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IMPROVEMENTS ON THE NATURAL ITERATION METHOD IN THE CLUSTER VARIATION METHOD

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Abstract By examining the relationship between grand potential and various distribution variables, this paper combines the Natural Iteration Method (NIM) with the Step Speeded Method and Dichotomous method, respectively, and proposes two methods, Step Speeded– and Dichotomous–NIMs, for improving the conventional NIM by making use of the absolute convergence of the NIM. The calculated results indicate the numbers of iteration in the two methods obviously decreased, and they are still with absolute convergence.

1. INTRODUCTION

The Cluster Variation Method (CVM), proposed by R. Kikuchi in 1951[1], has been proved to be an effective method to calculate entropy of mixing of solid solutions with short and long range order. In recent years this method has been given widespread attention by phase diagram researchers, and has been developed further and applied in phase equilibrium calculations[2,3]. When phase equilibria are calculated by the CVM, a set of complex non–linear simultaneous equations need to be solved. However, it is difficult to solve these equations by the conventional mathematical method such as Newton–Raphson iteration method. In 1974, R. Kikuchi proposed the Natural Iteration Method (NIM) with absolute convergence to realize phase equilibrium calculation by the CVM[4]. However,the NIM also has a serious shortcoming, i.e. more numbers of iteration and longer time of calculation, and it is especially difficult when the calculation of the CVM with larger clusters in multicomponent system is carried out in microcomputer. Therefore the application of the CVM was rather limited. In 1977 R. Kikuchi put forward a improved method for the NIM[5], and obvious effectiveness is achieved. However, this method can not be applied effectively until the Natural Iteration

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Calculation is operated to certain numbers of iteration. In this paper, we will propose two improved methods for the NIM, Step Speeded–NIM (SSNIM) and Dichotomous–NIM (DNIM), in order to increase the efficiency of the CVM calculation.

2. THE OUTLINE OF THE NIM AND ITS DRAWBACK

First, the CV–pair approximation is taken as an example, and the procedure of iterations of the NIM is illustrated in brief as follows.

For a system with N_0 lattice point (N_0 is Avogadro's number) and a coordination number 2ω, the molar grand potential G_m can be expressed by[2]

$$G_m = N_0\omega\sum_{ij}\varepsilon_{ij}y_{ij} - TR[(2\omega-1)\sum_i x_i \ln x_i - \omega\sum_{ij} y_{ij}\ln y_{ij}]$$

$$-\sum_i \mu_i x_i + \lambda(1-\sum_{ij} y_{ij}) \tag{2.1}$$

where x_i is molar fraction of component i, y_{ij} is probability of an $i-j$ atom pair, in solid solution, and the variables x_i and y_{ij} are related by the geometric relation

$$x_i = \sum_j y_{ij} \qquad \sum_i\sum_j y_{ij} = 1 \tag{2.2}$$

ε_{ij} is the nearest–neighbour interaction potential between the i and j atoms. λ is Lagrange multiplier due to normalizing the y_{ij}s in (2.2).

According to the equilibrium state condition, $\partial G_m / \partial y_{ij} = 0$, the following equation is obtained

$$y_{ij} = (x_i x_j)^{\frac{2\omega-1}{2\omega}} exp\left[-\frac{\varepsilon_{ij}}{RT} + \frac{\mu_i+\mu_j}{2\omega RT} + \frac{\lambda}{\omega RT}\right] \tag{2.3}$$

The NIM is constructed by eq.(2.3) combining with eq.(2.2), and is explained in detail by R.Kikuchi[4]. The procedure of iteration is shown in Fig.1 and two examples are given in Fig.2. The change of grand potential with the x_i in the Natural Iteration Calculation is given in Fig.2(a), in which the lowest point of grand potential is terminal in the

