

**LIQUID-LIQUID EQUILIBRIA.
CALCULATION OF THE COMPOSITION OF COEXISTING PHASES
AND OF THE CRITICAL POINT IN A TERNARY SYSTEM
FROM A DEPENDENCE OF GIBBS ENERGY ON COMPOSITION**

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An algorithm is formulated in the work for calculating the composition of coexisting liquid phases and of the critical point in a ternary system on the basis of a given dependence $G^E = G^E(x_1, x_2)$. The calculation includes also the case when the overall composition of a heterogeneous mixture is given for which the composition of the coexisting phases is to be found.

When calculating liquid-liquid equilibrium in a ternary system if we know $G^E = G^E(x_1, x_2)$, we must solve three nonlinear equations

$$\begin{aligned} a_1(x_1, x_2) &= a_1(z_1, z_2), \\ a_2(x_1, x_2) &= a_2(z_1, z_2), \\ a_3(x_1, x_2) &= a_3(z_1, z_2), \end{aligned} \tag{1}$$

where $a_i(x_1, x_2)$ is the activity of the i -th component in the first phase and $a_i(z_1, z_2)$ is the activity of the i -th component in the second, conjugate phase. For conciseness we shall use the symbol $\bar{a}_i = a_i(z_1, z_2)$, and so on, in some cases.

For a firmly chosen value of one variable of composition (*e.g.* x_1), we get the remaining unknowns x_2, z_1, z_2 by solving the system of equations (1).

Difficulties connected with the solution of system (1) are of several sorts:

a) For a chosen value of one variable of composition (*e.g.* x_1), there need not be any solution of the system (1). To put it in another way, the straight line $x_1 = (x_1)_{\text{chosen}}$ does not intersect at any point the binodal curve.

b) Even with a suitable choice of x_1 , the calculation procedure may converge to a so-called trivial solution (we do not consider here the critical point where this

solution makes physical sense), when holds

$$x_1 = z_1, \quad x_2 = z_2. \quad (2)$$

There is obviously an indefinite number of such solutions. Besides these indefinitely many trivial solutions, there exists at least one physical solution at a suitable choice of x_1 , when

$$x_i \neq z_i, \quad (3)$$

which is looked for. An attempt to eliminate the trivial solution for certain types of dependences of activity on composition was made by Procházka and coworkers¹.

c) For numerical solution of the system (1) we need to know a first approximation. An unsuitable first approximation can result in the divergence of iteration procedure or in the convergence to the trivial solution (Eq. 2). The range of the interval from which we can choose the first approximation, will depend considerably on the used form of equation and on the distance from the critical point. It is evident that the better the first approximation will be the more rapidly the solution of system (1) will converge.

d) A specific point on the binodal curve is the critical point which, however, is to be determined by a special procedure and which the last part of this work is devoted to.

Principle of the Method Proposed

The proposed method rises from the assumption that the calculation of the physical solution of the system (1) will be the more rapid the more accurate the first approximation will be.

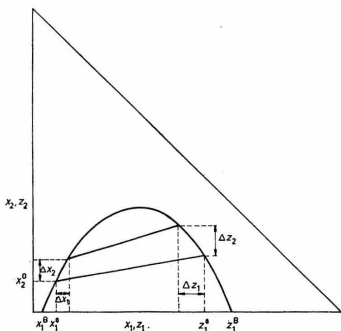


FIG. 1
Diagram of the Mutual Solubility of Components in a Ternary System

Let us consider a ternary system depicted schematically in Fig. 1. Let us assume that we know one couple of points of coexisting phases on the equilibrium curve, *i.e.* the points with coordinates x_1^0, x_2^0 and z_1^0, z_2^0 . Further we assume that we know the slopes of tangents to the equilibrium curve at these points, $dx_2/dx_1 = S_1$ and $dz_2/dz_1 = S_2$.

The approximation of a next point which should lie on the binodal curve is

$$(x_1)_{II} = x_1^0 + \Delta x_1 = x_1^0 + \delta/(1 + S_1^2)^{1/2}, \quad (4)$$

$$(x_2)_{II} = x_2^0 + \Delta x_2 = x_2^0 + S_1 \delta/(1 + S_1^2)^{1/2}, \quad (5)$$

where

$$\delta = \pm \sqrt{(\Delta x_1^2 + \Delta x_2^2)}. \quad (6)$$

If we want to increase x_1 we choose the sign + or $\delta > 0$ in Eq. (6), in the opposite case the sign - or $\delta < 0$.

