

17 Mixture Behavior, Stability, and Azeotropy

BASIC RELATIONS

As compounds mix to some degree in the liquid phase, the Gibbs energy of the system decreases toward a minimum at equilibrium. The Gibbs energy change obtained by forming a mixture starting from all the pure compounds can be written as

$$\Delta g_m \equiv g - g^0 = g - \sum_k x_k \mu_k^0 \quad (17.1)$$

The terms of Equation 17.1 can be written more explicitly as

$$\Delta g_m = \sum_1^c x_k (\bar{g}_k - g_k^0) = \sum_1^c x_k (\mu_k - \mu_k^0) = RT \sum_1^c x_k \ln \frac{f_k}{f_k^0} \quad (17.2)$$

For a binary system,

$$\frac{\Delta g_m}{RT} = x_1 \ln \frac{f_1}{f_1^0} + x_2 \ln \frac{f_2}{f_2^0} \quad (17.3)$$

Thus, expressing the fugacities in terms of the pure compound standard state, that is, defining the ideal behavior in Lewis's sense, from Equation 15.2 we write

$$\frac{\Delta g_m}{RT} = (x_1 \ln x_1 + x_2 \ln x_2) + (x_1 \ln \gamma_{1,0} + x_2 \ln \gamma_{2,0}) \quad (17.4a)$$

The first bracket of the right-hand side gives the contribution of the ideal mixture, Equation 15.19, and as both mole fractions are less than unity, its value is always negative. This suffices to prove that an ideal mixture is always a stable mixture. The second bracket gives the contribution of nonideality of the mixture, and it can be identified with the excess Gibbs energy in Lewis's sense, Equation 16.19. Thus,

$$\frac{\Delta g_m}{RT} = \frac{\Delta g_m^{id,0}}{RT} + \frac{g^E}{RT} \quad (17.4b)$$

POSITIVE AND NEGATIVE DEVIATIONS FROM IDEAL BEHAVIOR IN LEWIS'S SENSE

For negative deviations from ideality in Lewis's sense, $\gamma_{i,0} < 1$, the second bracket of the right-hand side of Equation 17.4a is also negative and makes the mixture still more stable than an ideal solution. For positive deviations from ideality in Lewis's sense, $\gamma_{i,0} > 1$, the second bracket of the right-hand side of Equation 17.4a is positive. If this contribution is large enough to overcome the contribution of the ideal mixture term, it produces instability, that is, liquid–liquid phase separation. A “good solvent” for a given compound should give negative deviations, ideal mixing, or at most weak positive deviations.

Although molecular effects are complex and resist generalizations, it is possible to establish some rules of thumb and be prepared to find exceptions. For the case of organic compounds, there are two main characteristics of their molecules that help in anticipating the behavior of their mixtures:

1. Length and shape of the hydrocarbon skeleton
2. Functional groups present

The effect of the functional group is so dominant that we classify the organic molecules in homologous families. In this respect, water can be considered the shortest alcohol, that is, an alcohol without a hydrocarbon chain. When mixing compounds, the group–group interactions govern the physical and chemical behavior of the mixture. Some group–group interactions are so strong as to cause a chemical reaction and the formation of new compounds. Good examples are the cases of groups COOH and OH, COO and H₂O, and CO and NH₂. We restrict our discussion here to nonre-active cases.

Large differences in the lengths of the hydrocarbon chains tend to give negative deviations. These are important in hydrocarbon–hydrocarbon systems, but they tend to be overshadowed by the larger effect of functional groups when these are present. The effect of the shape of the hydrocarbon skeleton is minor, and in most practical situations, it can be ignored. However, the effect of unsaturation in hydrocarbon structures may be important since unsaturated aliphatic compounds and also aromatic compounds can participate in electron donor–acceptor complexes and thus favor mixing.

BERG CLASSIFICATION OF LIQUIDS AND MIXTURE BEHAVIOR

Berg [1] proposed a classification of liquids in five groups that we extend here to six by differentiating between saturated and unsaturated hydrocarbons. The classification is based mostly on the capacity of the molecules to form hydrogen bonds and electron donor–acceptor complexes, but it also roughly orders the compounds on a scale of decreasing polarity. The modified Berg's classification is as follows:

- *Group 1:* Molecules forming tridimensional networks of H bonds. These are highly associated liquids, such as water, polyalcohols, polyphenols, hydroxyacids, amino alcohols, and amides.

