LIQUID–LIQUID EQUILIBRIUM. CALCULATION
OF EQUILIBRIUM COMPOSITION OF COEXISTING PHASES

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A new algorithm is proposed for determining the equilibrium curve on the basis of the knowledge of Gibbs' energy of N-component system. A known equilibrium composition is used during calculation to estimate the next approximation. The method is also modified for chemical-engineering applications when the composition of coexisting phases to a given overall composition is sought (flash calculations).

The difficulties in calculating the composition of coexisting phases have been one of the main hindrances of application of the thermodynamic description to the liquid–liquid phase equilibrium. This is as well the reason why up to the present appropriate attention has not been paid to this problem. The methods used of calculation of coexisting phases can be divided into three groups: *a*) non-derivative iterative methods, *b*) methods using the Newton solution of non-linear equations, *c*) methods based on seeking the minimum of Gibbs' energy.

To the first group pertain the methods proposed by Null[1], Boberg[2], Balder and coworkers[3]. They are very attractive at first sight because they require only a procedure for calculating activity coefficients. On the other hand this advantage is compensated by the need of a higher number of iterations. The methods seeking the minimum of Gibbs' energy[4] have not found a wider application hitherto even if they allow to determine in principle the correct solution.

The most rapid calculation is achieved by solving the non-linear equations

$$\ln a_i(\bar{x}) = \ln a_i(\bar{\bar{x}}), \quad i = 1, 2, ..., N \tag{1}$$

by the Newton method, where $a_i = x_i \gamma_i$ is the activity of i-th component. The efficiency of the Newton method excels especially at a suitable initial estimate of composition of coexisting phases. This method is used by Joy[5], Renon and coworkers[6], Novák and coworkers[7,8], Magnussen and coworkers[9]. The calculation is rather complicated as it requires the calculation of the activity coefficients and also their derivatives with respect to composition. These derivatives can be determined either numerically

or analytically. The numerical way of calculating extends considerably the calculation especially in case of multicomponent systems.

In applications we meet different types of problems. Let us consider an N-component system at a temperature T and pressure P which splits into two liquid phases. Such a system has $(N - 2)$ degrees of freedom. In agreement with the type of given variables we get different tasks from which the following three will form the object of this work:

1) Calculation of the equilibrium curve or surface for given values of x_1 (or x_2) in ternary system, x_1 and x_2 (or x_1 and x_3) in quaternary system, *etc.*

2) When calculating the extraction equipment the problem is very important when the overall composition $w_1, w_2, ..., w_{N-1}$ is given of a heterogeneous mixture which splits into two phases whose composition and relative amount ϕ is to be determined. From the material balance we have

$$w_i = (1 - \phi)\, \bar{x}_i + \phi \bar{\bar{x}}_i, \quad i = 1, 2, ..., N - 1, \tag{2}$$

where ϕ stands for the number of moles of the phase with composition $\bar{\bar{x}}_1, \bar{\bar{x}}_2, ..., \bar{\bar{x}}_{N-1}$ which is formed from 1 mol of mixture of overall composition $w_1, w_2, ..., w_{N-1}$.

3) The foregoing problem can be modified in such a way that we are to find the composition of coexisting phases which corresponds to the overall composition of mixture $w_1, w_2, ..., w_{N-2}$ (*i.e.* the overall composition is given incompletely!) and, simultaneously, ϕ mol of the phase of composition $\bar{\bar{x}}_1, \bar{\bar{x}}_2, ..., \bar{\bar{x}}_{N-1}$ and $(1 - \phi)$ mol of the phase of composition $\bar{x}_1, \bar{x}_2, ..., \bar{x}_{N-1}$ is to be formed.

In our calculations we start from the assumption that we know at least one pair of compositions of coexisting phases $\bar{x}^0 = (\bar{x}_1^0, \bar{x}_2^0, ..., \bar{x}_{N-1}^0)$ and $\bar{\bar{x}}^0 = (\bar{\bar{x}}_1^0, \bar{\bar{x}}_2^0, ..., \bar{\bar{x}}_{N-1}^0)$ for the given system. It will be also shown, how it is possible to obtain this approximation of composition of coexisting phases in N-component system from the knowledge of compositions of coexisting phases in binary heterogeneous system which are relatively easily available.

Determination of Equilibrium Curve

The system of equilibrium conditions (*1*) is a system of N equations for $2(N - 1)$ unknown values of mole fractions $\bar{x}_i, \bar{\bar{x}}_i, i = 1, 2, ..., N - 1$. Let us assume, as it has been said in introduction, that the vectors $\bar{x}^0$ and $\bar{\bar{x}}^0$ are one of solutions of system of equations (*1*). The next solution of this system can be obtained in the following way: Let us introduce the designation

$$\bar{x}_i = \bar{x}_i^0 + \Delta \bar{x}_i,$$
$$\bar{\bar{x}}_i = \bar{\bar{x}}_i^0 + \Delta \bar{\bar{x}}_i, \quad i = 1, 2, ..., N - 1 \tag{3}$$

where the increments $\Delta \bar{x}_i, \Delta \bar{\bar{x}}_i, i = 1, 2, ..., N - 1$ acquire small values, *i.e.* we seek such a solution of system of equations (*1*) which is not "too" far from the solution $\bar{x}^0, \bar{\bar{x}}^0$. By expanding the left-hand and right-hand sides of system of equations (*1*) into the Taylor series at the points $\bar{x}^0, \bar{\bar{x}}^0$ and neglecting the second and higher powers of increments $\Delta \bar{x}_i$ and $\Delta \bar{\bar{x}}_i$ we obtain the system of equations

$$\sum_{j=1}^{N-1} \left[\frac{\partial \ln a_i(\bar{x}^0)}{\partial x_j} \Delta \bar{x}_j - \frac{\partial \ln a_i(\bar{\bar{x}}^0)}{\partial x_j} \Delta \bar{\bar{x}}_j \right] = 0 . \quad i = 1, 2, ..., N \qquad (4)$$

The set dimension of solutions of the system of linear equations (*4*) is $N - 2$. Without detriment to generality let us assume that the values $\Delta \bar{\bar{x}}_2, \Delta \bar{\bar{x}}_3, ..., \Delta \bar{\bar{x}}_{N-1}$ have been chosen fixedly. Then by solving system of equations (*4*) we determine the values of remaining increments $\Delta \bar{x}_1, ..., \Delta \bar{x}_{N-1}, \Delta \bar{\bar{x}}_1$.

