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A GENERAL METHOD OF CALCULATING PHASE EQUILIBRIA IN A MULTICOMPONENT SYSTEM BY MEANS OF A HILL-CLIMBING MINIMIZATION PROCEDURE

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ABSTRACT

A generalization of the method of calculating the state of equilibrium of a multicomponent system, using a hill-climbing minimization procedure, is proposed. Moreover, an original method of calculating values for partial free energies from the state of equilibrium has been made an essential part of the general schedule.

INTRODUCTION

In most cases, the state of equilibrium of a multicomponent system is obtained through the minimization of the Gibbs free energy after all the independent variables have been prescribed. Several methods of calculation have already been used, in particular those of Hillert [1–3], Eriksson [4], Jansson [5], Sundman and Agren [6]. Most of these methods deal with the constraints of the system by producing supplementary unknowns.

A different method, using a hill-climbing minimization procedure [7], has been applied for many binary and ternary systems by Ansara [8]. In this method, the number of independent internal variables, which depends on the number and the nature of the phases, is reduced to its minimum value by means of constraints.

Here, a generalization of this method of calculation has been developed based on an automatic choice of the variables in relation to which the minimization will be done, and which yields the compositions of the phases in equilibrium in a multicomponent system. Moreover, an original method of calculating values for partial free energies has been made an essential part of the general schedule. We noted that these values must be known before analysis of the tendency for precipitation of other phases in relation to the calculated equilibrium can be made.

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EQUILIBRIUM STATE OF AN N-COMPONENT SYSTEM WITH Φ PHASES

A multicomponent system, containing Φ phases at a given temperature and submitted to an unchanging pressure, can be defined by

$$P_1 n + P_2 n + \ldots + P_f n + \ldots + P_\Phi n$$

where P_f is the fraction of n initial moles in phase f and satisfies the relation

$$\sum_{f=1}^{f=\phi} P_f = 1 \tag{1}$$

Taking the phases separately, one can determine the Gibbs free energy of the system, ΔG, which is equal to the summation of the Gibbs free energy of each phase, referred to the pure components in the same structural state. It can be expressed as

$$\Delta G = \sum_{f=1}^{\phi} P_f \Delta G^f = \sum_{f=1}^{\phi-1} P_f (\Delta G^f - \Delta G^\phi) + \Delta G^\phi \tag{2}$$

In order to define the Gibbs free energy of the system, the Gibbs free energy of each phase, ΔG^f, should be known as a function of temperature and composition. Usually, ΔG^f can be written at constant pressure

$$\Delta G^f = \Delta G^f\left(x_1^f, x_2^f, \ldots x_i^f, \ldots x_{N-1}^f, x_N^f, T\right) \tag{3}$$

Or in a condensed form

$$\Delta G^f = \Delta G^f\left(x_i^f, T\right) \tag{4}$$

with $i = 1, \ldots, N$.

Since x_i^f is the atomic fraction of i in phase f, we have

$$\sum_{i=1}^{N} x_i^f = 1 \tag{5}$$

In eqn. (3), the Gibbs free energy of phase f can be related to the pure components in a given structural state. In eqn. (4), the atomic fractions x_i^f may be constants, dependent variables or independent variables, according to the nature of the phase. The following inequality is proved by the number of independent variables, N_v^f, of phase f

$$0 \leqslant N_v^f \leqslant N - 1 \tag{6}$$

The dependent variables are expressed by linear combinations of the independent variables and the constants of the phases, as will be explained later.

On the assumption that the atomic fraction in phase f is

$$x_i^f = \frac{n_i^f}{nP_f} \tag{7}$$

and that

$$n_i = \sum_{f=1}^{\phi} n_i^f \tag{8}$$

the atomic fraction of component i of the initial melt is related to the different atomic fractions of the same component in the different phases by the equation

$$x_i = \sum_{f=1}^{\phi} P_f x_i^f = x_i^{\phi} + \sum_{f=1}^{\phi-1} P_f \left(x_i^f - x_i^{\phi} \right) \tag{9}$$

with $i = 1, \ldots, N$. These relations are called the generalized lever rule.

The compositions of the phases at the equilibrium are obtained by minimizing the Gibbs free energy of the system [expressed by eqn. (2)] in relation to the independent variables and on the assumption that the lever rule holds, using a hill-climbing technique described by Nelder and Mead [7].

GENERAL DESCRIPTION OF THE METHOD OF CALCULATION

In order to calculate the Gibbs free energy of the system one must calculate at each step of the minimization [shown by eqn. (2)], each atomic fraction x_i^f of the different phases in equilibrium and the $\phi - 1$ values of P_f, which are related by the $N - 1$ equations (9) (according to the relation $\sum_{i=1}^{i=N} x_i = 1$, the N equation is a linear combination of the other $N - 1$ equations).

