LIQUID-LIQUID EQUILIBRIUM. POSSIBILITIES OF THE REGULAR SOLUTION THEORY FOR MODELLING LIQUID-LIQUID EQUILIBRIUM IN TERNARY SYSTEMS

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The applicability of the regular solution model for the description of the liquid-liquid equilibrium in ternary system is discussed in the work and the conditions are established for the formation of two and three liquid phases. In the analysis it was found that certain forms of binodal curves cannot be obtained using only binary constants. On the other hand it appeared that the regular solution predicts a number of variants which have not been found experimentally yet. In the last part of the work, the effect of ternary constant is discussed as well.

Possible cases of liquid-liquid equilibrium will be investigated in this work in a ternary system whose concentration dependence of excess Gibbs energy is described by the relation

$$G^E/RT = x_1x_2b_{12} + x_1x_3b_{13} + x_2x_3b_{23} + x_1x_2x_3C\,. \qquad (1)$$

As far as the last term of Eq. (*1*) is also considered this is not, strictly speaking, the question of regular solution. This term was introduced for purely formal reasons because below the effect of the ternary constant C on the liquid-liquid equilibrium will be investigated, too.

As it is well known, the necessary condition for splitting into two liquid phases in a binary regular system is the non-equality $b > 2$. Since in ternary system the situation is more complicated the analysis of several special cases will be carried out. A general analytic solution does not exist even for this simplest dependence and a numerical solution would be rather not clearly arranged (four independent variables b_{12}, b_{13}, b_{23}, C are to be considered). Further these cases will be investigated: *a*) possibilities of the formation of two liquid phases in the system where it holds $b_{13} \neq 0$, $b_{12} = b_{23} = C = 0$, *b*) conditions for the formation of three liquid phases, *c*) possibilities of the formation of two or three liquid phases in the system where it holds $b_{13} \neq 0$, $b = b_{12} = b_{23} \neq 0$, $C = 0$, d) the effect of the ternary constant on liquid–liquid equilibrium.

Little attention has been paid by now to these problems in the literature. These questions were partly treated by Prigogine and Defay[1] in their monograph and Heidemann and Mandhame[2] analyzed qualitatively the van Laar equation from this point of view.

Before the investigation of the cases mentioned we will summarize some knowledge of thermodynamics of solutions[1,3,4] which will be used further.

Conditions of Phase Equilibrium and Conditions of Stability

For two equilibrium phases in a ternary system, the equality of temperature T, pressure P and activities of all the components, *i.e.*

$$a_i(x) = a_i(z)\,, \quad i = 1, 2, 3\,, \tag{2}$$

where x and z, respectively, give the compositions of single phases. If three phases are in equilibrium it must hold

$$a_i(x) = a_i(z)\,, \quad a_i(x) = a_i(w)\,, \quad i = 1, 2, 3\,, \tag{3}$$

where w stands for the composition of the third phase.

When calculating the composition of coexisting phases, the previously published procedure[5] has been applied which has appeared to be very advantageous for it has made it possible to calculate rapidly all the equilibrium curve and could be extended to the calculation of composition of three coexisting phases.

Analyzing Eq. (2) it is possible to show that the convex behaviour of the Gibbs energy of mixing G^M within the entire concentration range is a necessary and sufficient condition of homogeneity of mixtures in the whole concentration range. For a binary system, the function G^M is convex if holds

$$\partial^2(G^M/RT)/\partial x_1^2 > 0\,. \tag{4}$$

In ternary system, the function $G^M = G^M(x_1, x_2)$is convex if holds

$$\mathrm{G11} > 0\,, \quad \mathrm{G22} > 0\,,$$

$$D = \begin{vmatrix} \mathrm{G11} & \mathrm{G12} \\ \mathrm{G12} & \mathrm{G22} \end{vmatrix} = \mathrm{G11} \,.\, \mathrm{G22} - (\mathrm{G12})^2 > 0\,, \tag{5}$$

where $\mathrm{G}ij = \partial^2(G^M/RT)/\partial x_i\, \partial x_j$. Thus, if inequalities (5) are infringed in a certain concentration range then the system exhibits limited miscibility.

The equation

$$D = 0 \tag{6}$$

defines the spinodal curve which in a stable two-phase system lies inside the heterogeneous region (Fig. 1). The binodal curve is defined by the equilibrium conditions (*2*). The most important point of the spinodal and binodal curves is the critical point k (sometimes designated as plait point) at which both curves merge.

At the critical point, the relations[1,3,4] hold (providing that critical points of higher orders are excluded)

$$\mathrm{G11} > 0\,, \quad \mathrm{G22} > 0\,, \tag{7}$$

$$D = \begin{vmatrix} \mathrm{G11} & \mathrm{G12} \\ \mathrm{G12} & \mathrm{G22} \end{vmatrix} = \mathrm{G11}\,.\,\mathrm{G22} - (\mathrm{G12})^2 = 0\,, \tag{8}$$

$$D^* = \begin{vmatrix} \partial D/\partial x_1 & \partial D/\partial x_2 \\ \mathrm{G12} & \mathrm{G22} \end{vmatrix} = (\partial D/\partial x_1)\,.\,\mathrm{G22} - (\partial D/\partial x_2)\,.\,\mathrm{G12} = 0 \tag{9}$$

and

$$D^{\neq} = \begin{vmatrix} \partial D^*/\partial x_1 & \partial D^*/\partial x_2 \\ \mathrm{G12} & \mathrm{G22} \end{vmatrix} > 0\,. \tag{10}$$

The numerical procedure of calculating the critical point was as well discussed in the foregoing work[5].