The existence and uniqueness of this solution is ensured by the conditions of thermodynamic stability (excepting the cases which will be mentioned in conclusion of this chapter). As far as some of calculated increments is too large then it is sufficient to multiply all the increments by a reducing parameter $\eta \in \langle 0, 1 \rangle$, for the vectors $\eta \Delta \bar{x}$ and $\eta \Delta \bar{\bar{x}}$ are also the solution of system of equations (*4*), even for arbitrary $\eta \in (-\infty, \infty)$.

When determining η we can proceed *e.g.* in the following way: Let us denote

$$S_1 = \sqrt{\left[\sum_{i=1}^{N-1} (\Delta \bar{x}_i)^2 \right]}, \quad S_2 = \sqrt{\left[\sum_{i=1}^{N-1} (\Delta \bar{\bar{x}}_i)^2 \right]}, \quad S = \max (S_1, S_2) . \qquad (5)$$

If $S > \delta$, where δ represents the allowed "step" along the equilibrium curve which was usually chosen equal to 0·05, then we have for the reducing parameter η

$$\eta = \delta/S . \qquad (6)$$

In the opposite case $\eta = 1$.

Let us designate by the symbols $\bar{x}^1, \bar{\bar{x}}^1$, the vectors for which hold

$$\bar{x}_i^1 = \bar{x}_i^0 + \eta \Delta \bar{x}_i ,$$
$$\bar{\bar{x}}_i^1 = \bar{\bar{x}}_i^0 + \eta \Delta \bar{\bar{x}}_i , \quad i = 1, 2, ..., N - 1 , \qquad (7)$$

where the increments $\Delta \bar{\bar{x}}_2, ..., \Delta \bar{\bar{x}}_{N-1}$ are firmly chosen and the other ones are determined by the solution of system of equations (*4*). The vectors $\bar{x}^1$ and $\bar{\bar{x}}^1$ are then the initial approximation of solution of system of equations (*1*), where the values of variables $\bar{\bar{x}}_2, ..., \bar{\bar{x}}_{N-1}$ are firmly chosen. System of equations (*1*) is then a system of N equations for N unknowns $\bar{x}_1, ..., \bar{x}_{N-1}$ and $\bar{\bar{x}}_1$.

Consequently, in the first step of the Newton method we solve the system of N linear equations

$$\sum_{j=1}^{N-1} \frac{\partial \ln a_i(\bar{x}^1)}{\partial x_j} \Delta\bar{x}_j - \frac{\partial \ln a_i(\bar{x}^1)}{\partial x_1} \Delta\bar{x}_1 = \ln \frac{a_i(\bar{x}^1)}{a_i(\bar{x}^1)}, \quad i = 1, 2, ..., N \qquad (8)$$

for N increments $\Delta\bar{x}_1, ..., \Delta\bar{x}_{N-1}$ and $\Delta\bar{x}_1$. A new approximation of compositions of coexisting phases is then determined from the relation

$$\bar{x}_j^2 = \bar{x}_j^1 + \eta \Delta\bar{x}_j, \quad j = 1, 2, ..., N - 1$$
$$\bar{x}_1^2 = \bar{x}_1^1 + \eta \Delta\bar{x}_1, \qquad (9)$$

where $\eta \in (0, 1\rangle$ is the reducing parameter and the calculation is repeated. In the original Newton method, it is always $\eta = 1$. In the initial steps of the Newton method, however, it can happen that the values of increments are in absolute value too large and therefore it is suitable to choose η according to Eq. (6). The iteration procedure is repeated unless the values of increments are "sufficiently" small.

After solving system of equations (8) for the firmly chosen values of mole fractions $\bar{x}_2^1, ..., \bar{x}_{N-1}^1$ we choose further values of increments $\Delta\bar{x}_2, ..., \Delta\bar{x}_{N-1}$ and by solving system of equations (4) we obtain a good estimate of the next pair of compositions of coexisting phases and the whole cycle is repeated. When calculating $\Delta\bar{x}_1, \Delta\bar{x}_2, ..., \Delta\bar{x}_{N-1}$ and $\Delta\bar{x}_1$ according to Eqs (4) it is convenient to use the already obtained intermediate results, for the elements of the matrix of system of equations (4) are identical with those of the matrix of system of equations (8) in the last iteration step.

The first two steps along the equilibrium curve are outlined for ternary system in Fig. 1.

The number of iterations needed for solving the system of equations (8) was equal to $2-3$ in the calculations with the maximum step along the equilibrium curve $S = 0.05$ (Eq. (5)) when the condition for finishing the calculation was $|\Delta x_i| < 10^{-4}$ for all i.

System of equations (4) can be solved only in the case that the points $\bar{x}^0$ and $\bar{\bar{x}}^0$ are the inside points of N-component system, i.e. $\bar{x}_i, \bar{\bar{x}}_i \neq 0$ holds for all $i = 1, 2, ..., N$. This condition is not satisfied if e. g. we use the composition of coexisting phases of binary system as the initial approximation for calculating the equilibrium curve of ternary system. Without detriment to generality let us assume that $\bar{x}_k^0 = \bar{\bar{x}}_k^0 = 0$ holds for a component k, $k \neq N$. Then the value $\partial \ln a_k / \partial x_k$ in system of equations (4) is not finite, for $\ln a_k = \ln x_k + \ln \gamma_k$ holds. Then it is necessary to rearrange the corresponding k-th equation of system (4) in the following way: Instead of the equilibrium condition $\ln a_k(\bar{x}) = \ln a_k(\bar{\bar{x}})$ we consider the equivalent

condition $a_k(\bar{x}) = a_k(\bar{\bar{x}})$. It follows from the relation $a_k = x_k \gamma_k$

$$\partial a_k(\bar{x}^0)/\partial x_j = \partial a_k(\bar{\bar{x}}^0)/\partial x_j = 0, \quad j \neq k$$
$$\partial a_k(\bar{x}^0)/\partial x_k = \gamma_k(\bar{x}^0), \quad \partial a_k(\bar{\bar{x}}^0)/\partial x_k = \gamma_k(\bar{\bar{x}}^0), \quad (10)$$

where $\gamma_k(\bar{x}^0)$ and $\gamma_k(\bar{\bar{x}}^0)$ is the limiting activity coefficient of the k-th component. It follows from the analogous application of the Taylor series that the k-th equation of system (4) is considered in this case in the form

$$\gamma_k(\bar{x}^0) \Delta \bar{x}_k - \gamma_k(\bar{\bar{x}}^0) \Delta \bar{\bar{x}}_k = 0. \quad (11)$$

It would be possible to derive easily an analogous equation for $k = N$. However, the condition $k \neq N$ can be always satisfied by exchanging the order of compounds.

