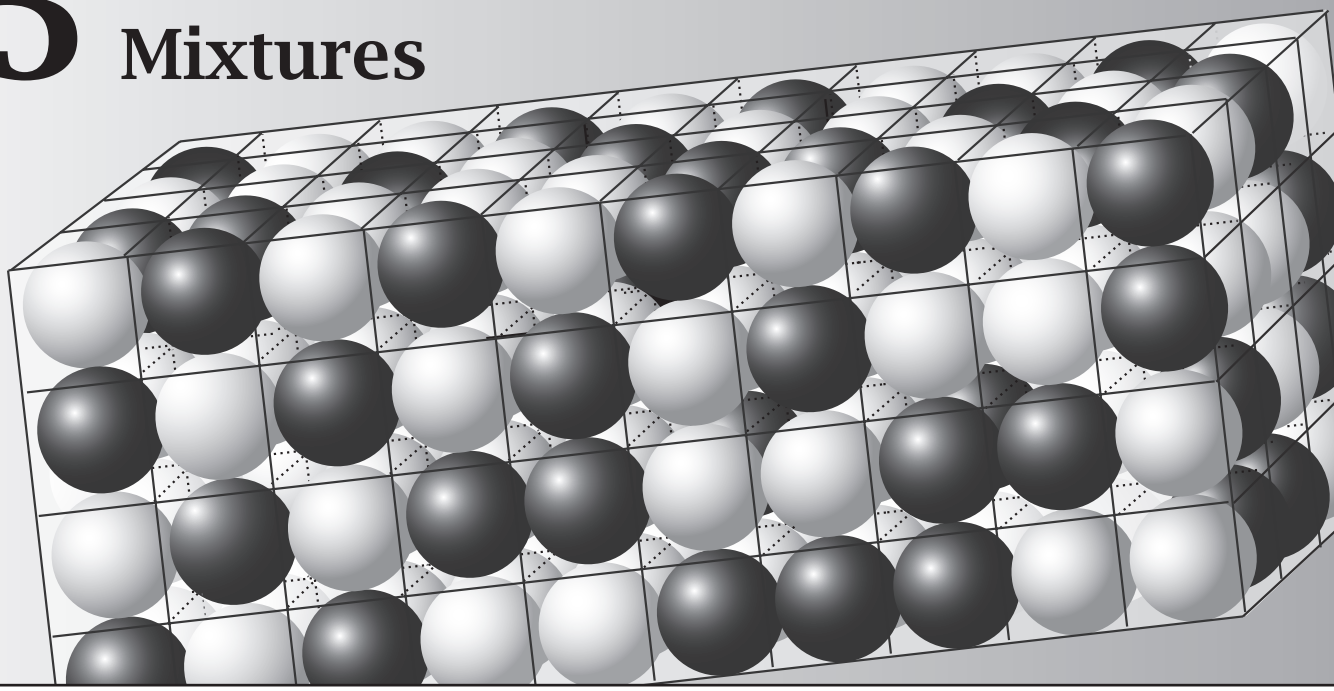
15 Solutions & Mixtures



A Lattice Model Describes Mixtures

In Chapter 14, we considered pure liquids or solids composed of a single chemical species. Here we consider *solutions*, i.e., homogeneous mixtures of more than one component. The fundamental result that we derive in this chapter, $\mu = \mu^\circ + kT \ln x$, is a relationship between a molecule's chemical potential μ and its concentration x in the solution. This relationship will help address questions in Chapters 16 and 25–31: When does one chemical species dissolve in another? When is it insoluble? How do solutes lower the freezing point of a liquid, elevate the boiling temperature, and cause osmotic pressure? What forces drive molecules to partition differently into different phases? We continue with the lattice model because it gives simple insights and because it gives the foundation for treatments of polymers, colloids, and biomolecules.

We use the $(T, V, \mathbf{N})$ ensemble, rather than $(T, p, \mathbf{N})$, because it allows us to work with the simplest possible lattice model that captures the principles of solution theory. The appropriate extremum principle is based on the Helmholtz free energy $F = U - TS$, where S is the entropy of solution and U accounts for the interaction energies between the lattice particles.

The Entropy of Solution

Suppose there are N_A molecules of species A and N_B molecules of species B. Particles of A and B are the same size—each occupies one lattice site—and

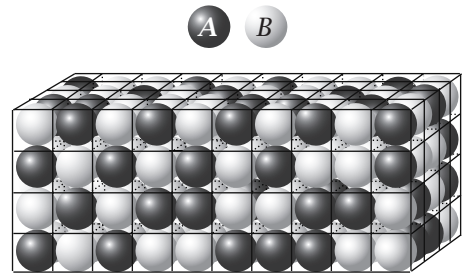


Figure 15.1 A lattice mixture of two components A and B. The number of A's is N_A and the number of B's is N_B. The total number of lattice sites is $N = N_A + N_B$. All sites are filled.

together they completely fill a lattice of N lattice sites (see Figure 15.1):

$$N = N_A + N_B. \tag{15.1}$$

(See Chapter 32 for the Flory–Huggins treatment for particles of different sizes, such as polymers in simple solvents.)