The number of independent variables can be defined by the relation

$$N_v^{(S)} = \sum_{f=1}^{\phi} N_v^f + (\phi - 1) - (N - 1)$$

where N_v^f is the number of independent variables of phase f, $\Phi - 1$ is the number of unknown P_f, and $N - 1$ is the number of independent equations (9).

In a simplified form, it becomes

$$N_v^{(S)} = \sum_{f=1}^{\phi} N_v^f - (N - \phi) \tag{10}$$

In order to choose the $N_v^{(S)}$ independent variables, $y_1, y_2, \ldots, y_K, \ldots, y_{N_v^{(S)}}$, $(N - \Phi)$ variables must be eliminated from the $\sum_{f=1}^{f=\Phi} N_v^f$ variables of the system.

STRATEGY FOR THE CHOICE OF INDEPENDENT VARIABLES OF THE MINIMIZATION PROCESS

This strategy is complex and is made in an automatic way; it is composed of two main steps:

(1) numbering eqns. (9) with the order of increasing number of independent variables and making the lines of constants appear in the first equations;

(2) suppressing $(N - \Phi)$ variables in the system with the new numeration.

Three particular examples are described in order to explain fully why these steps are necessary.

Examples of the choice of variables

Example 1

Let us consider a two phase equilibrium in a quaternary system. Relation (2) can thus be written

$$\Delta G = P_1 \Delta G^1 + (1 - P_1)\Delta G^2$$

Equations (9) become

$$x_1 = P_1 x_1^1 + (1 - P_1)x_1^2$$
$$x_2 = P_1 x_2^1 + (1 - P_1)x_2^2$$
$$x_3 = P_1 x_3^1 + (1 - P_1)x_3^2$$

In the description of the two phases, it has been supposed that the atomic fractions x_i^f are independent variables, so $N_v^1 = N_v^2 = 3$. The number of independent variables of the problem is equal to $6 - (4 - 2) = 4$ [eqn. (10)]. One should therefore eliminate two variables from the six independent variables of the system. In view of eqns. (9), x_1^1 and x_1^2 are chosen as variables for the calculation of P_1, and x_2^1 and x_3^1 are then eliminated by retaining x_2^2 and x_3^2 as variables. The first equation gives

$$P_1 = (x_1 - x_1^2)/(x_1^1 - x_1^2)$$

The last two equations are constraints and allow x_2^1 and x_3^1 to be expressed once P_1 has been calculated

$$x_2^1 = [x_2 - (1 - P_1)x_2^2]/P_1$$
$$x_3^1 = [x_3 - (1 - P_1)x_3^2]/P_1$$

The Gibbs free energy of the system is expressed by (2) as a function of the four independent variables x_1^1, x_1^2, x_1^3, x_1^4. $\Delta G(x_1^1, x_1^2, x_1^3, x_1^4)$ is minimized in relation to these variables.

Example 2

Let us consider again a two-phase equilibrium in a quaternary system. In the description of the two phases, it has been supposed that $x_1^1 = \alpha$, $x_2^1 = \beta$, $x_1^2 = \gamma x_2^2 + \delta$ (α, β, γ and δ being real constants), the other atomic fractions x_2^2, x_3^1 and x_3^2 being independent variables; so $N_v^1 = 1$, $N_v^2 = 2$. The number of independent variables of the problem is equal to $3 - (4 - 2) = 1$. One must therefore eliminate two variables from the three independent variables of the phases. The equations are numbered following the increasing number of independent variables and the constants are made to appear in the first equations, which are used to calculate P_f. Elimination of one variable in the third equation (9) is done in the same way as in example 1, after x_3^2 has been chosen as the variable of the problem.

$$x_3^1 = \left[x_3 - (1 - P_1)x_3^2\right]/P_1$$

This step is achieved after calculating P_1.

On the contrary, elimination of the single variable x_2^2 in the second equation cannot be made by the relation

$$x_2^2 = (x_2 - P_1\beta)/(1 - P_1)$$

since the first equation which should allow P_1 to be calculated gives

$$P_1 = \left(x_1 - x_1^2\right)/\left(\alpha - x_1^2\right)$$

Also, x_1^2 is dependent on x_2^2 which is known only after P_1 has been calculated. A linear combination of the first two equations gives

$$x_1 - \gamma x_2 = P_1(\alpha - \gamma\beta) + (1 - P_1)\left(x_1^2 - \gamma x_2^2\right)$$

$$x_1 - \gamma x_2 = P_1(\alpha - \gamma\beta) + (1 - P_1)\delta$$

so that

$$P_1 = (x_1 - \gamma x_2 - 1)/(\alpha - \gamma\beta - 1)$$

Once P_1 has been calculated $x_2^2 = (x_2 - P_1\beta)/(1 - P_1)$ and $x_1^2 = \gamma x_2^2 + \delta$ can be determined. The single variable of the minimization is x_3^2 and ΔG is minimized in relation to x_3^2.