This fact makes it possible that, on the basis of the knowledge of phase compositions in binary system, we can easily estimate the composition of phases in N-component system not too distant from this binary system. Or, when knowing the composition of phases in three-component system, we can easily estimate the phase compositions in four- and more-component system. This possibility is especially invaluable in multicomponent systems where determination of the first approximation of composition is especially complicated.

The proposed method of calculating the equilibrium curve is very efficient with regard to the fact that it ensures a good estimate of equilibrium composition on the basis of preceeding point. However, in some isolated cases it can happen that the calculation will not converge. According to our experience it can be caused by the following facts:

1) Incorrect variant of calculation. One such case in ternary system is shown in Fig. 2. As far as the estimated pairs of coexisting phases are given by the points $\bar{x}^1, \bar{\bar{x}}^1$ and

Fig. 1

Calculation of equilibrium curve for a firmly chosen value of $\bar{\bar{x}}_2$

the system of equations (4) is solved for $\bar{x}_2^1 = $ const., then we do not find any solution because the whole line $x_2 = \bar{x}_2^1$ lies in the homogeneous region. In such a case it is sufficient to choose another variant of solution of Eqs (4), e.g. $\bar{x}_1^1 = $ const. or, which is simplest, to exchange both phases and to solve the variant $\bar{x}_2 = $ const.

2) Thermodynamic instability of some of phases. The determinant of system of equations (8), D_8

$$D_8 = \begin{vmatrix} \dfrac{\partial \ln a_1(\bar{x})}{\partial x_1} & \dfrac{\partial \ln a_1(\bar{x})}{\partial x_2} & \cdots & \dfrac{\partial \ln a_1(\bar{x})}{\partial x_{N-1}} & - & \dfrac{\partial \ln a_1(\bar{x})}{\partial x_1} \\[3mm] \dfrac{\partial \ln a_2(\bar{x})}{\partial x_1} & \cdots & & & - & \dfrac{\partial \ln a_2(\bar{x})}{\partial x_1} \\[3mm] \vdots & & & & & \vdots \\[3mm] \dfrac{\partial \ln a_{N-1}(\bar{x})}{\partial x_1} & \cdots & & & - & \dfrac{\partial \ln a_{N-1}(\bar{x})}{\partial x_1} \\[3mm] \dfrac{\partial \ln a_N(\bar{x})}{\partial x_1} & \dfrac{\partial \ln a_N(\bar{x})}{\partial x_2} & \cdots & \dfrac{\partial \ln a_N(\bar{x})}{\partial x_{N-1}} & - & \dfrac{\partial \ln a_N(\bar{x})}{\partial x_1} \end{vmatrix} \quad (12)$$

is rearranged in this way: The i-th row $(i = 1, 2, \ldots, N)$ of the matrix is multiplied by the value $\bar{x}_i$. The other rows are added to the last row of the matrix so formed. On using the Gibbs–Duhem equation we get

$$D_8 = -(D_a/\bar{x}_N) \sum_{i=1}^{N} \bar{x}_i \, \partial \ln a_i(\bar{x})/\partial x_1 =$$

$$= -(D_a/\bar{x}_N) \sum_{i=1}^{N} (\bar{x}_i - \bar{x}_i) \, \partial \ln a_i(\bar{x})/\partial x_1 , \quad (13)$$
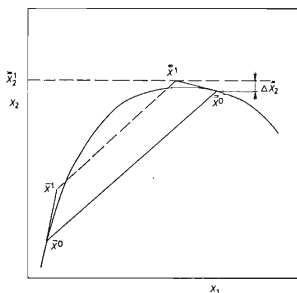
FIG. 2

Illustration of an incorrect variant of solution of system of equations (1) in a ternary system

where

$$D_a = \begin{vmatrix} \dfrac{\partial \ln a_1(\bar{x})}{\partial x_1} & \dfrac{\partial \ln a_1(\bar{x})}{\partial x_2} & \cdots & \dfrac{\partial \ln a_1(\bar{x})}{\partial x_{N-1}} \\[2mm] \dfrac{\partial \ln a_2(\bar{x})}{\partial x_1} & \dfrac{\partial \ln a_2(\bar{x})}{\partial x_2} & \cdots & \dfrac{\partial \ln a_2(\bar{x})}{\partial x_{N-1}} \\[2mm] \vdots & & & \vdots \\[2mm] \dfrac{\partial \ln a_{N-1}(\bar{x})}{\partial x_1} & & \cdots & \dfrac{\partial \ln a_{N-1}(\bar{x})}{\partial x_{N-1}} \end{vmatrix} \qquad (14)$$

By means of the determinant D_a, the thermodynamic stability of the first phase is defined by the relation[10,11]

$$D_a > 0. \qquad (15)$$

The equation

$$D_a = 0 \qquad (16)$$

defines a so-called spinodal surface (in ternary system at constant temperature and pressure, spinodal curve — see Fig. 3), which, in a stable two-phase system,
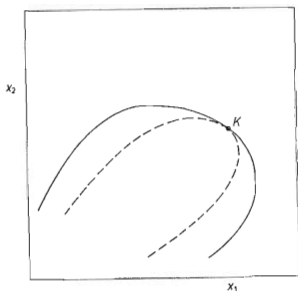
FIG. 3

The course of binodal (———) and spinodal (-----) curves in a ternary system; K critical point
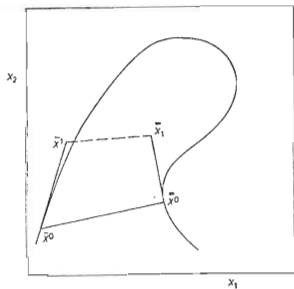
FIG. 4

