CALCULATION OF THE COMPOSITION OF COEXISTING PHASES

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A calculation of properties of conjugated phases from equations for the chemical equilibrium is rendered considerably difficult by the existence of side so called trivial solutions. A general procedure is proposed for eliminating these undesirable solutions. The procedure is demonstrated on the calculation of the composition of two liquid phases in a binary and ternary system for the Redlich–Kister and NRTL equations. The proposed method can be utilized in other areas, *e.g.* for calculating high-pressure vapour–liquid equilibria.

General Solution

During studying phase equilibria we use for calculations of densities or compositions of conjugated phases equalities between fugacities, chemical potentials or activities of components. The same functions are found on both left- and right-hand sides of equations of this type. The most simple general example of such a system of equations is given by

$$f_1(x^{(1)}) = f_1(x^{(2)}) , \qquad (1)$$
$$f_2(x^{(1)}) = f_2(x^{(2)}) ,$$

where f_1, f_2 are arbitrary functions. Usually we are searching for one solution $x_0^{(1)}, x_0^{(2)}$ of the system, which we will denote from now on as physical. It is verified easily that besides it, system (*1*) has infinitely many solutions $x^{(1)} = x^{(2)}$ independently of the real shape of functions f_1, f_2. These solutions we will denote as trivial ones.

It is obvious that the search for the physical solution may be complicated considerably by the existence of the trivial solutions. We will try to eliminate this difficulty by transforming system (*1*) into another system which would possess the same physical solution as (*1*) without having the trivial solutions.

If at least one function f is a polynomial

$$f_1 = a + bx + cx^2 + \dots ,$$

the transformation may be performed easily. Let us introduce an auxiliary variable

$$t = x^{(2)} - x^{(1)}$$

and rewrite Eq. (*1*) to

$$a + bx^{(1)} + c(x^{(1)})^2 + \ldots = a + b(t + x^{(1)}) + c(t + x^{(1)})^2 + \ldots \qquad (2)$$

After performing multiplications, only terms with first and higher powers of t remain in Eq. (*2*)

$$bt + 2x^{(1)}ct + ct^{(2)} + \ldots = 0\,. \qquad (3)$$

After factoring out t we obtain finally

$$b + 2x^{(1)}c + ct + \ldots = 0\,. \qquad (4)$$

This equation and the second equation of system (*1*) form a new system which has no trivial solution $t = 0$.

If neither f_1 nor f_2 in system (*1*) is a polynomial, we can remove the trivial solution by a "formal reduction", *i.e.* by rewriting Eq. (*1*) to the form

$$[f(x + t) - f(x)]/t = 0\,, \qquad (5)$$

employing an easily provable fact that the trivial solutions are always unifold.

There may be a physical solution $t = 0$ of system (*1*) for some numerical values of constants in f_1, f_2. This solution is preserved in Eqs (*4*), (*5*). For a numerical solution of the system in its vicinity it is safer to replace the expression on the lhs of Eq. (*5*) by a polynomial.

In a general case, the elimination of the trivial solution is more difficult. Let us have a system of equations

$$P_i(x_1^{(1)}, x_2^{(1)}, \ldots, x_n^{(1)}) = P_i(x_1^{(2)}, x_2^{(2)}, \ldots, x_n^{(2)}) \quad i = 1, 2, \ldots, 2n\,, \qquad (6)$$

where P_i's denote polynomials. It is obvious that Eqs (*6*) have a trivial solution

$$t_j = x_j^{(2)} - x_j^{(1)} = 0 \quad j = 1, 2, \ldots, n\,.$$

Similarly as in the case of the system of two equations we may rewrite Eq. (*6*) to

$$t_1 p_{i,1} + t_2 p_{i,2} + \ldots + t_n p_{i,n} = 0 \quad i = 1, 2, \ldots, 2n\,, \qquad (7)$$

where $p_{i,j}$'s are polynomials in variables $x_k^{(1)}$ and t_k ($k = 1, 2, \ldots, n$). Now we want to arrange system (7) in such a manner, so that it may be possible in at least one of the equations to factor out one of variables t_i. This equation and consequently the whole system will have no trivial solutions.