Example 3

For a two-phase equilibrium in a quinary system, eqns. (9) are

$$x_1 = P_1 x_1^1 + (1 - P_1)x_1^2$$

$$x_2 = P_1 x_2^1 + (1 - P_1)x_2^2$$

$$x_3 = P_1 x_3^1 + (1 - P_1)x_3^2$$

$$x_4 = P_1 x_4^1 + (1 - P_1)x_4^2$$

In the description of the two phases, it has been supposed that $x_1^1 = \alpha$, $x_1^2 = \beta$, $x_2^1 = \gamma$, $x_2^2 = \delta x_3^2 + \varepsilon$ (α, β, γ, δ and ε being real constants), the other

atomic fractions x_3^1, x_3^2, x_4^1, x_4^2 being independent variables; so $N_v^1 = 2$, $N_v^2 = 2$. The number of independent variables of the problem is $4 - (5 - 2) = 1$. One must therefore eliminate three variables from the four independent variables of the phases. The equations are numbered in the same way as in example 2. The first equation contains only constants and yields P_1 [$P_1 = (x_1 - \beta)/(\alpha - \beta)$; $\alpha \neq \beta$]. The other equations are then considered as constraints and one variable in each line should be taken off. Elimination of one variable in the last equation is made in the same way as in examples 1 and 2, after which x_4^2 is chosen as an independent variable of the problem.

$$x_4^1 = \left[x_4 - (1 - P_1)x_4^2\right]/P_1$$

On the contrary, eqn. (2) contains no independent variable; x_2^2 depends on x_3^2. Therefore, in order to take account of the constraint constituted by eqn. (2), one must eliminate the independent variable x_3^2 on which x_2^2 depends and which belongs to eqn. (3). Elimination of x_3^2 by means of x_2^2 is made in two steps

$$x_2^2 = (x_2 - P_1\gamma)/(1 - P_1)$$

followed by

$$x_3^2 = \left(x_2^2 - \varepsilon\right)/\delta$$

A variable in eqn. (3) is then eliminated; x_3^2 having already been taken off x_3^1 will be expressed by

$$x_3^1 = \left[x_3 - (1 - P_1)x_3^2\right]/P_1$$

The single independent variable of the problem is therefore x_4^2 and in the present case the two eliminated variables x_3^1 and x_3^2 are found to be in the same equation.

Numbering the equations of the generalized lever rule

Equations (9) are numbered in the order of increasing number of independent variables and such that the lines of constants appear in the first equations. In fact, in example 3 the first line contains only constants [$x_1 = \alpha P_1 + \beta(1 - P_1)$]. P_1 is fixed by this equation which must be placed in the first position. Moreover, it is noted that the existence of two lines of constants in this case makes the problem impossible unless the following condition is fulfilled by the atomic composition of the system (x_1, x_2). For

$$x_2 = \alpha' P_1 + \beta'(1 - P_1)$$

$$(x_1 - \beta)/(\alpha - \beta) = (x_2 - \beta')/(\alpha' - \beta')$$

Relations (9) become

$$x_j = \sum_{f=1}^{\phi} P_f x_j^f = x_j^{\phi} + \sum_{f=1}^{\phi-1} P_f\left(x_j^f - x_j^{\phi}\right) \qquad (11)$$

in which j is the new index of the numeration.

The following inequality is obtained from the number of independent variables, $N_v(j)$, of the different phases in line j.

$$j_1 \leqslant j_2 \Leftrightarrow N_v(j_1) \leqslant N_v(j_2) \tag{12}$$

Later, the new index j will be assigned to the components.

The choice of the variables $y_1, y_2, \ldots, y_k$ of the minimization will be done by eliminating $N - \Phi$ independent variables by means of the lines whose indexes are j, $j \geqslant \Phi$, making possible, on the one hand, calculation of the P_f values by means of the first $\Phi - 1$ equations, and on other, the remaining atomic fractions of the different phases by means of the last $N - \Phi$ equations, considered as constraints, and by means of the relations of dependence which are specific to the phases.

Techniques for eliminating an independent variable in a line

Let us consider a line j, $j \geqslant \Phi$: $x_j = \sum_{f=1}^{f=\Phi} P_f x_j^f$. Later, the independent variable $x_{j_2}^f$ will be linked to the variable $x_{j_1}^f$ if $x_{j_1}^f$ depends on $x_{j_2}^f$

$$x_{j_1}^f = \alpha x_j^f + \beta x_{j_2}^f + \ldots$$

Two cases must be distinguished as, according to the number of independent variables of the line j, $N_v(j)$ may be zero or non-zero.