If we know the position of the critical point we can easily represent with more precision the "course" of the binodal and spinodal curves at the critical point. The slope of tangent to the binodal and spinodal curves at the critical point is determined by the relation

$$(\mathrm{d}x_2/dx_1)_{\mathrm{bin,k}} = (\mathrm{d}x_2/\mathrm{d}x_1)_{\mathrm{spin,k}} = -(\mathrm{G11}/\mathrm{G12})_{\mathrm{k}} = -(\mathrm{G12}/\mathrm{G22})_{\mathrm{k}} = t_{\mathrm{k}}\,. \tag{11}$$

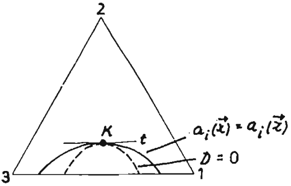


FIG. 1

Shape of Equilibrium ——— and Spinodal — — — Curve in Ternary System

As it was proved by Storonkin[3], in a certain vicinity of the critical point, the conode slopes are equal (except the second-order quantities) to the slope of tangent to the binodal curve at the critical point. For the curvature of the binodal and spinodal curves, Storonkin[3] derived the following relations

$$(\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{bin,k}} = -\alpha/(3\beta)\,, \tag{12}$$

$$(\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{spin,k}} = -(\alpha - 2\beta^2/\mathrm{G22})/\beta\,, \tag{13}$$

where

$$\alpha = (\partial/\partial x_1 + t_\mathrm{k}\,\partial/\partial x_2)^4\,(G^\mathrm{M}/\boldsymbol{R}T)\,, \tag{14}$$

$$\beta = \mathrm{G112} + 2t_\mathrm{k}\mathrm{G122} + t_\mathrm{k}^2\mathrm{G222} \tag{15}$$

($\mathrm{G112} = \partial^3(G^\mathrm{M}/\boldsymbol{R}T)/\partial x_1^2\,\partial x_2$, and the like).

Inequality (*10*) (*i.e.* the condition of minimum of G^M) can be expressed by the equivalent relation[3]

$$\alpha - 3\beta^2/\mathrm{G22} > 0\,. \tag{16}$$

By analyzing Eqs (*12*) and (*13*) it is possible to show easily that it holds

$$3 \geqq (\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{spin,k}}/(\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{bin,k}} \geqq 1\,, \tag{17}$$

while

$$(\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{spin,k}} = (\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{bin,k}} \tag{18}$$

occurs just in the case when it holds

$$D^{\neq} = 0\,. \tag{19}$$

If relations (*7*)–(*9*) are fulfilled but $D^{\neq} < 0$ then an unstable critical point is referred to, *i.e.* in the vicinity of the critical point, the spinodal curve lies outside the heterogeneous two phase region and in this case the splitting into three liquid phases takes place.

Shape of the liquid–liquid equilibrium curve for the system where $b_{13} \neq 0$, $b_{12} = b_{23} = C = 0$ *holds*. For this variant (see Appendix 1) holds

$$D = \mathrm{G11}\,.\,\mathrm{G22} - (\mathrm{G12})^2 = (1/x + 1/x_3 - 2b_{13})(1/x_2 + 1/x_3) - (1/x_3 - b_{13})^2\,. \tag{20}$$

Before starting the rearrangement of Eq. (*20*), we will utilize the fact that the system considered is symmetrical towards the components 1 and 3 and it is sufficient to investigate the behaviour of the determinant D along the line $x_1 = x_3$. If we choose as the independent variable $x_2 = x$ we get $x_1 = x_3 = (1 - x)/2$ and D in relation (*20*) is only a function of x. After small rearrangements of Eq. (*20*) we get

$$D = [-b_{13}^2 x(1 - x)^2 - 2b_{13}(1 - x)^2 + 4]\, x^{-1}(1 - x)^{-2} . \qquad (21)$$

Further we will examine the case $D = 0$. From Eq. (*21*) we obtain

$$b_{13(1)} = 2/(1 - x) , \qquad (22a)$$

$$b_{13(2)} = -2/[x(1 - x)] . \qquad (22b)$$

The dependence of b_{13} on x is given in Fig. 2 and in Fig. 3, the equilibrium curves for $b_{13} = 3$ and $b_{13} = -9$ are illustrated. Ternary system will be homogeneous as far as $b_{13} \in \langle -8; 2 \rangle$. For $b_{13} < -8$ we get a closed-loop equilibrium curve with

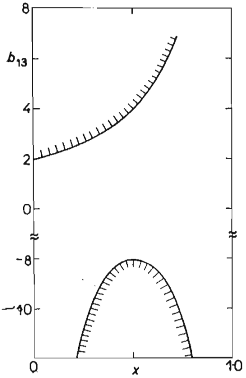


FIG. 2
Dependence of b_{13} on x According to Eq. (*22*)

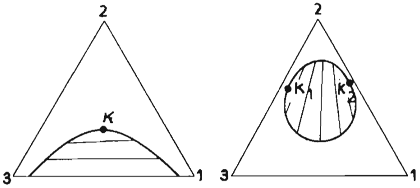


FIG. 3
Shape of Equilibrium Curve for $b_{13} = 3$ and $b_{13} = -9$

two critical points k_1 and k_2. This (to a certain extent paradoxical) result was reported already by Prigogine[1].

From the relation *(22a)*, it is further evident that the heterogeneous region will increase with increasing value of b_{13}. According to the relation *(22b)* it is on the contrary: The lower b_{13} will be, the larger the heterogeneous region in ternary system will be.

Conditions for the Formation of Three Liquid Phases

Usually it is assumed that the splitting into three liquid phases in ternary systems results from overlapping equilibrium curves which belong to single partially miscible binary systems. Besides this alternative, the regular model allows the formation of the three-phase region also in the cases when only one binary system is heterogeneous or even all three binary systems can be homogeneous, if the ternary constant is sufficiently high. These cases will be discussed below.