- *Group 2:* Molecules having both active hydrogen atoms and electron donor atoms, such as O, N, and F. These are associated liquids, such as nitrocompounds and nitriles with hydrogen atoms in the α position (i.e., in the adjacent C atom) with respect to the N atom, nitromethane and acetonitrile, phenols, acids (including HCN, HF, HCl, and HNO₃), alcohols, and primary and secondary amines.
- *Group 3:* Molecules having electron donor atoms (O, N, and F) but not having an active hydrogen atom. Nitriles and nitrocompounds without α -hydrogen, esters, ketones, aldehydes, esters, tertiary amines, and so forth, are in this group.
- *Group 4:* Molecules having an active hydrogen atom but not an electron donor atom, such as O, N, or F. These are polychlorinated compounds with Cl and H in the same or in adjacent carbon atoms.
- *Group 5:* Unsaturated hydrocarbons, aliphatic or aromatic.
- *Group 6:* Saturated hydrocarbons.

From group 3 down, mixtures of compounds from the same group are close to ideal with slight positive deviations. Within a same group, positive deviations increase as the difference between the molecules increases. For example, a mixture of two ketones will be more ideal than a mixture of one ketone and one nitrile. Long hydrocarbon chains in both molecules of the same group tend to reduce the nonideality. If the molecules have similar vapor pressures, their mixtures can exhibit maximum-pressure azeotropes.

When mixing compounds of different groups from group 3 down, there are two cases deserving special mention. Members of group 3 mixed with members of group 4 will always give negative deviations from ideality. If their vapor pressures are similar, they can exhibit minimum-pressure azeotropes. Second, polar solvents from group 3 (and also from group 2), when mixed with members of group 5, give electron donor–acceptor complexes and thus favor solubility.

Groups 1 and 2 contain the most difficult “personalities” among the chemical species. When members of groups 1 or 2 are mixed with members of groups 4, 5, or 6 they always exhibit positive deviations that can be strong enough to cause liquid phase separation. When members of groups 1 and 2 are mixed with members of group 3, there can be either weak positive or weak negative deviations. And this is also the situation when mixing members of group 1 among themselves, members of group 2 among themselves, and members of group 1 with members of group 2. Negative deviations that lead to azeotropic behavior are found in mixtures of water with strong acids or other associating liquids of group 2 and also in mixtures of organic acids or phenols with amines or alcohols.

While negative deviations from ideality in Lewis’s sense produce stable mixtures, strong positive deviations may cause instability, leading to the separation of the mixture into two liquid phases. Typical examples of a binary system formed by two partially miscible compounds are the cases of butanol and water and the more extreme case of petroleum and water. However, even in the case of strong positive deviations, two liquid compounds are miscible to a minor extent. Starting from one of the liquid compounds pure (solvent), it is always possible to dissolve in it a small concentration

of the second liquid compound (solute). However, if the concentration of the solute is increased above a certain limit, the liquid mixture may split into two separate liquid phases. Each liquid phase will be rich in one of the components and lean in the other. In ternary or higher systems, the additional components will distribute between the two liquid phases formed.

PARTIAL MISCIBILITY

In the mixing process of two completely miscible liquid compounds, or in the miscibility regions of two partially miscible liquid compounds, that is, in the range where the mixture is stable, the Gibbs energy decreases toward equilibrium; thus, for the formation of a stable binary mixture the Gibbs energy change is necessarily negative,

$$\Delta g_m < 0$$

Figure 17.1 presents a plot $(\Delta g_m/RT)$ versus x showing that for a system in which the two compounds are totally miscible in all of the composition range, the slope of the curve $\Delta g_m/RT$ versus x increases continuously with an increase in x . Thus,

$$\frac{d}{dx} \left[\frac{d\Delta g_m/RT}{dx} \right]_T \geq 0$$

So, the criterion for the stability of a binary mixture can be written as

$$\left[\frac{\partial^2(\Delta g_m/RT)}{\partial x^2} \right]_T \geq 0 \quad (17.5)$$

