LIQUID–LIQUID EQUILIBRIUM. THE CALCULATION
OF COMPOSITION OF COEXISTING PHASES IN BINARY SYSTEMS

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A detailed discussion of convergence of Newton's method employed for calculating the composition of coexisting phases is carried out, and a never-failing-to-converge method is proposed. The procedure is simpler and more reliable than iteration methods of the third order.

In our work[1], Newton's method was applied to the calculation of composition of coexisting liquid phases of N-component system. The equilibrium and balance conditions have a form of a system of nonlinear equations

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

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

where a_i is the activity of the i-th substance, $\bar{\mathbf{x}} = (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_{N-1})$ and $\bar{\bar{\mathbf{x}}} = (\bar{\bar{x}}_1, \bar{\bar{x}}_2, \ldots, \bar{\bar{x}}_{N-1})$ is the vector of mole fractions in the first and the second liquid phase, respectively, $\mathbf{w} = (w_1, w_2, \ldots, w_{N-1})$ is the given vector of overall composition, and the parameter ϕ, $\phi \in \langle 0, 1 \rangle$, indicates the relative magnitude of the second phase. System of equations (1) is a system of $2N - 1$ equations for $2N - 1$ unknowns $\bar{\mathbf{x}}, \bar{\bar{\mathbf{x}}}$ and ϕ. Methods have been proposed[1] which make it possible to determine the solution of system (1) if, as the first approximation of equilibrium composition, an arbitrary pair of coexisting points, *i.e.* the points $\bar{\mathbf{x}}^1$ and $\bar{\bar{\mathbf{x}}}^1$, is chosen for which the first N equations of system (1) hold. In practice it means that, as the first approximation of solution of system (1), it is possible to choose a solution of problem (1) with another vector of overall composition $\tilde{\mathbf{w}}$, and the norm $\|\mathbf{w} - \tilde{\mathbf{w}}\|$ need not be a small number. The method proposed makes it possible to carry out the calculation of system (1) for a number of different overall compositions, the result of foregoing calculation serving as the first approximation of next calculation. It was as well recommended in work[1] that the compositions of coexisting phases of the corresponding binary heterogeneous system should be used as the first approximation at the beginning of this numerical process. The solution of system (1) for binary system ($N = 2$)

is consequently important not only for obtaining information on the given binary system but also as an input value for multicomponent calculations.

In this work we deal with the solution of system (1) for $N = 2$. It will be shown that the convergence of Newton's method depends to a great extent on the values of the first approximation, even in the cases when the values of the first approximation lie in the homogeneous region and the relaxation (reducing, damping) parameter is used. Further, an always convergent method is proposed which in the vicinity of the solution turns continuously into classical Newton's method.

Discussion of Newton's Method of Solution of System (1)

In case of $N = 2$ it is possible to solve first the system of nonlinear equations

$$\ln a_1(\bar{x}_1) = \ln a_1(\tilde{x}_1) ,$$
$$\ln a_2(\bar{x}_1) = \ln a_2(\tilde{x}_1) , \qquad (2)$$

and the parameter ϕ can then be determined from the balance equation

$$(1 - \phi) \bar{x}_1 + \phi \tilde{x}_1 = w_1 . \qquad (3)$$

The system of equations (2) has besides the physical solution $\bar{x}_1 \neq \tilde{x}_1$, an infinite number of trivial solutions $\bar{x}_1 = \tilde{x}_1$. Thus, it is possible to expect a priori that the main task will consist in ensuring convergence of the numerical process to the physical solution, especially in the region of critical point, where the physical solution limits to the trivial one.