The multiplicity of states is the number of spatial arrangements of the molecules:

$$W = \frac{N!}{N_A! N_B!}. \tag{15.2}$$

The translational entropy of the mixed system can be computed by using the Boltzmann equation (5.1), $S = k \ln W$, and Stirling's approximation, Equation (B.3):

$$\begin{aligned}
\Delta S_{\text{solution}} &= k(N \ln N - N_A \ln N_A - N_B \ln N_B) \\
&= k(N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B) \\
&= -Nk\left[\frac{N_A}{N} \ln\left(\frac{N_A}{N}\right) + \frac{N_B}{N} \ln\left(\frac{N_B}{N}\right)\right] \\
&= -k\,(N_A \ln x_A + N_B \ln x_B). \qquad (15.3)
\end{aligned}$$

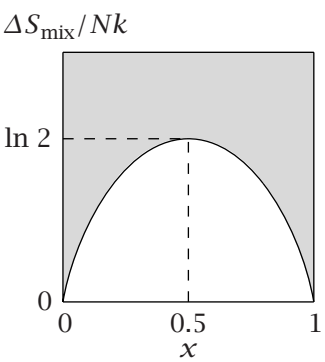


Figure 15.2 The entropy of solution as a function of the mole fraction x.

This entropy can be expressed in terms of the relative *concentrations* of A and B. We will express concentrations as *mole fractions* $x = N_A/N$ and $(1-x) = N_B/N$. Equation (15.3) gives the entropy of solution of a binary (two-component) solution as

$$\frac{\Delta S_{\text{solution}}}{Nk} = -x \ln x - (1-x) \ln(1-x). \tag{15.4}$$

Figure 15.2 shows how the entropy of solution $\Delta S_{\text{solution}}/Nk$ depends on x, the mole fraction of A, according to Equation (15.4).[1] The process is illustrated in Figure 15.3. Put N_A molecules of A into a container that has N_B molecules of B. The composition x is now fixed. If the two materials did not mix with each other, there would be no change in the entropy, relative to the two pure fluids: $\Delta S_{\text{solution}} = 0$. If the two materials do mix in the random way that we have assumed, the entropy will increase from 0, for the unmixed state, to $\Delta S_{\text{solution}}(x)$, the value shown for that particular composition x in Figure 15.2.

[1] $\Delta S_{\text{solution}}$ is often called the 'mixing entropy,' but the entropy actually arises from the greater volume available to each particle type [1]: N_A particles of A begin in N_A sites and end up distributed in $N_A + N_B$ sites, for example.

The components mix because of the multiplicity of ways of intermingling the A's with the B's. This is the driving force that causes atoms and molecules to mix.

Don't confuse x with a degree of freedom. The system doesn't change its composition toward $x = 1/2$ to reach the highest entropy. x is the composition that is fixed by the number of A and B molecules put into the solution. The solution entropy is maximal at $x = 1/2$ because this is the solution composition that gives the highest multiplicity of all possible compositions. Also, note that this entropy arises from arrangements of particles at fixed overall density and not from the mixing of holes and particles that we used to describe gas pressures.

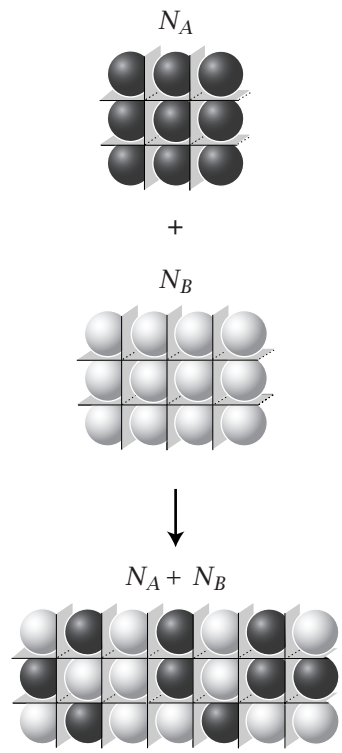


Figure 15.3 Mixing is a process that begins with N_A molecules of pure A and N_B molecules of pure B, and combines them into a solution of $N_A + N_B$ molecules.

EXAMPLE 15.1 Mixing entropy (entropy of solution). For a solution containing a mole fraction of 20% methanol in water, compute the entropy of solution. Equation (15.4) gives

$$\frac{\Delta S_{\text{solution}}}{N} = R(-0.2\ln 0.2 - 0.8\ln 0.8)$$

$$= \left(1.987\,\text{cal}\,\text{K}^{-1}\,\text{mol}^{-1}\right)(0.5) \approx 1.0\,\text{cal}\,\text{K}^{-1}\,\text{mol}^{-1}$$

If there were no interaction energy, the free energy of solution at $T = 300\,\text{K}$ would be

$$\frac{\Delta F_{\text{solution}}}{N} = \frac{-T\Delta S_{\text{solution}}}{N}$$

$$= -300\,\text{cal}\,\text{mol}^{-1}.$$

Ideal Solutions

A solution is called *ideal* if its free energy of solution is given by $\Delta F_{\text{solution}} = -T\,\Delta S_{\text{solution}}$, with $\Delta S_{\text{solution}}$ taken from Equation (15.4). Mixing an ideal solution involves no change in energy. And it involves no other entropies due to changes in volume, or structuring, or ordering in the solution. Chapter 25 describes solubility and insolubility in more detail. Now we move to a model of mixtures that is more realistic than the ideal solution model.