Let us consider first the simplest variant for which $b_{ij} = b$ and $C = 0$. Considering that the symmetrical dependence is treated, it must hold for the coordinates of points in Fig. 4:

$$A[x_1, x_2] = A[x, x]\,, \quad B[z_1, z_2] = B[1 - 2x, x]\,, \quad C[w_1, w_2] = C[x, 1 - 2x]\,.$$

The activity of all three components in these phases must be identical. With regard to the symmetrical dependence of Q on composition, it suffices, however, to solve just one equation, *e.g.* for the component 1. According to the relations in Appendix 1

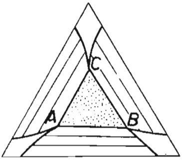


FIG. 4

Evolution of Three-Phase Region by Superposing Three Equally Nonideal Binary Systems

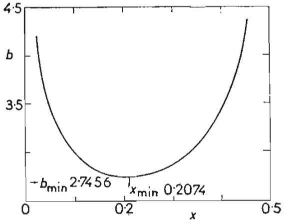


FIG. 5

Dependence of b on x Determined by Eq. *(24)*

we get

$$\ln x + bx(1 - x) + b(1 - x)(1 - 2x) - bx(1 - 2x) = \\ = \ln(1 - 2x) + bx(2x) + bx(2x) - bx^2 . \qquad (23)$$

After rearranging Eq. (*23*) we obtain

$$b = (1 - 3x)^{-1} \ln[(1 - 2x)/x] . \qquad (24)$$

The values of b in dependence on x are for this case given in Table I and plotted in Fig. 5. The minimum value of b for which three-phase region is formed is $b = 2{\cdot}7456$ with the value of $x = 0{\cdot}2074$. As it is evident from Fig. 5, we obtain for $b > 2{\cdot}7456$ always two values of x which two three-phase regions correspond to – see Fig. 6. It is possible to prove (and it also follows from Table I) that the minimum on the curve $b = b(x)$ in Fig. 5 merges in the minimum of the Gibbs energy of mixing $G^M = G^M(x)$ and for the given value of b, lower value of G^M corresponds to lower values of x. The consequence of this is a fact that the triangle $A'B'C'$ in Fig. 6 is metastable and the investigated three-phase region formed cannot be arbitrarily small.

In the foregoing example we have assumed the equality of all three binary constants. Let us consider now somewhat more real case, *viz.* $b_{12} = b_{23} = \mathrm{b}$ and $b_{13} \neq 0$

TABLE I

Values of b Determined from Eq. (*24*), Needed to Form Symmetrical Three-Phase Region According to Fig. 5

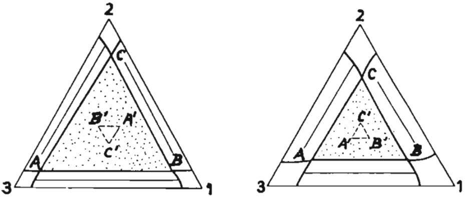
x	b	G^M/RT	x	b	G^M/RT
0·01	4·726	$-1{\cdot}876 \cdot 10^{-2}$	0·16	2·782	−0·1789
0·02	4·118	$-3{\cdot}588 \cdot 10^{-2}$	0·18	2·757	−0·1782
0·03	3·785	$-5{\cdot}165 \cdot 10^{-2}$	0·20	2·746	−0·1812
0·04	3·563	$-6{\cdot}628 \cdot 10^{-2}$	0·2074	2·7456	−0·1815
0·05	3·400	$-7{\cdot}985 \cdot 10^{-2}$	0·22	2·748	−0·1808
0·06	3·275	$-9{\cdot}246 \cdot 10^{-2}$	0·25	2·772	−0·1783
0·08	3·094	−0·1149	0·30	2·877	−0·1395
0·10	2·971	−0·1340	0·35	3·083	−0·0709
0·12	2·884	−0·1498	0·40	3·465	$5{\cdot}411 \cdot 10^{-2}$
0·14	2·823	−0·1625	0·45	4·297	0·308

($C = 0$). The three-phase region (if only one is formed) has now the shape which is illustrated in Fig. 7. With regard to the symmetry of the system holds

$$A[x_1, x_2]\,, \quad B[z_1, z_2] = B[1 - x_1 - x_2, x_2]\,, \quad C[w_1, w_2] = C[w_1, 1 - 2w_1]\,:$$

In this case it suffices to solve instead of six equations (*3*) only four but not even in this simple case the analytic solution has been found.

To cope at least partly with this problem let us consider a case in Fig. 8. Here the three-phase region formation (or decay) takes place on touching (or tearing off) two two-phase regions. A small increase in b_{13}, or b, will result in the formation of three-phase region. The point A is the critical point of the lower two-phase region and at



a) b)

FIG. 6

Three-Phase Region for *a*) $b = 3{\cdot}15$, *b*) $b = 2{\cdot}85$

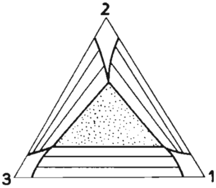


FIG. 7

Position of Three-Phase Region in System in Which Binary Subsystems 1—2 and 2—3 Exhibit the Same Deviations form Ideal Behaviour