The course of equilibrium curve with a concave part

lies inside the binodal surface (curve) which is defined by system of equations (1). It is evident that, if we include the points of spinodal surface into the calculation, the matrix of system of equations (8) is singular. When crossing the spinodal surface or curve, the increments change their sign. In case of binary system it is possible to show easily that, on using the points which do not meet condition (15), the calculation will converge to the trivial solution $\bar{x} = \bar{\bar{x}}$. We assume that the same will hold also in multicomponent systems. Therefore we recommend to check the signs of D_8 for both phases during calculation. As soon as condition (15) is not fulfilled, it can be most likely from these reasons: *a*) A part of binodal curve exhibits concave course (Fig. 4). When estimating next point $\bar{x}^1$ and $\bar{\bar{x}}^1$ we get deep into the heterogeneous region and it is necessary to reduce the allowed step δ along the equilibrium surface.

b) The two-phase region is overlapped by the three-phase one. The last points of calculated binodal curve $(A, B$ in Fig. 5) belong already to the metastable two-phase region which is overlapped by a more stable three-phase region. On the other hand, this fact is an invaluable advantage of this procedure because it allows to disclose the existence of three-phase region.

c) The calculation will also not converge in a certain vicinity of the critical point owing to the rounding errors. It is evident from Eq. (12) that in the vicinity of the critical point the determinant of system (8), D_8, approaches zero not only since the value of D_8 falls to zero but also the difference in composition of both phases limits to zero. However, in spite of it we can get relatively close to the critical point when using multiple precision.

Calculation of Composition of Coexisting Phases for a Given Overall Composition of Heterogeneous Mixture (Flash Calculations)

Let the overall composition of heterogeneous mixture $w = (w_1, w_2, \ldots, w_{N-1})$ be given. The equations of material balance have the vectorial record

$$(1 - \phi)\,\bar{x} + \phi\bar{\bar{x}} = w\,, \tag{17}$$

where $\phi \in \langle 0, 1 \rangle$. Therefore we seek the composition of such a pair of coexisting phases whose tie-line goes through the point w. The equilibrium conditions and the equations of material balance take then the form

$$\ln a_i(\bar{x}) = \ln a_i(\bar{\bar{x}})\,, \quad i = 1, 2, \ldots, N$$

$$(1 - \phi)\,\bar{x}_j + \phi\bar{\bar{x}}_j = w_j\,, \quad j = 1, 2, \ldots, N - 1 \tag{18}$$

The system of non-linear equations (18) is a system of $(2N - 1)$ equations for $(2N - 1)$ unknowns $\bar{x}_i, \bar{\bar{x}}_i, i = 1, 2, \ldots, N - 1$, and for the parameter ϕ. We assume again that we know the values of initial approximation of composition of coexisting phases $\bar{x}^0, \bar{\bar{x}}^0$. The equations of material balance can be rearranged into the form

$$(\bar{\bar{x}}_i - \bar{x}_i)/(\bar{\bar{x}}_1 - \bar{x}_1) = (w_i - \bar{x}_i)/(w_1 - \bar{x}_1), \quad i = 2, 3, \ldots, N - 1 \qquad (19)$$

which has arisen so that the parameter ϕ has been expressed from the first equation of system (17) and its value has been inserted into the remaining equations of material balance. Henceforth we will use Eqs (19) in the form

$$(\bar{\bar{x}}_i - \bar{x}_i)(w_1 - \bar{x}_1) = (w_i - \bar{x}_i)(\bar{\bar{x}}_1 - \bar{x}_1). \quad i = 2, 3, \ldots, N - 1 \qquad (20)$$

From the relations

$$\bar{x}_i = \bar{x}_i^0 + \Delta \bar{x}_i,$$
$$\bar{\bar{x}}_i = \bar{\bar{x}}_i^0 + \Delta \bar{\bar{x}}_i, \quad i = 1, 2, \ldots, N - 1 \qquad (21)$$

follows that the equations of material balance (20) can be expressed in the form

$$(\alpha_i + \Delta \bar{\bar{x}}_i - \Delta \bar{x}_i)(\beta_1 - \Delta \bar{x}_1) - (\beta_i - \Delta \bar{x}_i)(\alpha_1 + \Delta \bar{\bar{x}}_1 - \Delta \bar{x}_1) = 0,$$
$$i = 2, 3, \ldots, N - 1, \qquad (22)$$

where we have designated

$$\alpha_i = \bar{\bar{x}}_i^0 - \bar{x}_i^0, \quad \beta_i = w_i - \bar{x}_i^0. \quad i = 1, 2, \ldots, N - 1 \qquad (23)$$
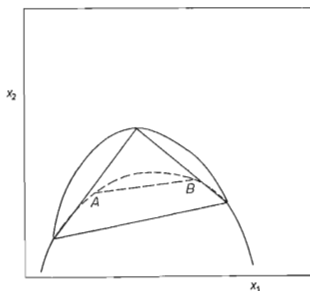

FIG. 5

Overlapping of two-phase region by a three-phase region

By multiplying the parentheses in Eq. (22) and neglecting the increments of the second order we obtain

$$\beta_1 \, \Delta \bar{x}_i + (\alpha_1 - \beta_1) \, \Delta \bar{x}_i - \beta_i \, \Delta \bar{\bar{x}}_1 - (\alpha_i - \beta_i) \, \Delta \bar{x}_1 = \beta_i \alpha_1 - \alpha_i \beta_1 \, .$$

$$i = 2, 3, \ldots, N - 1 \tag{24}$$

By replacing the equilibrium conditions (1) by the Taylor series at the points $\bar{x}^0$, $\bar{\bar{x}}^0$ and neglecting the second and higher powers of increments $\Delta \bar{x}_i$, $\Delta \bar{\bar{x}}_i$, $i = 1, 2, \ldots, N - 1$ we get the system of linear equations

$$\sum_{j=1}^{N-1} \left\{ \frac{\partial \ln a_i(\bar{x}^0)}{\partial x_j} \, \Delta \bar{x}_j - \frac{\partial \ln a_i(\bar{\bar{x}}^0)}{\partial x_j} \, \Delta \bar{\bar{x}}_j \right\} = \ln \frac{a_i(\bar{\bar{x}}^0)}{a_i(\bar{x})^0} \, . \qquad i = 1, 2, \ldots, N \tag{25}$$

By combining systems of equations (24) and (25) we obtain a linear system of $(2N - 2)$ equations for $(2N - 2)$ unknown increments $\Delta \bar{x}_i$, $\Delta \bar{\bar{x}}_i$.

