so-called hydrophobic effect is *not* due to repulsion between polar and nonpolar molecules. Neutral molecules *always* attract, at least through London dispersion forces. However, you can imagine that if we replace a solvent molecule by a solute molecule in the part of the lattice that initially contains solvent, and vice versa, then we change the *balance* of intermolecular forces. This is where the enthalpy of solution comes from.

Suppose that  $\epsilon_{11}$  is the energy associated with the intermolecular forces between nearest-neighbor solvent molecules,  $\epsilon_{22}$  is the energy associated with the forces between nearest-neighbor solute molecules, and  $\epsilon_{12}$  is the energy associated with the forces between a solute-solvent pair which are nearest neighbors to each other.<sup>2</sup> A typical convention would be that these energies are *negative*, with more negative values representing stronger intermolecular forces. Considering the initially segregated state described above, imagine that we swap a single solute and solvent pair in the lattice. Removing the solvent molecule from its environment would have an energetic cost of  $-z\epsilon_{11}$ . Similarly, removing the solute molecule from its environment would have an energetic cost of  $-z\epsilon_{22}$ .<sup>3</sup> Putting the solute molecule in the solvent environment then generates  $z$  new solute-solvent contacts, as does putting the solvent molecule in the solute environment. Thus, the energetic gain from these two operations is  $2z\epsilon_{12}$ . Overall, we have

$$2z\Delta\epsilon \approx z [2\epsilon_{12} - (\epsilon_{11} + \epsilon_{22})],$$

where the factor of 2 indicates that this is for the two molecules (one of solvent and one of solute), and the factor of  $z$  makes  $\Delta\epsilon$  the energy of solution per contact:

$$\Delta\epsilon \approx \epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22}). \tag{1}$$

Now we ask the question: How many solute-solvent contacts are there in the solution on average? Suppose that we focus on one particular solute molecule. The probability that any one of the nearest-neighbor lattice sites is occupied by a solvent molecule is  $N_1/(N_1 +$

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<sup>2</sup>We ignore longer-range intermolecular forces altogether.

<sup>3</sup>The assumption in this very simple model is that the solute and solvent are not only similar in size, but have identical coordination numbers. This is clearly the weakest part of the model for many solvent-solute systems.

$N_2 - 1) \approx N_1/(N_1 + N_2)$ , using the fact that  $N_1$  and  $N_2$  are both large. If we have a coordination number of  $z$ , then to the same degree of approximation, the average number of solute-solvent contacts per solute molecule should be just  $zN_1/(N_1 + N_2)$ . Since we have  $N_2$  solute molecules, the total number of contacts is therefore  $zN_1N_2/(N_1 + N_2)$ . Since each contact contributes  $\Delta\epsilon$  to the heat of solution, we have

$$\Delta_{\text{sol}}H = zN_1 \frac{N_2}{N_1 + N_2} \Delta\epsilon.$$

The fraction which occurs in this equation is obviously the mole fraction of the solute. However, since each lattice site has the same volume in our model, it is also the **volume fraction** of the solute,  $\phi_2$ :

$$\Delta_{\text{sol}}H = zN_1\phi_2\Delta\epsilon. \quad (2)$$

This is the **van Laar equation** for the heat of solution. This equation turns out to be a good initial approximation to the enthalpy of mixing, even when the solvent and solute are different in size. In fact, we will rederive it for polymers in the next lecture.

