

## How to write down the different thermodynamical models for given values of activity coefficient.

**Remark on the use of physical constants units.** There are at least two sets of physical units used in the thermodynamical calculations, depending on the source of the experimental data. The main attention should be paid to the units of the temperature  $T$  ( $^{\circ}\text{C}$  or  $\text{K}$ ), pressure  $P$  (atm, Pa, or mmHg), binary interaction coefficients  $A_{ij}$  (in cal/mol or J/mol), and the ideal gas constant :  $R=8.3144621 \text{ J / (K mol)}$  or  $R=1.9872036 \text{ cal/(mol K)}$ .

**I. Wilson.** In the examples below  $T$  is measured in  $^{\circ}\text{C}$ ,

$$R=8.3144621 \frac{\text{J}}{\text{K mol}}, \quad P_0=760 \text{ mmHg}.$$

To make the calculations, the following parameters should be specified:

- the matrix of binary interaction coefficients

$$\overline{A}_{ij} = \lambda_{ij} - \lambda_{ii}, \quad \overline{A}_{ii} = 0, \quad i, j = 1, 2, 3,$$

describing the interaction between  $i$ -th and  $j$ -th component. Here  $\lambda_{ij} - \lambda_{ii}$  corresponds to the constants in the Prausnitz book. The standard data (DECHEMA data base) are usually given in cal/mol units. Passing to the J/mol yields

$$A = 4.184 \overline{A}.$$

- molar liquid volumes  $v_i$ ,  $i=1, 2, 3$
- Antoine's equation constants  $a_i, b_i, c_i$ ,  $i=1, 2, 3$ , for partial molar pressures :

$$P_i = 10^{a_i - \frac{b_i}{T+c_i}}$$

So, in total we have to provide 18 constants for each ternary mixture.

Then, we set  $\Lambda_{ij} = \frac{v_j}{v_i} \exp\left(\frac{-A_{ij}}{R(T+273.15)}\right)$ , and then we use the formulae (6-165) from

[1] to compute  $y_i$ ,  $i=1, 2, 3$ . Finally,  $y_i = \frac{x_i P_i y_i}{P_0}$ , where  $x_3 = 1 - x_1 - x_2$ .

**II. NRTL.** In the examples below  $T$  is measured in  $^{\circ}\text{C}$ ,

$$R=8.3144621 \frac{\text{J}}{\text{K mol}}, \quad P_0=760 \text{ mmHg}.$$

To make the calculations, the following parameters should be specified:

- the matrix of binary interaction coefficients

$$\overline{A}_{ij} = g_{ij} - g_{ii}, \quad \overline{A}_{ii} = 0, \quad i, j = 1, 2, 3,$$

describing the interaction between  $i$ -th and  $j$ -th component. Again,  $g_{ij} - g_{ii}$  corresponds to the constants in the Prausnitz book [1]. The standard data (DECHEMA data base) are usually given in cal/mol units, so in order to pass to the J/mol we set

$$A = 4.184 \overline{A}.$$

- the symmetric  $(3 \times 3)$  matrix  $\alpha$  such that  $\alpha_{ii} = 0$ ,  $i=1, 2, 3$ .
- Antoine's equation constants  $a_i, b_i, c_i$ ,  $i=1, 2, 3$ , for partial molar pressures :

$$P_i = 10^{a_i - \frac{b_i}{T+c_i}}$$

So, in total we have to provide 18 constants for each ternary mixture.

Then, we set  $\tau_{ij} = \frac{A_{ij}}{R(T+273.15)}$ , and then we use the formulae (6-166) and

(6-169) from [1] to compute the matrix  $G$  and  $y_i$ ,  $i=1,2,3$ . Finally,  $y_i = \frac{x_i P_i y_i}{P_0}$ , where  $x_3 = 1 - x_1 - x_2$ .

**III. UNIQUAC.** In the examples below we use the modified Antoine equations, so it was more convenient to use T measured in K.

$$R = 1.9872036 \frac{\text{cal}}{\text{K mol}}, \quad P_0 = 1 \text{ atm} = 101325 \text{ Pa}.$$

To make the calculations, the following parameters should be specified for  $i=1,2,3$ :

- the matrix of binary interaction coefficients  $\overline{A}_{ij}$ ,  $\overline{A}_{ii}=0$ . Since the energy is measured in *cal*,  $A = \overline{A}$ . **Important:** the matrix  $A$  is not the same as in [1], instead the following formula should be used:

$$\tau_{ij} = \exp\left(-\frac{A_{ij}}{RT}\right). \quad (\text{U1})$$

- the Van-der-Waals volume  $r_i$  and area  $q_i$  of each component
- we set  $z=10$ ,  $q'_i = q_i$ ,  $\theta'_i = \theta_i$
- Antoine's equation constants  $a_i, b_i, c_i, d_i, e_i$  for partial molar pressures :

$$P_i = \exp\left(a_i + \frac{b_i}{T} + c_i \ln(T) + d_i T^{e_i}\right) \quad (\text{U2})$$

Finally, using formulae (6-173) from [1] we compute  $y_i$ ,  $i=1,2,3$ , and, as before,

$$y_i = \frac{x_i P_i y_i}{P_0}, \quad \text{where } x_3 = 1 - x_1 - x_2.$$

**Remark.** Of course, it would be better transform  $T$  to  $^{\circ}\text{C}$  in (U1) and (U2) replacing  $T \rightarrow T - 273.15$ . We can also unify the calculation using  $J$  for energy and hence

$A = 4.184 \overline{A}$ ,  $R = 8.3144621 \frac{J}{K \text{ mol}}$  as in other 2 models. The best thing is to adapt the computations to the set of units chosen by the user.

## References.

[1] J. M. Prausnitz, R.N. Lichtenthaler, E. Gomes de Azevedo. Molecular Thermodynamics of Fluid-Phase Equilibria. IIIrd edition, Published by Prentice Hall, 1998.

**Examples.** See in the attached PDF file.