From Walas, Phase Equilibrium in Chemical Engineering, 1985

for Margules 3-suffix:

$(\gamma_1 x_1)^* = (\gamma_1 x_1)$

$(\gamma_2 x_2)^* = \gamma_2 x_2$

$\ln\gamma_1^* + \ln x_1^* = \ln\gamma_1 + \ln x_1$

$\ln\gamma_2^* + \ln x_2^* = \ln\gamma_2 + \ln x_2$

$\ln\gamma_1 = [A + (B-A)x_1]\,x_2^2$ Applies in both phases

$\ln\gamma_2 = [B + (A-B)x_2]\,x_1^2$

$$\ln(\gamma_1/\gamma_1^*) = \ln(x_1^*/x_1) = [A + 2(B-A)x_1]x_2^2 - [A + 2(B-A)x_1^*]x_2^{*2} \tag{7.30}$$

$$= A\left[x_2^2\left(1 + 2\left(\frac{B}{A} - 1\right)x_1\right) - x_2^{*2}\left(1 + 2\left(\frac{B}{A} - 1\right)x_1^*\right)\right], \tag{7.31}$$

$$\ln(\gamma_2/\gamma_2^*) = \ln\frac{1 - x_1^*}{1 - x_1} = (B + 2(A-B)x_2)x_1^2 - (B + 2(A-B)x_2^*)x_1^{*2} \tag{7.32}$$

$$= B\left[x_1^2\left(1 + 2\left(\frac{A}{B} - 1\right)x_2\right) - x_1^{*2}\left(1 + 2\left(\frac{A}{B} - 1\right)x_2^*\right)\right]. \tag{7.33}$$

When these equations are ratioed, A/B remains the only variable, which has been solved for by Carlson & Colburn (1942) as

$$\frac{A}{B} = \frac{2\alpha_2 \ln(x_2^*/x_2) + \beta_1 \ln(x_1^*/x_1)}{2\alpha_1 \ln(x_1^*/x_1) + \beta_2 \ln(x_2^*/x_2)}, \tag{7.34}$$

where

$$\alpha_i = x_i^2 - x_i^{*2} - x_i^3 + x_i^{*3}, \tag{7.35}$$

$$\beta_i = x_i^2 - x_i^{*2} - 2x_i^3 + 2x_i^{*3}. \tag{7.36}$$

After a numerical value of A/B has been found, it is substituted into Eq. 7.31 to find A and then into Eq. 7.33 to find B, or $B = A/(A/B)$.

The solution of the van Laar equations is found in a similar manner. Thus,

$$\ln(\gamma_1/\gamma_1^*) = \ln(x_1^*/x_1) = AB^2\left[\left(\frac{x_2}{Ax_1 + Bx_2}\right)^2 - \left(\frac{x_2^*}{Ax_1^* + Bx_2^*}\right)^2\right], \tag{7.37}$$

$$\ln(\gamma_2/\gamma_2^*) = \ln(x_2{}^*/x_2)$$

$$= A^2B\left[\left(\frac{x_1}{Ax_1 + Bx_2}\right)^2 - \left(\frac{x_1^*}{Ax_1^* + Bx_2^*}\right)^2\right]. \tag{7.38}$$

The ratio of the parameters is

$$\frac{A}{B} = \frac{\left(\dfrac{x_1}{x_2} + \dfrac{x_1^*}{x_2^*}\right)\left(\dfrac{\ln(x_1^*/x_1)}{\ln(x_2/x_2^*)}\right) - 2}{\dfrac{x_1}{x_2} + \dfrac{x_1^*}{x_2^*} - \dfrac{2x_1 x_1^* \ln(x_1^*/x_1)}{x_2 x_2^* \ln(x_2/x_2^*)}} \tag{7.39}$$

and the value of A is

$$A = \frac{\ln(x_1^*/x_1)}{\dfrac{1}{\left(1 + \dfrac{A}{B}(x_1/x_2)\right)^2} - \dfrac{1}{\left(1 + \dfrac{A}{B}(x_1^*/x_2^*)\right)^2}}. \tag{7.39a}$$

When more than one set of equilibrium compositions is at hand, some method of nonlinear regression may be used to find the parameters. A suitable objective function is

$$F(A, B) = \Sigma\,(\gamma_1 x_1 - \gamma_1^* x_1^*)_i^2 + \Sigma\,(\gamma_2 x_2 - \gamma_2^* x_2^*)_i^2 = \text{minimum}. \tag{7.40}$$