When using Newton's method to solve system (2), we obtain in the i-th iteration step the system of linear equations

$$(\partial \ln \bar{a}_1/\partial x_1) \Delta \bar{x}_1 - (\partial \ln \bar{a}_1/\partial x_1) \Delta \tilde{x}_1 = \ln (\tilde{a}_1/\bar{a}_1) ,$$
$$(\partial \ln \bar{a}_2/\partial x_1) \Delta \bar{x}_1 - (\partial \ln \bar{a}_2/\partial x_1) \Delta \tilde{x}_1 = \ln (\tilde{a}_2/\bar{a}_2) , \qquad (4)$$

where $\Delta \bar{x}_1 = \bar{x}_{1,i+1} - \bar{x}_{1,i}$, $\Delta \tilde{x}_1 = \tilde{x}_{1,i+1} - \tilde{x}_{1,i}$, $\bar{x}_{1,i}$, $\tilde{x}_{1,i}$ being the i-th approximation of equilibrium composition of coexisting phases. The values of derivatives and right-hand sides are determined at the point $\bar{x}_{1,i}$ or $\tilde{x}_{1,i}$. For the sake of simplicity we denote $\bar{a}_1 = a_1(\bar{x}_1)$ and the like.

Between the dimensionless Gibbs energy of mixing G, $G = G^M/(RT)$ and the activity of i-th substance hold in binary system the following relations[2-5]

$$\ln a_1 = G + x_2 G1 , \quad \ln a_2 = G - x_1 G1 ,$$
$$\partial \ln a_1/\partial x_1 = x_2 G11 , \quad \partial \ln a_2/\partial x_1 = -x_1 G11 ,$$

$$G(0) = G(1) = 0 \, ,$$

$$\lim_{x_1 \to 0_+} G1 = -\infty \, , \quad \lim_{x_1 \to 1_-} G1 = \infty \, , \tag{5}$$

where $G1 = \partial G/\partial x_1$, $G11 = \partial^2 G/\partial x_1^2$, $x_2 = 1 - x_1$, and all the derivatives are taken at constant temperature and pressure. A typical diagram of the dependence of function $G = G(x_1)$ for a partially miscible system is given in Fig. 1. The tangent constructed at a general non-equilibrium point $\bar{x}_1$ intercepts segment lines of the length $\ln \bar{a}_2$ and $\ln \bar{a}_1$ on the axes $x_1 = 0$ and $x_1 = 1$, respectively. Analogous statement holds for the point $\bar{\bar{x}}_1$. From relation (2) and Fig. 1 follows the well-known thermodynamic knowledge that the targents in the diagram of function G constructed at equilibrium points are identical. In the homogeneous and metastable regions, the condition of thermodynamic stability holds which has in the case considered the form[3-5]

$$G11 > 0 \, . \tag{6}$$

If the condition of thermodynamic stability (6) applies in the whole concentration interval $(0, 1)$, i.e. the solution considered is homogeneous in the entire concentration range, then system (2) has naturally no physical solution $\bar{x}_1 \neq \bar{\bar{x}}_1$. If the condition (6) does not hold in the entire concentration interval, then, in a general case, more solutions of system of equations (2) may exist for which $\bar{x}_1 \neq \bar{\bar{x}}_1$ holds. One of such cases when six pairs $(\bar{x}_1, \bar{\bar{x}}_1)$, $\bar{x}_1 \neq \bar{\bar{x}}_1$ exist which satisfy system of equations (2), is illustrated in Fig. 2. The physical solution is then such a pair which is connected with the
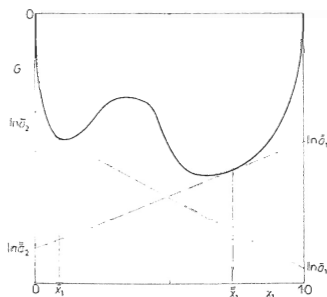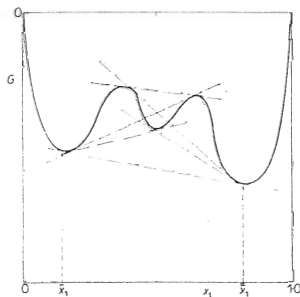

Fig. 1

Diagram of the $G(x_1)$ function

Fig. 2

Diagram of the $G(x_1)$ function with a multiple solution

lowest value of Gibbs energy of the system. (The given pair is designated in Fig. 2). The diagram of the function G in Fig. 2 is a consequence of incorrect description of the concentration dependence of activity which in actual cases arises *e.g.* when using the NRTL equation[6,7]. These "pathological" cases will not be dealt with in this work, and we shall always assume that system of equations (2) has just one physical solution, or saying it in other words, that the function $G(x_1)$ has just two inflex points in the interval $(0, 1)$.