Since the values of initial approximation $\bar{x}^0$ and $\bar{\bar{x}}^0$ can differ significantly from the solution of system of equations (18), it is necessary, at least in several initial iteration steps of the Newton method, to use the reducing parameter η (Eqs (5) and (6)).

Further it is possible to proceed in two ways: In the first variant (henceforth designated as V1) we obtain a new approximation of equilibrium composition of co-
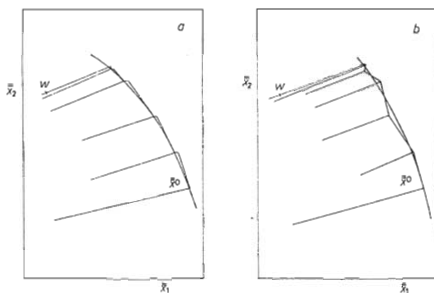
existing phases $\bar{x}^1$, $\bar{\bar{x}}^1$ by inserting into Eqs (7) after determining $\Delta\bar{x}_i$, $\Delta\bar{\bar{x}}_i$, $i = 1, 2, \ldots$
$\ldots, N - 1$, from systems of equations (24) and (25). With this approximation of composition we solve system of equations (1), e.g. for chosen values $\bar{x}_2, \ldots, \bar{x}_{N-1}$ as in the first part. The calculated compositions are used as a new approximation $\bar{x}^0$ and $\bar{\bar{x}}^0$ for the next step.

In the second variant (V2) we start all the time from systems of equations (24) and (25) and do not return on the equilibrium surface (but doing so we use all the time the reducing parameter which is determined by Eq. (6)). The difference between both the procedures in a ternary system is shown in Fig. 6.

On comparing these two variants it is possible to say that the first one will be more reliable even though slower (after each step on the equilibrium surface it is necessary to solve completely system of equations (1)). However, using sufficiently low δ, this variant fails (if it is not too far from w) only in the cases when the method described in the foregoing part fails, too (unsuitable numbering of components, concave segments on the equilibrium surface, close occurrence of three-phase region, rounding errors in the vicinity of critical point). On the other hand, the variant V2 will be much more rapid but it can be recommended just only for "smooth" equilibrium curves or surfaces. Before using it we recommend to make sure of its applicability for the given system.

Convergence of the Newton method is always subject to a factor of uncertainty and therefore as the most sure we recommend the following third variant (V3). This variant can be especially advantageous in the case when the vector w is "very" far from conode $\bar{x}^0$, $\bar{\bar{x}}^0$. The convergence can be ensured if we proceed in the following way:

a) We construct the line segment $\overline{w, w^0}$ whose one end point is the point w and the second one a hitherto particularly undetermined point w^0 on the line segment $\overline{\bar{x}^0, \bar{\bar{x}}^0}$ — see Fig. 7. The construction of the point w^0 will be explained later. b) On the line segment $\overline{w, w^0}$, for the points ξ of which holds $\xi = (1 - \varphi) w^0 + \varphi w$, where $\varphi \in \langle 0, 1 \rangle$, we choose M equidistant points $w^1, w^2, \ldots, w^M$. If e.g. $M = 9$ is chosen (and consequently the parameter φ takes gradually the values $0{\cdot}1, 0{\cdot}2, \ldots, 0{\cdot}9$) we have

$$w^1 = 0{\cdot}9w^0 + 0{\cdot}1w \,,$$
$$w^2 = 0{\cdot}8w^0 + 0{\cdot}2w \,,$$
$$\ldots \tag{26}$$
$$w^9 = 0{\cdot}1w^0 + 0{\cdot}9w \,.$$

c) Let us solve first the system of non-linear equations (18) where, however, the point w will be replaced by w^1. The solution obtained will then be used as the initial approximation for solving the system of non-linear equations (18), where the point w

is substituted by the point w^2, *etc.* It is evident that a sufficiently large value of M guarantees the convergence of numerical process. During practical calculations we proceed so that we choose such M, $M \geqq 0$, that the distance of adjoining points should not be larger than *e.g.* 0·05. Since the initial approximation in the given procedure is very close to the true solution, it is possible to use the modified Newton method.

The coordinates of the point w^0 are best chosen so that the line segment $\overline{w, w^0}$ should be normal to the line segment $\overline{\bar{x}^0, \bar{x}^0}$, *i.e.* the point w^0 should exhibit the shortest distance from point w of all the points of line segment $\overline{\bar{x}^0, \bar{x}^0}$. For the point w^0 holds

$$w^0 = \left(1 - \phi_0\right) \bar{x}^0 + \phi_0 \bar{x}^0 , \tag{27}$$

where ϕ_0 is a number from the interval $(0, 1)$. Let us construct the function

$$f(\phi_0) = \sum_{i=1}^{N-1} (w_i - w_i^0)^2 = \sum_{i=1}^{N-1} \left[w_i - \left(1 - \phi_0\right) \bar{x}_i^0 - \phi_0 \bar{x}_i^0\right]^2 \tag{28}$$

which gives square of the distance of point w from point w^0. From the condition $df/d\phi_0 = 0$ follows

$$\phi_0 = \sum_{i=1}^{N-1} \left(\bar{x}_i^0 - w_i\right)\left(\bar{x}_i^0 - \bar{x}_i^0\right) / \sum_{i=1}^{N-1} \left(\bar{x}_i^0 - \bar{x}_i^0\right)^2 . \tag{29}$$

By inserting this value of ϕ_0 into Eq. (27) we obtain the point w^0. As far as we get $\phi_0 < 0$ or $\phi_0 > 1$, then we choose $w^0 = \bar{x}^0$ or $w^0 = \bar{x}^0$, respectively.

