When a two-liquid system is brought to boil, the vapor constitutes a third phase, which coexists with the two liquids. The equilibrium criterion at this point applies to all three phases, and thus we have,

$$\begin{array}{lllll} f_1^{\mathrm{I}} = f_1^{\mathrm{II}} = f_1^V & & x_1^{\mathrm{I}}\gamma_1^{\mathrm{I}}P_1^{\mathrm{sat}} = x_1^{\mathrm{II}}\gamma_1^{\mathrm{II}}P_1^{\mathrm{sat}} = y_1P, \\ & \Rightarrow & \\ f_2^{\mathrm{I}} = f_2^{\mathrm{II}} = f_2^V & & x_2^{\mathrm{I}}\gamma_2^{\mathrm{I}}P_2^{\mathrm{sat}} = x_2^{\mathrm{II}}\gamma_2^{\mathrm{II}}P_2^{\mathrm{sat}} = y_2P. \end{array} \tag{13.2}$$

These equations fix the equilibrium compositions of the three phases. As a consequence of these relationships, and as long as both liquid phases are present, the system boils as an azeotrope: the boiling temperature and the composition of all phases remain constant and the only change is that the vapor phase increases at the expense of the liquid. When one of the two liquids boils off completely, the system consists of a single liquid and a vapor and behaves as usual, namely, its boiling temperature and the composition of the two phases vary continuously as more liquid is converted into vapor.

To perform calculations with partially miscible liquids we need expressions for the activity coefficients. These may be calculated by any of the models discussed in Chapter 12, with the notable exception of the Wilson model, which is not capable of describing partially miscible liquids. If the activity coefficients are known, LLE and VLLE calculations are fundamentally no different from the VLE calculations discussed in the previous chapter.

Example 13.1: Solubility Limits Using Activity Coefficients

Methanol and carbon disulfide at 10 °C exhibit partial miscibility. The activity coefficients may be represented by the NRTL equation with $\alpha = 0.2$ and $\tau_{12} = 49.62R$, $\tau_{21} = 940.7R$, where R is the ideal-gas constant. Determine the composition of the equilibrium phases at 10 °C.

Solution Using $\alpha = 0.2$ and the values of τ_{ij} given in the problem statement we find

$$G_{12} = 0.96556, \quad G_{21} = 0.514543.$$

The corresponding NRTL expressions for the activity coefficients are

$$\ln\gamma_1 = \frac{0.870055(1-x_1)^2}{(0.503811\,(1-x_1)+x_1)^2} + \frac{0.222994(1-x_1)^2}{(1-0.0456573x_1)^2},$$

$$\ln\gamma_2 = \frac{1.72695x_1^2}{(0.503811\,(1-x_1)+x_1)^2} + \frac{0.212813x_1^2}{(1-0.0456573x_1)^2}.$$

To obtain the mutual solubility of methanol and carbon disulfide, we solve eq. (13.1) for x_1^{I} and x_1^{II} using these activity coefficients. This requires a numerical solution and it is best done using a mathematical package. The solution is

$$x_1^{\mathrm{I}} = 0.040724, \quad x_2^{\mathrm{II}} = 0.742787.$$

change subscript to "1"