For a while we will distinguish variables t_k which are present in system (7) explicitly from those which occur in the equations through $p_{i,j}$. The first equation of the system will be rewritten to the form

$$t_1 = -(1/p_{1,1})(t_2 p_{2,1} + \ldots + t_n p_{n,1}) \quad (8)$$

and inserted into the second to n-th ones for all explicit t_1's. Similarly we express t_2 from the second equation and insert into the third to n-th ones. In this manner we proceed further until finally only t_n remains explicitly in the n-th equation and this will be factored out. The last equation and $2n - 1$ equations (7) form the resulting system deprived of the trivial solutions.

If the functions in system (6) are not polynomials, the outlined algorithm cannot be employed in the general case directly as the transition from Eq. (6) to (7) is not generally possible. The removal of the trivial solutions must be preceded by approximating the functions by polynomials (*e.g.* Taylor or orthogonal polynomial expansions). It is, however, not necessary in some particular cases (see the following paragraph).

Further we show the use of the outlined general procedure in calculating liquid–liquid equilibria. The procedure may be also employed for calculating one- and multicomponent high-pressure vapour–liquid equilibria and in all other cases where identical functions become equal in different points.

Application in Liquid–Liquid Equilibria

The following equilibrium conditions hold in a two-phase binary liquid system

$$\ln a_i(x^{(1)}) = \ln a_i(x^{(2)}) \quad i = 1, 2, \quad (9)$$

where a_i is the activity of the i-th component and $x^{(j)}$ is the mole fraction of the first component in the j-th phase. For calculating the composition of the coexisting phases we rewrite Eq. (9) to the form of (compare with Eq. (5))

$$(\ln a_i(x^{(1)}) - \ln a_i(x^{(2)}))/t = 0 \quad i = 1, 2, \quad (10)$$

where $t = x^{(2)} - x^{(1)}$. System (10) has already no trivial solution $t = 0$. The system possesses, however, a physical solution $t = 0$ in the critical point. A numerical solution of system (10) is unstable in the vicinity of this point and it is therefore safer to replace expressions on the rhs by polynomials.

Now we show an arrangement of system (10) which is suitable for calculations also in the vicinity of the critical point for the case of the Redlich–Kister[1] and NRTL (ref.[2]) equations. If the activities of the components are expressed by the Redlich–Kister three-constant relation

$$\ln a_1 = \ln x_1 + x_2^2[b + c(4x_1 - 1) + d(x_1 - x_2)(6x_1 - 1)]\,,$$
$$\ln a_2 = \ln x_2 + x_1^2[b + c(1 - 4x_1) + d(x_1 - x_2)(1 - 6x_2)]\,. \qquad (11)$$

Eq. (*9*) will be rewritten to

$$\ln(1 - t/x_1) + (x_2 + t)^2\,[b + c(4x_1 - 4t - 1) + d(x_1 - x_2 - 2t)$$
$$(6x_1 - 6t - 1)] - x_2^2[b + c(4x_1 - 1) + d(x_1 - x_2)(6x_1 - 1)] = 0\,, \quad (12a)$$

$$\ln(1 + t/x_2) + (x_1 - t)^2\,[b + c(1 - 4x_2 - 4t_1) + d(x_1 - x_2 - 2t)$$
$$(1 - 6x_2 - 6t)] - x_1^2[b + c(1 - 4x_2) + d(x_1 - x_2)(1 - 6x_2)] = 0\,, \quad (12b)$$

where, for simplicity of the notation, we omit superscript 1 in mole fractions. After performing the multiplications, t may be factored out from the polynomial part of Eq. (*12a*), which leads to

$$0 = [\ln(1 - t/x_1)]/t - 4x_2^2[c + d(4x_1 - 2x_2 - 3t)] +$$
$$+ (t + 2x_2)\,[b + c(4x_1 - 4t - 1) + d(x_1 - x_2 - 2t)(6x_1 - 6t - 1)]\,. \quad (13)$$