In the calculation procedure proposed we have eliminated the parameter ϕ in system of equations (18) and solved the system of $2(N - 1)$ equations for $2(N - 1)$ unknown mole fractions. Thus, an attractive possibility offers to reduce further the number of equations (variant V4). From equations of material balance (17) follows

$$\bar{x}_i = w_i/\phi - \left[(1 - \phi)/\phi\right] \bar{x}_i . \quad i = 1, 2, ..., N - 1 \tag{30}$$

If we insert this relation into the equilibrium conditions, we obtain

$$\ln a_i(\bar{x}) = \ln a_i(w/\phi - \left[(1 - \phi)/\phi\right] \bar{x}) , \quad i = 1, 2, ..., N \tag{31}$$

which is a system of N equations only for N unknowns ϕ, $\bar{x}_i$, $i = 1, 2, ..., N - 1$. However, the determination of initial approximation of parameter ϕ is a problem in the case when w is "very" far from the line segment $\overline{\bar{x}^0, \bar{x}^0}$. When we proceed during calculation by the method of constructing the points w^1, w^2, ..., the solution of system of equations (31) is simple. In the first step (*i.e.* $w = w^1$) we should deter-

mine the value ϕ_0 according to Eq. (29) (where $w_i = w_i^1$) as an initial approximation of parameter ϕ, in the second step $w = w^2$, etc. For numerical reasons it is suitable to choose the order of phases so that $\phi < 0.5$, for the parameter ϕ occurs in the denominator on the right-hand side of Eq. (30).

In conclusion of this part we would like to draw attention to the fact that according to the establishment of point w, three cases can occur which are shown for ternary system in Fig. 8:

A) The given overall composition lies inside the heterogeneous region (point A in Fig. 8). In this case

$$0 < \phi < 1. \tag{32}$$

B) The given overall composition lies in the homogeneous region but there exists at least one tie-line which goes through this point (point B in Fig. 8). In this case the calculated ϕ meets the condition

$$\phi \notin \langle 0, 1\rangle. \tag{33}$$

C) The given point lies in the homogeneous region and no tie-line goes through it. In this case the calculation converges to the trivial solution $\bar{x} = \bar{\bar{x}}$.
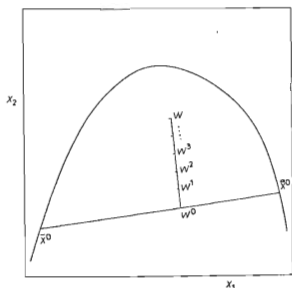

FIG. 7

The course of line segments $\overline{\bar{x}^0, \bar{\bar{x}}^0}$ and $\overline{w^0, w}$ in a ternary system
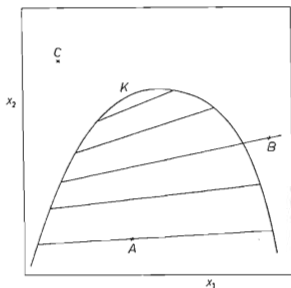
FIG. 8

Solvability of the problem of calculating the coexisting phases for a given overall system composition

*Calculation of Equilibrium Composition of Phases when the Incomplete
Overall Composition* $(w_1, w_2, ..., w_{N-2})$ *and the Relative Amount
of Phases Are Given*

The problem for a ternary system is outlined in Fig. 9 and can be formulated as follows: Determine the vector of overall composition (and composition of coexisting phases corresponding to it) of a ternary system so that the first component of this vector should be equal to w_1 and the relative amount of the first phase should be $(1 - \phi)$.

The algorithm of solution of this problem in a general N-component two-phase system is relatively simple. From the equilibrium conditions (1) and the first $(N - 2)$ equations of material balance (2), we form a system of equations

$$\ln a_i(\bar{x}) = \ln a_i(\bar{\bar{x}}), \qquad i = 1, 2, ..., N$$
$$(1 - \phi)\,\bar{x}_i + \phi\bar{\bar{x}}_i = w_i, \quad i = 1, 2, ..., N - 2 \qquad (34)$$

which is a system of $2(N - 1)$ equations for $2(N - 1)$ unknown values of mole fractions $\bar{x}_i, \bar{\bar{x}}_i, i = 1, 2, ..., N - 1$. Then we determine the value of w_{N-1} from the found solution of system of equations (34) and from the last equation of material balance

$$(1 - \phi)\,\bar{x}_{N-1} + \phi\bar{\bar{x}}_{N-1} = w_{N-1} . \qquad (35)$$

System of equations (34) is solved by the Newton method with reducing parameter η. From Eq. (21) follows

$$(1 - \phi)\,(\bar{x}_i^0 + \Delta\bar{x}_i) + \phi(\bar{\bar{x}}_i^0 + \Delta\bar{\bar{x}}_i) = w_i . \quad i = 1, 2, ..., N - 2 . \qquad (36)$$
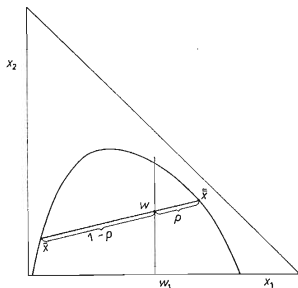

FIG. 9

Calculation of composition of coexisting phases for an incompletely given overall system composition

By combining systems of equations (25) and (36), a system of $2(N - 1)$ equations for $2(N - 1)$ increments $\Delta \bar{x}_i$, $\Delta \bar{\bar{x}}_i$, $i = 1, 2, ..., N - 1$ is formed. To calculate a new approximation of equilibrium composition of both phases, the reducing parameter is again used in the same way as in foregoing chapter. The calculation is carried out till the values of increments are "sufficiently" small.