According to the Eqs (4) and (5), with a suitably chosen δ , we obtain a very accurate approximation of the next point on the first branch of the binodal curve. For the calculation, of course, an approximation of the point $(z_1, z_2)_{II}$ is needed, too. One possibility would be to retain the values z_1^0, z_2^0 . Knowing the slope $S_2 = dz_2/dz_1$ and on the assumption that the tie-line slope t^0 changes only very little, it is possible to improve the estimate even in this case.

Then

$$t^0 = (z_2^0 - x_2^0)/(z_1^0 - x_1^0) \approx [(z_2)_{II} - (x_2)_{II}]/[(z_1)_{II} - (x_1)_{II}], \quad (7)$$

$$S_2 = dz_2/dz_1 \approx [(z_2)_{II} - z_2^0]/[(z_1)_{II} - z_1^0]. \quad (8)$$

By combining the relations (4)–(8) we obtain

$$(z_1)_{II} = [z_2^0 - (x_2)_{II} - S_2 z_1^0 + t^0(x_1)_{II}]/(t^0 - S_2), \quad (9)$$

$$(z_2)_{II} = (x_2)_{II} + t^0[(z_1)_{II} - (x_1)_{II}]. \quad (10)$$

When applying Eqs (4), (5), (9) and (10) it is necessary to determine the tangent slopes S_1 and S_2 to the equilibrium curve. For these slopes one can find in the literature²⁻⁴ the relations

$$S_1 = dx_2/dx_1 = -(G11 + t G12)/(G12 + t G22), \quad (11)$$

or

$$S_2 = dz_2/dz_1 = -(\bar{G}11 + t \bar{G}12)/(\bar{G}12 + t \bar{G}22), \quad (12)$$

where t is the slope of tie-line (defined beforehand), see Eq. (7). G_{11} , G_{12} , G_{22} , and \bar{G}_{11} , \bar{G}_{12} , \bar{G}_{22} are the second order derivatives of the molar Gibbs energy G with respect to composition at constant temperature and pressure

$$G_{11} = \partial^2(G/RT)/\partial x_1^2; \quad G_{12} = \partial^2(G/RT)/\partial x_1 \partial x_2; \quad (13)$$

$$G_{22} = \partial^2(G/RT)/\partial x_2^2; \quad \bar{G}_{11} = \partial^2(G/RT)/\partial z_1^2;$$

and so on.

We have issued from the assumption that the composition of at least one couple of conjugate phases is known. However, if we have no information on the compositions of the conjugate phases in the ternary system it is possible to choose the composition of coexisting phases in the binary system as the first approximation. For the slopes S_1 and S_2 to the binodal curve we get in this case the simple relations

$$\lim_{x_2 \rightarrow 0} dx_2/dx_1 = -G_{11}/G_{12}, \quad (14)$$

$$\lim_{z_2 \rightarrow 0} dz_2/dz_1 = -\bar{G}_{11}/\bar{G}_{12}. \quad (15)$$

Before passing to the solution of the system (1) itself, it is desirable to estimate the magnitude of δ in Eq. (6) with more precision. To this purpose we will utilize the results of the calculation of two equilibrium curves depicted in Fig. 2. The dependence of G^E on composition is given by the relation (35) and $b_{13} = 3$. When calculating we started with the binary mixture 1-3 and the last calculated equilibrium compositions are indicated by arrows with inscribed values of δ . On solving the system

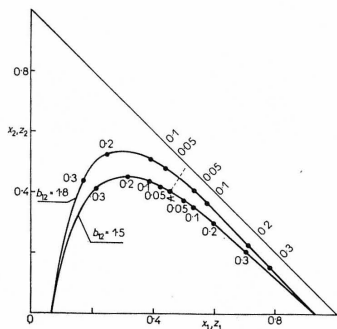


FIG. 2
The Effect of the Value of δ on the Feasibility of Calculating the Coexisting Phases K Critical point.

(1) further, we obtained the trivial solution. It is evident that by choosing sufficiently low values δ , it is possible to approach to the critical point as close as desired.

During the calculations the number of iterations to the solution of system (1) was as well observed. At $\delta = 0.05$ four iterations were usually needed (an admissible error was 10^{-4}). In the vicinity of the critical point or when estimating the ternary composition from binary data, the number of iterations was always higher. At $\delta = 0.3$ the number of iterations rose on the average to 10. If these results should be generalized the value $\delta = 0.05$ to 0.1 is to be recommended. If we are not interested in a close proximity of the critical point it is possible to choose even $\delta = 0.2$ to speed up the computations.