This equation and Eq. (*12b*) form a system deprived of the trivial solutions. For calculations in the vicinity of the critical point it is sufficient to expand the logarithm in Eqs (*12a,b*) into the series

$$(1/t)\ln(1 - t/x_1) = -(1/x_1) + \ldots \qquad (14)$$

The NRTL equation for activities may be rearranged similarly

$$\ln a_1 = \ln x_1 + x_2^2[t_{21}g_{21}^2(x_1 + x_2g_{21})^{-2} + t_{12}g_{12}(x_2 + x_1g_{12})^{-2}]\,,$$
$$\ln a_2 = \ln x_2 + x_1^2[t_{12}g_{12}^2(x_2 + x_1g_{12})^{-2} + t_{21}g_{21}(x_1 + x_2g_{21})^{-2}]\,, \qquad (15)$$

where $g_{ij} = \exp(-\alpha t_{ij})$. After introducing the auxiliary variable t, Eqs (*9*) pass over to

$$\ln(1 - t/x_1) + (x_2 + t)^2\,\{t_{21}g_{21}[x_1 + x_2g_{21} - (1 - g_{21})\,t]^{-2} +$$
$$+ t_{12}g_{12}[x_2 + x_1g_{12} + (1 - g_{12})\,t]^{-2}\} - x_2^2[t_{21}g_{21}^2(x_1 + x_2g_{21})^{-2} +$$
$$+ t_{12}g_{12}(x_2 + x_1g_{12})^{-2}] = 0\,, \qquad (16a)$$

$$\ln(1 + t/x_2) + (x_1 - t)^2\,\{t_{12}g_{12}^2[x_2 + x_1g_{12} + (1 - g_{12})\,t]^{-2} +$$
$$+ t_{21}g_{21}[x_1 + x_2g_{21} + (g_{21} - 1)\,t]^{-2}\} - x_1^2[t_{12}g_{12}^2(x_2 + x_1g_{12})^{-2} +$$
$$+ t_{21}g_{21}(x_1 + x_2)^{-2}] = 0\,. \qquad (16b)$$

After a rearrangement we may again factor out t from Eq. (*16a*) without being compelled to approximate the expression by a polynomial in t

$$\begin{aligned}(1/t)\ln(1 - t/x_1) + t_{21}g_{21}[(2x_2 + t)(x_1 + x_2g_{21})^2 + \\ + 2x_2^2(1 - g_{21})(x_1 + x_2g_{21}) - (1 - g_{21})^2 tx_2^2](x_1 + x_2g_{21})^{-2} \,. \\ \cdot [x_1 + x_2g_{21} - (1 - g_{21})t]^{-2} + \\ + t_{12}g_{12}\{(2x_2 + t)(x_2 + x_1g_{12})^2 - x_2^2[2(1 - g_{12})(x_2 + x_1g_{12}) + t(1 - g_{12})^2]\} \\ [x_2 + x_1g_{12} + t(1 - g_{12})]^{-2}(x_2 + x_1g_{12})^{-2} = 0 \,. \qquad (17)\end{aligned}$$

The system formed by Eqs (*17*) and (*16b*) has already no trivial solutions. For calculations in the vicinity of the critical point it is necessary to replace the logarithm in Eq. (*17*) by relation (*14*).

An elimination of the trivial solutions in calculations of the composition of coexisting phases in ternary systems is more laborious. It is necessary to solve the system of three equations

$$\ln a_i(x_1^{(1)}, x_2^{(1)}) = \ln a_i(x_1^{(2)}, x_2^{(2)}) \quad i = 1, 2, 3 \qquad (18)$$

for given $x_1^{(1)}$ and unknowns $x_1^{(2)}, x_2^{(1)}, x_2^{(2)}$. Again we introduce auxiliary variables

$$t_1 = x_1^{(2)} - x_1^{(1)} \,,$$

$$t_2 = x_2^{(2)} - x_2^{(1)} \,.$$

Function $\ln a_i$ for the Redlich–Kister expansion is the sum of a polynomial in t_1, t_2 and a logarithmic function of variable t_i. This fact allows us to transform arbitrary two of Eqs (*18*) into the form of Eqs (*7*)