Inserting the relations involved in Eqs (5) into system of equations (4) we get

$$(1 - \bar{x}_1)\,\bar{G}11\,\Delta\bar{x}_1 - (1 - \bar{\bar{x}}_1)\,\bar{\bar{G}}11\,\Delta\bar{\bar{x}}_1 = \bar{\bar{G}} + (1 - \bar{\bar{x}}_1)\,\bar{\bar{G}}1 - \bar{G} - (1 - \bar{x}_1)\,\bar{G}1\,,$$

$$-\bar{x}_1\bar{G}11\,\Delta\bar{x}_1 + \bar{\bar{x}}_1\bar{\bar{G}}11\,\Delta\bar{\bar{x}}_1 = \bar{\bar{G}} - \bar{\bar{x}}_1\bar{\bar{G}}1 - \bar{G} + \bar{x}_1\bar{G}1\,, \qquad (7)$$

where $\bar{G} = G(\bar{x}_1)$, $\bar{G}1 = G1(\bar{x}_1)$, $\bar{G}11 = G11(\bar{x}_1)$ and in an analogous way for the second phase. The determinant of matrix of system (7) is equal to $(\bar{\bar{x}}_1 - \bar{x}_1)\,\bar{G}11\bar{\bar{G}}11$. This fact is in harmony with work[1] where it was proved for an N-component system that the determinant of matrix which originates from the solution of system (1) by Newton's method is zero on the spinodal curve (surface). Applying the Cramer rule to system (7) we obtain the resulting relations

$$\Delta\bar{x}_1 = (t - \bar{G}1)/\bar{G}11\,, \quad \Delta\bar{\bar{x}}_1 = (t - \bar{\bar{G}}1)/\bar{\bar{G}}11\,, \qquad (8)$$

where

$$t = (\bar{\bar{G}} - \bar{G})/(\bar{\bar{x}}_1 - \bar{x}_1) \qquad (9)$$

is the slope of line connecting the points $[\bar{x}_1, \bar{G}]$ and $[\bar{\bar{x}}_1, \bar{\bar{G}}]$. Since for a convergent iteration process holds $\Delta\bar{x}_1 \to 0$, $\Delta\bar{\bar{x}}_1 \to 0$, relation (8) confirms again the formerly mentioned knowledge that the tangents of diagram of function G constructed at equilibrium points are identical , *i.e.* it holds

$$t = \bar{G}1 = \bar{\bar{G}}1\,. \quad [\text{equilibrium}] \qquad (10)$$

The simplicity of relation (8) makes possible at least partial analysis of features of iteration process. Without detriment of generality let us assume $\bar{x}_1 < \bar{\bar{x}}_1$ and divide the interval $(0, 1)$ into five subintervals I_j, $j = 1, 2, ..., 5$, where (Fig. 3)

$$I_1 = (0, \alpha)\,, \quad I_2 = \langle\alpha, \beta\rangle\,, \quad I_3 = \langle\beta, \gamma\rangle\,,$$

$$I_4 = (\gamma, \delta\rangle\,, \quad I_5 = (\delta, 1)\,, \qquad (11)$$

$\bar{x}_1 = \alpha$, $\bar{\bar{x}}_1 = \delta$ being the equilibrium compositions of coexisting phases, and the function $G(x_1)$ has an inflex point at the points $x_1 = \beta$ and $x_1 = \gamma$, *i.e.* $G11(\beta) = G11(\gamma) = 0$. The existence of at least two inflex points of function G in the interval

(α, δ) follows from the well-known theorem of mathematic analysis. The function G can exhibit, in principle, even more than two inflex points in the interval (α, δ). This „pathological" case, as it has been said, will not be dealt with. In the intervals $I_1 \cup I_2$ and $I_4 \cup I_5$, the condition of thermodynamic stability (6) holds, i.e. the function G is convex. In the interval I_3, the function G is concave, i.e. $G11 \leqq 0$ is valid (the equality sign refers only to the points β and γ).