Equations 1 and 2 provide some important clues on the factors which will be important in determining the solubility. The main variable in the van Laar equation is  $\Delta\epsilon$ . This will be negative (favorable) whenever the solute and solvent have stronger interactions with each other than the average of the like-molecule interactions. If, on the other hand, like-molecule interactions are particularly strong for one of the two solutes, then the enthalpy of solution could be very positive, which would in turn make the free energy of solution positive. An example would arise if trying to dissolve a hydrocarbon in water. Hydrocarbons are nonpolar (or nearly so, depending on the geometry), so they are mostly subject to London dispersion forces. On the other hand, water molecules have very strong hydrogen bonding interactions with each other. Water-hydrocarbon interactions would mostly be due to dipole-induced dipole forces, which are much weaker than hydrogen bonding. Thus,  $\epsilon_{11}$  is very negative, and  $\epsilon_{12}$  is much smaller in magnitude, so hydrocarbons won't dissolve in water to any appreciable extent. If we add some alcohol groups to the hydrocarbon on the other hand, the solute will now be able to make hydrogen bonds as well. This will tend to make both  $\epsilon_{22}$  and  $\epsilon_{12}$  more negative. Depending on the number and placement of the alcohol groups, this may result in a decrease in  $\Delta\epsilon$ , particularly since  $\epsilon_{22}$  is weighted by a factor of  $\frac{1}{2}$ , which might eventually lead to solubility of the compound in water. For example, neither hexane nor 1-hexanol is very soluble in water, but hexanediols are.

## 2.2 Entropy of solution

The entropy of solution is almost embarrassingly easy to calculate using the Boltzmann formula. If we have an  $N_0$ -site lattice containing  $N_1$  molecules of solvent and  $N_2$  molecules of solute, the total number of microstates is

$$W = \frac{N_0!}{N_1!N_2!}.$$

The entropy is therefore

$$S = k \ln W = k (\ln N_0! - \ln N_1! - \ln N_2!).$$

The entropy of the original segregated arrangement is 0 (only one microstate), so  $\Delta_{\text{sol}}S = S$ . We can use Stirling's approximation to rewrite the factorials, as well as the relationship  $N_0 = N_1 + N_2$ :

$$\begin{aligned}\Delta_{\text{sol}}S &= k[(N_1 + N_2) \ln(N_1 + N_2) - (N_1 + N_2) - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2] \\ &= k \left[ N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right] \\ &= -k \left[ N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} \right]. \\ \therefore \Delta_{\text{sol}}S &= -k [N_1 \ln X_1 + N_2 \ln X_2],\end{aligned}\tag{3}$$

where  $X_1$  and  $X_2$  are the mole fractions of the solvent and solute, respectively. You may have derived an equation which looks identical to equation 3 in your previous courses in thermodynamics for the entropy of mixing of two gases. In fact, this equation turns up again and again when we mix two substances, regardless of the details of what is being mixed or how.

Note that  $\Delta_{\text{sol}}S$  is always positive, as we expect, since the mole fractions are, by definition, less than 1.

With a slight rearrangement, we can rewrite equation 3 as a function of  $X_2$  only, using the fact that  $X_1 + X_2 = 1$ :

$$\frac{\Delta_{\text{sol}}S}{N_1 + N_2} = -k [(1 - X_2) \ln(1 - X_2) + X_2 \ln X_2].$$

You can easily verify that this function reaches a maximum at  $X_2 = \frac{1}{2}$ . Thus

$$\Delta_{\text{sol}}S \leq k(N_1 + N_2) \ln 2.\tag{4}$$

For a given size of system, there is a maximum possible entropy of solution given by inequality 4.  $\Delta_{\text{sol}}H$  on the other hand is not subject to any particular bound, so the latter quantity is the one which determines the solubility of a compound in a solvent.

Finally note that, in the context of the lattice model,  $X_i = \phi_i$ , the volume fraction, so equation 3 can also be written

$$\Delta_{\text{sol}}S = -k [N_1 \ln \phi_1 + N_2 \ln \phi_2].$$

This form of the entropy of solution will reappear when we treat polymer solutions in the next lecture.

### Exercises

1. Prove inequality 4.
2. Prove that  $\Delta_{\text{sol}}G$  always becomes negative if  $\phi_2$  is sufficiently small. Is this physically reasonable?

Hint: Divide  $\Delta_{\text{sol}}G$  by  $N_1 + N_2$  and relate as many of the terms as possible to  $\phi_2$ .