## Example 05.09 Compare experimental VLE to Wilson Equation Results

**problem:**

Compare the experimental vapor phase mole fractions published by Hiaki et al. for the system acetone (1) - chloroform (2) - methanol (3) at 1 atm with the calculated ones using the binary Wilson parameters $\lambda_{ij}$ listed in  assuming ideal vapor phase behavior.
The calculation should be performed for the following composition at T=331.42 K:
$x_1$ = 0.229, $x_2$ = 0.175, $x_3$ = 0.596, $y_1$ = 0.250, $y_2$ = 0.211, $y_3$ = 0.539.

**general constants and definitions:**

$$cm := 0.01m \qquad R := 8.31433 \frac{J}{K \cdot mol}$$

$$mmHg := \frac{1}{760} atm \qquad kPa := 1000Pa$$

**input data**

$$ncomp := 3 \qquad i := 1..ncomp \qquad j := 1..ncomp \qquad k := 1..ncomp$$

Experimental data:

$$T := 331.42K \qquad x := \begin{pmatrix} 0.229 \\ 0.175 \\ 0.596 \end{pmatrix} \qquad y := \begin{pmatrix} 0.250 \\ 0.211 \\ 0.539 \end{pmatrix}$$

Antoine constants of the components:

$$Ant := \begin{pmatrix} 7.1327 & 1219.97 & 230.653 \\ 6.95465 & 1170.97 & 226.232 \\ 8.08097 & 1582.27 & 239.7 \end{pmatrix}$$

Antoine function for vapor pressure calculation:

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

Liquid molar volumes of the components:

$$v := \begin{pmatrix} 74.04 \\ 80.67 \\ 40.73 \end{pmatrix} \frac{cm^3}{mol}$$

Interaction parameter matrix:

$$a_\lambda := \begin{pmatrix} 0 & 375.2835 & 31.1208 \\ -1722.58 & 0 & -1140.79 \\ 747.217 & 3596.17 & 0 \end{pmatrix} K \quad b_\lambda := \begin{pmatrix} 0 & -3.78434 & -0.67704 \\ 6.405502 & 0 & 2.59359 \\ -0.256645 & -6.2234 & 0 \end{pmatrix}$$

$$c_\lambda := \begin{pmatrix} 0 & 7.91073 \cdot 10^{-3} & 8.68371 \cdot 10^{-4} \\ -7.47788 \cdot 10^{-3} & 0 & 3.10 \cdot 10^{-5} \\ -1.24796 \cdot 10^{-3} & 3.00 \cdot 10^{-5} & 0 \end{pmatrix} K^{-1}$$

## Solution

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

$$\Delta\lambda(T) := a_\lambda + b_\lambda \cdot T + c_\lambda \cdot T^2 \qquad \Delta\lambda(T) = \begin{pmatrix} 0 & -10.014 & -97.883 \\ -421.033 & 0 & -277.817 \\ 525.085 & 1.537 \times 10^3 & 0 \end{pmatrix} K$$

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

$$\Delta\Lambda(T,i,j) := \frac{v_j}{v_i} \cdot e^{\left[\frac{\left(-\Delta\lambda(T)_{i,j}\right)}{T}\right]} \qquad \Delta\Lambda(T,1,2) = 1.123$$

Calculation of the activity coefficient as function of temperature and composition can be performed using the expression given in Table 5.6:

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

$$\gamma(T,x) = \begin{pmatrix} 1.223 \\ 1.101 \\ 1.205 \end{pmatrix}$$

Calculation of partial pressures, total pressure and vapor mole fractions::

$$P(T,x,i) := x_i \cdot \gamma(T,x)_i \cdot Ps(T,i) \qquad P_{tot}(T,x) := \sum_i P(T,x,i) \qquad y_{calc}(T,x,i) := \frac{P(T,x,i)}{P_{tot}(T,x)}$$

$P(T,x,i) =$

| |
|---|
| 0.3 |
| 0.175 |
| 0.558 |

atm

$P_{tot}(T,x) = 1.032\,atm$

$y_{calc}(T,x,i) =$

| |
|---|
| 0.29041 |
| 0.16943 |
| 0.54016 |

The results can now be compared to the experimental data given by Hiaki et al.. The measurements were performed at 1 atm, which is 3.2% lower than the calculated value. The experimental vapor phase compositions of the first two components differ strongly (by about 4 mol%) from the experimental findings:

$$y_{exp} := \begin{pmatrix} 0.250 \\ 0.211 \\ 0.539 \end{pmatrix}$$

$$y_{exp_i} - y_{calc}(T, x, i) =$$

| |
|---|
| -0.04 |
| 0.042 |
| $-1.165 \cdot 10^{-3}$ |

$$\frac{y_{exp_i} - y_{calc}(T, x, i)}{y_{exp_i}} \cdot 100 =$$

| |
|---|
| -16.164 |
| 19.703 |
| -0.216 |

This also results in serious discrepances between the experimental and calculated separation factors:

$$\alpha_{exp_{i,j}} := \frac{y_{exp_i} \cdot x_j}{x_i \cdot y_{exp_j}} \qquad \alpha_{exp} = \begin{pmatrix} 1 & 0.905 & 1.207 \\ 1.104 & 1 & 1.333 \\ 0.828 & 0.75 & 1 \end{pmatrix}$$

$$\alpha_{calc_{i,j}} := \frac{y_{calc}(T, x, i) \cdot x_j}{x_i \cdot y_{calc}(T, x, j)} \qquad \alpha_{calc} = \begin{pmatrix} 1 & 1.31 & 1.399 \\ 0.763 & 1 & 1.068 \\ 0.715 & 0.936 & 1 \end{pmatrix}$$

Although the vapor phase concentration was nearly correct, all separation factors are very unrealistic. Either the model parameters or the experimental results are therefor not acceptable.