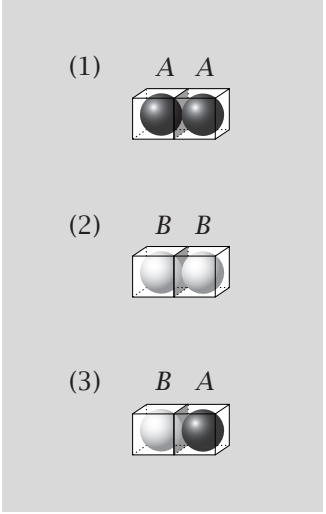


Figure 15.4 Three types of contact (or bond) occur in a lattice mixture of components A and B.

The Energy of Solution

In practice, few solutions are truly ideal. Real solutions involve energies of solution. In the lattice model, the total energy of solution is the sum of the contact interactions of noncovalent bonds of all the pairs of nearest neighbors in the mixture. For a lattice solution of components A and B, Figure 15.4 shows the three possible types of contact: an AA bond, a BB bond, or an AB bond. There are no other options, because the lattice is completely filled by A's and B's.

The total energy of the system is the sum of the individual contact energies over the three types of contact:

$$U = m_{AA}w_{AA} + m_{BB}w_{BB} + m_{AB}w_{AB}, \tag{15.5}$$

where m_{AA} is the number of AA bonds, m_{BB} is the number of BB bonds, m_{AB} is the number of AB bonds, and w_{AA}, w_{BB}, w_{AB} are the corresponding contact energies. As noted in Chapter 14, the quantities w are negative.

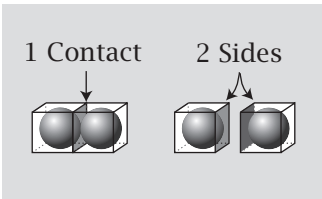


Figure 15.5 One contact between lattice particles involves two lattice site sides.

In general, the numbers of contacts, m_{AA}, m_{BB}, and m_{AB}, are not known. To put Equation (15.5) into a more useful form, you can express the quantities m in terms of N_A and N_B, the known numbers of A's and B's. Each lattice site has z 'sides,' just as in Chapter 14. Figure 15.5 shows that every contact involves two sides. The total number of sides of type A particles is zN_A, which can be expressed in terms of the numbers of contacts as

$$zN_A = 2m_{AA} + m_{AB}, \tag{15.6}$$

because the total number of A sides equals

$$(\text{number of } AA \text{ bonds}) \times \left(\frac{2\ A \text{ sides}}{AA \text{ bond}}\right) + (\text{number of } AB \text{ bonds}) \times \left(\frac{1\ A \text{ side}}{AB \text{ bond}}\right).$$

Similarly, for type B particles,

$$zN_B = 2m_{BB} + m_{AB}. \tag{15.7}$$

Solve Equations (15.6) and (15.7) for the number of AA bonds m_{AA} and for the number of BB bonds m_{BB}:

$$m_{AA} = \frac{zN_A - m_{AB}}{2} \qquad \text{and} \qquad m_{BB} = \frac{zN_B - m_{AB}}{2}. \tag{15.8}$$

Substitute Equations (15.8) into Equation (15.5) to arrive at an expression for the total interaction energy, in which the only unknown term is now m_{AB}, the number of AB contacts:

$$\begin{aligned} U &= \left(\frac{zN_A - m_{AB}}{2}\right) w_{AA} + \left(\frac{zN_B - m_{AB}}{2}\right) w_{BB} + m_{AB}w_{AB} \\ &= \left(\frac{zw_{AA}}{2}\right) N_A + \left(\frac{zw_{BB}}{2}\right) N_B + \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right) m_{AB}. \end{aligned} \tag{15.9}$$

Now we use the Bragg–Williams, or *mean-field*, approximation to evaluate m_{AB} [2–4].

The Mean-Field Approximation

Different arrangements of the system's particles will have different values of m_{AB}. In principle, we should consider each configuration of the system, and we should account for its appropriate Boltzmann weight (for more discussion, see page 278). This would lead to sophisticated models. Here we explore a much simpler approach that gives many of the same insights. We make an assumption, called the mean-field approximation, that for any given numbers N_A and N_B, the particles are mixed as randomly and uniformly as possible. This gives us a way to estimate m_{AB}.