$$t_1 f_{11} + t_2 p_{12} = 0 \,, \qquad (19)$$

$$t_1 p_{21} + t_2 f_{22} = 0 \,,$$

where

$$f_{11} = \frac{1}{t_1}\ln(1 - t_1/x_1) + p_{11} \,,$$

$$f_{22} = \frac{1}{t_2}\ln(1 - t_2/x_2) + p_{22}$$

and $p_{i,j}$ $(i, j = 1, 2)$ are polynomials of the variables x_1, x_2, t_1, t_2. For the sake of simplicity the upper index of the mole fraction denoting the phase was again omitted. From the first Eq. (*19*) we express

$$t_1 = -t_2(p_{12}/f_{12})$$

and substitute into the second Eq. (*19*) which upon dividing by t_2 is transformed into

$$f_{22} - \frac{p_{12}p_{21}}{f_{11}} = 0\,.$$

This equation, together with arbitrary two equations (*18*) forms the desired system without a trivial solution. In the vicinity of the critical point Eq. (*13*) must be used for logarithms in f_{11} and f_{12}.

Transformation of the system (*17*) was performed for the Redlich–Kister expansion with twelve binary and three ternary constants in total. Relations for polynomials p_{ij} are presented in the Appendix. Analogous procedure can also be employed for a NRTL equation.

APPENDIX

Relations for polynom'als p_{ij} in Eqs (*19*)

$$\begin{aligned} p_{11} = {} & (b_{12} - b_{13})\,x_2 + b_{13}(x_3 + 1 - \bar{x}_1) + 2c_{12}x_2(x_1 - x_2 - 1 + \bar{x}_1) + \\ & + c_{13}\{x_3[2(x_1 - x_3) - 1] + \bar{x}_1 + (\bar{x}_1 - \bar{x}_3 - 2x_3)(1 - 2\bar{x}_1)\} - \\ & - 2c_{23}x_2(\bar{x}_2 - \bar{x}_3 - x_3) + d_{12}x_2[3(x_1 - x_2)(x_1 - x_2 - 1 + \bar{x}_1) - 2\bar{x}_1 + \\ & + (\bar{x}_2 - \bar{x}_1)(1 - 3\bar{x}_1)] + d_{13}\{[2x_1 + (\bar{x}_1 - \bar{x}_3)(1 - 3\bar{x}_1)](\bar{x}_1 - \bar{x}_3 - 2x_3) + \\ & + x_3(x_1 - x_3)[3(x_1 - x_3) + 6\bar{x}_1 - 4]\} + 3d_{23}x_2\{x_3[2(\bar{x}_2 - \bar{x}_3) + t_1] - \\ & - (x_2 - x_3)^2\} - e_{12}x_2\{[2(\bar{x}_1 - \bar{x}_2) + t_1][3\bar{x}_1 + (\bar{x}_1 - \bar{x}_2)(1 - 4\bar{x}_1)] - \\ & - 4(x_1 - x_2)^2(x_1 - x_2 - 1 + \bar{x}_1)\} + e_{13}\{[3\bar{x}_1 + (\bar{x}_1 - \bar{x}_3)(1 - 4\bar{x}_1)][(\bar{x}_1 - \bar{x}_3)^2 - \\ & - 4x_3(\bar{x}_1 - \bar{x}_3 + t_1)] - x_3(x_1 - x_3)^2[5 - 4(x_1 - x_3) - 8\bar{x}_1]\} - \\ & - 4e_{23}\{x_2(x_2 - x_3)^3 + \bar{x}_2\bar{x}_3[3(x_2 - x_3)(t_1 + 4t_2 - x_2 + x_3) - t_1^2 - \\ & - 6t_1t_2 - 12t_2^2]\} - Cx_2[3(x_1 - x_3 - t_1) - 1 - x_1 + x_3 + t_1] - \\ & - C_1\{[3(x_1 - x_3 - t_1) - 2]\,x_1x_2 + \bar{x}_2\bar{x}_3(2 - 3\bar{x}_1)\} - C_2x_2^2[3(x_1 - x_3 - t_1) - 1] \end{aligned}$$