As well as in the previous chapter mentioned, even in this case we can meet with the problems of convergence of the Newton method if the initial approximation $\bar{x}^0$, $\bar{\bar{x}}^0$ is not "sufficiently" close to the solution of system of equations (34). Also in this case we can use the procedure as in previous chapter. First we determine the values w_i^0, $i = 1, 2, ..., N - 1$ from the relation:

$$(1 - \phi) \bar{x}_i^0 + \phi \bar{\bar{x}}_i^0 = w_i^0 . \quad i = 1, 2, ..., N - 2 . \tag{37}$$

The points $w = (w_1, w_2, ..., w_{N-2})$ and $w^0 = (w_1^0, w_2^0, ..., w_{N-2}^0)$ are connected by a line segment. M equidistand points w^1, w^2, ..., w^M are chosen on the line segment $\overline{w, w^0}$ for points ξ of which holds $\xi = (1 - \varphi) w^0 + \varphi w$, $\varphi \in \langle 0, 1 \rangle$. Then it holds

$$w^k = (1 - \varphi_k) w^0 + \varphi_k w, \quad k = 1, 2, ..., M , \tag{38}$$

where $0 < \varphi_1 < \varphi_2 < ... < \varphi_M < 1$. Let us solve first system of equations (34) where, however, the values w_i, $i = 1, 2, ..., N - 2$ are replaced by the values w_i^1. The vectors $\bar{x}^0$ and $\bar{\bar{x}}^0$ are used as the initial approximation. The solution obtained is then used as the initial approximation for solving the same system of equations where the values w_i are replaced by the values w_i^2, $i = 1, 2, ..., N - 2$, etc. It is again evident that a sufficiently large value of M guarantees the convergence of numerical procedure. In practical calculations we usually proceed so that the distance of two neighbouring points w^k and w^{k+1} is chosen e.g. 0·05. Just as in foregoing chapter we can use here the modified Newton method, too.

CONCLUSION

A new method for calculating the equilibrium curve is proposed whose principle consists in using the values of thermodynamic functions of preceeding calculated pair of compositions of coexisting phases for estimating the next pair of compositions of coexisting phases.

Besides, the relations are derived which enable to estimate the equilibrium composition in N-component system on the basis of knowledge of composition of co-existing phases in binary system only.

In the second part four variants of calculating the coexisting phases for a given overall composition (flash calculations) are proposed which are important in chemi-

cal-engineering practice. Each of these variants has certain advantages, the most reliable being probably the variant V3, the most rapid the variant V2. These methods have not only a direct chemical-engineering application but can also be employed when determining the parameters according to the procedure proposed by Varhegyi and Eon[12].

Direct comparison of the method proposed here and those reported in the literature[1-9] was not carried out because each one has its specific properties and choice of the most suitable method depends on the system, type of problem, computer used, accuracy required, *etc*. However, it is evident from an *a priori* comparison that the method proposed here is better than that proposed previously (but the differences disappear in the cases when the slopes of tie-lines change only little). In case of ternary systems and calculations of equilibrium curve, the procedures by Joy[5] and Magnussen and coworkers[9] are probably somewhat more advantageous, however, the procedure proposed here can easily be applied to multicomponent systems and can easily be modified to be used in flash calculations.

In Appendix the relations for activity coefficients and their derivatives for the most common empirical and semi-empirical equations are given. The relations for the Redlich–Kister equation have already been published[7].

APPENDIX

Relations for $Q = G^E/(RT)$, $\ln \gamma_a$ and $\partial \ln \gamma_a / \partial x_b$ of some empirical and semi-empirical equations

1) Wilson Modified Equation[13,14]

$A_{ki} \neq A_{ik}$, $b_{ki} = b_{ik}$ parameters characterizing the binary system $i-k$ ($A_{ii} = A_{kk} = 1$, $b_{kk} = b_{ii} = 0$)

$$Q = -\sum_{k=1}^{N} x_k \ln \sum_{i=1}^{N} x_i A_{ki} + (1/2) \sum_{k=1}^{N} \sum_{i=1}^{N} x_k x_i b_{ki} = \sum_{k=1}^{N} x_k \ln S_k +$$
$$+ (1/2) \sum_{k=1}^{N} x_k R_k \, ,$$

$$S_k = \sum_{i=1}^{N} x_i A_{ki} \, , \qquad R_k = \sum_{i=1}^{N} x_i b_{ki} \, ,$$

$$\ln \gamma_a = 1 - \ln S_a - \sum_{k=1}^{N} x_k A_{ka}/S_k + R_a - (1/2) \sum_{k=1}^{N} x_k R_k \, ,$$

$$\partial \ln \gamma_a / \partial x_b = -A_{ab}/S_a - A_{ba}/S_b + A_{aN}/S_a + A_{Na}/S_N + \sum_{k=1}^{N} \left[x_k A_{ka}(A_{kb} - A_{kN})/S_k^2 \right]$$
$$+ b_{ab} - b_{aN} + R_N - R_b \, ,$$
$$a = 1, 2, \ldots, N \, , \quad b = 1, 2, \ldots, N-1 \, .$$

2) NRTL Equation[15]

$\tau_{ik} \neq \tau_{ki}$, $\alpha_{ik} = \alpha_{ki}$ parameters characterizing the binary system $i-k$ ($\tau_{ii} = \tau_{kk} = 0$)

$$Q = \sum_{k=1}^{N} \left[x_k \sum_{i=1}^{N} x_i \tau_{ik} G_{ik} \Big/ \sum_{i=1}^{N} x_i G_{ik} \right] = \sum_{k=1}^{N} x_k C_k / J_k ,$$

$$G_{ik} = \exp\left(-\alpha_{ik} \tau_{ik} \right) , \quad C_k = \sum_{i=1}^{N} x_i \tau_{ik} G_{ik} , \quad J_k = \sum_{i=1}^{N} x_i G_{ik} ,$$

$$\ln \gamma_a = C_a / J_a + \sum_{k=1}^{N} x_k G_{ak} \left[\tau_{ak} - C_k / J_k \right] / J_k ,$$

$$\partial \ln \gamma_a / \partial x_b = \left(\tau_{ba} G_{ba} - \tau_{Na} G_{Na} \right) / J_a - C_a \left(G_{ba} - G_{Na} \right) / J_a^2 +$$
$$+ G_{ab} \left(\tau_{ab} - C_b \right) / J_b^2 - G_{aN} \left(\tau_{aN} - C_N \right) / J_N^2 +$$
$$+ \sum_{k=1}^{N} x_k G_{ak} \left[\tau_{Nk} G_{Nk} - \tau_{bk} G_{bk} + 2 \left(G_{bk} - G_{Nk} \right) \left(C_k - \tau_{ak} \right) / J_k^2 \right] ,$$

$$a = 1, 2, \ldots, N , \quad b = 1, 2, \ldots, N - 1 .$$

3) UNIQUAC Equation[16]