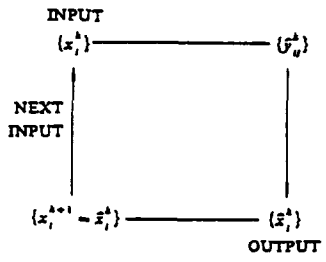


Fig.1 Iteration proccdure of the NIM

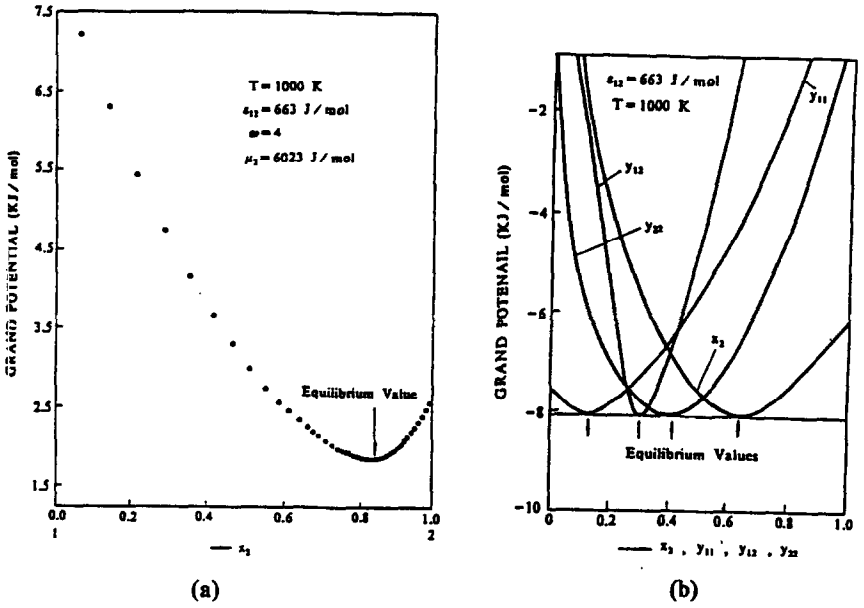


Fig.2 The iteration procedure in the NIM. (a) The relation between grand potential and the x_i in the CV–pair approximation; (b) The relation between grand potential and the x_i , y_{ij} in CV–tetrahedron approximation

iteration procedure and corresponds to the equilibrium value of certain chemical potential. It can be seen from Fig.2(a) that no matter what the initial point is the iteration procedure will finally converge. Fig.2(b) gives the change of the grand potential with the x_i and y_{ij} in the CV–tetrahedron approximation, and it is shown that all y_{ij} s will also reach the equilibrium value besides the x_i when the grand potential reaches the minimum value.

Many variables, x_i , y_{ij} , z_{ijkl} and so on, are introduced in phase equilibrium calculation by the CVM, and the output values of these variables at previous iteration act as the input values for the next. However, the grand potential decreases by a little margin at such a iteration procedure, thus the efficiency of the CVM calculation by the NIM is lower, and it is very difficult for Natural Iteration Calculation to be carried out on a microcomputer for larger clusters. This is only a shortcoming of the NIM. Therefore, how to decrease the numbers of iteration and increase calculated efficiency of the NIM, at the same time keeping absolute convergence is a problem of important significance.

3. STEP SPEEDED NATURAL ITERATION METHOD

3.1 CV–Pair Approximation in Binary System

The basic principle of the Step Speeded Natural Iteration Method (SSNIM) is as follows: The relative position between the present point of iteration and equilibrium point can be judged by the difference between input and output values of distribution variables, because the grand potential will decrease during the iteration procedure due to the absolute convergence of the NIM. Therefore the output value from a previous iteration adding a step along the direction tending to the equilibrium point acts as the input values for the next iteration, and this procedure makes sure that the equilibrium value is approached at each iteration. The principle of the SSNIM is shown in Fig.3.

It is assumed that points A and A′ correspond to the input and output values x_2^1 and $\hat{x}_2^1$, respectively (a caret is placed for an output quantity in order to facilitate the disposition in this paper), and the difference between the output and input values, $\hat{x}_2^1 - x_2^1$, is less than zero, which indicates that the equilibrium values E is at the left side of the output value $\hat{x}_2^1$, thus a value which is less than $\hat{x}_2^1$, $\hat{x}_2^1 - \Delta x_2^1$, which approaches equilibrium value, rather than $\hat{x}_2^1$ is regarded as the input value of the latter (B–B′) iteration, x_2^2 (where Δx_2^k can be a step at kth iteration). Similarly, the point E is judged at the right side of the $\hat{x}_2^2$ by means of the difference between the $\hat{x}_2^2$ and x_2^2, a value which is more than $\hat{x}_2^2$, $\hat{x}_2^2 + \Delta x_2^2$, is used as the