$$\begin{aligned} p_{12} = {} & (b_{12} - b_{13})(\bar{x}_1 - 1) - b_{23}(\bar{x}_2 - \bar{x}_3 + t_2) - c_{12}[\bar{x}_1 + (1 - 2\bar{x}_1)(\bar{x}_1 - \bar{x}_2 - x_2)] + \\ & + c_{13}[\bar{x}_1 + (1 - 2\bar{x}_1)(\bar{x}_1 - \bar{x}_3 - x_3)] - 2c_{23}[x_2(\bar{x}_2 - \bar{x}_3 - 2x_3) - \bar{x}_3(\bar{x}_2 - \bar{x}_3)] + \\ & + d_{12}\{x_2(x_1 - x_2)(1 - 3\bar{x}_1) - (\bar{x}_1 - \bar{x}_2 - x_2)[2\bar{x}_1 + (\bar{x}_1 - \bar{x}_2)(1 - 3\bar{x}_1)]\} + \\ & + d_{13}\{(\bar{x}_1 - \bar{x}_3 - x_3)[2\bar{x}_1 + (\bar{x}_1 - \bar{x}_3)(1 - 3\bar{x}_1)] - x_3(x_1 - x_3)(1 - 3\bar{x}_1)\} + \\ & + 3d_{23}[4x_2x_3(x_2 - x_3 - t_2) - (\bar{x}_2 - \bar{x}_3)^2(\bar{x}_2 - \bar{x}_3 + t_2)] + \\ & + e_{12}\{[3\bar{x}_1 + (\bar{x}_1 - \bar{x}_2)(1 - 4\bar{x}_1)][2x_2(x_1 - x_2) + t_2x_2 - (\bar{x}_1 - \bar{x}_2)^2] + \\ & + x_2(x_1 - x_2)^2(1 - 4\bar{x}_1)\} + e_{13}\{[3\bar{x}_1 + (\bar{x}_1 - \bar{x}_3)(1 - 4\bar{x}_1)][(\bar{x}_1 - \bar{x}_2)^2 - \end{aligned}$$

$$- 2x_3(x_1 - x_3) + t_2x_3] - x_3(x_1 - x_3)^2 (1 - 4\bar{x}_1)\} -$$
$$- 4e_{23}\{(x_2 - x_3)^3(\bar{x}_2 - \bar{x}_3 + t_2) - \bar{x}_1\bar{x}_3[6(x_2 - x_3)^2 + 8t_2^2 - 12t_2(x_2 - x_3)]\} +$$
$$+ C(1 - 2\bar{x}_1)(\bar{x}_2 - \bar{x}_3 + t_2) + C_1x_1(2 - 3\bar{x}_1)(\bar{x}_2 - \bar{x}_3 + t_2) +$$
$$+ C_2(1 - 3\bar{x}_1)[x_2^2 - \bar{x}_3(x_2 + \bar{x}_2)]$$