$N_v(j) \neq 0$

Let us suppose that x_j^1 is the independent variable that we will suppress. Two cases must be distinguished

(1) x_j^1 is not linked to any dependent variable

x_j^1 can be taken off and expressed by means of the previously calculated values of P_f and by means of the other atomic fractions of the different phases of line j.

$$x_j^1 = \left(x_j - \sum_{f=2}^{f=\Phi} P_f x_j^f \right) / P_1$$

These last variables (x_j^f, $f \neq 1$) will have been chosen previously as independent variables of the minimization if they are independent, or if they are dependent, the independent variables which are linked to these variables will be chosen as independent variables in order to calculate them. Therefore it will no longer be possible to eliminate another variable in the same line.

(2) x_j^1 is linked to one or more dependent variables

(2a) none of these variables lies in the $\Phi - 1$ first equations: x_j^1 can be suppressed (see above) and the dependent variables which are linked to x_j^1 will be expressed, after the calculation of x_j^1, by means of the relation

$$x_{j_1}^1 = \alpha x_j^1 + \beta x_{j_2}^1 + \ldots \; (j \geqslant \Phi)$$

The variables $x_{j_2}^1$ will have been chosen previously as independent variables of the problem.

(2b) One or more of these variables lie in the $\Phi - 1$ first equations: let $x_{j_1}^1$ be this variable ($j_1 \leqslant \Phi - 1$). We can only suppress x_j^1 if the linear combination of the lines j, j_1, j_2 is realizable (cf. example 2), which means the resulting line $x_{j_1} - \alpha x_j - \Sigma_{j_2} \beta_{j_2} x_{j_2}$ contains only variables defined before calculation of the values of P_f. For this to be possible, two conditions have to be satisfied by the line j:

α, none of the independent variables of the line j has yet been suppressed;

β, none of the dependent variables of the line j is linked to an already suppressed independent variable, because the latter cannot be calculated before P_f.

Once these two conditions are satisfied, the independent variables $x_{j_2}^1$ which is linked to $x_{j_1}^1$ have to be examined.

If $j_2 \leqslant \Phi - 1$, the variables $x_{j_2}^1$ are taken as independent variables of the minimization.

If $j_2 \geqslant \Phi$, line j_2 must satisfy the same conditions (α, β) as line j. It follows that the variable $x_{j_2}^1$ will be suppressed in line j_2 in this step of the operation.

If all the conditions necessary to suppress the variable x_j^1 are satisfied, the other variables of line j are then calculated in the same way as in (1).

$N_v(j) = 0$

After the numeration, a line j ($j \geqslant \Phi$) may contain only constants or dependent variables [$N_v(j) = 0$]. An independent variable must be eliminated in another line by means of a dependent variable of line j (cf. example 3).

Let x_j^1 be a dependent variable

$$x_j^1 = \sum_{p=1}^{q} \alpha_p x_{j_p}^1 + \alpha_{q+1}$$

We will therefore suppress one variable out of the independent variables $x_{j_p}^1$. If this elimination is possible, x_j^1 will be calculated by means of the relation

$$x_j^1 = \left(x_j - \sum_{f=2}^{f=\Phi} P_f x_j^f \right) / P_1$$

and the suppressed independent variable $x_{j_1}^2$ will be calculated by

$$x_{j_1}^1 = \left(x_j^1 - \sum_{p=2}^{q} \alpha_p x_{j_p}^1 - \alpha_{q+1} \right) / \alpha_1$$

The following conditions must now be satisfied for $x_{j_1}^1$ to be suppressed.

(a) The variable of line j_1 which is calculated by means of the constraint established by line j_1 must not have been suppressed already because the calculation requires that all the other atomic fractions be known.

(b) $x^1_{j_1}$ can be eliminated if another independent variable of line j_1 is taken off, in order for the constraint of line j_1 to be verified. Thus, the variables $x^2_{j_1}$, ... $x^{\Phi}_{j_1}$ must be examined in order to see if one of these variables can be suppressed later on.

(c) $x^1_{j_1}$ must not be linked to a dependent variable which lies in the $\Phi - 1$ first equations because it has to be known before the calculation of the values of P_f. This inconvenience cannot be palliated by a linear combination, because another variable must be taken off in line j_1.

In the event that $x^1_{j_1}$ cannot be suppressed, $x^1_{j_2}$, ...$x^1_{j_q}$ will be analyzed. In the case of impossibility, a new dependent variable x^2_j of line j will be analyzed.