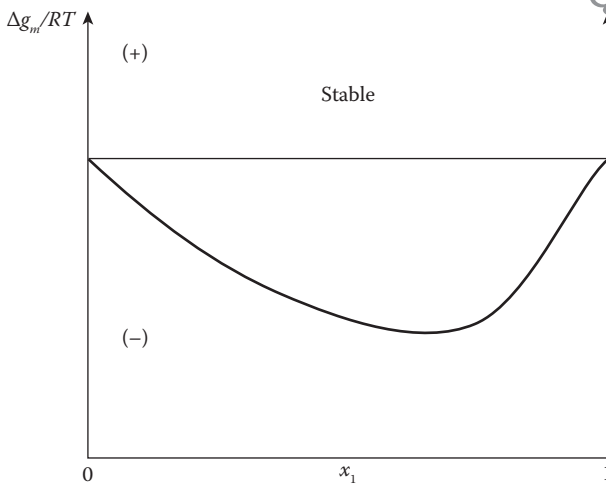


FIGURE 17.1 Stable system.

where x refers to x_1 or to x_2 . When Equation 17.5 is satisfied over all of the concentration range, the compounds are miscible in all proportions. Binary systems having strong positive deviations from ideality in Lewis's sense may exhibit immiscibility if Equation 17.5 fails to be satisfied. If this happens, the mixture will be unstable and split into two phases. This behavior is depicted in Figure 17.2, where between points 1 and 2, the slope of the curve of $(\Delta g_m/RT)$ versus x decreases with composition. In this case, the Gibbs energy of the system is less when there are two phases present instead of one.

For a binary liquid mixture, Equation 17.1 takes the form

$$\Delta g_m \equiv g - x_1\mu_1^0 - x_2\mu_2^0 \quad (17.1a)$$

Taking the second derivative with respect to either x_1 or x_2 , for the condition of stability we obtain

$$\left[\frac{\partial^2 \Delta g_m}{\partial x^2} \right]_T = \left[\frac{\partial^2 g}{\partial x^2} \right]_T \geq 0 \quad (17.6)$$

This result shows a very important conclusion; that is, both the plots of Δg_m versus x and g versus x convey the same information regarding a possible instability of the system. If at any concentration range the second derivative of the function becomes negative, that is, the curve presents an inflection point, the mixture becomes unstable and separates into two phases.

In Chapter 6, we discussed the relations between molar properties and partial molar properties, taking the molar volume as an example, but observing that the conclusions were also valid for all other molar and partial molar quantities. Hence, by analogy to what was shown in Figure 6.1, Figure 17.3 shows that a tangent line to

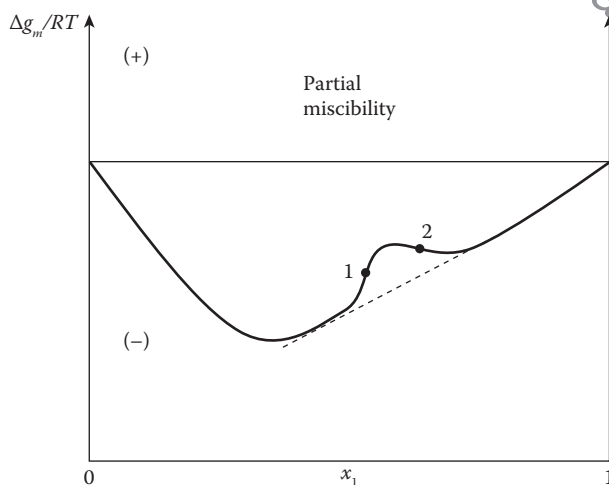


FIGURE 17.2 System showing instability gap k .

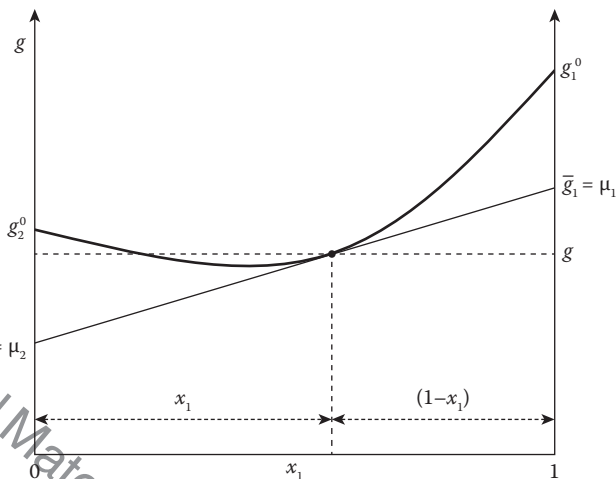


FIGURE 17.3 Stable binary system.