Let us consider the following cases:

1) $\bar{x}_{1,1}, \tilde{x}_{1,1} \in I_3$. Both the points which represent the first approximation of composition of coexisting phases lie in labile region. From the concavity of function G in the interval I_3 follows

$$\bar{\bar{G}}1 < t < \bar{G}1 , \quad \bar{G}11 \leqq 0 , \quad G11 \leqq 0 , \tag{12}$$

and therefore it holds (see Eq. (8))

$$\Delta \bar{x}_1 > 0 , \quad \Delta \tilde{x}_1 < 0 \tag{13}$$

with the exception of the case $\bar{x}_{1,1} = \beta$ or $\tilde{x}_{1,1} = \gamma$, when the values of increments are not defined. It is evident from relation (13) and Fig. 3 that the signs of increments have incorrect value, and therefore in case of sufficiently low values of relaxation parameters $\lambda_i, \lambda_i \in (0, 1\rangle$, the iteration process

$$\begin{aligned}
\bar{x}_{1,i+1} &= \bar{x}_{1,i} + \lambda_i \Delta \bar{x}_1 , \\
\tilde{x}_{1,i+1} &= \tilde{x}_{1,i} + \lambda_i \Delta \tilde{x}_1 \quad i = 1, 2, \ldots
\end{aligned} \tag{14}$$

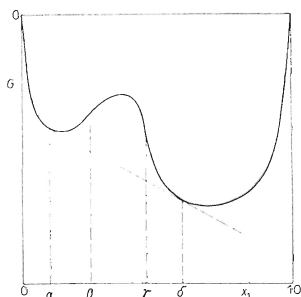converges to the trivial non-physical solution $\bar{x}_1 = \tilde{x}_1$.

FIG. 3

Important points of the $G(x_1)$ function

2) $\bar{x}_{1,1} \in I_1$, $\bar{\bar{x}}_{1,1} \in I_5$. Both the points lie in the respective homogeneous regions. Then from the convexity of the function G follows

$$\bar{G}1 < t < \bar{\bar{G}}1, \quad \bar{G}11 > 0, \quad \bar{\bar{G}}11 > 0, \tag{15}$$

and again Eq. (13) holds, which in this case means that the increments have right signs. However, later we will show that this does not guarantee the convergence of iteration process to a physical solution neither in case of low values of relaxation parameter.

3) The other cases. In remaining cases it is not possible to establish unambiguously the signs of increments for different variants of the relation between values of $\bar{G}1$, $\bar{\bar{G}}1$ and t can occur. From the general convergence theorem of Newton's method, we only know that there exists always some vicinity of solution, and as far as the first approximation of solution lies in this vicinity, then the iteration process converges.

As an example let us consider a simple symmetrical system

$$G = x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1) + 2 \cdot 25 x_1 (1 - x_1), \tag{16}$$

where it holds

$$G1 = \ln x_1 - \ln (1 - x_1) + 2 \cdot 25 (1 - 2x_1),$$

$$G11 = 1/x_1 + 1/(1 - x_1) - 4 \cdot 5,$$

$$\alpha = 0 \cdot 2244, \quad \beta = 0 \cdot 333\bar{3}, \quad \gamma = 0 \cdot 666\bar{6}, \quad \delta = 0 \cdot 7756,$$

$$G(\alpha) = G(\delta) = -0 \cdot 1408,$$

$$G(\beta) = G(\gamma) = -0 \cdot 1365, \quad G(0 \cdot 5) = -0 \cdot 1306. \tag{17}$$

