Chemical Thermodynamics for Process Simulation
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Example 08.03 SLE of Benzene - Ethanol Using UNIQUAC

problem:

Calculate the solubility of benzene(2) in ethanol(1) at 260 K. The activity coefficients in the liquid phase should be taken into account by the UNIQUAC equation.

general constants and definitions:

$kPa := 1000Pa \qquad dm := 0.1m \qquad R := 8.31433 \frac{J}{K \cdot mol}$

input data

$ncomp := 2 \qquad i := 1 .. ncomp$

$T := 260K$

$T_{m_2} := 278.68K$

$\Delta h_{m_2} := 9952 \frac{J}{mol}$

$\Delta u := \begin{pmatrix} 0 & -43.04 \\ 384.09 & 0 \end{pmatrix} K$

$r := \begin{pmatrix} 2.1055 \\ 3.1878 \end{pmatrix}$

$q := \begin{pmatrix} 1.972 \\ 2.400 \end{pmatrix}$

Solution

First calculate the activity (x*γ) of solid benzene at T = 260K:

$$\ln x\gamma_2 := \frac{-\Delta h_{m_2}}{R \cdot T}\left(1 - \frac{T}{T_{m_2}}\right) \qquad \ln x\gamma_2 = -0.3086$$

$$x\gamma_2 := e^{\ln x\gamma_2} \qquad x\gamma_2 = 0.734$$

Now we need a function to calculate the activity coefficients as f(x,T) using UNIQUAC:

$$\gamma(x,T) := \left|\begin{array}{l}
\text{for } i \in 1..ncomp \\
\quad \text{for } j \in 1..ncomp \\
\qquad \tau_{i,j} \leftarrow e^{\frac{-\Delta u_{i,j}}{T}} \\
\text{for } i \in 1..ncomp \\
\quad \left|\begin{array}{l}
V_i \leftarrow \dfrac{r_i}{\sum_{j=1}^{ncomp} r_j \cdot x_j} \\
F_i \leftarrow \dfrac{q_i}{\sum_{j=1}^{ncomp} q_j \cdot x_j}
\end{array}\right. \\
\text{for } i \in 1..ncomp \\
\quad \left|\begin{array}{l}
\ln\gamma_i \leftarrow 1 - V_i + \ln(V_i) - 5 \cdot q_i \cdot \left(1 - \dfrac{V_i}{F_i} + \ln\left(\dfrac{V_i}{F_i}\right)\right) \ldots \\
\qquad + q_i \cdot \left(1 - \ln\left(\dfrac{\sum_{j=1}^{ncomp} q_j \cdot x_j \cdot \tau_{j,i}}{\sum_{j=1}^{ncomp} q_j \cdot x_j}\right) - \sum_{j=1}^{ncomp} \dfrac{q_j \cdot x_j \cdot \tau_{i,j}}{\sum_{k=1}^{ncomp} q_k \cdot x_k \cdot \tau_{k,j}}\right) \\
\gamma_i \leftarrow e^{\ln\gamma_i}
\end{array}\right. \\
\gamma
\end{array}\right.$$

We use the root function to find the mole fraction of component 2 for which the liquid activity is equal to the solid activity in the mole fraction range from 0 to 1. As a starting value we set the mole fraction to the solid activity.

$$x2 := x\gamma_2$$

$$x2 := \mathrm{root}\left[x\gamma_2 - \gamma\left[\begin{pmatrix} 1 - x2 \\ x2 \end{pmatrix}, T\right]_2 \cdot x2, x2, 0, 1\right] \qquad x2 = 0.244$$

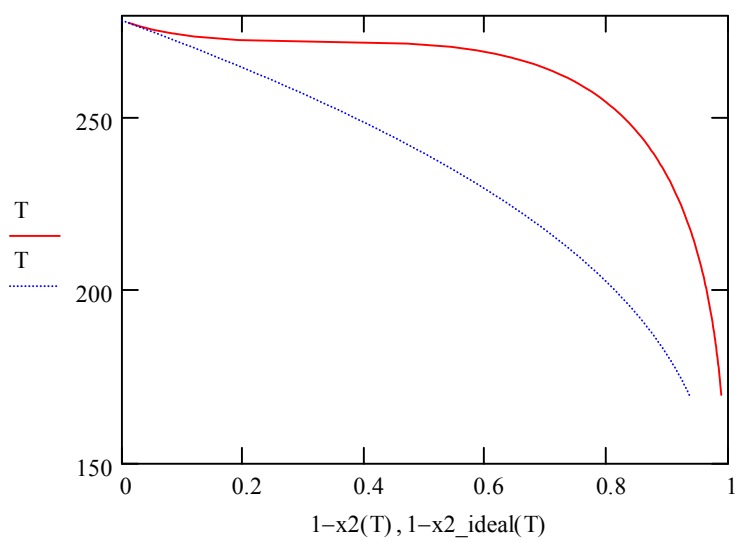
$$\gamma\left[\begin{pmatrix} 1 - x2 \\ x2 \end{pmatrix}, T\right]_2 = 3.016$$

For a graphical representation, this calculations can be defined as function of temperature

$$x\gamma_2(T) := \exp\left[\frac{-\Delta h_{m_2}}{R \cdot T}\left(1 - \frac{T}{T_{m_2}}\right)\right]$$

starting value for root

$$x := .5$$

$$x2(T) := \mathrm{root}\left[x\gamma_2(T) - \gamma\left[\begin{pmatrix} 1 - x \\ x \end{pmatrix}, T\right]_2 \cdot x, x, 0, 1\right] \qquad T := 170K .. 280K$$

$$x2_ideal(T) := x\gamma_2(T)$$