Consider a specific site next to an A molecule. What is the probability that a B occupies that neighboring site? In the Bragg–Williams approximation, you assume that the B's are randomly distributed throughout all the sites. The probability p_B that any site is occupied by B equals the fraction of all sites that are occupied by B's:

$$p_B = \frac{N_B}{N} = x_B = 1-x. \tag{15.10}$$

Because there are z nearest-neighbor sites for each molecule of A, the average number of AB contacts made by that particular molecule of A is $zN_B/N = z(1-x)$. The total number of molecules of A is N_A, so

$$m_{AB} \approx \frac{zN_AN_B}{N} = zNx(1-x). \tag{15.11}$$

Now compute the total contact energy of the mixture from the known quantities N_A and N_B by substituting Equation (15.11) into Equation (15.9):

$$\begin{aligned} U &= \left(\frac{zw_{AA}}{2}\right)N_A + \left(\frac{zw_{BB}}{2}\right)N_B + z\left(w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right)\frac{N_AN_B}{N} \\ &= \left(\frac{zw_{AA}}{2}\right)N_A + \left(\frac{zw_{BB}}{2}\right)N_B + kT\chi_{AB}\frac{N_AN_B}{N}, \end{aligned} \tag{15.12}$$

where we define a dimensionless quantity called the **exchange parameter** χ_{AB}:

$$\chi_{AB} = \frac{z}{kT}\left(w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right) \tag{15.13}$$

(see also page 275).

How does the Bragg–Williams approximation err? If AB interactions are more favorable than AA and BB interactions, then B's will prefer to sit next to A's more often than the mean-field assumption predicts. Or, if the self-attractions are stronger than the attractions of A's for B's, then A's will tend to cluster together, and B's will cluster together, more than the random mixing assumption predicts. Nevertheless, the Bragg–Williams mean-field expression is often a reasonable first approximation.

The Free Energy of Solution

Now combine terms to form the free energy $F = U - TS$, using Equation (15.3) for the entropy and Equation (15.12) for the energy:

$$\begin{aligned} \frac{F(N_A,N_B)}{kT} &= N_A\ln\left(\frac{N_A}{N}\right) + N_B\ln\left(\frac{N_B}{N}\right) \\ &\quad + \left(\frac{zw_{AA}}{2kT}\right)N_A + \left(\frac{zw_{BB}}{2kT}\right)N_B + \chi_{AB}\frac{N_AN_B}{N}. \end{aligned} \tag{15.14}$$

$F(N_A,N_B)$ is the free energy of a mixed solution of N_A A's and N_B B's, totaling $N = N_A + N_B$ particles.

Typically, we are interested in the free energy *difference* between the mixed final state and the initial pure states of A and B, $\Delta F_{\text{solution}}$ (see Figure 15.3):

$$\Delta F_{\text{solution}} = F(N_A,N_B) - F(N_A,0) - F(0,N_B). \tag{15.15}$$

$F(N_A, 0) = zw_{AA}N_A/2$ is the free energy of a pure system of N_A A's, which is found by substituting $N = N_A$ and $N_B = 0$ into Equation (15.14). Similarly, $F(0, N_B) = zw_{BB}N_B/2$ is the free energy of a pure system of N_B B's. $F(N_A, N_B)$, the free energy of the mixed final state, is given by Equation (15.14). Substitute these three free energy expressions into Equation (15.15) and divide by N to get the free energy of solution in terms of the mole fraction x and the interaction parameter χ_{AB}:

$$\frac{\Delta F_{\text{solution}}}{NkT} = x \ln x + (1-x)\ln(1-x) + \chi_{AB}x(1-x). \tag{15.16}$$

This model was first described by JH Hildebrand in 1929, and is called the *regular solution model* [5]. While ideal solutions are driven only by the entropy of solution of particles of roughly equal size, regular solutions are driven also by the energy of the mean-field form described above. Solutions having free energies of solution of the form in Equation (15.16) are called regular solutions. Sometimes energies are more complicated than in this simple model: in electrolytes, for example; or when molecules are rod-shaped, as in solutions of liquid crystals; or when A has a very different size than B, as in polymer solutions. Polymers are described in the last chapters of this book. Here's an application of Equation (15.16).

EXAMPLE 15.2 Oil and water don't mix. Show that oil and water don't mix unless one component is very dilute. A typical value is $\chi \approx 5$ for hydrocarbon/water interactions. If $x_{\text{oil}} = 0.3$ and $T = 300\,\text{K}$, Equation (15.16) gives the free energy of solution as

$$\begin{aligned}\frac{\Delta F_{\text{solution}}}{N} &= [0.3\ln 0.3 + 0.7\ln 0.7 + 5(0.3)(0.7)](8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K}) \\ &= 1.1\,\text{kJ}\,\text{mol}^{-1}.\end{aligned}$$

Because this value is positive, it predicts that oil and water won't mix to form a random solution of this composition. If the oil is very dilute, $x_{\text{oil}} = 10^{-4}$, then

$$\begin{aligned}\frac{\Delta F_{\text{solution}}}{N} &= \left[10^{-4}\ln 10^{-4} + 0.9999\ln 0.9999 + 5(10^{-4})(0.9999)\right] \\ &\quad \times (8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K}) = -1.3\,\text{J}\,\text{mol}^{-1},\end{aligned}$$

which is negative, so mixing is favorable.

In general, determining solubility is not as simple as these calculations imply, because another option is available to the system—it may separate into phases with different compositions. Phase separation, for which this model is a starting point, is described in Chapter 25.

