Example 05.13 Azeotropic Points of the System Acetone - Methanol

problem:

Determine the azeotropic points of the system acetone (1) - methanol (2) at 50, 100 and 150°C by the ratio of the activity coefficients and vapor pressures using the Wilson equation. To simplify the calculation, the vapor phase should be treated as ideal, although this assumption will lead to higher deviations at 150°C.

general constants and definitions:

$$R_{gas} := 8.31433 \frac{J}{K \cdot mol} \qquad mmHg := \frac{1}{760} atm$$

input data

$$n_{comp} := 2 \qquad i := 1 .. n_{comp} \qquad j := 1 .. n_{comp} \qquad k := 1 .. n_{comp}$$

Azeotropes should be found at the following temperatures:

$$T1 := (50 + 273.15)K \qquad T2 := (100 + 273.15)K \qquad T3 := (150 + 273.15)K$$

Antoine constants of the components:

$$Ant := \begin{pmatrix} 7.1327 & 1219.97 & 230.653 \\ 8.08097 & 1582.27 & 239.7 \end{pmatrix}$$

Antoine function for vapor pressure calculation:

$$Ps(T, i) := 10^{\left(Ant_{i,1} - \frac{Ant_{i,2}}{\frac{T}{K} - 273.15 + Ant_{i,3}}\right)} mmHg$$

It should be noted that a correct prediction of the azeotropic behavior for this narrow boiling mixture requires a precise description of the pure component vapor pressures. This is difficult to achieve over a wide temperature range of 100 K using the Antoine equation with only three parameters. In cases like this, the extended Antoine equation or the Wagner equation are usually preferred.

Liquid molar volumes of the components:

$$v := \begin{pmatrix} 74.04 \\ 40.73 \end{pmatrix} \frac{cm^3}{mol}$$

Interaction parameter matrix:

$$a_\lambda := \begin{pmatrix} 0 & -60.756 \\ 863.79 & 0 \end{pmatrix} \frac{cal}{mol} \qquad b_\lambda := \begin{pmatrix} 0 & -0.06114 \\ -1.0533 & 0 \end{pmatrix} \frac{cal}{mol \cdot K}$$

Solution

Calculation of the interaction parameters $\Delta\lambda$ as function of temperature:

$$\Delta\lambda(T) := a_\lambda + b_\lambda \cdot T \qquad \Delta\lambda(323.15K) = \begin{pmatrix} 0 & -80.513 \\ 523.416 & 0 \end{pmatrix} \frac{cal}{mol}$$

Calculation of the interaction parameters $\Delta\Lambda$ as function of temperature:

$$\Delta\Lambda(T,i,j) := \frac{v_j}{v_i} \cdot e^{\left[\frac{\left(-\Delta\lambda(T)_{i,j}\right)}{R_{gas} \cdot T}\right]} \qquad \Delta\Lambda(323.15K,1,2) = 0.624$$

Calculation of the activity coefficient as function of temperature and composition:

