Example 05.22a VLE of Hexane-Butanone-2 Via UNIFAC - Step by Step

Calculate the vapor-liquid equilibrium of the system n-hexane (1) - 2-butanone (2) at 60°C for a mole fraction of x_1 = 0.5 with the help of the UNIFAC method assuming ideal behavior of the vapor phase.

System: n-hexane (1) - 2-butanon (2)

System temperature: $T := 333.15K$

Pure component vapor pressures: $Ps := \begin{pmatrix} 75.85 \\ 51.90 \end{pmatrix} kPa$

Composition: $x := \begin{pmatrix} .5 \\ .5 \end{pmatrix}$

Definitions: $kPa := 1000Pa$

$ncomp := 2$

$nmgroups := 2$

$nsgroups := 3$

$i := 1..2 \quad j := 1..2$

$k := 1..3 \quad m := 1..3 \quad n := 1..3$

Structural information:

Groups:

Subgroup 1	CH3	Maingroup 1	CH3
Subgroup 2	CH2	Maingroup 2	CH2CO
Subgroup 3	CH3CO		

Subgroup i belongs to maingroup $nord_i$:

$$nord := \begin{pmatrix} 1 \\ 1 \\ 2 \end{pmatrix}$$

Number of subgroups of type i in component j ($\nu_{i,j}$):

$$\nu := \begin{pmatrix} 2 & 1 \\ 4 & 1 \\ 0 & 1 \end{pmatrix}$$

R- and Q-values for subgroups:

$$R := \begin{pmatrix} 0.9011 \\ 0.6744 \\ 1.6724 \end{pmatrix} \qquad Q := \begin{pmatrix} 0.848 \\ 0.540 \\ 1.488 \end{pmatrix}$$

Interaction parameters between maingroups:

$$a := \begin{pmatrix} 0 & 0 & 476.4 \\ 0 & 0 & 476.4 \\ 26.76 & 26.76 & 0 \end{pmatrix} K \qquad \psi_{n,m} := \exp\left(-\frac{a_{n,m}}{T}\right) \qquad \psi = \begin{pmatrix} 1 & 1 & 0.239 \\ 1 & 1 & 0.239 \\ 0.923 & 0.923 & 1 \end{pmatrix}$$

Calculation of the combinatorial part (Guggenheim and Stavermann):

Relative van der Waals volume and surface of the components:

$$r_i := \sum_k \nu_{k,i} \cdot R_k \qquad r = \begin{pmatrix} 4.5 \\ 3.248 \end{pmatrix} \qquad q_i := \sum_k \nu_{k,i} \cdot Q_k \qquad q = \begin{pmatrix} 3.856 \\ 2.876 \end{pmatrix}$$

$$V_i := \frac{r_i}{\sum_j r_j \cdot x_j} \qquad V = \begin{pmatrix} 1.162 \\ 0.838 \end{pmatrix} \qquad F_i := \frac{q_i}{\sum_j q_j \cdot x_j} \qquad F = \begin{pmatrix} 1.146 \\ 0.854 \end{pmatrix}$$

$$\ln\gamma C_i := 1 - V_i + \ln(V_i) - 5 \cdot q_i \cdot \left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \qquad \ln\gamma C = \begin{pmatrix} -0.0099 \\ -0.0121 \end{pmatrix}$$

Calculation of the residual part:

Mixture:

Calculation of group fractions in the mixture:

$$XM_m := \frac{\sum_j \nu_{m,j} \cdot x_j}{\sum_j \sum_n \nu_{n,j} \cdot x_j} \qquad XM = \begin{pmatrix} 0.333 \\ 0.556 \\ 0.111 \end{pmatrix}$$

Calculation of group surface fractions in the mixture:

$$\theta M_m := \frac{Q_m \cdot XM_m}{\sum_n Q_n \cdot XM_n} \qquad \theta M = \begin{pmatrix} 0.378 \\ 0.401 \\ 0.221 \end{pmatrix}$$

Group activity coefficients in the mixture:

$$\ln\Gamma M_k := Q_k \cdot \left(1 - \ln\left(\sum_m \theta M_m \cdot \psi_{m,k} \right) - \sum_m \frac{\theta M_m \cdot \psi_{k,m}}{\sum_n \theta M_n \cdot \psi_{n,m}} \right) \qquad \ln\Gamma M = \begin{pmatrix} 0.08 \\ 0.051 \\ 0.929 \end{pmatrix}$$

Pure Components:

Calculation of group fractions in the pure components:

$$X_{m,i} := \frac{\nu_{m,i}}{\sum_n \nu_{n,i}} \qquad X = \begin{pmatrix} 0.333 & 0.333 \\ 0.667 & 0.333 \\ 0 & 0.333 \end{pmatrix}$$

Calculation of group surface fractions in the pure components:

$$\theta_{m,i} := \frac{Q_m \cdot X_{m,i}}{\sum_n Q_n \cdot X_{n,i}} \qquad \theta = \begin{pmatrix} 0.44 & 0.295 \\ 0.56 & 0.188 \\ 0 & 0.517 \end{pmatrix}$$

Group activity coefficients in the pure components:

$$\ln\Gamma_{k,i} := Q_k \cdot \left(1 - \ln\left(\sum_m \theta_{m,i} \cdot \psi_{m,k} \right) - \sum_m \frac{\theta_{m,i} \cdot \psi_{k,m}}{\sum_n \theta_{n,i} \cdot \psi_{n,m}} \right) \qquad \ln\Gamma = \begin{pmatrix} 0 & 0.29 \\ 0 & 0.185 \\ 2.243 & 0.262 \end{pmatrix}$$

$$\ln\gamma R_i := \sum_k \nu_{k,i} \cdot \left(\ln\Gamma M_k - \ln\Gamma_{k,i} \right) \qquad \ln\gamma R = \begin{pmatrix} 0.366 \\ 0.323 \end{pmatrix} \qquad \exp(\ln\gamma R) = \begin{pmatrix} 1.442 \\ 1.381 \end{pmatrix}$$

Calculation of the activity coefficients:

$$\ln\gamma_i := \ln\gamma C_i + \ln\gamma R_i \qquad \ln\gamma = \begin{pmatrix} 0.356 \\ 0.311 \end{pmatrix} \qquad \gamma_i := \exp(\ln\gamma_i) \qquad \gamma = \begin{pmatrix} 1.428 \\ 1.365 \end{pmatrix}$$

Calculation of the total pressure:

$$P := \sum_i x_i \cdot \gamma_i \cdot Ps_i \qquad P = 89.555\,kPa$$

Calculation of the vapor composition:

$$y_i := \frac{x_i \cdot \gamma_i \cdot Ps_i}{P} \qquad y = \begin{pmatrix} 0.605 \\ 0.395 \end{pmatrix}$$

Calculation of the K-factors:

$$K_i := \frac{y_i}{x_i} \qquad K = \begin{pmatrix} 1.209 \\ 0.791 \end{pmatrix}$$

Calculation of the separation factors:

$$\alpha_{i,j} := \frac{K_i}{K_j} \qquad \alpha = \begin{pmatrix} 1 & 1.529 \\ 0.654 & 1 \end{pmatrix}$$