The physical solution are therefore the values $\bar{x}_1 = 0 \cdot 2244$ and $\bar{\bar{x}}_1 = 0 \cdot 7756$. Let us choose classical Newton's method as an iteration method:

$$\bar{x}_{1,i+1} = \bar{x}_{1,i} + \Delta \bar{x}_1$$
$$\bar{\bar{x}}_{1,i+1} = \bar{\bar{x}}_{1,i} + \Delta \bar{\bar{x}}_1, \quad i = 1, 2, \ldots, \tag{18}$$

where the prescription for increments is given by relation (8), and the relaxation parameter λ equals unity in each iteration step. The values $\bar{x}_{1,i}$ and $\bar{\bar{x}}_{1,i}$ for different sets of the first approximation $(\bar{x}_{1,1}, \bar{\bar{x}}_{1,1})$ are given in Table I. The value $\bar{x}_{1,1}$ is in all cases an excellent approximation of solution, whereas the value $\bar{\bar{x}}_{1,1}$ lies deep in the homogeneous region. In the first case $(\bar{x}_{1,1} = 0 \cdot 22)$ the calculated value of $\Delta \bar{x}_1$ is such that the next approximation $\bar{x}_{1,2}$ lies in the metastable region I_2 near the inflex point $\beta = 0 \cdot 333\bar{3}$. Therefore the value of the second derivative $G11$ at the point $\bar{x}_{1,2}$ is

equal to a positive but "very small" number, and consequently a new value $\Delta \bar{x}_1$ is very high. This entails that the next approximation $\bar{x}_{1,3}$ lies outside the physical interval $(0, 1)$. The value of $\bar{x}_1$ does not change too much during the iteration process for the value of G11 is, at the point $\bar{x}_1 = 0.99$, "very high".

Thus it is evident that it is necessary to determine the relaxation parameter λ, $\lambda \in \langle 0, 1 \rangle$ so that the iteration process has the form

$$\bar{x}_{1,i+1} = \bar{x}_{1,i} + \lambda \Delta \bar{x}_1 ,$$
$$\bar{x}_{1,i+1} = \bar{x}_{1,i} + \lambda \Delta \bar{x}_1 , \quad i = 1, 2, \dots . \qquad (19)$$

where the value of parameter λ is usually chosen in each iteration step by the following strategy: Let us denote $D = |\Delta \bar{x}_1| + |\Delta \bar{x}_1|$. Then we require

$$D < \sigma \Rightarrow \lambda = 1 ,$$
$$D \geqq \sigma \Rightarrow \lambda = \sigma/D , \qquad (20)$$

where σ is a measure of the length of iteration step. We most often choose $\sigma = 0.05$. The value of relaxation parameter λ may be different in each iteration step (in Eq. (19) we should write more precisely $\lambda_i \Delta \bar{x}_{1,i}$, which is not done for the sake of simplicity), $\lambda = 1$ being always at the end of iteration process. Use of relaxation parameter ensures in many cases the convergence to the physical solution, however, it is not always so. The important iteration steps of numerical process (8), (19) and (20) and $\sigma = 0.05$ are given in Table II for problem (16) with the first approximation (0·22, 0·99). The value of unknown quantity $\bar{x}_1$ is changed very slowly because $\bar{\bar{G}}11 \gg 1$ applies. However, the value of $\bar{x}_1$ changes comparatively rapidly, and already in the fourth iteration step lies in the labile region I_3. This fact cannot be prevented even by choosing lower value of the relaxation parameter. If $\bar{x}_1 \in I_3$, i.e. $\bar{G}11 < 0$, then the numerical value of $\Delta \bar{x}_1$ depends on the dependence of t and $\bar{G}1$. It follows

TABLE I

Results of iteration process (18) for different input approximation

i	$\bar{x}_{1,i}$	$\bar{x}_{1,i}$	$\bar{x}_{1,i}$	$\bar{x}_{1,i}$	$\bar{x}_{1,i}$	$\bar{x}_{1,i}$
1	0·22	0·99	0·2244	0·99	0·23	0·99
2	0·329	0·967	0·337	0·967	0·347	0·967
3	1·753	0·923	−1·570	0·923	−0·159	0·923

from relation (8)

$$t < \bar{G}1 \Rightarrow \Delta\bar{x}_1 > 0 \, ,$$
$$t > \bar{G}1 \Rightarrow \Delta\bar{x}_1 < 0 \, . \tag{21}$$