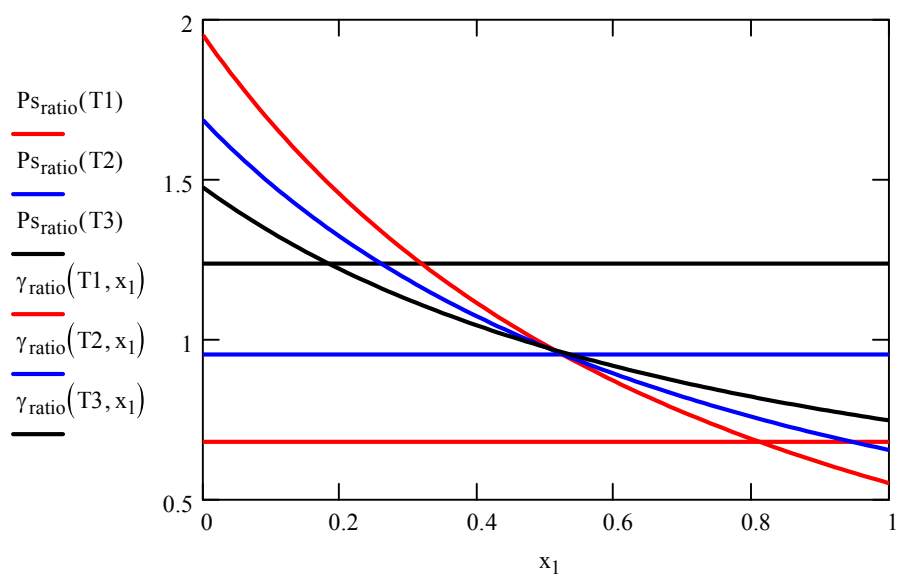
$$\gamma(T,x) := \left| \begin{array}{l} \text{for } i \in 1..n_{comp} \\ \quad \gamma_i \leftarrow \exp\left[-\ln\left(\sum_j x_j \cdot \Delta\Lambda(T,i,j)\right) + 1 - \sum_k \frac{\left(x_k \cdot \Delta\Lambda(T,k,i)\right)}{\left(\sum_j x_j \cdot \Delta\Lambda(T,k,j)\right)}\right] \\ \gamma \end{array} \right.$$

In order to plot the the ratios of the vapor pressures and the ratio of the activity coefficients, the following functions are defined:

$$Ps_{ratio}(T) := \frac{Ps(T,2)}{Ps(T,1)} \qquad x(x_1) := \begin{pmatrix} x_1 \\ 1 - x_1 \end{pmatrix} \qquad \gamma_{ratio}(T,x_1) := \frac{\gamma(T,x(x_1))_1}{\gamma(T,x(x_1))_2}$$

The values of both functions as function of composition are shown for the three different temperatures below. The azeotropic composition can be found at the intersection of same colored lines.

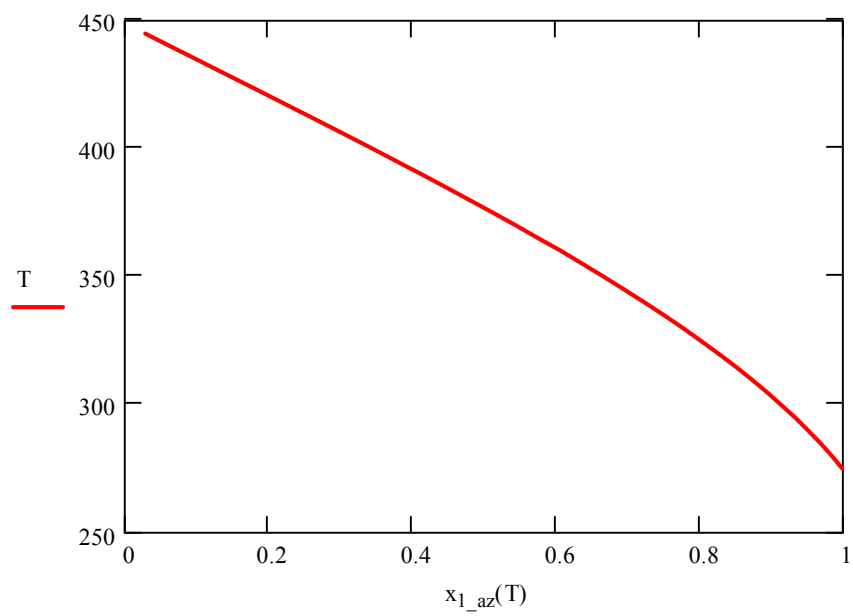
$$x_1 := 0, 0.01 .. 1$$



In order to find the exact values, the root function can be applied in the limited mole fraction range of 0 to 1:

$$x_{1_az}(T) := \mathrm{root}\left(Ps_{ratio}(T) - \gamma_{ratio}(T, x_1), x_1, 0, 1\right)$$

$x_{1_az}(T1) = 0.811$ $\quad$ $x_{1_az}(T2) = 0.524$ $\quad$ $x_{1_az}(T3) = 0.183$

The following plot shows the dependence of the azeotropic composition on temperature:

$$T := 270K, 275K .. 470K$$