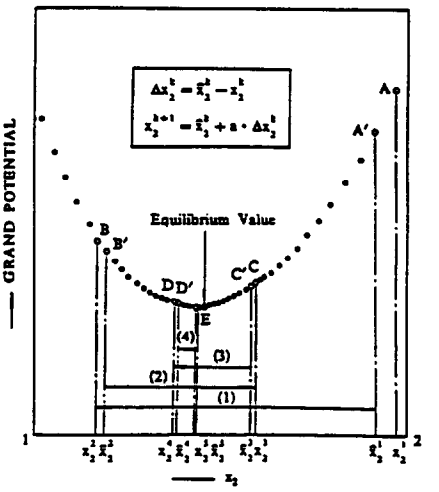


Fig.3 Schematic diagram of the SSNIM

input value at the C–C′ iteration, x_2^3. This iteration procedure can quickly proceed the equilibrium point E, as shown in Fig.3, and is not, however, the natural iteration. In this paper, it is called the Step Speeded Natural Iteration Method.

How to choose the step Δx_2^k is a key in the SSNIM. In this paper we choose the difference between the output and input values, i.e. $\Delta x_2^k = \hat{x}_2^k - x_2^k$ (and $\Delta y_{ij}^k = \hat{y}_{ij}^k - y_{ij}^k$) as a step, the advantages of such a step is following:

(a) When iteration procedure tends to equilibrium value, the Δx_2^k ($= \hat{x}_2^k - x_2^k$) become smaller and smaller, and when the numbers of iteration $k \to \infty$, $\Delta x_2^k \to 0$. Thus, convergence of iteration can be assured.

(b) The Δx_2^2 can automatically change its sign with the iteration procedure, thus each iteration is effectively ensured to approach equilibrium value.

In order to decrease the numbers of iteration in maximum extent, the value, $a\Delta x_2^k$, is often regarded as the speeded step and the coefficient a is generally

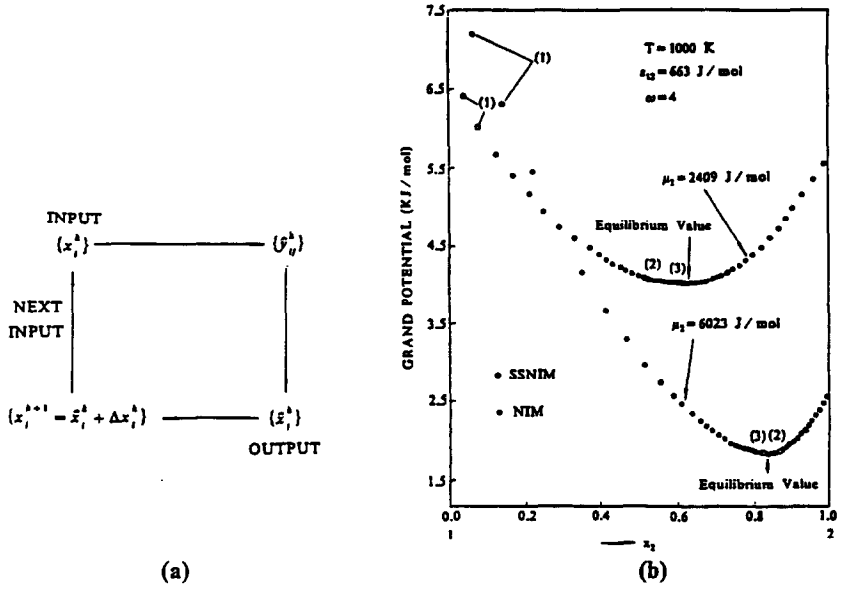


Fig.4 Iteration procedure in the SSNIM. (a) Iteration procedure in CV–pair approximation; (b) Comparison between the SSNIM and NIM

chosen as 5–10. The comparison of iteration procedures of the SSNIM and NIM is shown in Fig.4. Table 1 gives a comparison of the iteration numbers between the NIM and SSNIM. It can be seen that calculating efficiency of the SSNIM is 10–15 times than the NIM.