Since in the fourth iteration step the second implication holds, the value of $\bar{x}_1$ „returns" in the fifth step back into the interval $I_1 \cup I_2$. In next steps (except the seventh one), the first implication applies in Eq. (21), and the iteration process converges to the point $\bar{x}_1 = \bar{\bar{x}}_1 = \gamma = 0.666\bar{6}$.

Proposal of New Algorithm of Solution of System (2)

It has been proved in foregoing part that both classical Newton's method and Newton's method with reducing parameter do not ensure convergence to the physical solution of system (2). Then it is necessary to choose such an iteration process that the values $\bar{x}_{1,i}$ and $\bar{\bar{x}}_{1,i}$ should lie in each iteration step in the interval $I_1 \cup I_2$ and $I_4 \cup I_5$, respectively. Let us consider the iteration method

$$\bar{x}_{1,i+1} = \bar{x}_{1,i} + \bar{\mu}\bar{\psi}(\bar{x}_{1,i}, \bar{\bar{x}}_{1,i}) \, ,$$
$$\bar{\bar{x}}_{1,i+1} = \bar{\bar{x}}_{1,i} + \bar{\bar{\mu}}\bar{\bar{\psi}}(\bar{x}_{1,i}, \bar{\bar{x}}_{1,i}) \, , \quad i = 1, 2, \ldots \tag{22}$$

where

$$\bar{\psi} = \bar{\bar{G}} - \bar{G} - \bar{G}1(\bar{\bar{x}}_1 - \bar{x}_1) \, ,$$
$$\bar{\bar{\psi}} = \bar{\bar{G}} - \bar{G} - \bar{\bar{G}}1(\bar{\bar{x}}_1 - \bar{x}_1) \, , \tag{23}$$

and $\bar{\mu}, \bar{\bar{\mu}}$ are nonzero parameters whose value may change during the iteration process. Equilibrium conditions (2) can be expressed in terms of relation (5) in an equivalent

TABLE II
Important iteration steps of process (8), (19), (20) and $\sigma = 0.05$

i	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$	i	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$
1	0.22	0.99	8	0.359	0.904
2	0.261	0.981	9	0.397	0.892
3	0.301	0.971	10	0.428	0.873
4	0.342	0.962	11	0.457	0.852
5	0.296	0.959	14	0.541	0.785
6	0.331	0.944	18	0.634	0.699
7	0.375	0.938	∞	0.666	0.666

form $\overline{\overline{\psi}} = 0$ and $\overline{\psi} = 0$. Consequently, if the iteration process (22) converges, then it converges to the solution of system (2). From the theory of iteration processes follows[8,9] that the necessary condition of convergence are "small" absolute values of coefficients of matrix **A**

$$\mathbf{A} = \begin{pmatrix} \partial \overline{F}/\partial \overline{x}_1, \ \partial \overline{F}/\partial \overline{\overline{x}}_1 \\ \partial \overline{\overline{F}}/\partial \overline{x}_1, \ \partial \overline{\overline{F}}/\partial \overline{\overline{x}}_1 \end{pmatrix}, \tag{24}$$

where the relations

$$\overline{F} = \overline{x}_1 + \overline{\mu}\overline{\psi}, \quad \overline{\overline{F}} = \overline{\overline{x}}_1 + \overline{\overline{\mu}}\overline{\overline{\psi}} \tag{25}$$

hold true, and the parameters $\overline{\mu}$ and μ are considered to be constants. On inserting Eq. (23) into Eqs (24) and (25) we find that

