

To confirm that these satisfy the equilibrium criterion we calculate the activity coefficients of methanol in the two phases:

$$\begin{aligned}\ln \gamma_1^{\text{I}} &= 19.9129, & \ln \gamma_1^{\text{II}} &= 1.09174, \\ \ln \gamma_2^{\text{I}} &= 1.01025, & \ln \gamma_2^{\text{II}} &= 3.76774.\end{aligned}$$

These indeed satisfy eq. (13.1):

$$\begin{aligned}\text{methanol:} & & (0.040724)(19.9129) & = & (0.742787)(1.09174) & = & 0.810932, \\ \text{carbon disulfide:} & & (1 - 0.040724)(1.01025) & = & (1 - 0.742787)(3.76774) & = & 0.969113.\end{aligned}$$

Therefore, the solubility of carbon disulfide in methanol at 10 °C is

$$x_1^{\text{I}} = 0.0407 = 4.07\% \text{ by mol,}$$

and the solubility of methanol in carbon disulfide is

$$x_2^{\text{I}} = 1 - 0.743 = 0.257 = 25.7\% \text{ by mol.}$$

*Comments* The numerical solution of eq. (13.1) requires some attention. These equations are always satisfied at  $x_1^{\text{I}} = x_1^{\text{II}}$  but such solutions are trivial and do not represent the composition of true coexisting phases. Trivial solutions must be identified and rejected, whenever the numerical method happens to converge to one of them.

## 13.2 Gibbs Free Energy and Phase Splitting

In practice it is useful to know before mixing whether we will obtain a homogeneous solution, or whether phase splitting will occur. One way to answer this question is suggested in the previous example: if eq. 13.1 has a nontrivial solution, the system phase separates into two liquids whose compositions are given by the solution to these equations. If no solution exists, then the liquids form a homogenous solution at all compositions. Alternatively, the determination of phase splitting can be done by examining the Gibbs energy of mixing. Recall that the equilibrium state of a system at fixed pressure and temperature has the minimum possible Gibbs free energy. With this in mind, we analyze the problem of phase splitting as follows. We form 1 mol of solution by mixing  $x_1$  mol of liquid component 1 and  $x_2$  mol of liquid component 2 ( $x_1 + x_2 = 1$ ). If components are fully miscible at this composition, the result is a single liquid with composition  $(x_1, x_2)$ . The Gibbs free energy of this single-phase system is

$$\begin{aligned}G &= G^{\text{id}} + G^{\text{E}} = \underbrace{x_1 G_1 + x_2 G_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)}_{G^{\text{id}}} + \underbrace{RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)}_{G^{\text{E}}} \\ &= x_1 G_1 + x_2 G_2 + \underbrace{RT(x_1 \ln(x_1 \gamma_1) + x_2 \ln(x_2 \gamma_2))}_{\Delta G_{\text{mix}}}.\end{aligned}$$