Table 1 The comparison of iteration numbers between the SSNIM and NIM in the CV–pair approximation of binary system

Conditions / Numbers / Methods	T = 1000K ε_{12} = 663 J / mol ω = 6 a = 10			
	μ_2 = −6023 J / mol	μ_2 = 2409	μ_2 = 6023	μ_2 = 7228
NIM	136	181	145	129
SSNIM	8	13	9	7

3.2 CV–Tetrahedron Approximation in Binary System

The expression of molar grand potential for a disordered fcc structure is given by R.Kikuchi[2]. The following equation can be obtained according to the equilibrium condition, $\partial G_m / \partial z_{ijkl} = 0$.

$$z_{ijkl} = exp\left[-\frac{\varepsilon_{ijkl}}{2RT} + \frac{\mu_i + \mu_j + \mu_k + \mu_l}{8RT} \right] Y^{1/2} X^{-5/8}$$

where

$$Y = y_{ij} y_{ik} y_{il} y_{jk} y_{jl} y_{kl}$$
$$X = x_i x_j x_k x_l$$
$$\varepsilon_{ijkl} = \varepsilon_{ij} + \varepsilon_{ik} + \varepsilon_{il} + \varepsilon_{jk} + \varepsilon_{jl} + \varepsilon_{kl}$$

The variables for the output and input have the y_{ij} besides the x_i in the CV–tetrahedron approximation, and the y_{ij} changes at iteration procedure as shown in Fig.2(b). Thus, the variables y_{ij}s also require to be speeded besides the x_i, i.e.

$$\left.\begin{aligned} x_i^{k+1} &= \hat{x}_i^k + a \cdot \Delta x_i^k \\ y_{ij}^{k+1} &= \hat{y}_{ij}^k + a \cdot \Delta y_{ij}^k \end{aligned}\right\} \tag{3.1}$$

In the NIM, the equation $x_i^k = \sum_j y_{ij}^k$ is assured to hold at each iteration. However, the above equation still holds after the x_i and y_{ij} are respectively

speeded. An analysis is given as follows:

It is assumed that the equation $x_i^{k+1} = \sum_j y_{ij}^{k+1}$ is held in the SSNIM, thus the following equations are obtained by combining with the eq.(3.1)

$$\left.\begin{aligned} \hat{x}_1^k + a \cdot \Delta x_1^k &= \hat{y}_{11}^k + a \cdot \Delta y_{11}^k + \hat{y}_{12}^k + a \cdot \Delta y_{12}^k \\ \hat{x}_2^k + a \cdot \Delta x_2^k &= \hat{y}_{21}^k + a \cdot \Delta y_{21}^k + \hat{y}_{22}^k + a \cdot \Delta y_{22}^k \end{aligned}\right\} \tag{3.2}$$

It can be known from eq.(3.2) that in the initial stage of iteration, although the Δx_i^k and Δy_{ij}^k have certain values, the equation $\Delta x_i^k = \Sigma \Delta y_{ij}^k$ holds; and when iteration procedure approaches the equilibrium value, the Δx_i^k and Δy_{ij}^k respectively tend to zero. Thus, equation $\Delta x_i^{k+1} = \sum_j y_{ij}^{k+1}$ can be assured to hold at whole iteration procedure in the SSNIM, it is assured to obatin the correct equilibrium point.

In the CV–tetrahedron approximation for ordered phase, when the distribution variables in different sub–lattice are simultaneously speeded, the calculating efficiency can be also raised. However, the effect may be not very obvious because of more distribution variables and the restriction among them. From our results the efficiency can be generally increased to about 5 times than the NIM.