r_i, q_i parameters characterizing the volume and surface of component i, $\Delta u_{ik} \neq \Delta u_{ki}$ parameters characterizing the binary system $i-k$, ($\Delta u_{ii} = \Delta u_{kk} = 0$), $z = 10$ (coordination number)

$$Q = \sum_{k=1}^{N} x_k \left\{ \ln \left(\phi_k / x_k \right) + (z/2) q_k \ln \left(\Theta_k / \phi_k \right) - q_k \ln S_k \right\} ,$$

$$r = \sum_{i=1}^{N} x_i r_i , \quad q = \sum_{i=1}^{N} x_i q_i , \quad \phi_k = x_k r_k / r , \quad \Theta_k = x_k q_k / q ,$$

$$\tau_{ik} = \exp \left[-\Delta u_{ik} / (RT) \right] , \quad S_k = \sum_{i=1}^{N} \Theta_i \tau_{ik} ,$$

$$\ln \gamma_a = 1 - \phi_a / x_a + \ln \left(\phi_a / x_a \right) + (z/2) q_a \left[\ln \left(\Theta_a / x_a \right) + \phi_a / \Theta_a - 1 \right] +$$
$$+ q_a \left[1 - \ln S_a - \sum_{k=1}^{N} \Theta_k \tau_{ak} / S_k \right] ,$$

$$\partial \ln \gamma_a / \partial x_b = \phi_N / x_N - \phi_b / x_b - \phi_a \phi_N / (x_a x_N) + \phi_a \phi_b / (x_a x_b) +$$
$$+ (z/2) q_a \left(1 - \phi_a / \Theta_a \right) \left[(\phi_b - \Theta_b) / x_b + (\Theta_N - \phi_N) / x_N \right] +$$
$$+ (q_a / q) \left\{ q_b \left[1 - \tau_{ba} / S_a - \tau_{ab} / S_b + \sum_{i=1}^{N} \Theta_i \tau_{ai} \tau_{bi} / S_i^2 \right] -$$
$$- q_N \left[1 - \tau_{Na} / S_a - \tau_{aN} / S_N + \sum_{i=1}^{N} \Theta_i \tau_{ai} \tau_{Ni} / S_i^2 \right] \right\} ,$$

$$a = 1, 2, \ldots, N , \quad b = 1, 2, \ldots, N - 1 .$$

4) Group-Contribution Method UNIFAC[9,17]

N number of components in system, NG number of groups in system; R_i, Q_i volume and surface of group i; r_k, q_k volume and surface of molecule of component k; v_{ik} number of groups i in molecule k; $a_{ij} \neq a_{ji}$ group interaction parameters characteristic of groups $i-j$, $(a_{ii} = a_{jj} = 0)$, $z = 10$ (coordination number)

$$r_k = \sum_{i=1}^{NG} v_{ik} R_i , \quad q_k = \sum_{i=1}^{NG} v_{ik} Q_i ,$$

$$RI_j = r_j / (\sum_{i=1}^{N} x_i r_i) , \quad QI_j = q_j / (\sum_{i=1}^{N} x_i q_i) ,$$

$$G_{jk} = QI_j v_{jk} , \quad \tau_{ji} = \exp(-a_{ji}/T) , \quad S_{ik} = \sum_{j=1}^{NG} G_{jk} \tau_{ji} ,$$

$$\Theta_i = \sum_{j=1}^{N} x_j G_{ij} , \quad \eta_i = \sum_{j=1}^{N} x_j S_{ij} ,$$

$$\ln \gamma_a = 1 - RI_a + \ln RI_a + q_a \{1 - \ln QI_a - (z/2) [1 - RI_a/QI_a +$$
$$+ \ln (RI_a/QI_a)] \} - \sum_{i=1}^{NG} [\Theta_i S_{ia}/\eta_i - G_{ia} \ln (S_{ia}/\eta_i)] ,$$

$$\partial \ln \gamma_a / \partial x_b = -(RI_b - RI_N)(1 - RI_a) + q_a(QI_b - QI_N) -$$
$$- (z/2) q_a [RI_b - RI_N - (QI_b - QI_N)](RI_a/QI_a - 1) +$$
$$- \sum_{i=1}^{NG} [S_{ia}(G_{ib} - G_{iN}) + (S_{ib} - S_{iN})(G_{ia} - S_{ia}\Theta_i/\eta_i)]/\eta_i ,$$

$$a = 1, 2, ..., N , \quad b = 1, 2, ..., N - 1 .$$

5) Group-Contribution Method ASOG[18]

N number of components in system, NG number of groups in system; v_k^{FH} number of atoms (different from hydrogen) in molecule of component k; v_{ik} number of atoms (different from hydrogen) in group i of molecule of component k; $a_{ij} \neq a_{ji}$ group interaction parameters characteristic of the groups $i-j$ $(a_{ii} = a_{jj} = 0)$

$$r_k = \sum_{i=1}^{NG} v_{ik} , \quad r = \sum_{k=1}^{N} x_k r_k , \quad q = \sum_{k=1}^{N} x_k v_k^{FH} ,$$

$$S_{ik} = \sum_{j=1}^{NG} a_{ij} v_{jk} , \quad \Theta_i = \sum_{k=1}^{N} x_k v_{ik} , \quad \eta_i = \sum_{k=1}^{N} x_k S_{ik} ,$$

$$\ln \gamma_a = \ln (v_a^{FH}/q) + 1 - v_a^{FH}/q + r_a \ln (r/r_a)$$
$$- \sum_{i=1}^{NG} \{ v_{ia}[\ln (\eta_i/S_{ia}) - 1] + \Theta_i S_{ia}/\eta_i \} ,$$

$$\partial \ln \gamma_a / \partial x_b = \left(\nu_b^{FH} - \nu_N^{FH} \right) \left(\nu_a^{FH}/q - 1 \right) / q + \left(r_b - r_N \right) r_a / r -$$

$$- \sum_{i=1}^{NG} \left[\left(S_{ib} - S_{iN} \right) \left(\nu_{ia} - \Theta_i S_{ia}/\eta_i \right) + S_{ia} (\nu_{ib} - \nu_{iN})/\eta_i \right],$$

$$a = 1, 2, ..., N, \quad b = 1, 2, ..., N - 1.$$

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