The Chemical Potentials

The chemical potential for A in this lattice model of a two-component mixture is found by taking the derivative $\mu_A = (\partial F/\partial N_A)_{T,N_B}$ (see Equation (9.31)) of F

(Equation (15.14)) with respect to N_A, holding N_B (not N) constant:

$$\begin{aligned}\frac{\mu_A}{kT} &= \left[\frac{\partial}{\partial N_A}\left(\frac{F}{kT}\right)\right]_{T,N_B} \\ &= \ln\left(\frac{N_A}{N}\right) + 1 - \frac{N_A}{N} - \frac{N_B}{N} + \frac{zw_{AA}}{2kT} + \chi_{AB}\frac{(N_A+N_B)N_B - N_AN_B}{(N_A+N_B)^2} \\ &= \ln x_A + \frac{zw_{AA}}{2kT} + \chi_{AB}(1-x_A)^2. \qquad (15.17)\end{aligned}$$

Similarly, the chemical potential for B is

$$\frac{\mu_B}{kT} = \left[\frac{\partial}{\partial N_B}\left(\frac{F}{kT}\right)\right]_{T,N_A} = \ln x_B + \frac{zw_{BB}}{2kT} + \chi_{AB}(1-x_B)^2. \qquad (15.18)$$

The main result is an equation of the form

$$\mu = \mu^\circ + kT\ln \gamma x, \qquad (15.19)$$

where γ (not to be confused with the surface tension) is called the *activity coefficient*.

The lattice model leads to a small ambiguity. In principle, our degrees of freedom are (T, V, N_A, N_B). But the volume is not independent of the total particle number because the lattice is fully filled and constrained by $N_A + N_B = N$. Because the lattice contains no empty sites, this model does not treat pV effects. We regard the relevant constraints as (T, N_A, N_B) and neglect the pV term. This is why you hold N_B constant, rather than N, when taking the derivative with respect to N_A.

Equations (15.17)–(15.19) provide the foundation for our treatment of mixing, solubility, partitioning, solvation, and colligative properties in Chapter 16. We will find that the chemical potential describes the escaping tendency for particles to move from one phase or one state to another. Particles are driven by at least two tendencies. First particles of A tend to leave regions of high concentration of A and move toward regions of low concentration of A to gain solution entropy (this is described by the term $kT\ln x$). Second, particles of A are attracted to regions or phases for which they have high chemical affinity, described in the next chapter by the quantities μ° and χ_{AB}.

What's the physical interpretation of the exchange parameter χ_{AB}? From the steps leading to Equation (15.13), you can determine that χ_{AB} describes the energetic cost of beginning with the pure states of A and B and transferring one B into a medium of pure A's and one A into a medium of pure B's (see Figure 15.6):

$$\tfrac{1}{2}z(AA) + \tfrac{1}{2}z(BB) \longrightarrow z(AB), \qquad \text{and} \qquad \chi_{AB} = -\ln K_{\text{exch}}, \qquad (15.20)$$

where K_{exch} is the equilibrium constant for the exchange process. Think of the A's as little boys at a dance and the B's as little girls at a dance. When $\chi_{AB} > 0$, it means the boys and girls don't want to mix. The larger the value of χ_{AB}, the more they don't want to mix. On the other hand, *older* boys and girls at a dance *do* want to mix, so in those cases $\chi_{AB} < 0$. When $\chi_{AB} = 0$, it means there is no preference either way, and mixing happens freely. χ_{AB} does not include the translational entropy, so imagine beginning this exchange by choosing a particular A and B located at fixed spatial positions in their respective media.

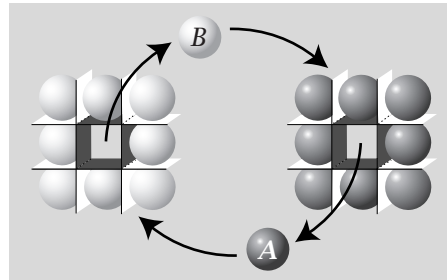


Figure 15.6 The quantity $2\chi_{AB}$ is the energy divided by kT for the process that begins with pure components A and B, and exchanges an A for a B.

If this process is favorable in the direction of the arrow in Equation (15.20) and Figure 15.6, $K_{\text{exch}} > 1$. In that case, χ_{AB}, which has units of energy divided by kT, is negative. According to *Hildebrand's principle*, for most systems the AB affinity is weaker than the AA and BB affinities, so usually $\chi_{AB} > 0$. The quantity χ_{AB} also contributes to the interfacial free energy between two materials, which we take up in the next section.

In the next few chapters, we apply this theory of mixtures to liquids. However, this lattice theory is also widely used for studying properties of solids. For example, metal alloys are mixtures of metals: *brass* is copper and zinc; *bronze* is tin and copper; *solder*, used in electronics, is tin and lead; and *sterling silver* is mostly silver with a little copper. Metals are driven by the solution entropy to form these alloys.