3.3 The Application of the SSNIM in Multicomponent System

The main problem for improving the NIM in multicomponent system is to seek the path by which the grand potential decreases most quickly. Through studying the relationships between the grand

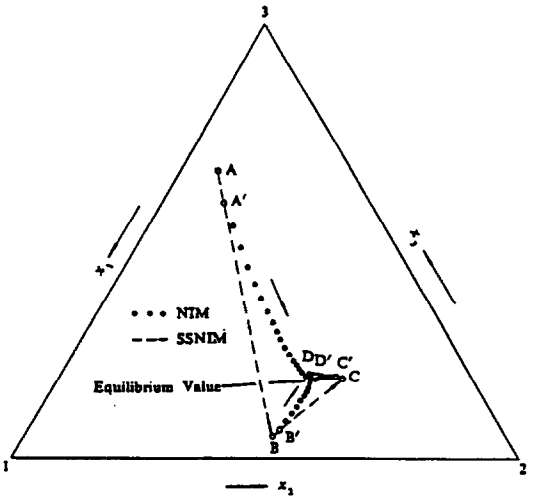


Fig.5 Schematic diagram of the SSNIM in ternary system

potential and distribution variables, we find that the direction of connected line between the input and output values is the path in which the approximated grand potential decreases most quickly, the output values of various variables acts as the input values for the next interation, thus equilibrium value can be quickly sought. The advantage of this method is that it does not require the differentiation of grand potential with respect to the variables to determine the decreased direction of grand potential. The SSNIM in ternary system is shown in Fig.5.

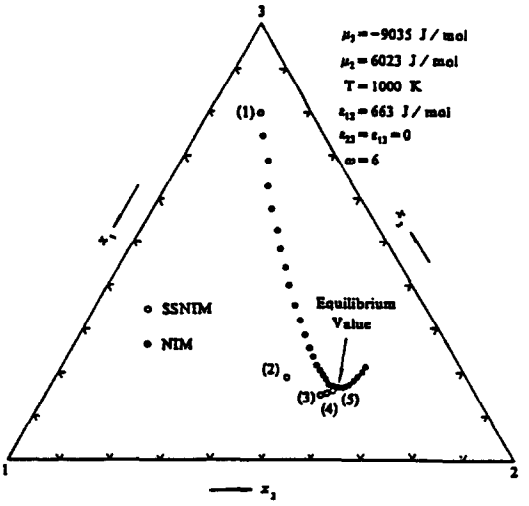


Fig.6 Comparison of iteration procedure between the SSNIM and NIM in ternary system

In CV–pair approximation, the Δx_i^k $(=\hat{x}_i^k - x_i^k)$ is still chosen as the speeded step in this paper

$$x_i^{k+1} = \hat{x}_i^k + a \cdot \Delta x_i^k$$
$$(i = 1, 2, \cdots, n)$$

thus the x_i^{k+1} can be assured in the connected line between the output and input values at the kth iteration. The goal to increase speed can be reached.

The iteration procedure of the CV–pair approximation in ternary system by the above method is shown

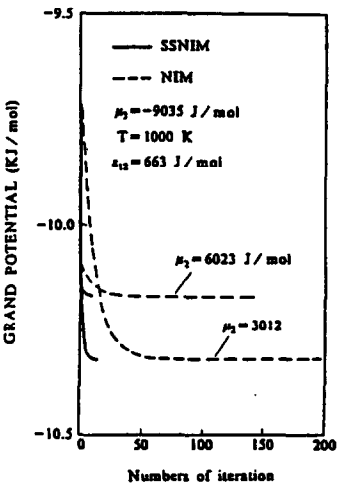


Fig.7 Comparison of iteration numbers between the SSNIM and NIM in ternary system

in Fig.6. It is shown that the numbers of iteration in the SSNIM obviously decreases as shown in Fig.7 and Table 2, and the calculating efficiency increases 10–15 times than that of the NIM.

Table 2 The comparison of iteration numbers between the SSNIM and NIM in the CV–pair approximation of ternary system

Numbers \ Conditions / Methods	$T=1000K \quad \varepsilon_{12}=663\,J/mol \quad \omega=6$ $\mu_3=-9035J/mol \quad a=10$			
	$\mu_2=3012J/mol$	$\mu_2=-3012$	$\mu_2=6023$	$\mu_2=7228$
NIM	190	195	143	98
SSNIM	13	15	11	7

For the CV–tetrahedron approximation, the y_{ij} is also speeded, i.e.

$$y_{ij}^{k+1}=\hat{y}_{ij}^{k}+a\cdot\Delta y_{ij}^{k} \qquad (i=1,2,\cdots,n)$$

Thus calculating efficiency also obviously increases.