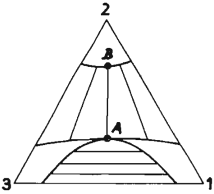


FIG. 8

Beginning of Evolution of Three-Phase Region by Superposing Two Two-Phase Regions the same time the coexisting point to B. Let the coordinates $A[x_1, x_2] = A[(1 - x)/2, x]$ correspond to the point A and $B[z_1, z_2] = B[(1 - z)/2, z]$ to the point B. From the equality of activities of components 1 and 2 we obtain

$$\ln [(1 - x)/(1 - z)] + (b - b_{13}/4)(x^2 - z^2) = 0\,, \qquad (25)$$

$$\ln (x/z) + (b - b_{13}/4)[(1 - x)^2 - (1 - z)^2] = 0\,. \qquad (26)$$

It follows from the analysis of Eqs (*25*) and (*26*) that they can yield a common solution just in the case when $x + z = 1$ holds, which means that the points A and B are placed symmetrically around $x_2 = 0{\cdot}5$. From the equality (*25*) we get ($z = 1 - x$)

$$b - b_{13}/4 = (1 - 2x)^{-1} \ln [(1 - x)/x]\,. \qquad (27)$$

Since we look for a point which equilibrium curves in Fig. 8 will touch at we need still to determine at what values of b and b_{13}, the critical point of the lower binodal curve will be identical with the point A. From the discussion given below follows that Eq. (*22a*) holds even for non-zero value of b. By combining Eqs (*22a*) and (*27*) we get

$$b_\Delta = 2(1 - x)^{-1} + (1 - 2x)^{-1} \ln [(1 - x)/x]\,, \qquad (28)$$

or

$$b_\Delta = b_{13}/4 + [b_{13}/(4 - b_{13})] \ln [(2/(b_{13} - 2)]\,. \qquad (29)$$

The values of b_Δ and the corresponding values of b_{13} as a function of x are given in Table II. For $b > b_\Delta$ the formation of three-phase region takes place. The apex

TABLE II

Values of b_Δ and b_{13} Determined from Eqs (*28*) and (*29*)

x	b_Δ	b_{13}	x	b_Δ	b_{13}
0·02	4·564	2·040	0·16	3·034	2·381
0·04	3·975	2·083	0·18	2·979	2·439
0·06	3·658	2·127	0·20	2·950	2·470
0·08	3·451	2·174	0·30	2·832	2·857
0·10	3·302	2·223	0·40	2·861	3·333
0·12	3·190	2·272	0·50	3·000	4·000
0·14	3·103	2·325			

of the triangle is given by the point B and its base is the tie-line of the lower two-phase region.

In this way the problem is solved when the three-phase region is formed when touching mutually two binodals on the line $x_1 = x_3$. As it has been said in the introduction of this chapter, the three-phase region can be formed under certain circumstances even when only one binary system is heterogeneous. Let us consider the case $b_{13} = 3$ and $b_{12} = b_{23} = b$. It is possible to prove easily that regardless of the value of b, at the point $x_1 = x_2 = 1/3$ it will hold not only $D = 0$ but also $D^* = 0$. However, for $b > 1{\cdot}875$, the condition *(10)* is no more fulfilled and therefore the stable critical point is not referred to. It is evident in Fig. 9*a* that for $b > 1{\cdot}875$ "the equilibrium points" of two phase region occurring in the vicinity of the point $x_i = 1/3$ lie inside the spinodal curve and consequently they are not stable. In this case the two-phase region turns into a three-phase one.

The condition for the three-phase region formation can be in this case formulated by the relation

$$(\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{bin},k} \geqq (\mathrm{d}^2x_2/\mathrm{d}x_1^2)_{\mathrm{spin},k} \qquad (30)$$

or

$$D^* \leqq 0\,, \qquad (31)$$

where the subscript k emphasizes that the curvature is taken at the point at which $D = D^* = 0$ holds. For the case considered here ($b_{12} = b_{23} = b$, $b_{13} \neq 0$, $C = 0$), it is possible, from the equality in relations *(30)* or *(31)* on the line $x_1 = x_3 = (1 - x)/2$, to derive the relation

$$b'_\Delta = b_{13}(b_{13} + 2)/[8(b_{13} - 2)]\,, \qquad (32)$$

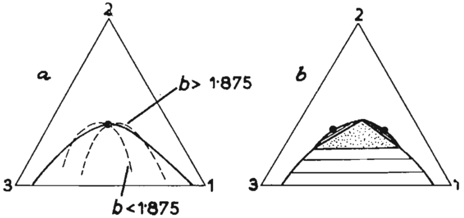


FIG. 9

Evolution of Three-Phase Region by Splitting Two-Phase Region where $b = b'_{\Delta}$ just when $D^{*} = 0$. For $b < b'_{\Delta}$, the spinodal curve lies in the heterogeneous region. If $b > b'_{\Delta}$ there is a three-phase region at the apex of the heterogeneous two-phase region (Fig. 9*b*). The values of b'_{Δ} are given in Table III.

Three important facts follow from relation (*32*): *a*) Three-phase region can arise even in the case that $b < 2$. The minimum value $b_{\text{min}} = 1{\cdot}4576$ and the corresponding value $b_{13} = 4{\cdot}828$. *b*) Eq. (*32*) is quadratic with respect to b_{13} and has two solutions for $b > 1{\cdot}4576$. So *e.g.* for $b = 2{\cdot}1$ we get $b_{13(1)} = 11{\cdot}12$ and $b_{13(2)} = 2{\cdot}877$. The three-phase region will be formed only for $b_{13} \in (2{\cdot}877;\ 11{\cdot}12)$. *c*) The values of b_{Δ} calculated from the relation (*29*) for $b_{13} < 2{\cdot}47$ are lower than the corresponding value of b'_{Δ} from the relation (*32*). Accordingly, when increasing b for a firmly chosen value of b_{13}, the formation of the three-phase region takes place by overlapping the two-phase regions (Fig. 8). For $b_{13} > 2{\cdot}47$, the three-phase region formation takes place at $b \geqq b'_{\Delta}$ on increasing the value of b, *i.e.* the three-phase region arises at the apex of heterogeneous region corresponding to the binary system $1-3$.

Also in this case the formation of three-phase region on the line $x_1 = x_3$ was investigated. As far as the three-phase region begins to form on the side two-phase regions we are entirely dependent on numerical calculations. The indicator of the formation of three-phase region is in such a case instability (invalidity of conditions (*16*)) of calculated coexisting phases.