$$\mathbf{A} = \begin{pmatrix} 1 - \overline{\mu}\overline{G}11(\overline{x}_1 - \overline{\overline{x}}_1), \ \overline{\mu}(\overline{\overline{G}}1 - \overline{G}1) \\ \overline{\overline{\mu}}(\overline{G}1 - \overline{G}1), \ 1 - \overline{\overline{\mu}}\overline{\overline{G}}11(\overline{x}_1 - \overline{\overline{x}}_1) \end{pmatrix} \tag{26}$$

holds. If we choose

$$\overline{\mu} = 1/[\overline{G}11(\overline{x}_1 - \overline{\overline{x}}_1)], \quad \overline{\overline{\mu}} = 1/[\overline{\overline{G}}11(\overline{x}_1 - \overline{\overline{x}}_1)], \tag{27}$$

i.e. annual the diagonal members of matrix (26), then by inserting Eq. (27) into (22), we obtain Newton's method (18) where the prescription for increments is given by relation (8). Since at the point of solution, $\overline{G}1 = \overline{\overline{G}}1$ applies, the matrix **A** is in case of Newton's method equal to a null matrix at the point of solution. Hereof follows the theorem of local convergence of Newton's method as it has been given formerly. At the beginning of iteration process, however, the values of $\overline{G}1$ and $\overline{\overline{G}}1$ can differ significantly, which means that the non-diagonal members of matrix (26) differ substantially from zero in case of Newton's method. If, *e.g.*, $\overline{x}_1 = 0.22$ and $\overline{\overline{x}}_1 = 0.99$, then it is possible to establish easily from Eq. (17) that $\overline{G}1 = -0.0057$ and $\overline{\overline{G}}1 = 2.39$. Providing that $\overline{\overline{x}}_1 = 0.999$ is chosen, then $\overline{\overline{G}}1 = 4.66$ would hold, *etc.* Therefore it is more suitable for the type of the problem studied to choose in every iteration step the parameters $\overline{\mu}$ and $\overline{\overline{\mu}}$ so that the sum of squares of elements of matrix (26) should be as small as possible in each row. It is possible to derive easily that then

$$\overline{\mu} = \overline{G}11(\overline{x}_1 - \overline{\overline{x}}_1)/\{[\overline{G}11(\overline{x}_1 - \overline{\overline{x}}_1)]^2 + (\overline{\overline{G}}1 - \overline{G}1)^2\},$$

$$\overline{\overline{\mu}} = \overline{\overline{G}}11(\overline{x}_1 - \overline{\overline{x}}_1)/\{[\overline{\overline{G}}11(\overline{x}_1 - \overline{\overline{x}}_1)]^2 + (\overline{\overline{G}}1 - \overline{G}1)^2\}. \tag{28}$$

In a sufficiently narrow vicinity of solution ($\overline{\overline{G}}1 = \overline{G}1$), relations (27) and (28) are identical, and in the final steps of the iteration process, all the advantages of Newton's method are retained (especially the rapidity of convergence — Newton's method is

a method of second order). By inserting Eq. (28) into Eqs (22) and (23), it is possible to derive easily that for increments in each iteration step holds

$$\Delta \bar{x}_1 = \bar{\mu}(\bar{x}_1 - \bar{x}_1)(t - \bar{G}1),$$
$$\Delta \bar{\bar{x}}_1 = \bar{\bar{\mu}}(\bar{x}_1 - \bar{x}_1)(t - \bar{\bar{G}}1), \tag{29}$$

and when $\bar{G}1 = \bar{\bar{G}}1$, Eqs (29) and (8) are identical.

The values of $\bar{x}_1$ and $\bar{\bar{x}}_1$ in single iteration steps of method (29), (28) at differently chosen values of the first approximation in problem (16) are given in Table III. An advantage of iteration process (29) is the fact that prescription (29) does not contain the unknown relaxation parameter whose value would have to be determined in each iteration step. Iteration process (29) was tested for a number of variants of expressing the function G, $\bar{x}_{1,1} = \varepsilon$, $\bar{\bar{x}}_{1,1} = 1 - \varepsilon$ having been chosen as the first approximation. The value ε was chosen so that $\bar{x}_{1,1} \in I_1$ and $\bar{\bar{x}}_{1,1} \in I_5$ should apply, *i.e.* the first approximation should lie in homogeneous region. Since the intervals I_1 and I_5 are not known *a priori*, we always chose $\varepsilon = 0.00001$. Except some cases when the solution lies near the critical point $(|\bar{x}_1 - \bar{x}_1| < 0.1)$, the proposed iteration process was always convergent. This failure can be removed by inserting two relaxation parameters λ_1, $\lambda_2 \in \langle 0, 1 \rangle$ of such a value that