Interfacial Tension Describes the Free Energy of Creating Surface Area

The boundary between two condensed phases is an *interface*. The interfacial tension γ_{AB} is the free energy cost of increasing the interfacial area between phases A and B. If γ_{AB} is large, the two media will tend to minimize their interfacial contact. Let's determine γ_{AB} by using the lattice model for molecules of types A and B that are identical in size.

Suppose there are N_A molecules of A, n of which are at the interface, and there are N_B molecules of B, n of which are at the interface in contact with A (see Figure 15.7). (Because the particles have the same size in this model, there will be the same number n of each type for a given area of interfacial contact). The total energy of the system is treated as it was for surface tension

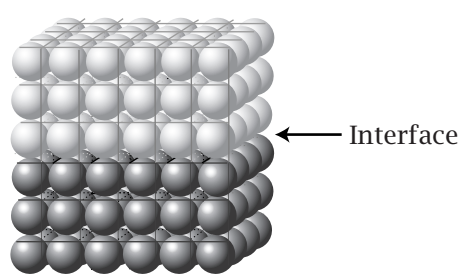


Figure 15.7 Lattice model of interfacial tension.

(see Equation (14.26)), with the addition of n AB contacts at the interface:

$$U = (N_A - n)\left(\frac{zw_{AA}}{2}\right) + n\left(\frac{(z-1)w_{AA}}{2}\right) + nw_{AB}$$
$$+ (N_B - n)\left(\frac{zw_{BB}}{2}\right) + n\left(\frac{(z-1)w_{BB}}{2}\right). \tag{15.21}$$

Because the entropy of each bulk phase is zero according to the lattice model, the interfacial tension is defined by

$$\gamma_{AB} = \left(\frac{\partial F}{\partial \mathcal{A}}\right)_{N_A,N_B,T} = \left(\frac{\partial U}{\partial \mathcal{A}}\right)_{N_A,N_B,T} = \left(\frac{\partial U}{\partial n}\right)_{N_A,N_B,T}\left(\frac{dn}{d\mathcal{A}}\right), \tag{15.22}$$

where $\mathcal{A}$ is the total area of the surface in lattice units. You have $dn/d\mathcal{A} = 1/a$, where a is the area per molecule exposed at the surface. Take the derivative $(\partial U/\partial n)$ using Equation (15.21):

$$\left(\frac{\partial U}{\partial n}\right)_{N_A,N_B,T} = w_{AB} - \frac{w_{AA} + w_{BB}}{2}. \tag{15.23}$$

You can assemble an expression for γ_{AB} from Equations (15.13), (15.22), and (15.23):

$$\gamma_{AB} = \frac{1}{a}\left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right) = \left(\frac{kT}{za}\right)\chi_{AB}. \tag{15.24}$$

When there are no molecules of B, $w_{AB} = w_{BB} = 0$, and γ_{AB} reduces to the surface tension given by Equation (14.29), $-w_{AA}/2a$.

EXAMPLE 15.3 Estimating χ_{AB} from interfacial tension experiments. The interfacial tension between water and benzene at 20°C is 35 dyn cm^{-1}. Suppose $z = 6$ and the interfacial contact area of a benzene with water is about 3 Å × 3 Å= 9.0 Å^2. Determine χ_{AB} at 20°C. Equation (15.24) gives

$$\chi_{AB} = \frac{za\gamma_{AB}}{kT} = \frac{(6)(9\,\text{Å}^2)(35 \times 10^{-7}\,\text{J cm}^{-2})\left(\frac{1\,\text{cm}}{10^8\,\text{Å}}\right)^2}{(1.38 \times 10^{-23}\,\text{J K}^{-1})(293\,\text{K})} = 4.7.$$

χ_{AB} is a dimensionless quantity, and $RT\chi_{AB} = 11.3\,\text{kJ mol}^{-1} = 2.7\,\text{kcal mol}^{-1}$ is the exchange energy.

EXAMPLE 15.4 Where does the interfacial tension matter? Interfacial tension—from either covalent or noncovalent bonding—holds paint on walls and barnacles on ships. It holds your cells together so your body doesn't fall apart, and it helps snails and other slimy critters to crawl. Cell-adhesion proteins help hold cells to surfaces and other cells; they are critical in cancer. Water on your waxed car shapes itself into spherical beads to minimize its contact with the wax, because χ_{AB} between water and wax is large. Water beads are flatter on a rusty hood than a waxed hood, since χ_{AB} is smaller between water and rusty metal. Figure 15.8 shows how impurities in metals and other solids

can migrate to *grain boundaries* and *dislocations*, which are interfaces between different microparticles of solid materials. This can lead to weakening or breakage of solid materials, sometimes causing catastrophic structural failures of materials.