TABLE III

Values of b'_{Δ} in Their Dependence on b_{13} Determined by Eq. (*32*) and Mole Fraction x at Critical Point

b_{13}	b'_{Δ}	x	b_{13}	b'_{Δ}	x
12	2·10	0·8332	2·90	1·9736	0·3103
11·1	2.00	0·8198	2·877	2·00	0·3048
10	1·875	0·80	2·80	2·10	0·2857
8	1·666	0·75	2·70	2·266	0·2592
6	1·50	0·6666	2·60	2·492	0·2307
5	1·458	0·60	2·596	2·50	0·2296
4·8284	1·4571	0·5857	2·50	2·8152	0·20
4	1·50	0·50	2·40	3·30	0·1666
3·50	1·604	0·4286	2·30	4·121	0·1304
3	1·875	0·333	2·20	5·775	0·091
			2·10	10·762	0·0476

Shape of the Liquid–Liquid Equilibrium Curve for a System Where $b_{13} \neq 0$, $b_{12} = b_{23} = b \neq 0$, $C = 0$ *Hold*

First we will investigate again the position of spinodal curve, or the set of points at which the determinant $D = 0$. In this case holds

$$D = (1/x_1 + 1/x_3 - 2b_{13})(1/x_2 + 1/x_3 - 2b) - (1/x_3 - b_{13})^2 . \qquad (33)$$

With respect to the symmetry between the components 1 and 3 we can write $x_1 = x_3 = (1 - x)/2$ and if we investigate the case $D = 0$ it is possible to obtain, after rearranging Eq. (*33*), the relation

$$4 - 8bx(1 - x) - 2b_{13}(1 - x)^2 + 4bb_{13}(1 - x)^2 x - b_{13}^2 x(1 - x)^2 = 0 . \qquad (34)$$

This equation is a quadratic equation with respect to b_{13} and its solution yields

$$b_{13(1)} = 2/(1 - x) , \qquad (35a)$$

$$b_{13(2)} = 4b - 2/[x(1 - x)] . \qquad (35b)$$

Eq. (*35a*) is identical with Eq. (*22a*) and have been applied in foregoing part. The second solution of Eq. (*35b*) reduces naturally to Eq. (*22b*) for $b = 0$. The dependence of b_{13} on x for various values of b is presented in Fig. 10.

Before passing to the discussion of some special subvariants, let us denote the value b_{13} which corresponds to the maximum on curves $b_{13(2)} = f(x)$ (Fig. 10) by the symbol $b_E = 4b - 8$. If $b_{13} < b_E$ the determinant D is zero at two values of x

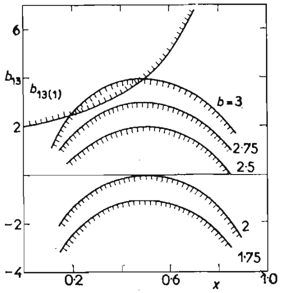


FIG. 10

Dependence of b_{13} on x According to Eq. (*36*) placed symmetrically about $x_2 = 0{\cdot}5$ (between these values the determinant D is negative). These values, however, do not correspond to the critical point because Eq. (*9*) is not fulfilled. As far as $b_{13} < b_E < 2$ holds a closed-loop region of limited miscibility will be in the ternary system (Fig. 3*b*). Unlike the variant with $b = 0$, which has been discussed at the beginning of this work, the values of b_{13} need not be in this case so low. For example for $b_{12} = b_{23} = b = 1{\cdot}75$, we obtain the closed-loop region already at $b_{13} < -1$. For $b_{13} = b_E < 2$, the closed loop curve reduces to a point with coordinates $x_1 = x_3 = 0{\cdot}25$. An interesting case occurs at $b_{13} = b_E = 0$, $b = 2$: Then $D = 0$ holds even for all points $x_2 = 0{\cdot}5$ (x_1 and x_3 are in this case arbitrary) and the critical "point" turns in this case into the critical "line".

Let us investigate, in addition, a special subvariant, *viz.* $b = b_{12} = b_{13} = b_{23}$. In this case all three binary systems behave in the same manner and it is sufficient to examine only the behaviour of one equilibrium curve. The cases which can occur are summarized in Fig. 11. At $b < 2$ the system is always homogeneous. For $18/7 > b > 2$, three two-phase regions are formed which increase with increasing b. At $b = 18/7 = 2{\cdot}571$ (as follows from Eq. (*32*)), a three-phase region begins to form at the apex of each heterogeneous region and this is accompanied by two smaller two-phase regions. With further increase of the value of b, the three-phase regions

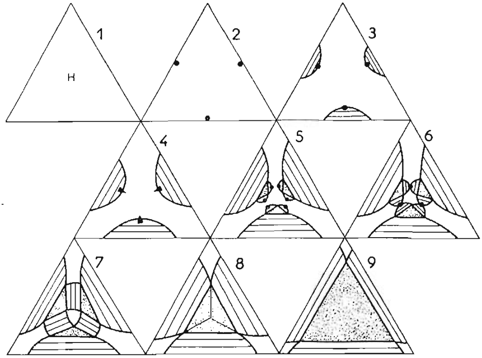


FIG. 11

Shapes of Liquid–Liquid Equilibrium Curves in Dependence on $b = b_{12} = b_{13} = b_{23}$

1 $b < 2$; 2 $b = 2$; 3 $2 < b < 2{\cdot}572$; 4 $b = 2{\cdot}572$; 5 $2{\cdot}572 < b < 2{\cdot}666$; 6 $b = 2{\cdot}666$; 7 $2{\cdot}666 < b < 2{\cdot}745$; 8 $b = 2{\cdot}745$; 9 $b > 2{\cdot}745$.

increase and at $b = b_E = 8/3 = 2{\cdot}666$ (as it follows from Eq. (*35b*)), the side two-phase regions will touch. At $2{\cdot}7456 > b > 2{\cdot}666$ three three-phase regions occur in the system together with six two-phase ones. At $b = 2{\cdot}7456$ (which follows from Eq. (*24*)), the three-phase region will merge and as a result we have one three-phase region.

