Example 05.10 Thermodynamic Consistency Using the Area Test

problem:

Check the isothermal VLE data of the system ethanol (1) water (2) measured by Mertl et al. at 70°C for thermodynamic consistency using the area test.

general constants and definitions:

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

input data

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

Vapor pressure of the pure components at 70°C:

$Ps_1 := 72.30kPa \qquad Ps_2 := 31.09kPa$

Experimental data:

$$x^{\langle 1 \rangle} := \begin{pmatrix} 0.062 \\ 0.095 \\ 0.131 \\ 0.194 \\ 0.252 \\ 0.334 \\ 0.401 \\ 0.593 \\ 0.680 \\ 0.793 \\ 0.810 \\ 0.943 \\ 0.947 \end{pmatrix} \qquad y^{\langle 1 \rangle} := \begin{pmatrix} 0.374 \\ 0.439 \\ 0.482 \\ 0.524 \\ 0.552 \\ 0.583 \\ 0.611 \\ 0.691 \\ 0.739 \\ 0.816 \\ 0.826 \\ 0.941 \\ 0.945 \end{pmatrix} \qquad P := \begin{pmatrix} 48.33 \\ 53.2 \\ 56.53 \\ 60.12 \\ 62.39 \\ 64.73 \\ 66.34 \\ 70.11 \\ 71.23 \\ 72.35 \\ 72.41 \\ 72.59 \\ 72.59 \end{pmatrix} kPa$$

(the data are given here without pure component vapor pressures, which were not reported by the author)

$n_{data} := rows(x) \qquad j := 1 .. n_{data}$

$x_{j,2} := 1. - x_{j,1} \qquad y_{j,2} := 1. - y_{j,1}$

Solution

In the first step the activity coefficients are calculated from the experimental data points using the assumption of ideal vapor phase behavior.

$$\gamma_{j,i} := \frac{y_{j,i} \cdot P_j}{x_{j,i} \cdot Ps_i}$$

$\gamma =$

4.032	1.037
3.4	1.061
2.877	1.084
2.246	1.142
1.89	1.202
1.563	1.304

To perform the area test, the logarithm of the ratio of the activity coefficients is first regressed using a flexible mathematical expression (polynomial). Please note that expressions for g^E like Redlich-Kister or Legendre-polynomials cannot be used in this case as they can only describe thermodynamically consistent behavior. In this case the convenient MathCad functions "regress" and "interp" are used.

$$\ln\gamma_{ratio_j} := \ln\left(\frac{\gamma_{j,1}}{\gamma_{j,2}}\right)$$

Data regression

$$par := regress\left(x^{\langle 1 \rangle}, \ln\gamma_{ratio}, 4\right)$$

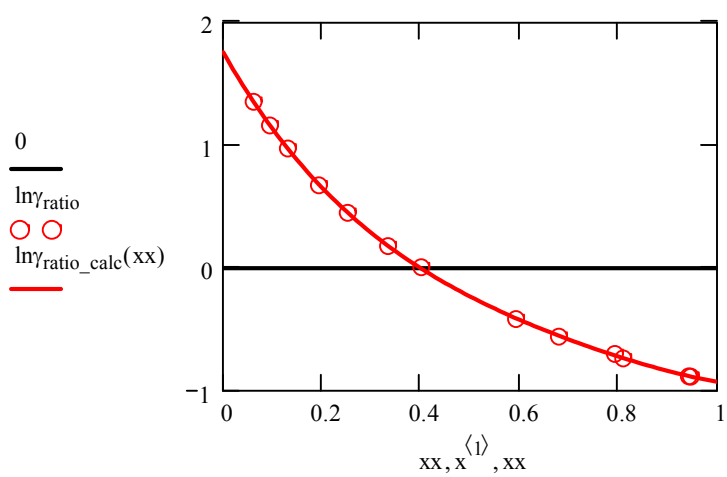
$$\ln\gamma_{ratio_calc}(xx) := interp\left(par, x^{\langle 1 \rangle}, \ln\gamma_{ratio}, xx\right)$$

Sum of squared deviations (SSD):

$$SSD := \sum_j \left[\ln\gamma_{ratio_j} - \ln\gamma_{ratio_calc}\left[\left(x^{\langle 1 \rangle}\right)_j\right]\right]^2$$

$$SSD = 4.747 \times 10^{-4}$$

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



Calculation of the relative area deviation in the above plot:

$$area_{dev} := \frac{\int_0^1 \ln\gamma_{ratio_calc}(x)\,dx}{\int_0^1 \left|\ln\gamma_{ratio_calc}(x)\right|\,dx} \qquad area_{dev} = -0.055$$

In this test, a relative area deviation of -5.5% is found. In case of isothermal data sets, consistency is assumed for relative area deviations below 10%. For isobaric data sets, this percentage is increased by $(T_{max}-T_{min})/T_{min}$ * 150%. The data can thus be considered to be thermodynamically consistent from the point of view of an area test.

Further discussion of these tests can be found in:

Redlich, O., Kister, A.T., Ind. Eng. Chem. 40 (1948) 345
Herington, E.F.G., Nature 160 (1947) 610
Herington, E.F.G., J. Inst. Petrol. 37 (1951) 457