the curve of g versus x intercepts the vertical axis located at $x_1 = 0$ at a value equal to the chemical potential of compound 2, and the vertical axis located at $x_1 = 1$ at a value equal to the chemical potential of compound 1 at the particular composition where it touches the curve. If the curve of g versus x does not have any inflection point, the system presents complete miscibility in all the composition range. In this case, the slope of the curve with respect to x_1 will continuously increase with respect to an increase in x_1 or with respect to an increase of x_2 . However, if Equation 17.6 is not satisfied in some composition range, as shown in Figure 17.4, the tangent will touch the curve in two points representing two liquid phases of different compositions having identical values for the chemical potential of compound 1 and also identical values for the chemical potential of compound 2. Thus, if the condition for stability is not satisfied, the mixture will split into two liquid phases of different compositions.

The points of contact of the tangent line with the curve for the molar Gibbs energy, describing the compositions of the liquid phases at equilibrium, are called binodal points, and the inflection points are called spinodal points. For modeling purposes, it is of interest to relate stability to the excess Gibbs energy in the Lewis convention. From Equations 17.4b and 17.5, we conclude that to show *instability* in some range of composition, the following condition must be met:

$$\frac{\partial^2 \Delta g_m}{\partial x^2} = \frac{\partial^2 \Delta g_m^{id,0}}{\partial x^2} + \frac{\partial^2 g^E}{\partial x^2} < 0$$

or

$$\frac{\partial^2 g^E}{\partial x^2} < -\frac{\partial^2 \Delta g_m^{id,0}}{\partial x^2}$$

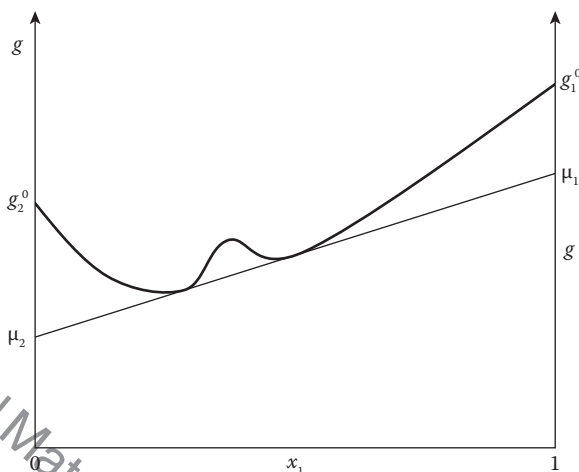


FIGURE 17.4 System showing instability gap.

Taking the second derivative of the contribution of the ideal mixture, Equation 15.19, with respect to either x_1 or x_2 , we obtain

$$\frac{\partial^2 \Delta g_m^{id,0}}{\partial x^2} = \frac{RT}{x_1 x_2}$$

As the right-hand side of this expression is always positive, we confirm that the ideal mixture is stable in all of the composition range. The most interesting conclusion, however, is obtained when we combine this later result with that obtained for the second derivative of the excess Gibbs energy and write that for *instability*,

$$\frac{\partial^2 g^E}{\partial x^2} < -\frac{RT}{x_1 x_2} \quad (17.7)$$

Equation 17.7 shows that in order to represent liquid–liquid separation in a binary system, that is, in order to represent *instability*, an excess Gibbs energy function must have a negative value of its second derivative *in at least part of the composition range*. This is equivalent to say that in some part of the composition range, excess Gibbs energy function must present two inflection points in which its derivative changes sign. Notably, the two-parameter expression of Wilson [2], which is one of the most successful for the representation of vapor–liquid equilibrium, fails to meet this condition, and thus it is unable to represent liquid–liquid equilibrium. In fact, for a binary system, the Wilson equation for the excess Gibbs energy can be written as

$$g_{Wilson}^E = -RT [x_1 \ln (x_1 + x_2 \Lambda_{12}) + x_2 \ln (x_1 \Lambda_{21} + x_2)]$$

where Λ_{12} and Λ_{21} are temperature dependent but composition independent adjustable binary parameters. Taking the second derivative of this expression, one obtains

$$\frac{\partial^2 [g^E]_{Wilson}}{\partial x^2} = RT \left[x_1 \frac{(1 - \Lambda_{12})^2}{(x_1 + x_2 \Lambda_{12})^2} + x_2 \frac{(1 - \Lambda_{21})^2}{(x_1 \Lambda_{21} + x_2)^2} \right]$$

The right-hand side of this expression is always positive, no matter the values of the binary parameters Λ_{12} and Λ_{21} . Hence, the Wilson equation in its two-parameter form cannot satisfy Equation 17.7.