Solution of the System (1)

By means of the relations (4), (5), (9) and (10) a next couple of the compositions of coexisting phases on the binodal curve is estimated. Before passing to the solution of the system (1) it is necessary to choose a suitable variant. With respect to the mole fraction which will be held constant, we have four possibilities. Let us discuss now some variants. Let us consider Fig. 3a. If we start at the point $A[x_1^0, x_2^0]$ the next approximation will be the point $B[x_1^0 + \Delta x_1, x_2^0 + \Delta x_2]$. As far as we should solve

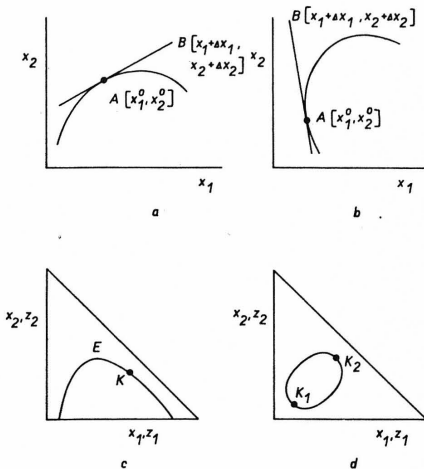


FIG. 3

The Effect of the Shape of Binodal Curve on the Solvability of the System (16)

the system (I) on the assumption that $x_2 = x_2^0 + \Delta x_2 = \text{const}$ we shall not find a solution (the numerical procedure will not converge or we shall obtain the trivial solution). These difficulties we will not encounter if we hold constant mole fraction of the first component when solving the system (I).

In Fig. 3b an opposite alternative is illustrated, where on the contrary the choice $x_1 = \text{const}$ fails.

From these cases it is evident that the difficulties, when solving the system of equations (I), may occur when:

- a) $dx_2/dx_1 \rightarrow 0$; we solve the system (I) for $x_2 = \text{const}$.
 b) $dx_2/dx_1 \rightarrow \infty$; we solve the system (I) for $x_1 = \text{const}$.

Therefore it is necessary to choose constant, for the solution of the system (I), that mole fraction which does not exhibit an extreme on the corresponding branch of the binodal curve. For the system in Fig. 3c it can be x_1, z_1, z_2 but in no case x_2 because we would not get behind the point E during solution. Another extreme case is presented in Fig. 3d. Here none of considered variables would be suitable. In such a case it is sometimes desirable to carry out a change of components. If we hold in this case the third component constant when solving the system (I) the computation will take place without complications.

Usually we know (at least) approximately the course of the binodal curve and therefore we can choose right a corresponding variant. A qualitative course of the binodal curve can be conceived on the basis of the knowledge of the critical point (see below), of the mutual solubility of pure components and of the limiting slopes determined by means of the relations (14) and (15).

Now if we have an estimate of equilibrium composition and know which of mole fractions is to be held constant we can proceed to the solution of the system (I). On making use the Newton method to the logarithms of activities and choosing e.g. $x_1 = \text{const}$ we get

$$\begin{aligned} [\partial \ln a_i / \partial z_1] \Delta z_1 + [\partial \ln a_i / \partial z_2] \Delta z_2 - [\partial \ln a_i / \partial x_2] \Delta x_2 = \\ = \ln [x_i \gamma_i / (z_i \bar{v}_i)], \quad i = 1, 2, 3 \end{aligned} \quad (16)$$

The derivatives $\partial \ln a / \partial x$ can be expressed in terms of the quantities G11, G12, G22 defined beforehand. It holds

$$\begin{aligned} \partial \ln a_1 / \partial x_1 &= G11(1 - x_1) - G12 \cdot x_2, \\ \partial \ln a_1 / \partial x_2 &= G12(1 - x_1) - G22 \cdot x_2, \\ \partial \ln a_2 / \partial x_1 &= G12(1 - x_2) - G11 \cdot x_1, \\ \partial \ln a_2 / \partial x_2 &= G22(1 - x_2) - G12 \cdot x_1, \end{aligned} \quad (17)$$

$$\begin{aligned}\partial \ln a_3 / \partial x_1 &= -G11 \cdot x_1 - G12 \cdot x_2, \\ \partial \ln a_3 / \partial x_2 &= -G12 \cdot x_1 - G22 \cdot x_2,\end{aligned}$$

By determining the coefficients in system of equations (16) and by subsequent solving, we obtain Δz_1 , Δz_2 , Δx_2 . Let hold

$$S = |\Delta z_1| + |\Delta z_2| + |\Delta x_2|. \quad (18)$$

Now three cases may occur according to the magnitude of S . If S is less than the chosen value (e.g. 10^{-4}) then the system of equations (16) can be considered solved.