It is evident from Fig. 11 that the variety of shapes of heterogeneous regions and consequently also of equilibrium curves, is large. In Fig. 12 we give these alternatives which can occur in this case in ternary system. From Figs 13*a* and 13*b* it is possible to determine at what values of the parameters it is possible to realize the given shapes.

In Figs 13*a* and 13*b*, the curves are given which delimit the single regions. The curve *a* presents the dependence between b_{13} and b which conform to the relation (*32*). The curve *b* expresses relation (*29*). The straight line c is determined by the rela-

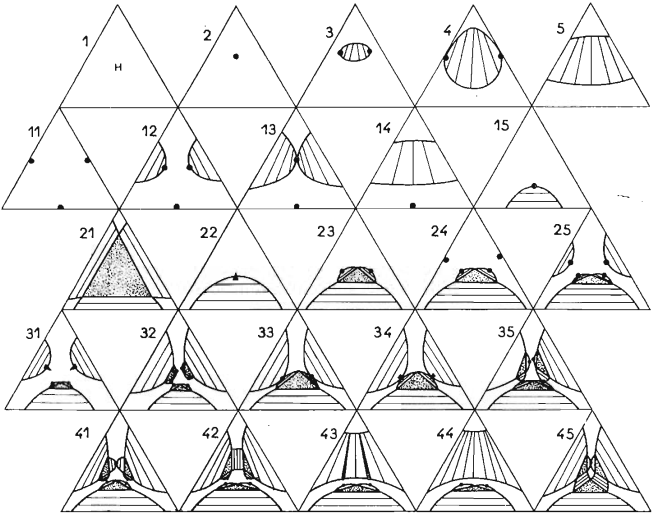
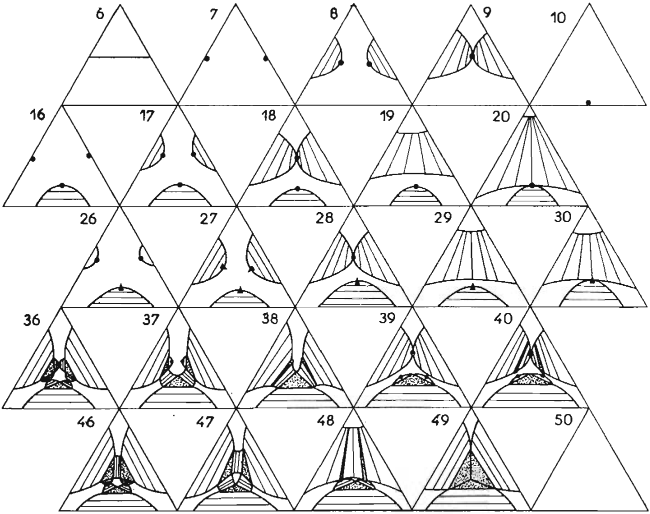


FIG. 12

Possible Shapes of Liquid–Liquid Equilibrium Curves in Ternary System with $b_{13} \neq 0$ and $b = b_{12} = b_{23} \neq 0$

tion $b_{13} = b_E = 4b - 8$ and follows from Eq. (*35b*). The curve *d* has been found tentatively and gives the values of parameters at which the side two-phase regions touch (in Fig. 11 it is at $b = 2{\cdot}666$). The curves e delimit the range of parameters at which the three-phase region is formed or disappears even at the side two-phase regions and has been found tentatively as well.

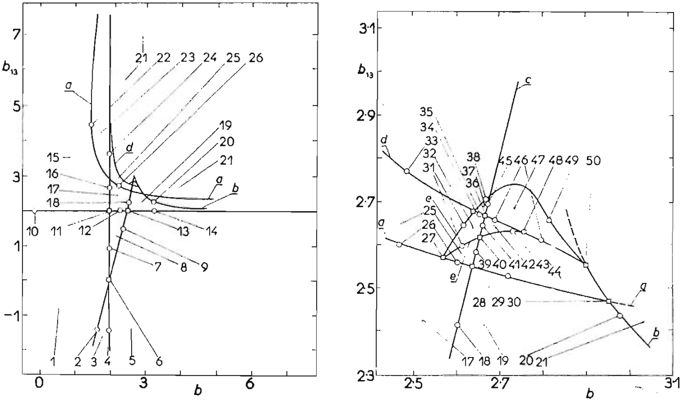
Some variants given in Fig. 12 are exotic but majority is common in practice. In Fig. 14 we give two examples from the Francis monograph[4]. The system n-C_6H_{14}–C_6H_5OH–H_2O remainds of the type No 23 in Fig. 12 and n-decanol–nitromethane–glycol the type No 18. We presume that even the variant No 6 is real to a certain extent and the systems H_2O–organic compound at the critical temperature will resemble to it if D_2O is taken as the third component. This type of system would be especially suitable to study thermodynamic or transport properties in the critical



1 Whole system is homogeneous, *6* for all points $x_2 = 0{\cdot}5$, it holds $D = 0$ ($b = 2$, $b_{13} = 0$), 24 for $b_{13} = 4$, critical points of side two-phase regions merge with critical points of binary systems 1–2 and 2–3.

region. No system has been found probably up to now in which more than one three-phase region would exist.