General algorithm

The data related to the description of the different phases are contained in a file which is read by the program. In that file an indicator is used for each component of each phase to distinguish the constants, the dependent variables and the independent variables. The program then calculates the number of variables of the minimization (10) and then, after the equations of the generalized lever rule have been numbered (see above), composes a table of independent variables which is linked to the dependent variables of the $\Phi - 1$ first equations. Then, $N - \Phi$ variables are eliminated by means of the $N - \Phi$ last equations (see above) with the new numeration and, when possible, in the order:

(1) taking off an independent variable which is not linked to any dependent variable;

(2) taking off an independent variable which does not involve a linear combination of the lines;

(3) taking off an independent variable which involves a linear combination of the lines, the indices of the lines which are implicated in the linear combination and the order of calculation of the concerned variables being memorized.

For the lines which contain only dependent variables, the independent variable is suppressed in another line as described above. The independent variables which are conserved in the precedent algorithm are then numbered. These variables, named $y_1, y_2 \ldots, y_{N'^{(S)}}$, are the variables of the minimization.

CALCULATION OF THE PARTIAL GIBBS FREE ENERGIES OF THE COMPONENTS IN THE Φ-PHASE EQUILIBRIUM

Principles of the calculation of the partial Gibbs free energies

The state of equilibrium of a given multiphase system is represented in an N dimensional space (X_i, $i = 1$ to $N - 1$, Y) by a point, labelled $^*S$, whose

coordinates are defined by the N relations

$$\left|\begin{array}{l} x_j = {}^*x_j^{\phi} + \sum_{f=1}^{\phi-1} P_f\left({}^*x_j^f - {}^*x_j^{\phi}\right) \qquad j = 1, \ldots, N-1 \\ \Delta^*G = \Delta^*G^{\phi} + \sum_{f=1}^{\phi-1} P_f\left(\Delta^*G^f - \Delta^*G^{\phi}\right) \end{array}\right. \tag{13}$$

The superscript * indicates that the corresponding values are calculated at the equilibrium.

Equations (13) define a point, labelled $^*S$, which represent a Φ-phase equilibrium in an N-component system in an N-dimensional space whose coordinates are $(x_1, x_2, \ldots, x_j, \ldots x_{N-1}, \Delta G)$. When the whole composition of the system varies, this point defines a $\phi - 1$-dimensional space, contained in an hyperplane tangential to the hypersurfaces representing the Gibbs free energies of the different phases of the system. The point of tangency of phase f has the coordinates $^*x_j^f$, Δ^*G^f, with $j = 1, \ldots, N-1$. If this hyperplane can be defined, the partial Gibbs free energies of the components, $Y_i = \overline{\Delta G}_i$, with $i = 1$–N, are calculated using the intersections of this hyperplane with the straight lines $x_j = \delta_{ij}$, where δ_{ij} is the Kröenecher's symbol ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$).

Equation of the N $-$ *1-dimensional hyperplane tangential to the hypersurfaces representing the Gibbs free energies of the* ϕ *phases in equilibrium*

A hyperplane in an N-dimensional space is completely defined by a point and $N - 1$ independent director vectors. Any vector which is tangential to a hypersurface representing a phase f at the point $(^*x_j^f, \Delta^*G^f)$ is contained in the hyperplane which is tangential to the f phases in the equilibrium state. Especially, if x_i^f is an independent variable of phase f, the vector whose coordinates are

$$\left(\frac{{}^*\partial x_j^f}{\partial x_i^f}\right), \left(\frac{{}^*\partial \Delta G^f}{\partial x_i^f}\right)$$

with $j = 1, \ldots, N-1$, can be taken as a director vector of the tangential hyperplane.

The $\Phi - 1$ first director vectors are chosen by taking a free system of $\Phi - 1$ vectors contained in the linear variety defined by relations (13). This system is completed by $N - \Phi$ vectors which are tangential to the hypersurfaces of equation $\Delta G^f = \Delta G^f(x_j^f)$ at equilibrium.

Determination of the $\Phi - 1$ *first director vectors*

Equations (13) define a parametric representation of the $\Phi - 1$ dimensional space which has been previously described. The independent parame-

ters are $P_1, P_2, \ldots, P_{\Phi-1}$. The $\Phi - 1$ vectors $\vec{\mathbf{V}}_1, \vec{\mathbf{V}}_2, \ldots, \vec{\mathbf{V}}_K, \ldots, \vec{\mathbf{V}}_{\Phi-1}$, whose components are

$$\vec{\mathbf{V}}_k \left| \begin{array}{l} {}^*x_1^k - {}^*x_1^\phi \\ \hline {}^*x_j^k - {}^*x_j^\phi \\ \hline {}^*x_{N-1}^k - {}^*x_{N-1}^\phi \\ \Delta^*G^k - \Delta^*G^\phi \end{array} \right. \tag{14}$$

constitute a system of independent directors of this space.