For an inaccurate estimation of coexisting compositions or in the proximity of sides of the concentration triangle it can occur that we should get too high value of S ($S > \Delta_1$). In such a case it is recommended to use for the next iteration corrected values of increments given by the relation

$$\begin{aligned}(\Delta \varphi)_{\text{correct}} &= (\Delta \varphi)_{\text{calc}} \cdot \Delta_1 / S, \\ \varphi &= x_2, z_1, z_2,\end{aligned} \quad (19)$$

where Δ_1 is a chosen reducing parameter. During the computations carried out by the authors $\Delta_1 = 0.05$ was used.

In terms of the found values Δz_1 , Δz_2 , Δx_2 we will obtain a next approximation of equilibrium compositions and the solution of the system is repeated. As it has been said the usual number of iterations to reach $S < 10^{-4}$ was 4 to 5.

After having solved the system (16) we obtain a base for calculating the next iteration according to Eqs (4), (5), (9) and (10) and we solve the system (16) once again. In this way we proceed along the equilibrium curve and the computation is very rapid.

The needed relations for calculating the activity coefficients, G11, G12 and G22 are given in Appendix 1 for the Redlich-Kister equation⁵. In Appendix 2 the relations are presented between the constants of the Margules⁶ and the Redlich-Kister equations which enable one to use the relations given in Appendix 1 as well for the systems for which the constants of the Margules equation (see e.g.^{7,8}) are known. For n-component systems, analogous relations (for the NRTL equation^{9,10} as well) will be published elsewhere¹¹.

It might seem that we considerably complicate the calculation by this procedure because besides the activity coefficients we need in addition the second derivatives of the Gibbs energy for calculating S_1 and S_2 . However, it is necessary to realize that these derivatives are required as well for calculating the coefficients in system (16) and for the determination of the next point approximation on the equilibrium curve according to Eqs (4), (5), (9) and (10) and thus we have already calculated them.

Calculation of the Compositions of Coexisting Phases for a Given Composition of a Heterogeneous Mixture

According to the procedure outlined in a foregoing part, it is possible to determine the location of the equilibrium curve. We often meet the problem to find the composition of coexisting phases for a mixture whose overall composition lies in the heterogeneous region.

In Fig. 4 two coexisting phases correspond to the point $W[w_1, w_2]$ and their composition is to be found. Let us assume again that we know a couple of coexisting compositions x_1^0, x_2^0 and z_1^0, z_2^0 (this couple can be also the compositions of coexisting phases in the binary mixture). Let us define a function Φ by the relation

$$\Phi = x_2^0 + t^0(w_1 - x_1^0). \quad (20)$$

This quantity gives the value of mole fraction of the component 2 in the heterogeneous region as a function of the composition of coexisting phase at composition x_1^0, x_2^0 , of the slope of tie-line t^0 and of mole fraction w_1 . If $\Phi = w_2$ holds then the point of the binodal curve x_1^0, x_2^0 is identical with the point A . On combining Eqs (4), (5) with (20) we get

$$\Phi = x_2^0 + S_1 \delta / (1 + S_1^2)^{1/2} + t^0 [w_1 - x_1^0 - \delta / (1 + S_1^2)^{1/2}]. \quad (21)$$

From this equation we get (by putting $\Phi = w_2$)

$$\delta = [x_2^0 - w_2 + t^0(w_1 - x_1^0)] (1 + S_1^2)^{1/2} / (t^0 - S_1). \quad (22)$$

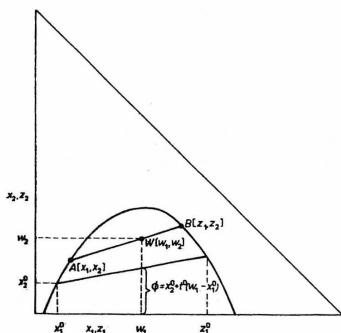


FIG. 4
Calculation of Coexisting Phases for a Given Heterogeneous Composition

With δ determined in this way we will obtain the next approximation of composition according to Eqs (4), (5), (9) and (10). On solving the system (16) we will get a new composition and repeat the calculation.

The experience which has been obtained with respect to the optimum value of δ holds of course in this case as well. At the beginning we get usually δ too high (in absolute value) and it is necessary to diminish its value. The optimum value depends on the properties of the system, on the distance from the critical point and from the sides of triangle, etc.