CONDITION FOR STABILITY OF LIQUID MIXTURES

Particularly useful forms of the stability condition are those written in terms of the fugacities of the compounds. For clarity, before giving the final forms, we present three alternative formulations of the Gibbs–Duhem equation for a binary liquid mixture under isothermal conditions. From Equation 14.19, for this case we write

$$x_1 d \ln f_1 + x_2 d \ln f_2 = 0$$

and for an infinitesimal change in composition of the mixture,

$$x_1 \frac{d \ln f_1}{dx_1} + x_2 \frac{d \ln f_2}{dx_1} = 0 \quad (14.19a)$$

Replacing x_2 by $(1 - x_1)$ and rearranging, we write

$$x_1 \left[\frac{d \ln f_1}{dx_1} - \frac{d \ln f_2}{dx_1} \right] = \frac{d \ln f_2}{dx_2} \quad (14.19b)$$

while replacing x_1 by $(1 - x_2)$ in Equation 14.19a, we obtain

$$x_2 \left[\frac{d \ln f_1}{dx_1} - \frac{d \ln f_2}{dx_1} \right] = \frac{d \ln f_1}{dx_1} \quad (14.19c)$$

Taking the derivative of Equation 17.3 with respect to x_1 ,

$$\frac{d(\Delta g_m / RT)}{dx_1} = (\ln f_1 - \ln f_2) + \left(x_1 \frac{d \ln f_1}{dx_1} + x_2 \frac{d \ln f_2}{dx_1} \right) - (\ln f_1^0 - \ln f_2^0)$$

We recognize here that the second bracket of the right-hand side is null, according to Equation 14.19a above, and the third bracket is a constant, independent of composition. Thus, for the second derivative, the only important term is the first bracket. Hence,

$$\frac{d^2(\Delta g_m / RT)}{dx_1^2} = \frac{d \ln f_1}{dx_1} - \frac{d \ln f_2}{dx_1}$$

Comparison of this result with inequality (Equation 17.5) shows that the *condition for stability* can be written as

$$\left(\frac{d \ln f_1}{dx_1} - \frac{d \ln f_2}{dx_1} \right) > 0 \quad (17.8a)$$

or, equivalently, as $dx_1 = -dx_2$,

$$\left(\frac{d \ln f_1}{dx_1} + \frac{d \ln f_2}{dx_2} \right) > 0 \quad (17.8b)$$

Combining the inequality in Equation 17.8a with Equations 14.19b and 14.19c of the Gibbs-Duhem equation written above, for stability it is necessary that

$$\frac{d \ln f_1}{dx_1} > 0 \quad (17.9)$$

and

$$\frac{d \ln f_2}{dx_2} > 0 \quad (17.10)$$

According to the inequalities in Equations 17.9 and 17.10, in a stable liquid mixture the fugacity of a compound always increases with an increase in its concentration.

AZEOTROPY

For the purposes of this discussion, we start with Equation 16.4, which is valid at moderate conditions of temperature and pressure. Adding the equations for both compounds in a binary mixture, we obtain

$$P = x_1 \gamma_{1,0} P_1^s + x_2 \gamma_{2,0} P_2^s \quad (17.11)$$

For an ideal mixture, then,

$$P^{id} = x_1 P_1^s + x_2 P_2^s = P_2^s + (P_1^s - P_2^s) x_1$$

Thus, at constant temperature, in a plot of P versus x_1 , the equilibrium pressure of an ideal mixture will be a straight line. On the other hand, if the activity coefficients are larger than unity, that is, for positive deviations from ideality, the equilibrium pressure will be a curve above the straight line. If the activity coefficients are smaller than unity, that is, negative deviations from ideality, the equilibrium pressure will be a curve below the straight line. In an ideal solution, the different kinds of molecules do not distinguish each other and they mix without heat effects or volume change. In the case of positive deviations, the two compounds attract each other with forces that are weaker than those existing in an ideal solution. Similarly, in the case of negative deviations, the two compounds attract each other with forces that are stronger