In Fig. 12 a type of system is missing which is presented in Fig. 15. As it is proved in Appendix 2 it is not possible to describe this system by making use of the binary



a *b*

FIG. 13

Delimitation of Single Types of Equilibrium Curves Given in Fig. 12 in Their Dependence on b_{13} and $b = b_{12} = b_{23}$

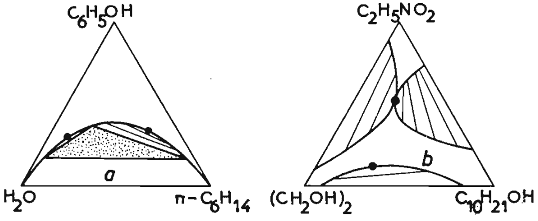


FIG. 14

Two Examples of More Complicated Shapes of Equilibrium Curves in Ternary System *a* $t = 75°C$; *b* $t = 6°C$.

constants b_{ij}. Heidemann and Mandham[2] succeeded in obtaining this diagram in terms of the van Laar equation but on using in addition the ternary constant C. Also in this case it can be described considering the ternary constant.

Effect of Ternary Constant ($b_{ij} = 0$)

The analysis of this variant having rather academic character, is carried out for the reason to compare limiting values of binary constants b_{ij} and the ternary constant C for homogeneous solution. For the determinant D, we obtain after rearranging the relation

$$D = 1/(x_1x_2) + 1/(x_1x_3) + 1/(x_2x_3) - 6C + \\ + C^2(1 - 2x_1^2 - 2x_2^2 - 2x_3^2)\,. \qquad (36)$$

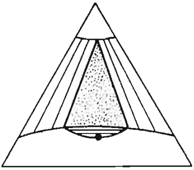


FIG. 15

Further Possible Alternative Shape of Equilibrium Curve in Ternary System

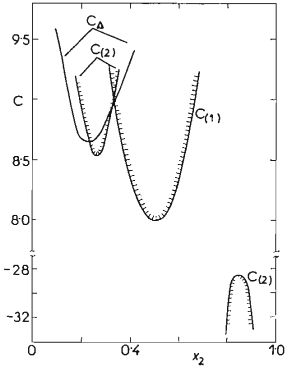


FIG. 16

Dependence of C on x According to Eqs (*38*) and (*40*)

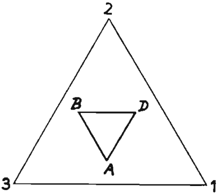


FIG. 17

Position of Three-Phase Region in Ternary System if Effect of Ternary Constant Only is Considered

Since symmetrical system is considered it is sufficient to investigate D along the line $x_1 = x_3 = (1 - x)/2$. We obtain the relation

$$D = 4/[x(1 - x)] + 4/(1 - x)^2 - 6C + C^2[1 - (1 - x)^2 - 2x^2]. \qquad (37)$$

From Eq. (37) and the condition $D = 0$ we get a quadratic equation for the parameter C having these two solutions

$$C_{(1)} = 2/[x(1 - x)], \qquad (38a)$$

$$C_{(2)} = 2/[x(1 - x)(2 - 3x)]. \qquad (38b)$$

The dependence of C on x is given in Fig. 16. For $-28{\cdot}5 < C < 8$ the system is homogeneous, for $C > 8$ or $C < -28{\cdot}5$ we obtain three heterogeneous regions.

Before passing to a more detailed discussion of possible variants, it is necessary to find conditions at which the given three regions merge to form a three-phase region. The resulting three-phase region will have the shape indicated in Fig. 17. With regard to the total asymmetry, the apexes of the three-phase region will have the following coordinates: $A[x_1, x_2] = A[(1 - x)/2, x]$; $B[z_1, z_2] = B[x, (1 -$

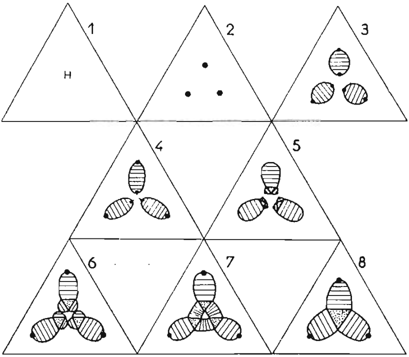


FIG. 18

Shapes of Equilibrium Curves in Ternary System in Dependence on Constant C

1 $-2{\cdot}8 < C < 8$; 2 $C = 8$; 3 $8 < C < 8{\cdot}393$; 4 $C = 8{\cdot}393$; 5 $8{\cdot}393 < C < 8{\cdot}520$; 6 $C = 8{\cdot}520$; 7 $8{\cdot}520 < C < 8{\cdot}634$; 8 $C \geqq 8{\cdot}634$.

$- x)/2]$; $D[w_1, w_2] = D[(1 - x)/2, (1 - x)/2]$. From the equality of activities of component 1 at the point A and B we will get (the value of C will be denoted by C_Δ)

$$\ln[(1 - x)/2] + C_\Delta x^2(1 - x)/2 = \ln x + C_\Delta(1 - 2x)[(1 - x)/2]^2 \qquad (39)$$

and for the constant C_Δ we will obtain the relation

$$C_\Delta = 4(1 - x)(1 - 3x)^{-1} \ln[(1 - x)/(2x)]\,. \qquad (40)$$

The dependence of C_Δ on x (for the point A, x merges in x_2) is presented as well in Fig. 16. This dependence exhibits a minimum at $x_2 = 0{\cdot}235$ and $C = 8{\cdot}634$. It is possible to show that this minimum corresponds to the minimum value of the Gibbs energy of mixing $G^M = G^M(x)$. For $C_\Delta > 8{\cdot}634$ we get two values of x from Eq. (*40*) and consequently also two different triangles which correspond to two three-phase regions. The inner triangle is metastable and the larger value of G^M corresponds to it (see analogous case for relation (*24*)).

In Fig. 18 we give a sequence of diagrams which result gradually from increasing the parameter C (negative values of C have not been investigated). Three closed-loop two-phase regions are formed at $C > 8$. If $C \approx 8{\cdot}39$ then a three-phase region appears on the inner side of the closed-loop curve and this is accompanied by two two-phase regions on its sides. At $C = 8{\cdot}5202$ ($x = 0{\cdot}26$) these side two-phase regions will touch. When increasing the parameter C on, these regions increase and simultaneously all three three-phase regions increase, too. If $C = 8{\cdot}634$ then these three-phase regions merge and an only triangle is formed. The coordinates of its apexes are determined from Eq. (*40*). The critical point of the two-phase regions can be determined from relation (*38a*).