$$p_{21} = (b_{12} - b_{23})(\bar{x}_2 - 1) - b_{13}(\bar{x}_1 - \bar{x}_3 + t_1) + c_{12}[\bar{x}_2 - (1 - 2\bar{x}_2)(\bar{x}_1 + x_1 - \bar{x}_2)] -$$
$$- 3c_{13}[(\bar{x}_1 - \bar{x}_3)(\bar{x}_1 - \bar{x}_3 + t_1) - 2x_1x_3] + c_{23}[\bar{x}_2 + (1 - 2\bar{x}_2)(\bar{x}_2 - x_3 - \bar{x}_3)] +$$
$$+ d_{12}\{[2\bar{x}_2 - (\bar{x}_1 - \bar{x}_2)(1 - 3\bar{x}_2)](\bar{x}_1 - \bar{x}_2 + x_1) - x_1(x_1 - x_2)(1 - 3\bar{x}_2)\} +$$
$$+ d_{23}\{[2\bar{x}_2 + (\bar{x}_2 - \bar{x}_3)(1 - 3\bar{x}_2)](\bar{x}_2 - \bar{x}_3 - x_3) + x_3(x_2 - x_3)(1 - 3\bar{x}_2)\} +$$
$$+ 3d_{13}[4x_1x_3(x_1 - x_3 - t_1) - (\bar{x}_1 - \bar{x}_3)^2(\bar{x}_1 - \bar{x}_3 + t_1)] +$$
$$+ e_{12}\{[3\bar{x}_2 - (\bar{x}_1 - \bar{x}_2)(1 - 4\bar{x}_2)][2x_1(x_1 - x_2) - t_1x_1 + (\bar{x}_1 - \bar{x}_2)^2] -$$
$$- x_1(x_1 - x_2)^2(1 - 4\bar{x}_2)\} + e_{23}\{[3\bar{x}_2 + (\bar{x}_2 - \bar{x}_3)(1 - 4\bar{x}_2)][(\bar{x}_2 - \bar{x}_3)^2 -$$
$$- 2x_3(x_2 - x_3) + t_1x_3] - x_3(x_2 - x_3)^2(1 - 4\bar{x}_2)\} + 4e_{13}\{\bar{x}_1\bar{x}_2[6(x_1 - x_3)^2 +$$
$$+ 8t_1^2 - 12t_1(x_1 - x_3)] - (x_1 - x_3)^3(\bar{x}_1 - \bar{x}_3 - t_1)\} + C(1 - 2\bar{x}_2)(\bar{x}_1 - \bar{x}_3 + t_1) +$$
$$+ C_1(1 - 3\bar{x}_2)[x_1^2 - \bar{x}_3(x_1 + x_1)] + C_2(2 - 3\bar{x}_2)(\bar{x}_1 - \bar{x}_3 + t_1)x_2$$

$$p_{22} = (b_{12} - b_{13})x_1 + b_{23}(1 - \bar{x}_2 + x_3) + 2c_{12}x_1(x_1 - x_2 - \bar{x}_2 + 1) +$$
$$+ c_{23}[\bar{x}_2 + (\bar{x}_2 - \bar{x}_3 - 2x_3)(1 - 2\bar{x}_2) + 2x_3(x_2 + x_3) - x_3] -$$
$$- 2c_{13}x_1(\bar{x}_1 - \bar{x}_3 - x_3) + d_{12}x_1[3(x_1 - x_2)(x_1 - x_2 - \bar{x}_2 + 1) + 2\bar{x}_2 +$$
$$+ (\bar{x}_1 - \bar{x}_2)(1 - 3\bar{x}_2)] + d_{23}\{[2\bar{x}_2 + (\bar{x}_2 - \bar{x}_3)(1 - 3\bar{x}_2)](\bar{x}_2 - \bar{x}_3 - 2x_3) +$$
$$+ x_3(x_2 - x_3)[3(x_2 - x_3) + 6\bar{x}_2 - 4]\} + 3d_{13}x_1[2x_3(\bar{x}_1 - \bar{x}_3) +$$
$$+ t_2x_3 - (\bar{x}_1 - \bar{x}_3)^2] - e_{13}x_1\{[(\bar{x}_2 - \bar{x}_1)(1 - 4\bar{x}_2) + 3\bar{x}_2][2(\bar{x}_1 - \bar{x}_3) - t_2] -$$
$$- 4(x_1 - x_2)^2(x_1 - x_2 - \bar{x}_2 + 1)\} + e_{23}\{[3\bar{x}_2 + (\bar{x}_2 - \bar{x}_3)(1 - 4\bar{x}_2)] .$$
$$. [(\bar{x}_2 - \bar{x}_3)^2 - 4x_3(\bar{x}_2 - \bar{x}_3 + t_2)] + x_3(x_2 - x_3)^2[4(x_2 - x_3) + 8\bar{x}_2 - 5]\} -$$
$$- 4e_{13}\{(x_1 - x_3)^3 x_1 + \bar{x}_1\bar{x}_3[3(x_1 - x_3)(4t_1 + t_2 - x_1 + x_3) - t_2^2 - 6t_1t_2 -$$
$$- 12t_1^2]\} + Cx_1[1 + 2(x_3 - \bar{x}_2) + C_1x_1^2[1 - 3(\bar{x}_2 - x_3) - C_2\{[3x_1x_2(\bar{x}_2 - x_3) -$$
$$- 2x_1x_2 + \bar{x}_1\bar{x}_2(2 - 3\bar{x}_2)]$$

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