As these $\Phi - 1$ first equations (13) are independent, a new parametric representation of the space can be obtained, whose independent parameters are $x_1, x_2, \ldots, x_{\Phi-1}$, by writing

$$\left[P_f\right] = \left[{}^*x_k^f - {}^*x_k^\phi\right]^{-1}\left[x_k - {}^*x_k^\phi\right] \tag{15}$$

in this matrix notation, $[P_f]$ and $[x_k - {}^*x_k^\phi]$ are columns with $\Phi - 1$ lines and $[{}^*x_k^f - {}^*x_k^\Phi]$ a square matrix of $\Phi - 1$ order. The inverse matrix will be noted $[m_{k,f}]$, so that

$$\left[P_f\right] = \left[m_{k,f}\right]\left[x_k - {}^*x_k^\phi\right] \tag{16}$$

The expression of P_f can be written as

$$P_f = \sum_{k=1}^{k=\phi-1} m_{k,f}\left(x_k - {}^*x_k^\phi\right) \tag{17}$$

with $f = 1, 2, \ldots, \Phi - 1$.

The new parametric representation is

$$\left| \begin{array}{l} x_k = x_k, \text{ with } k = 1, \ldots, \phi - 1 \\ x_l = {}^*x_l^\phi + \displaystyle\sum_{f=1}^{f=\phi-1} \sum_{k=1}^{k=\phi-1} m_{k,f}\left(x_k - {}^*x_k^\phi\right)\left({}^*x_l^f - {}^*x_l^\phi\right) \qquad l = \phi, \ldots, N-1 \\ \Delta G = \Delta^*G^\phi + \displaystyle\sum_{f=1}^{f=\phi-1} \sum_{k=1}^{k=\phi-1} m_{k,f}\left(x_k - {}^*x_k^\phi\right)\left(\Delta^*G^f - \Delta^*G^\phi\right) \end{array} \right. \tag{18}$$

So, it follows

$$\left| \begin{array}{l} x_k = x_k \text{ with } k = 1, \ldots, \phi - 1 \\ x_l = \displaystyle\sum_{k=1}^{k=\phi-1} \alpha_{l,k} x_k + \kappa_l \qquad l = \phi, \ldots, N-1 \\ \Delta G = \displaystyle\sum_{k=1}^{k=\phi-1} \alpha_{N,k} x_k + \kappa'_N \end{array} \right. \tag{19}$$

and

$$\alpha_{l,k} = \sum_{f=1}^{f=\phi-1} m_{k,f}\left({}^*x_l^f - {}^*x_l^\phi\right) \quad l = \phi, \ldots N-1 \qquad k = 1, \ldots \phi - 1 \tag{20}$$

$$\alpha_{N,k} = \sum_{f=1}^{f=\phi-1} m_{k,f}\left(\Delta^*G^f - \Delta^*G^\phi\right) \tag{21}$$

$$\kappa_l = {}^*x_l^\phi - \sum_{k=1}^{\phi-1} \alpha_{l,k}\,{}^*x_k^\phi \tag{22}$$

$$\kappa'_N = \Delta^*G^\phi - \sum_{k=1}^{\phi-1} \alpha_{N,k}\,{}^*x_k^\phi \tag{23}$$

In the new parametric representation, the free system of $N-1$ independent vectors $\vec{\mathbf{W}}_1, \vec{\mathbf{W}}_2, \ldots, \vec{\mathbf{W}}_K, \ldots, \vec{\mathbf{W}}_{\Phi-1}$ is defined by a matrix of N lines and $\Phi - 1$ columns.

$$\begin{vmatrix}
1, & \ldots & \ldots & 0, & \ldots & \ldots & 0 \\
0, & 1, & \ldots & 0, & \ldots & & 0 \\
\vdots & & \ddots & & & & \vdots \\
0, & \ldots & & 1, & \ldots & & 0 \\
0, & \ldots & & 0, & 1, \ldots & & 0 \\
\vdots & & & & \ddots & & \vdots \\
0, & \ldots & & 0, & \ldots & 1, & 0 \\
 & & & & & \ddots & \\
0, & \ldots & \ldots & 0, & \ldots & \ldots & 1 \\
\alpha_{\phi,1}, & \ldots & & \alpha_{\phi,k}, & \ldots & & \alpha_{\phi,\phi-1} \\
\cdot & & & & & & \cdot \\
\alpha_{l,1}, & \ldots & & \alpha_{l,k}, & \ldots & & \alpha_{l,\phi-1} \\
\cdot & & & & & & \cdot \\
\alpha_{N,1}, & \ldots & & \alpha_{N,k}, & \ldots & & \alpha_{N,\phi-1}
\end{vmatrix} \tag{24}$$

The elements of column k are the components of the vector $\vec{\mathbf{W}}_k$.