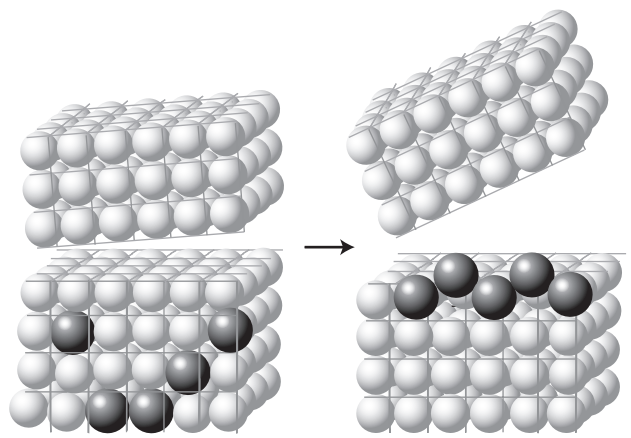


Figure 15.8 Impurity atoms (large dark spheres) in metals and solids (atoms shown as small spheres) can migrate to boundaries between individual crystals. This is a major source of the microscopic cracks and fractures that cause the weakening and breakage of solid materials.

What Have We Left Out?

There are two main ways in which our lattice model is a simplification. First, the partition function Q should be a sum over all the possible states of the system. It should be a sum of the number of states with small numbers of AB contacts, m_{AB}, and states with large m_{AB}, rather than a mean-field estimate of the number of uniformly mixed conformations (see Figure 15.9). In this way, we have made the approximation that

$$\begin{aligned} Q &= \sum_{m_{AB}} W(N_A, N_B, m_{AB}) e^{-E(N_A,N_B,m_{AB})/kT} \\ &\approx \frac{N!}{N_A!N_B!} e^{-U/kT}, \end{aligned} \tag{15.25}$$

where E is the energy of a configuration having m_{AB} contacts and W is the density of states, the number of configurations having the given value of m_{AB} (see page 177). U is the mean-field average energy from Equation (15.12).

The second approximation that we made was leaving out the quantum mechanical degrees of freedom: rotations, vibrations, and electronic configurations. Those degrees of freedom normally are the same in the pure phase as in the mixed phase. In *differences* of thermodynamic quantities, like $\Delta F_{\text{solution}}$, such terms cancel, so you are at liberty to leave them out in the first place. It is only the quantities that *change* in a process that need to be taken into account. Only the intermolecular interactions and the translational entropy change in simple mixing processes. But for chemical reactions in solution,

quantum mechanics contributes too (see Chapter 16). Taking internal degrees of freedom into account gives

$$Q = q_A^{N_A} q_B^{N_B} \sum_{m_{AB}} W(N_A, N_B, m_{AB}) e^{-E(N_A,N_B,m_{AB})/kT}$$

$$\approx q_A^{N_A} q_B^{N_B} \frac{N!}{N_A! N_B!} e^{-U/kT}, \tag{15.26}$$

where q_A and q_B are the partition functions for the rotations, vibrations, and electronic states of molecules A and B, respectively. Using $F = -kT \ln Q$ (Equation (10.42)) with Equation (15.26), you get a general expression for the free energy of solution that includes the quantum mechanical contributions in the mean-field lattice model:

$$\frac{F}{kT} = N_A \ln\left(\frac{N_A}{N}\right) + N_B \ln\left(\frac{N_B}{N}\right) + \left(\frac{zw_{AA}}{2kT}\right) N_A + \left(\frac{zw_{BB}}{2kT}\right) N_B$$

$$+ \chi_{AB} \frac{N_A N_B}{N} - N_A \ln q_A - N_B \ln q_B. \tag{15.27}$$

Similarly, the generalizations of Equation (15.17) for the chemical potential are

$$\frac{\mu_A}{kT} = \ln\left(\frac{x_A}{q_A}\right) + \frac{zw_{AA}}{2kT} + \chi_{AB}(1 - x_A)^2,$$

and

$$\frac{\mu_B}{kT} = \ln\left(\frac{x_B}{q_B}\right) + \frac{zw_{BB}}{2kT} + \chi_{AB}(1 - x_B)^2. \tag{15.28}$$

The quantum mechanical components cancel in quantities such as $\Delta F_{\text{solution}}$ when the internal degrees of freedom are unaffected by the mixing process. To see this, use Equation (15.27) to get the pure state components for Equation (15.15),

$$F(N_A, 0) = N_A[(zw_{AA}/2) - \ln q_A] \text{ and } F(0, N_B) = N_B[(zw_{BB}/2) - \ln q_B],$$

and subtract. You get the same result as in Equation (15.16):

$$\frac{\Delta F_{\text{solution}}}{NkT} = x \ln x + (1 - x) \ln(1 - x) + \chi_{AB} x(1 - x).$$

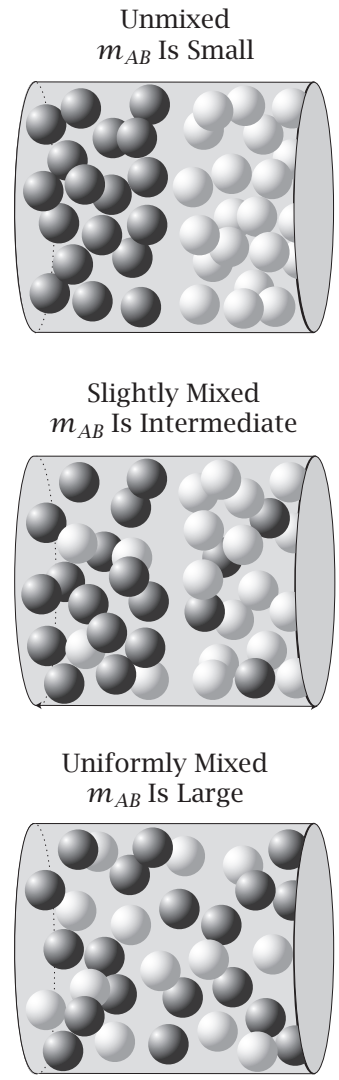


Figure 15.9 Particles of A and B can mix to different degrees to have different numbers m_{AB} of AB contacts. The partition function Q is a sum over all these states, but the mean-field model assumes uniform mixing.