Calculation of the Critical Point

The knowledge of the critical point, *i.e.* the point at which both phases merge, is significant both from the theoretical and practical point of view. The determination of the accurate position of the critical point is unrealizable by means of a procedure which would consist in the calculation of coexisting phases. From the thermodynamic viewpoint the critical point is defined on the basis of the validity of the relations²⁻⁴

$$D = \begin{vmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{vmatrix} = G_{11} \cdot G_{22} - (G_{12})^2 = 0, \quad (23)$$

$$\begin{aligned} D^* &= \begin{vmatrix} \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2} \\ G_{12} & G_{22} \end{vmatrix} = \frac{\partial D}{\partial x_1} \cdot G_{22} - \frac{\partial D}{\partial x_2} \cdot G_{12} = \\ &= D_1 \cdot G_{22} - D_2 \cdot G_{12} = 0, \end{aligned} \quad (24)$$

assuming that

$$\begin{vmatrix} \frac{\partial D^*}{\partial x_1} & \frac{\partial D^*}{\partial x_2} \\ G_{12} & G_{22} \end{vmatrix} > 0. \quad (25)$$

The quantities G_{11} , G_{12} , G_{22} have the meaning defined before and $D_1 = \partial D / \partial x_1$ and $D_2 = \partial D / \partial x_2$. Eqs (23) and (24) are two nonlinear equations which are sufficient to determine x_{1k} and x_{2k} . From the numerical standpoint we have a much simpler problem than in case of the system (16). Its laboriousness consists only in the fact that for calculating D^* we need to know the third derivatives of the Gibbs energy with respect to composition and when applying the Newton method, even the fourth derivatives.

On using the Newton method Eqs (23) and (24) turn into the system of equations

$$(D_1)_{x_1^0, x_2^0} \Delta x_1 + (D_2)_{x_1^0, x_2^0} \Delta x_2 = -(D)_{x_1^0, x_2^0}, \quad (26)$$

$$(\frac{\partial D^*}{\partial x_1})_{x_1^0, x_2^0} \Delta x_1 + (\frac{\partial D^*}{\partial x_2})_{x_1^0, x_2^0} \Delta x_2 = -(D^*)_{x_1^0, x_2^0}, \quad (27)$$

where x_1^0 , x_2^0 are the first approximations of composition of the critical point.

For the derivatives of D and D^* in Eqs (23) and (24) we get

$$\partial D/\partial x_1 = D1 = G111 \cdot G22 + G11 \cdot G122 - 2 \cdot G12 \cdot G112, \quad (28)$$

$$\partial D/\partial x_2 = D2 = G112 \cdot G22 + G11 \cdot G222 - 2 \cdot G12 \cdot G122, \quad (29)$$

$$\partial D^*/\partial x_1 = D11 \cdot G22 + D1 \cdot G122 - D12 \cdot G12 - D2 \cdot G112, \quad (30)$$

$$\partial D^*/\partial x_2 = D12 \cdot G22 + D1 \cdot G222 - D22 \cdot G12 - D2 \cdot G122, \quad (31)$$

where

$$D11 = \partial^2 D/\partial x_1^2 = G1111 \cdot G22 + 2 \cdot G111 \cdot G122 + G11 \cdot G1122 + \\ - 2(G112)^2 - 2 \cdot G12 \cdot G1112, \quad (32)$$

$$D12 = \partial^2 D/\partial x_1 \partial x_2 = G1112 \cdot G22 + G111 \cdot G222 + G11 \cdot G1222 + \\ - G122 \cdot G112 - 2 \cdot G12 \cdot G1122, \quad (33)$$

$$D22 = \partial^2 D/\partial x_2^2 = G1122 \cdot G22 + 2 \cdot G112 \cdot G222 + G11 \cdot G2222 + \\ = 2(G122)^2 - 2 \cdot G12 \cdot G1222. \quad (34)$$

For the sake of concise denotation of the higher-order derivatives of the molar Gibbs energy with respect to the composition we use analogous abbreviations as formerly, *e.g.*

$$G112 = \partial^3(G/RT)/\partial x_1^2 \partial x_2,$$

$$G1112 = \partial^4(G/RT)/\partial x_1^3 \partial x_2, \quad \text{and so on.}$$

The relations for the third and fourth derivatives of the Gibbs energy with respect to composition of the Redlich–Kister equation are as well given in Appendix 1.

The critical points for a number of systems were calculated in this way. Considering that with "normal" systems there exists only one or no solution. The calculation is not so sensitive to the first approximation. Only in some few cases, when the first approximation corresponded to the heterogeneous composition or provided that the critical point was in the vicinity of sides of the concentration triangle, 20 iterations were not sufficient.

As one of interesting results we present the critical curve of a system which would conform to the relation

$$G^E/RT = b_{13}x_1x_3 + b_{12}x_1x_2 \quad (35)$$

for $b_{13} = 3$ in the dependence on b_{12} . The calculated compositions of the critical point are given in Table I.

It is evident from the table that low values of b_{12} influence the critical point only little. When b_{12} approaches to the "critical" value $b_{12} = 2$, then its influence on the position of the critical point increases.