From the shapes of equilibrium curves in Fig. 18 it is evident that in this case different diagrams from those given in Fig. 12 are obtained. In this fact we can see the justification of the last term in Eq. (*1*). By incorporating the ternary constant it is also possible to model the diagram in Fig. 15 which has been proved not to be possible to be obtained only in terms of binary constants b_{ij} in Eq. (*1*).

It would be possible to investigate further variants with ternary constant but it is outside the framework of this work. Just to inform we give several orientation values of the ternary constant for $b = b_{12} = b_{13} = b_{23}$ which are possible as a maximum for a homogeneous system:

b	0	1	1·5	1·75
C	8	5·95	4·5	3·67

APPENDIX 1

The relations following from Eq. (*1*) for the thermodynamic quantities given below:

$$\begin{aligned}
Q &= \mathrm{G}^{\mathrm{E}}/RT = x_1x_2b_{12} + x_1x_3b_{13} + x_2x_3b_{23} + Cx_1x_2x_3\\
\ln a_1 &= \ln x_1 + b_{12}x_2(1 - x_1) + b_{13}x_3(1 - x_1) - b_{23}x_2x_3 + Cx_2x_3(1 - 2x_1)\\
\ln a_2 &= \ln x_2 + b_{12}x_1(1 - x_2) - b_{13}x_1x_3 + b_{23}x_3(1 - x_2) + Cx_1x_3(1 - 2x_2)\\
\ln a_3 &= \ln x_3 - b_{12}x_1x_2 + b_{13}x_1(1 - x_3) + b_{23}x_2(1 - x_3) + Cx_1x_2(1 - 2x_3)\\
\mathrm{G11} &= \partial^2(G^{\mathrm{M}}T)/\partial x_1^2 = 1/x_1 + 1/x_3 - 2b_{13} - 2Cx_2\\
\mathrm{G12} &= \partial^2(G^{\mathrm{M}}/RT)/\partial x_1\, \partial x_2 = 1/x_3 + b_{12} - b_{13} - b_{23} + \mathrm{C}(x_3 - x_1 - x_2)\\
\mathrm{G22} &= \partial^2(G^{\mathrm{M}}/RT)/\partial x_2^2 = 1/x_2 + 1/x_3 - 2b_{23} - 2Cx_1\\
\mathrm{G111} &= \partial^3(G^{\mathrm{M}}/RT)/\partial x_1^3 = 1/x_3^2 - 1/x_1^2\\
\mathrm{G112} &= \partial^3(G^{\mathrm{M}}/RT)/\partial x_1^2\, \partial x_2 = \mathrm{G122} = \partial^3(\mathrm{G}^{\mathrm{M}}/RT)/\partial x_1\, \partial x_2^2 = 1/x_3^2 - 2C\\
\mathrm{G222} &= \partial^3(G^{\mathrm{M}}/RT)/\partial x_2^3 = 1/x_3^2 - 1/x_2^2\\
\mathrm{G1111} &= 2/x_1^3 + 2/x_3^3\\
\mathrm{G1112} &= \mathrm{G1122} = \mathrm{G1222} = 2/x_3^2\\
\mathrm{G2222} &= 2/x_2^3 + 2/x_3^3\,.
\end{aligned}$$

APPENDIX 2

We shall show that in the case of $b_{12} = b_{23} = b$, $b_{13} < 2$ and $C = 0$ it is not possible to obtain the ternary diagram in Fig. 15. It is so because in the given case, the critical point can occur on the line $x_1 = x_3 = (1 - x)/2$, $(x_2 = x)$ just at $x = 0{\cdot}5$ and $b_{13} = b_{\mathrm{E}} = b - 8$, which corresponds to the ternary diagrams No 9, 18, 28, 36, 39, 40, 41, and 45 in Fig. 12. This statement can be attained by the following consideration: At the critical point, $D = 0$ and $D^* = 0$ must hold. The first equation is fulfilled if it holds

$$b_{13} = 2/(1 - x)\,, \tag{35a}$$

$$b_{13} = 4b - 2/[x(1 - x)\,x]\,. \tag{35b}$$

The solution (*35a*) has been eliminated because it corresponds to the heterogeneous binary system 1—3. For the determinant D^* holds

$$D^* = (\partial D/\partial x_1)\,\mathrm{G22} - \mathrm{G12}(\partial D/\partial x_2)\,. \tag{9}$$

It is possible to make sure easily that on the line $x_1 = x_3$ holds: $(\partial D/\partial x_1) = 0$ (consequence of the symmetry of system) and $\mathrm{G12} \neq 0$ (since $b_{13} < 2$). Consequently, it must hold $\partial D/\partial x_2 = 0$ so that the second equation may be fulfilled. On differentiating relation (*33*) and rearranging we get

$$2(1 - x)^3\, x^2(\partial D/\partial x_2) = 6x - 2 + b_{13}(1 - x)^3 + 4bx^2(1 - x)\,. \tag{A—1}$$

Putting the right-hand side of relation (*A—1*) equal to zero and inserting from relation (*35b*) for the expression $4b$, we obtain the relation

$$(1 - x)\,(1 - 2x)\,b_{13} = 2(1 - 2x)\,. \tag{A—2}$$

Eq. (*A—2*) is fulfilled only for $x = 0{\cdot}5$ (see above-mentioned diagrams) and for $b_{13} = 2/(1 - x)$, which implies the heterogeneous binary system 1—3 which has been excluded from our considerations. In this way our statement is proved.

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