



Choosing the reference state for each component to be the pure liquid (i.e., $G_1 = G_2 = 0$), the Gibbs energy of a single phase system simplifies to

$$G = \Delta G_{\text{mix}} = RT(x_1 \ln(x_1 \gamma_1) + x_2 \ln(x_2 \gamma_2)). \quad (13.3)$$

If the liquids are only partially miscible, then two phases are formed, phase I with composition $(x_1^{\text{I}}, x_2^{\text{I}})$, and phase II with composition $(x_1^{\text{II}}, x_2^{\text{II}})$. The number of moles in each phase are related by the mass-balance equations in the form of the familiar lever rule:

$$n^{\text{I}} = \frac{x_1 - x_1^{\text{II}}}{x_1^{\text{I}} - x_1^{\text{II}}}, \quad n^{\text{II}} = \frac{x_1^{\text{I}} - x_1}{x_1^{\text{I}} - x_1^{\text{II}}}.$$

Notice that $n^{\text{I}} + n^{\text{II}} = 1$ because we are working with a total of 1 mol. As an extensive property, the Gibbs free energy of the two-phase system is the sum of the two phases:

$$G^{\text{I+II}} = n^{\text{I}} G^{\text{I}} + n^{\text{II}} G^{\text{II}} = n^{\text{I}} G^{\text{I}} + (1 - n^{\text{I}}) G^{\text{II}}, \quad (13.4)$$

where G^{I} and G^{II} are the molar Gibbs free energies of each liquid phase. These are given by eq. (13.3) using the composition of the corresponding phase.

To decide whether the system forms a single phase or two liquid phases we compare the Gibbs free energy for each case:

- If $G < G^{\text{I+II}}$, the single-phase system is more stable;
- If $G > G^{\text{I+II}}$, the two-phase system is more stable.

To demonstrate the application of this criterion, we reanalyze the system methanol/carbon disulfide of Example 13.1. The Gibbs free energy of the solution is calculated from eq. (13.3) using the NRTL equation with the constants given in Example 13.1 and is plotted in Figure 13-2 as a function of the mol fraction of methanol.

Suppose that we mix 0.3 mol of methanol with 0.5 mol of ~~n-hexane~~. If the system forms a single phase, its state would be represented by point A on the Gibbs line. If it forms two phases, say, liquids B' and C', the overall state is represented by point A'. Points B' and C' lie on the Gibbs curve (both states are a single-phase liquid) and their composition satisfies the condition $x_{B'} < x_A < x_{C'}$. Point A' lies on the straight line that connects points B' and C'. The molar Gibbs energy that corresponds to this point (read off the vertical axis at point A') is the overall molar Gibbs energy of the two-phase system.¹ Comparing the two states, state A' has lower Gibbs energy. According to the Gibbs inequality, state A' is more stable than A. Liquid states B' and C' were selected arbitrarily in this trial. Many other

carbon disulfide

1. To convince yourself of this, look at eq. (13.4) and notice that $G^{\text{I+II}}$ moves on a straight line between G^{I} and G^{II} as n^{I} is varied between 1 and 0.