Summary

We have developed a model for the thermodynamic properties of ideal and regular solutions. Two components A and B will tend to mix because of the favorable entropy resulting from the many different ways of interspersing A and B particles. The degree of mixing also depends on whether the AB attractions are stronger or weaker than the AA and BB attractions. In the next chapters, we will apply this model to the properties of solutions.

Problems

1. Ternary lattice mixtures. Consider a lattice model liquid mixture of three species of spherical particles: A, B, and C. As with binary mixtures, assume that all $N = n_A + n_B + n_C$ sites are filled.

(a) Write an expression for the entropy of solution.
(b) Using the Bragg–Williams approximation, write an expression for the energy U of solution in terms of the binary interaction parameters χ.
(c) Write an expression for the chemical potential μ_A of A.

2. Enthalpy of solution. For a mixture of benzene and n-heptane having equal mole fractions $x = 1/2$ and temperature $T = 300\,\text{K}$, the enthalpy of solution is $\Delta H_{\text{solution}} = 220\,\text{cal mol}^{-1}$. Compute χ_{AB}.

3. Plot $\mu(x)$. Plot the chemical potential versus x for:

(a) $\chi_{AB} = 0$,
(b) $\chi_{AB} = 2$,
(c) $\chi_{AB} = 4$.

4. Limit of $x \ln x$ terms in solution entropies and free energies. What is the value of $x \ln x$ as $x \to 0$? What is the implication for the entropy of solution?

5. Hydrophobic entropy. The experimentally determined total entropy of dissolving benzene in water at high dilution is approximately $14\,\text{cal K}^{-1}\,\text{mol}^{-1}$ at $T = 15°\text{C}$.

(a) How does this total entropy compare with the solution entropy component?
(b) Speculate on the origin of this entropy.

6. Solubility parameters. The quantity χ_{AB} describes AB interactions relative to AA and BB interactions. If instead of a two-component mixture, you had a mixture of N different species $A, B, \ldots$, then, to obtain the pairwise quantities χ_{ij} for all of them, you would need $\sim N^2$ experiments involving mixtures of all the components $i = 1, 2, \ldots, N$ with all the components $j = 1, 2, \ldots, N$. However, sometimes this can be much simpler. If all the species are nonpolar, you can make the approximation $w_{AB} \approx \sqrt{w_{AA} w_{BB}}$ (see Chapter 24). Show how this reduces the necessary number of experiments to only ~N.

7. Self-assembly of functional electrical circuits. G Whitesides and colleagues have pioneered the formation of nano- and mesoscale structures based on the self-assembly of patterned components [6]. Consider a circuit made from the self-assembly of N different building block components. When shaken up together, each component must find its proper place in a two-dimensional square lattice for the circuit to function correctly. Using Figure 15.10, suppose that if the letters are correctly ordered as on the left, each unit interacts pairwise with its neighbor through an interaction energy w_{match}. However, if a letter is surrounded by an incorrect neighbor, it interacts more weakly, with an energy w_{mismatch}. Find the contact energy difference

$$\Delta w = w_{\text{match}} - w_{\text{mismatch}},$$

necessary to ensure that the circuit can be reliably self-assembled. That is, the fraction of working circuits should be higher than δ, where δ is some small value. Ignore shape and surface effects (assume each of the N components makes $z = 4$ contacts) and only consider the equilibrium between a perfectly formed circuit and all possible misformed circuits in which two components have swapped places. Assume that N is large enough that the defective components are not in contact with one another.

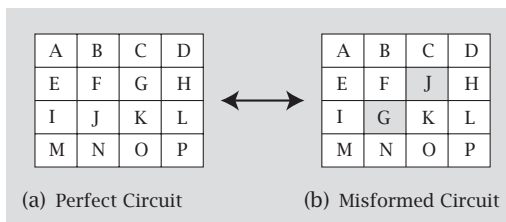


Figure 15.10 Comparing a correctly self-assembled two-dimensional circuit of parts with an incorrectly assembled circuit [6]. (a) A perfect Whitesides circuit. (b) One of the possible misformed Whitesides circuits.

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Suggested Reading

Excellent discussions of the lattice model of mixing:

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Good treatments of liquids, regular solutions, and surfaces:

JS Rowlinson and FL Swinton, *Liquids and Liquid Mixtures*, 3rd edition, Butterworth, London, 1982. A complete and extensive discussion of mixing, including much experimental data.

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