4. DICHOTOMOUS NATURAL ITERATION METHOD

4.1 The CV–Pair Approximation in Binary System

The basic principle of the Dichotomous Natural Iteration Method (DNIM) is to combine the NIM with the Dichotomous Method, thus the calculating efficiency is increased by making use of the advantages of these two methods. The DNIM is shown in Fig.8.

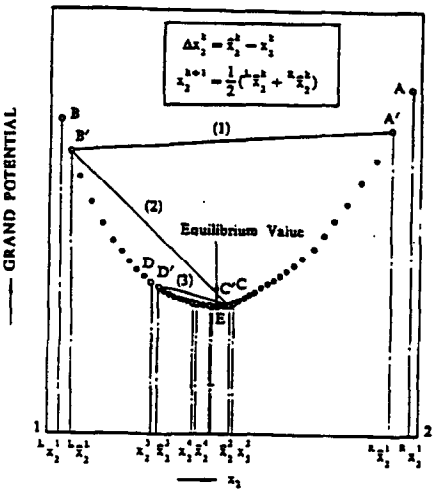


Fig.8 Schematic diagram of the DNIM

It is assumed that the ${}^{L}x_2^1$ and ${}^{R}x_2^1$ are respectively the initial guess values, and are called 1st iteration points, and then the $({}^{L}\hat{x}_2^1 + {}^{R}\hat{x}_2^1)/2$, other than ${}^{L}\hat{x}_2^1$ (or ${}^{R}\hat{x}_2^1$) is regarded as the input value at 2nd iteration. Provided that $x_2^2 = ({}^{L}\hat{x}_2^1 + {}^{R}\hat{x}_2^1)/2, \Delta^{L}x_2^1 = {}^{L}\hat{x}_2^1 - {}^{L}x_2^1, \Delta^{R}x_2^1 = {}^{R}\hat{x}_2^1 - {}^{R}x_2^1$, the input value x_2^2 corresponds to the output value $\hat{x}_2^2$, and the difference $\Delta x_2^2 = \hat{x}_2^2 - x_2^2$. If the Δx_2^2 and ${}^{L}\Delta x_2^1$ have the same signs, which indicates that the equilibrium point is between the $\hat{x}_2^2$ and ${}^{R}\Delta\hat{x}_2^1$, thus the ${}^{L}\hat{x}_2^1$ is substituted by $\hat{x}_2^2$, and the $(\hat{x}_2^2 + {}^{R}\hat{x}_2^2)/2$ acts as the input value for the 3rd iteration. If the Δx_2^2 and $\Delta^{R}\hat{x}_2^1$ have same signs, which indicates the equilibrium point is between the $\hat{x}_2^2$ and ${}^{L}\hat{x}_2^1$, thus the ${}^{R}\hat{x}_2^1$ is substituted by the $\hat{x}_2^2$, and the $(\hat{x}_2^2 + {}^{L}\hat{x}_2^2)/2$ acts as the input value at the 3rd iteration. When the ${}^{L}\hat{x}_2^1$ (or ${}^{R}\hat{x}_2^1$) is substituted with the $\hat{x}_2^2$, the $\Delta^{L}x_2^2$ (or $\Delta^{R}\hat{x}_2^2$) is also substituted by the Δx_2^2; and then the difference between the output and input values at the 3rd iteration is compared, as above, with the retained Δx_2^2 and $\Delta^{L}x_2^1$ (or $\Delta^{R}x_2^1$). This procedure is repeated until Δx_2^k is less than a given measure of convergence. The iteration procedure as above mentioned is shown in Fig.9(a).

The calculated results indicate that the numbers of iteration in te DNIM decrease 10–15 times than that in the NIM, as shown in Table 3. Fig.9(b) gives the comparison between the DNIM and NIM.