This effect, in our opinion, explains the disagreeing view on the problem whether it is possible to predict the liquid-liquid equilibrium and, consequently, the critical point from the vapour-liquid equilibrium. If the effect of constants of the corresponding binary systems 1-2 and 2-3 on the liquid-liquid equilibrium is relatively small then the prediction is possible. With systems which are sensitive to the values of the above-mentioned parameters, the prediction is made difficult or even impossible.

The proposed method for the calculation of coexisting phases speeds up considerably the computation of all the curve of limited miscibility and at the same time enables to approach even very close to the critical point. A comparison with the methods published in the literature (Null¹⁰, Renon and coworkers¹¹) cannot be well done because with the last methods, the first approximation is not uniquely specified, which has a substantial effect on the duration of computations.

TABLE I
Dependence of the Critical Point Position on the Parameter b_{12} (for $b_{13} = 3$)

b_{12}	x_{1k}	x_{2k}	x_{3k}	$\Delta x_{1k}/\Delta b_{12}$	$\Delta x_{2k}/\Delta b_{12}$	$\Delta x_{3k}/\Delta b_{12}$
-0.2	0.3202	0.3342	0.3456	0.065	-0.007	-0.059
0	0.3333	0.3333	0.3333	0.067	0	-0.067
0.2	0.3470	0.3342	0.3188	0.070	0.009	-0.079
0.4	0.3613	0.3369	0.3018	0.073	0.018	-0.091
0.6	0.3764	0.3416	0.2819	0.078	0.028	-0.106
0.8	0.3924	0.3487	0.2589	0.082	0.042	-0.124
1.0	0.4093	0.3585	0.2322	0.086	0.058	-0.144
1.2	0.4269	0.3718	0.2012	0.090	0.076	-0.166
1.4	0.4452	0.3898	0.1650	0.092	0.106	-0.196
1.5	0.4544	0.4011	0.1445	0.093	0.123	-0.216
1.6	0.4637	0.4144	0.1219	0.092	0.145	-0.237
1.7	0.4729	0.4301	0.0969	0.092	0.173	-0.265
1.8	0.4821	0.4490	0.0689	0.091	0.209	-0.300
1.9	0.4911	0.4719	0.0369	0.090	0.255	-0.345
2.0	0.5	0.5	0	0.09	0.29	-0.38

APPENDIX 1.

The First to Fourth Derivatives of the Gibbs Energy with respect to Composition in a Ternary System

$$Q = G^E/(RT) = x_1x_2[b_{12} + c_{12}(x_1 - x_2) + d_{12}(x_1 - x_2)^2] + \\ + x_1x_3[b_{13} + c_{13}(x_1 - x_3) + d_{13}(x_1 - x_3)^2] + \\ + x_2x_3[b_{23} + c_{23}(x_2 - x_3) + d_{23}(x_2 - x_3)^2] + \\ + x_1x_2x_3[C + C_1x_1 + C_2x_2]$$

$$\ln \gamma_1 = b_{12}x_2(1 - x_1) + b_{13}x_3(1 - x_1) - b_{23}x_2x_3 + \\ + c_{12}x_2[x_1 + (x_1 - x_2)(1 - 2x_1)] - 2x_2x_3(x_2 - x_3)c_{23} + \\ + c_{13}x_3[x_1 + (x_1 - x_3)(1 - 2x_1)] - 3x_2x_3(x_2 - x_3)^2d_{23} + \\ + d_{12}x_2(x_1 - x_2)[2x_1 + (x_1 - x_2)(1 - 3x_1)] + \\ + d_{13}x_3(x_1 - x_3)[2x_1 + (x_1 - x_3)(1 - 3x_1)] + \\ + x_2x_3[C(1 - 2x_1) + C_1x_1(2 - 3x_1) + C_2x_2(1 - 3x_1)]$$

$$\ln \gamma_2 = b_{12}x_1(1 - x_2) - b_{13}x_1x_3 + b_{23}x_3(1 - x_2) + \\ + c_{12}x_1[-x_2 + (x_1 - x_2)(1 - 2x_2)] - 2x_1x_3(x_1 - x_3)c_{13} + \\ + c_{23}x_3[x_2 + (x_2 - x_3)(1 - 2x_2)] - 3x_1x_3(x_1 - x_3)^2d_{13} + \\ + d_{12}x_1(x_1 - x_2)[-2x_2 + (x_1 - x_2)(1 - 3x_2)] + \\ + d_{23}x_3(x_2 - x_3)[2x_2 + (x_2 - x_3)(1 - 3x_2)] + \\ + x_1x_3[C(1 - 2x_2) + C_1x_1(1 - 3x_2) + C_2x_2(2 - 3x_2)]$$