Determination of the remaining N − Φ *director vectors*

When choosing the independent variables of the problem, one independent variable of one of the phases of the system was suppressed for each of the $N - \Phi$ last lines of the lever rule. Let z_l^f be this variable. The vector $\vec{\mathbf{W}}_l$

defined by

$$\vec{\mathbf{W}}_l \left| \begin{array}{l} *\left(\dfrac{\partial x_j^f}{\partial z_l^f}\right) \quad \text{with } j = 1, \ldots N-1 \\ *\left(\dfrac{\partial \Delta G^f}{\partial z_l^f}\right) \end{array} \right. \tag{25}$$

will be taken as a director vector of the tangential hyperplane. So the remaining $N - \Phi$ director vectors are $\vec{\mathbf{W}}_\Phi, \ldots \vec{\mathbf{W}}_{N-1}$.

In the event that all the suppressed variables for the $N - \Phi$ last lines are independent variables of these lines, i.e. if $z_l^f = x_l^f$ for line l, the matrix of vectors $\vec{\mathbf{W}}_1, \ldots, \vec{\mathbf{W}}_{N-1}$ has the form

$$\left| \begin{array}{ccccccccc} 1, & \ldots, & 0, & \ldots, & 0,0, & \ldots, & 0, & \ldots, & 0 \\ 0,1, & \ldots, & 0, & \ldots, & 0,0, & \ldots, & 0, & \ldots, & 0 \\ \vdots & \ddots & & & & & & & \vdots \\ 0, & \ldots, & 1, & \ldots, & 0,0, & \ldots, & 0, & \ldots, & 0 \\ \vdots & & & \ddots & & & & & \vdots \\ 0, & \ldots, & 0, & \ldots, & 1,0, & \ldots, & 0, & \ldots, & 0 \\ & & & & \ddots & & & & \\ \alpha_{\phi,1}, & \ldots, & \alpha_{\phi,k}, & \ldots, & \alpha_{\phi,\phi-1}, 1, & \ldots, & 0, & \ldots, & 0 \\ \vdots & & & & & \ddots & & & \vdots \\ \alpha_{l,1}, & \ldots, & \alpha_{l,k}, & \ldots, & \alpha_{l,\phi-1}, 0, & \ldots, & 1, & \ldots, & 0 \\ \vdots & & & & & & & \ddots & \vdots \\ \alpha_{N-1,1}, & \ldots, & \alpha_{N-1,k}, & \ldots, & \alpha_{N-1,\phi-1}, 0, & \ldots, & 0, & \ldots, & 1 \\ \alpha_{N,1}, & \ldots, & \alpha_{N,k}, & \ldots, & \alpha_{N,\phi-1}, \alpha_{N,\phi}, & \ldots, & \alpha_{N,1}, & \ldots, & \alpha_{N,N-1} \end{array} \right| \tag{26}$$

This matrix is formed by N lines and $N - 1$ columns and will be designated as $[\alpha_{i,p}]$, with $i = 1, \ldots N$ and $p = 1, \ldots, N-1$.

The $N - 1$ vectors are then independent. In the event that several of the suppressed variables for line l are not independent variables of this line, it may be possible that the system formed by the vectors is not a free system. The vector which is correlated to the suppressed variable will be replaced by a vector which is correlated to another independent variable of line 1. If, following this process, a system of $N - 1$ independent vectors cannot be constructed, the tangential hyperplane at equilibrium cannot be defined.

Equation of the hyperplane

A system of $N - 1$ independent vectors, $\vec{\mathbf{W}}_p$, has been determined. These vectors are director vectors of the hyperplane tangential to the hypersurfaces representing the Gibbs free energies of the Φ phases at equilibrium.

The vectorial equation of the hyperplane can be written as

$$\vec{\mathbf{V}} = {}^*\vec{S} + \sum_{p=1}^{N-1} \omega_p \vec{W}_p \tag{27}$$

where $\vec{\mathbf{V}}$ is a vector of the hyperplane, ${}^*\vec{S}$ represents the equilibrium state of the system, and $\{\omega_p\}_{p=1,\ldots,N-1}$ are parameters of R^{N-1}. This equation can be replaced by the following relations in N-dimensional space.

$$\left|\begin{array}{l} X_j = x_j + \sum_{p=1}^{p=N-1} \omega_p \alpha_{j,p} \quad \text{with } j = 1, \ldots, N-1 \\ Y = \Delta^*G + \sum_{p=1}^{p=N-1} \omega_p \alpha_{N,p} \end{array}\right. \tag{28}$$

Calculation of the partial Gibbs free energies of the components in the Φ-phase equilibrium

The ensemble of relation (28) is a parametric representation of the tangential hyperplane. The Cartesian equation of the hyperplane is

$$Y = \sum_{i=1}^{N} X_i Y_i \tag{29}$$

where $Y_i = \overline{\Delta G_i}$ represents the partial Gibbs free energy of component i referred to a given structure of component i. Y can be identified as the Gibbs free energy of the system when X_i is the whole composition of the system and as the Gibbs energy of phase f when X_i is the composition of phase f at equilibrium.