4.2 The CV–Tetrahedron Approximation in Binary System

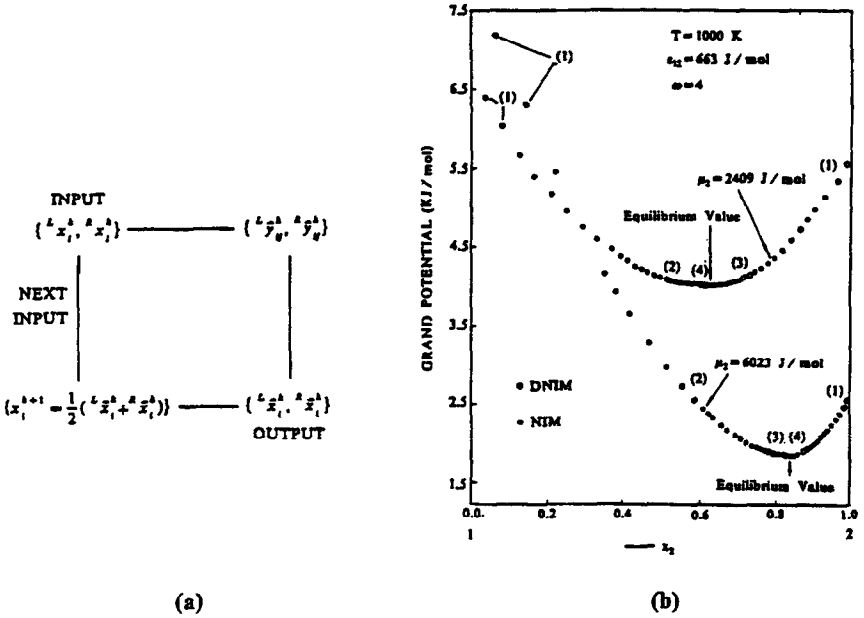
For the CV–tetrahedron approximation, the y_{ij} is also dichotomized besides the x_i, i.e.

$$x_i^{k+1} = ({}^{L}\hat{x}_i^k + {}^{R}\hat{x}_i^k)/2$$

$$y_{ij}^{k+1} = ({}^{L}\hat{y}_{ij}^k + {}^{R}\hat{y}_{ij}^k)/2$$

The equation $x_i^{k+1} = \sum_j y_{ij}^{k+1}$ in the DNIM also holds due to ${}^{L}\hat{x}_i^k = \sum_j {}^{L}\hat{y}_{ij}^k$,

${}^{R}\hat{x}_i^k = \sum_j {}^{R}\hat{y}_{ij}^k$, therefore, the correct convergence value can be assured, and actual calculated procedure is the same with the CV–pair approximation. The numbers of iteration in the DNIM for the CV–tetrahedron approximation obviously decreased too.



(a) (b)

Fig.9 Iteration procedure of the DNIM. (a) Iteration procedure in CV–pair approximation; (b) Comparison between the DNIM and NIM

Table 3 The comparison of iteration numbers between the DNIM and NIM in the CV–pair approximation of binary system

Conditions / Numbers / Methods	T = 1000K ε_{12} = 663 J / mol ω = 6			
	μ_2 = −6023 J / mol	μ_2 = 2409	μ_2 = 6023	μ_2 = 7228
NIM	136	181	145	127
DNIM	13	14	13	13

5. THE COMPARISON BETWEEN THE SSNIM AND DNIM

The SSNIM and DNIM in binary systems for the CV–pair approximation almost have the same effect. Calculating speeds of these two methods increase 10–15 times than that of the NIM. However, the SSNIM has two advantages as follows:

(a) The SSNIM can be applied to the CVM calculation in multicomponent system and the DNIM can not.

(b) The SSNIM can be obtained with slight revision of the programs using the NIM.

The DNIM in Binary system for the CV–tetrahedron approximation has better convergence than the SSNIM, but is not, however, suitable to apply in multicomponent system.

6. CONCLUSIONS

(1) Two methods, the SSNIM and DNIM, for the improvement of the NIM are proposed, and the calculating efficiency obviously increases.

(2) The SSNIM and DNIM are still imbued with the absolute convergence at the same time increasing speed.

ACKOWLEDGEMENT

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