$$\ln \gamma_3 = -b_{12}x_1x_2 + b_{13}x_1(1 - x_3) + b_{23}x_2(1 - x_3) + \\ - 2c_{12}x_1x_2(x_1 - x_2) + c_{13}x_1[-x_3 + (x_1 - x_3)(1 - 2x_3)] + \\ + c_{23}x_2[-x_3 + (x_2 - x_3)(1 - 2x_3)] - 3d_{12}x_1x_2(x_1 - x_2)^2 + \\ + d_{13}x_1(x_1 - x_3)[-2x_3 + (x_1 - x_3)(1 - 3x_3)] + \\ + d_{23}x_2(x_2 - x_3)[-2x_3 + (x_2 - x_3)(1 - 3x_3)] + \\ + x_1x_2[C(1 - 2x_3) + C_1x_1(1 - 3x_3) + C_2x_2(1 - 3x_3)]$$

$$G11 = \partial^2(G/RT)/\partial x_1^2 = 1/x_1 + 1/x_3 - 2b_{13} + 2c_{12}x_2 - 6c_{13}(x_1 - x_3) + \\ - 2c_{23}x_2 + 2d_{12}x_2(3x_1 - 2x_2) + 2d_{13}[4x_1x_3 - 5(x_1 - x_3)^2] + \\ + 2d_{23}x_2(3x_3 - 2x_2) + 2x_2[-C + C_1(x_3 - 2x_1) - C_2x_2]$$

$$\begin{aligned}
 G12 &= \partial^2(G/RT)/\partial x_1 \partial x_2 = 1/x_3 + b_{12} - b_{13} - b_{23} \\
 &+ 2c_{12}(x_1 - x_2) - 2c_{13}(2x_1 - x_3) - 2c_{23}(2x_2 - x_3) + \\
 &+ d_{12}[3(x_1 - x_2)^2 - 2x_1x_2] + d_{13}[4x_1x_3 - (x_1 - x_3) \cdot \\
 &\cdot \{4x_1 + 3(x_1 - x_3)\}] + d_{23}[4x_2x_3 - (x_2 - x_3) \{4x_2 + 3(x_2 - x_3)\}] + \\
 &+ C(x_3 - x_1 - x_2) + C_1x_1(2x_3 - 2x_2 - x_1) + C_2x_2(2x_3 - 2x_1 - x_2)
 \end{aligned}$$

$$\begin{aligned}
 G22 &= \partial^2(G/RT)/\partial x_2^2 = 1/x_2 + 1/x_3 - 2b_{23} + \\
 &- 2c_{12}x_1 - 2c_{13}x_1 - 6c_{23}(x_2 - x_3) + 2d_{12}x_1(3x_2 - 2x_1) + \\
 &+ 2d_{13}x_1(3x_3 - 2x_1) + 2d_{23}[4x_2x_3 - 5(x_2 - x_3)^2] + \\
 &+ 2x_1[-C - C_1x_1 + C_2(x_3 - 2x_2)]
 \end{aligned}$$

$$\begin{aligned}
 G111 &= \partial^3(G/RT)/\partial x_1^3 = 1/x_3^2 - 1/x_1^2 - 12c_{13} + 6d_{12}x_2 - 48d_{13}(x_1 - x_3) + \\
 &- 6d_{23}x_2 - 6C_1x_2
 \end{aligned}$$

$$\begin{aligned}
 G112 &= \partial^3(G/RT)/\partial x_1^2 \partial x_2 = 1/x_3^2 + 2c_{12} - 6c_{13} - 2c_{23} + \\
 &+ 2d_{12}(3x_1 - 4x_2) + 4d_{13}(5x_3 - 7x_1) - 2d_{23}(7x_2 - 3x_3) + \\
 &- 2C - 2C_1(2x_1 + x_2 - x_3) - 4C_2x_2
 \end{aligned}$$

$$\begin{aligned}
 G122 &= \partial^3(G/RT)/\partial x_1 \partial x_2^2 = 1/x_3^2 - 2c_{12} - 2c_{13} - 6c_{23} + \\
 &- 2d_{12}(4x_1 - 3x_2) - 2d_{13}(7x_1 - 3x_3) - 4d_{23}(7x_2 - 5x_3) + \\
 &- 2C - 4C_1x_1 + 2C_2(x_3 - x_1 - 2x_2)
 \end{aligned}$$

$$\begin{aligned}
 G222 &= \partial^3(G/RT)/\partial x_2^3 = 1/x_3^2 - 1/x_2^2 - 12c_{23} + 6d_{12}x_1 + \\
 &- 6d_{13}x_1 - 48d_{23}(x_2 - x_3) - 6C_2x_1
 \end{aligned}$$