$$\bar{x}_{1,i+1} = \bar{x}_{1,i} + \lambda_1 \bar{\mu}(\bar{x}_1 - \bar{x}_1)(t - \bar{G}1),$$
$$\bar{\bar{x}}_{1,i+1} = \bar{\bar{x}}_{1,i} + \lambda_2 \bar{\bar{\mu}}(\bar{x}_1 - \bar{x}_1)(t - \bar{\bar{G}}1) \quad i = 1, 2, \ldots \tag{30}$$

TABLE III
Iteration process (28), (29) with differently chosen values of the first approximation

i	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$	$\bar{x}_{1,i}$	$\bar{\bar{x}}_{1,i}$
1	0·220	0·990	0·220	0·999	0·2244	0·99999	0·00001	0·99999
2	0·236	0·967	0·226	0·994	0·226	0·9999	0·0001	0·9999
3	0·257	0·923	0·238	0·979	0·229	0·9992	0·0008	0·999
4	0·264	0·867	0·254	0·943	0·233	0·995	0·005	0·995
5	0·233	0·817	0·267	0·880	0·242	0·982	0·020	0·980
6	0·226	0·786	0·250	0·835	0·256	0·949	0·057	0·943
7	0·224	0·776	0·225	0·796	0·269	0·897	0·113	0·887
8			0·225	0·778	0·256	0·842	0·170	0·830
9			0·224	0·776	0·225	0·780	0·209	0·791
10					0·224	0·776	0·223	0·777
11							0·224	0·776

hold, the generally different relaxation parameters λ_1 and λ_2 being chosen in each step so that $\bar{x}_{1,i} \in I_1 \cup I_2$ and $\bar{x}_{1,i} \in I_4 \cup I_5$, $i = 1, 2, \ldots$. In conclusion of iteration process obviously always $\lambda_1 = \lambda_2 = 1$ applies. This procedure is easily practicable if we know the position of both inflex points of the G function which can be found by solving one equation for one unknown quantity $G11(x_1) = 0$. We have not found a case when iteration process (30) would not converge.

In this work we have dealt with the methods of second order whose typical representative is Newton's method. With the methods of second order, it is necessary to know in addition the first and second derivatives of function G, $i.e.$ $G1$ and $G11$, besides the function G. We also treated iteration methods of third order[8,9] whose principle consists in a quadratic approximation of the left- and right-hand sides of system (2). The improvement as to the extension of the convergence region and speeding-up the convergence of iteration process is, however, comparatively small in comparison with the methods of second order without the relaxation parameter, and does not correspond to the considerable complication of iteration prescription and the need of knowledge of the function $G111$ (the third derivative of function G). For this reason the methods of third order have not been dealt with in this work.

CONCLUSION

The carried out detailed analysis of use of Newton's method for calculating the composition of coexisting phases from the dependence of Gibbs energy on composition has shown that both classical Newton's method and Newton's method with relaxation parameter do not converge to the physical solution in some cases. Considering that the composition of coexisting phases in binary system can be used as the first approximation for calculating the composition of coexisting phases in multicomponent system, it is advantageous to have at one's disposal a never-failing-to-converge method for binary system. This requirement is met by the newly proposed method in which the increments in composition of both phases are determined in terms of Eq.(29) or (30).

It is necessary to state that the solution of system (2), even in case of binary system, is not simple. The greater difficulties can be expected with multicomponent systems. One of the necessary conditions of success is a good first approximation which can be established $e.g.$ by a procedure presented in our previous paper[1].

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