Tip 85 – MSE Density Parameter Update

Notes updated by Peiming Wang (OLI) March 11, 2009

In UNIQUAC term, the excess molar volume, v_{UNIQ}^{ex}, is assumed to be analogous to that of the excess Gibbs energy, i.e.

$$v_{UNIQ}^{ex} = -\left[\sum_i q_i x_i \, ln\left(\sum_j \theta_j \tau_{ji}^v\right)\right] \quad \text{(Combinatorial term omitted)} \qquad (1)$$

where τ_{ji}^v is a different interaction parameter from that of τ_{ji} in the g_{UNIQ}^{ex} model.

The symmetrically normalized v^{ex} (subscript *UNIQ* is omitted in the following text) needs to be converted to the unsymmetrically normalized value ($v^{ex,*}$) for density calculations in MSE.

Conversion from v^{ex} to $v^{ex,*}$:

Standard state chemical potentials in the two normalizations are related by

$$\mu_i^* = \mu_i^0 + RT \, ln \, \gamma_i^\infty \qquad (\text{or} \qquad \mu_i^* = \mu_i^0 + \mu_i^{ex,\infty})$$

which is derived from equality of chemical potentials in two normalizations, and using $\gamma_i^* = 1$ in the infinite dilution limit. Derivatives of μ_i's with respect to pressure give volumes, i.e.

$$\frac{\partial \mu_i^*}{\partial P} = \frac{\partial \mu_i^0}{\partial P} + \frac{\partial \mu_i^{ex,\infty}}{\partial P} \quad \Rightarrow \quad v_i^* = v_i^0 + v_i^{ex,\infty}$$

Here is how to calculate $v_i^{ex,\infty}$:

Analogous to $RT \, ln \, \gamma_i = \frac{\partial (ng^{ex})}{\partial n_i} = \mu_i^{ex}$, v_i^{ex} can be defined as $v_i^{ex} = \left(\frac{\partial (nv^{ex})}{\partial n_i}\right)_T$ and derived from Eq. (1) as:

$$v_i^{ex} = q_i\left[1 - ln\left(\sum_j \theta_j \tau_{ji}^v\right) - \sum_j \frac{\theta_j \tau_{ij}^v}{\sum_k \theta_k \tau_{kj}^v}\right] \qquad (2a)$$

At infinite dilution,

$$v_i^{ex,\infty} = v_i^{ex}\Big|_{x_i \to 0, x_w \to 1} = q_i\left(1 - ln \, \tau_{w,i}^v - \tau_{i,w}^v\right) \qquad (2b)$$

Now, $v^{ex,*}$ can be calculated from Eq. (3) by combining Eq (1) and (2b):

$$v^{ex,*} = v^{ex} + \sum_i x_i v_i^{ex,\infty} \qquad (3)$$

In Eq. (1) and (2),

$$\tau_{ji}^{v} = exp\left(-\frac{a_{ji}^{v}}{RT}\right) \qquad a_{ji}^{v} = a_{ji}^{v0} + a_{ji}^{v1}T + a_{ji}^{v2}T^{2}$$ (Correspond to D0JI, D1JI, D2JI)

Equation (3) is equivalent to the equation:

$$v^{ex,*} = v^{ex} - RT\sum_{i} x_i \left(\frac{\partial \ln \gamma_i^{\infty}}{\partial P}\right)_T \text{, with } \left(\frac{\partial \ln \gamma_i^{\infty}}{\partial P}\right)_{T,x} = -\frac{v_i^{ex,\infty}}{RT}$$

Solution volume is then calculated by

$$v = \sum_{i} x_i \bar{v}_i^{*} + v^{ex,*} \qquad (4)$$

Here $v^{ex,*}$ is calculated from contributions of UNIQUAC and “middle-range” terms, if applicable, and $\bar{v}_i^{*}$ is from either HKF or as described in 2002 paper for organic component.