$$G1111 = \partial^4(G/RT)/\partial x_1^4 = 2/x_1^3 + 2/x_3^3 - 96d_{13}$$

$$G1112 = \partial^4(G/RT)/\partial x_1^3 \partial x_2 = 2/x_3^3 + 6d_{12} - 48d_{13} - 6d_{23} - 6C_1$$

$$G1122 = \partial^4(G/RT)/\partial x_1^2 \partial x_2^2 = 2/x_3^3 - 8d_{12} - 20d_{13} - 20d_{23} - 4C_1 - 4C_2$$

$$G1222 = \partial^4(G/RT)/\partial x_1 \partial x_2^3 = 2/x_3^3 + 6d_{12} - 6d_{13} - 48d_{23} - 6C_2$$

$$G2222 = \partial^4(G/RT)/\partial x_2^4 = 2/x_2^3 + 2/x_3^3 - 96d_{23}$$

APPENDIX 2.

Conversion of Constants of the Margules and the Redlich-Kister Equations

Three-Suffix Margules Equation

$$G^E/(RT) = x_1x_2(A_{21}x_1 + A_{12}x_2) + x_1x_3(A_{31}x_1 + A_{13}x_3) + \\ + x_2x_3(A_{32}x_2 + A_{23}x_3) + x_1x_2x_3(A_{21} + A_{13} + A_{32} - C_M)$$

For recalculation the following equations hold:

$$\begin{aligned} A_{12} &= b_{12} - c_{12} & A_{13} &= b_{13} - c_{13} & A_{23} &= b_{23} - c_{23} \\ A_{21} &= b_{12} + c_{12} & A_{31} &= b_{13} + c_{13} & A_{32} &= b_{23} + c_{23} \\ C_M &= -C + c_{12} - c_{13} + c_{23} \\ b_{12} &= (A_{12} + A_{21})/2 & b_{13} &= (A_{13} + A_{31})/2 & b_{23} &= (A_{23} + A_{32})/2 \\ c_{12} &= (A_{21} - A_{12})/2 & c_{13} &= (A_{31} - A_{13})/2 & c_{23} &= (A_{32} - A_{23})/2 \\ C &= -C_M + (A_{21} - A_{12} + A_{13} - A_{31} - A_{23} + A_{32})/2 \end{aligned}$$

Four-Suffix Margules Equation

$$\begin{aligned} G^E/(RT) &= x_1x_2(A_{21}x_1 + A_{12}x_2 - D_{12}x_1x_2) + \\ &+ x_1x_3(A_{31}x_1 + A_{13}x_3 - D_{13}x_1x_3) + \\ &+ x_2x_3(A_{32}x_2 + A_{23}x_3 - D_{23}x_2x_3) + \\ &+ x_1x_2x_3(A_{21} + A_{13} + A_{32} - x_1C_M - x_2C_{1M} - x_3C_{2M}) \\ A_{12} &= b_{12} - c_{12} + d_{12} & A_{13} &= b_{13} - c_{13} + d_{13} & A_{23} &= b_{23} - c_{23} + d_{23} \\ A_{21} &= b_{12} + c_{12} + d_{12} & A_{31} &= b_{13} + c_{13} + d_{13} & A_{32} &= b_{23} + c_{23} + d_{23} \\ D_{12} &= 4d_{12} & D_{13} &= 4d_{13} & D_{23} &= 4d_{23} \\ C_M &= -C - C_1 + c_{12} + c_{23} - c_{13} + 2d_{12} + 2d_{13} + d_{23} \\ C_{1M} &= -C - C_2 + c_{12} - c_{13} + c_{23} + 2d_{12} + d_{13} + 2d_{23} \\ C_{2M} &= -C + c_{12} - c_{13} + c_{23} + d_{12} + 2d_{13} + 2d_{23} \\ b_{12} &= (A_{12} + A_{21} - D_{12}/2)/2 & b_{13} &= (A_{13} + A_{31} - D_{13}/2)/2 \\ c_{12} &= (A_{21} - A_{12})/2 & c_{13} &= (A_{31} - A_{13})/2 \\ d_{12} &= D_{12}/4 & d_{13} &= D_{13}/4 \\ b_{23} &= (A_{23} + A_{32} - D_{23}/2)/2 \\ c_{23} &= (A_{32} - A_{23})/2 \\ d_{23} &= D_{23}/4 \end{aligned}$$

$$C = -C_{2M} + (A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23} + D_{12}/2 + D_{13} + D_{23})/2$$

$$C_1 = C_{2M} - C_M + (D_{12} - D_{23})/4$$

$$C_2 = C_{2M} - C_{1M} + (D_{12} - D_{13})/4$$

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