can be arranged in space; this term is also known as the combinatorial contribution. The second term on the right-hand side is the enthalpic contribution and arises from differences between polymer-polymer and polymer-solvent interactions; this term is also referred to as the residual contribution (not to be confused with the residual properties introduced earlier, which measure deviations from the ideal-gas state). Even if this term is zero (i.e., $\chi = 0$), the solution is nonideal due to the size difference between polymer and solvent.

UNIQUAC

The name of this model is an acronym of *universal quasichemical*, the name of the theory used to drive it. Like the Flory-Huggins model, UNIQUAC separates nonideal contributions to the excess Gibbs free energy into a combinatorial and a residual term:

$$\frac{G^{\mathrm{E}}}{RT} = g^{R} + g^{C}. \tag{12.46}$$

The combinatorial term accounts for differences in size and shape of the molecules and depends entirely on properties of the pure components. The residual term accounts for binary interactions and contains parameters characteristic for a pair of components. For binary solution these are given by the expressions

$$g^{C} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \frac{z}{2}\left(x_1 q_1 \ln \frac{\theta_1}{\Phi_1} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2} \right), \tag{12.47}$$

$$g^{R} = -q_1 x_1 \ln\left(\theta_1 \tau_{11} + \theta_2 \tau_{21}\right) - q_2 x_2 \ln\left(\theta_2 \tau_{12} + \theta_2 \tau_{22}\right). \tag{12.48}$$

The activity coefficients is also expressed as a sum of residual and combinatorial contributions,

are

$$\ln \gamma_i = \ln \gamma_i^{C} + \ln \gamma_i^{R}, \tag{12.49}$$

These terms are given by the following expressions:

$$\ln \gamma_1^{C} = \ln \frac{\Phi_1}{x_1} + 1 - \frac{\Phi_1}{x_1} - 5 q_1 \left(\ln \frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1} \right), \tag{12.50}$$

$$\ln \gamma_1^{R} = q_1 \left(1 - \ln(\theta_1 + \theta_2 \tau_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2 \tau_{12}}{\theta_1 \tau_{12} + \theta_2} \right), \tag{12.51}$$

with

$$\Phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2}, \tag{12.52}$$

$$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}, \tag{12.53}$$

$$\tau_{ij} = \exp\left(-a_{ij}/T\right). \tag{12.54}$$

Second printing corrections for Matsoukas, Fundamentals of Chemical Engineering Thermodynamics (9780132693066).