The quantities $Y_i = \overline{\Delta G_i}$ are calculated by using the intersection of the tangential hyperplane with the straight lines whose equations are

$$X_j = \delta_{i,j} \tag{30}$$

$\delta_{i,j}$ being the Krönecker symbol.

From substitution in relations (28), it follows

$$\left|\begin{array}{l} \delta_{i,j} = x_j + \sum_{p=1}^{p=N-1} \omega_{p,i} \alpha_{j,p} \quad \text{with } j = 1, \ldots N-1 \\ Y_i = \Delta^*G + \sum_{p=1}^{N-1} \omega_{p,i} \alpha_{N,p} \end{array}\right. \tag{31}$$

As the $N-1$ vectors $\vec{\mathbf{W}}_p$ are independent, the matrix $[\alpha_{j,p}]$ can be inversed and the inversed matrix is labelled $[\beta_{j,p}]$, with $j, p = 1, \ldots N-1$.

It can be written

$$\omega_{p,i} = \sum_{j=1}^{j=N-1} \beta_{j,p}(\delta_{i,j} - x_j) \tag{32}$$

and it follows that

$$Y_i = \Delta\overline{G}_i = \Delta^* G + \sum_{p=1}^{p=N-1} \sum_{j=1}^{j=N-1} \beta_{j,p}(\delta_{i,j} - x_j)\alpha_{N,p} \tag{33}$$

This formula defines in a more general manner the partial Gibbs free energy of a component i referred to a given structure for the phases in equilibrium in a multicomponent system. These quantities are needed to study the stability of the calculated equilibrium related to the other phases of the system which can precipitate.

STUDY OF THE STABILITY OF AN Φ-PHASE EQUILIBRIUM RELATED TO THE OTHER PHASES OF THE SYSTEM

Gibbs rule, which defines the variance or number of independent variables on which the state of a system depends, is given by

$$V = N + 2 - \phi \tag{34}$$

This indicates that the maximum number of phases which can coexist at the equilibrium is equal to N at a given temperature and pressure. Moreover, in a multicomponent system, the number of phases which can exist may be numerous, the possible phases being either the stable or metastable phases of the lower order limiting systems, or the specific multicomposed phases. The problem is therefore to search through all the possible phases for those which are stable at a given temperature and pressure. For a given whole composition, the more stable equilibrium corresponds to a minimum of the Gibbs free energy of the system.

The stability of an Φ-phase equilibrium related to the other phases of the system has been studied by defining a new quantity $d^{(f)}$ which characterizes the tendency towards precipitation of phases f related to this equilibrium.

Let us consider Φ phases in an N-component system. Equation (29) having been taken into consideration, the system will be stable relative to any phase f of the multicomponent system which is characterized by its Gibbs free energy $\Delta G^f(x_i^f)$ if the quantity $\delta^{(f)}$ defined by

$$\delta^{(f)} = \Delta G^f(x_i^f) - \sum_{i=1}^{N} x_i^f Y_i \tag{35}$$

is positive for each value of the independent variables of phase f, i.e.

$$d^{(f)} = \text{minimum}\left[\delta^{(f)}\right] > 0 \tag{36}$$

related to the independent variables of phase f.

CONCLUSION

The method which has been presented here yields at any temperature and for a given pressure the state of equilibrium of a multicomponent system, i.e. the compositions of the phases in equilibrium and the activity of each component. It allows analysis of the tendency for precipitation of the other phases of the system. This method has already been successfully applied to several quaternary or quinary systems, especially for the C–Cr–Fe–Ni [9] and C–Cr–Nb–Ni–W [10,11] systems. The principal advantage of this program is to yield execution times which are very rapid for most of the cases studied up to now.

One drawback of the program is the fact that for each phase in equilibrium, the Gibbs free energy must be known as an explicit function of the composition and temperature. For phases which have internal variables other than the composition, it is necessary to think of generalizing the automatic choice of these new variables or calling at each step of the minimization a subroutine which allows calculation of the Gibbs free energy for each phase. However, it seems that this drawback is not fundamental because the method of calculation never depends on the thermodynamic model which has been used for the description of each phase.

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