

A NUMERICAL CRITERION FOR EXISTENCE OF THE EQUILIBRIUM STATE IN AN OPEN CHEMICAL SYSTEM

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ABSTRACT — A numerical criterion for verifying attainability of equilibrium in an open chemical system is proposed. The criterion may also be used for testing compatibility of minerals (constant composition phases) in given phase assemblages.

Equilibrium computations, Open systems, Numerical criterion, Existence of equilibrium

Un critère numérique de l'existence d'un état d'équilibre pour un système chimique ouvert

RÉSUMÉ — On propose un critère numérique pour vérifier que l'équilibre d'un système chimique ouvert peut être atteint. Il est possible aussi d'utiliser ce critère pour tester la possibilité de la coexistence des minéraux (phases à composition constante) dans une association donnée.

Calcul d'équilibres, Systèmes ouverts, Critère numérique, Existence d'équilibres

INTRODUCTION

By an open chemical system we shall understand a system capable to exchange certain components (species) with the environment. For a thermodynamic description of an open system we use the « canonical » model proposed by KORZHINSKII (1965). The main points of the model are as follows :

- An exchange of substance between the system and the environment is possible by the transfer of some species through their dividing boundary. These species are known as perfectly mobile components.
- The mole quantities of perfectly mobile components in the environment are unlimited, while their chemical potentials are constant (not depending on the system composition).
- The equilibrium in an open system ensures the equality of chemical potentials of perfectly mobile components inside the system (for actual ones) and in the environment, except providing the usual equilibrium conditions inside the system.

D.S. Korzhinskii showed that such a system's thermodynamic potential is the function K , derived from the potential of the corresponding closed system by subtracting the parts of energy included with perfectly mobile components into all the phases of the system (Legendre transformation). The easiest way for determination of these contributions is to include the perfectly mobile components into the set of basic substances (in this case basic substances being not perfectly mobile are called inert components). By the way, a similar transformation of potentials is also applied to simplifications of algorithms for equilibrium computations in closed systems (e.g. SHVAROV, 1981 ; DE CAPITANI and BROWN, 1987).

So the equilibrium calculation for an open system of considered type comes to minimization of potential K for valid compositions set which is determined by the mass balance equations for inert components and the non-negativity conditions for the mole quantities of all the system components (species). If the temperature and pressure are independent parameters then the potential K is derived by the transformation of Gibbs free energy,

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and the equilibrium calculation for such an open system can be conducted with the help of the programs which are used for minimizing the free energy of closed systems (with the appropriate modification of mass balance equations and standard potentials of species).

DISCUSSION

The equilibrium state in a closed chemical system can always be found because the solution to the problem of calculating phase equilibrium in such system exists if the mass balance equations are compatible, i.e. if there is at least one composition satisfied with mass balance and electroneutrality equations (the last is needed if the system contains charged species). However, this condition is not sufficient for open chemical systems because infinite decreasing of the system potential may follow infinite absorption of one or more perfectly mobile components from the system environment. Let us consider, for example, an open isobaric-isothermal system involving an aqueous solution. If H_2O (gas) in the environment is assumed to be perfectly mobile and its partial pressure is taken more than the pressure of saturated vapor over pure water, then equilibrium in this system will never be reached and the quantity of water in the system will infinitely increase. It is clear that the last problem is not correct, but in a general case, when the number of perfectly mobile components is large and their stoichiometric compositions are complex, the question of the existence of the equilibrium state is not so obvious as here.

In nature, of course, the situation discussed above is impossible, because the idea of the environment as an unlimited reservoir of components with constant chemical potentials is a mathematical abstraction. Nevertheless this type of open system models is so convenient for theoretical and numerical analysis, that the system's ability to absorb the perfectly mobile components infinitely is not a sufficient reason for rejecting this concept. Indeed, if equilibrium in the open system is reached, no contradiction appears. However, if the calculations show that the volume of the open system increases infinitely, there must be defects in the system model, e.g. wrong choice of the mobile components, incorrect determination of their chemical potentials or errors in the stoichiometry, free energies and so on.

It would be wrong to think that the simplest method for calculating equilibria in open systems based on the Henry's law (link between the activity of a dissolved species and the given fugacity of the corresponding gas — perfectly mobile component !) is flawless. This method effectively uses the same canonical model of an open system, and the previous discussion can be also applied.

A similar problem appears in calculating equilibrium compositions of systems involving both solutions and constant composition (pure) phases. With respect to numerical procedures, the constant composition phases differ from perfectly mobile components only in the presence of non-negativity conditions for their mole quantities. At the same time these quantities can be found only after determining the equilibrium compositions of the solutions. As the computation of the equilibrium composition of a solution is an iterative process, the non-negativity restrictions for the quantities of the constant composition phases are not activated until iterations converge. Thus in fact the solutions are considered as open ones with respect to the phases of constant composition during the calculation. Therefore there can be such phase assemblages for which equilibrium compositions of solutions cannot be found by the reason discussed above. It was noted in the first paper devoted to equilibrium calculations in multicomponent systems with unknown phases (BOYNTON, 1960) that for some solid phase assemblages it was impossible to find an equilibrium composition of the aqueous solution. It is quite likely that the reason for this has already been shown above. It is possible, of course, to calculate the mole quantities of the constant composition phases and to verify their non-negativity at each iteration, but this approach is also problematic because one may delete a phase which has become temporarily negative, in any step of solving the non-linear equations.

CRITERION CONSTRUCTING

The above considerations show the necessity of a numerical criterion which allows to predict the presence of the equilibrium state in an open system before the start of the essential calculations. However as far as the author knows, this question was neither solved nor considered. So let the initial equilibrium problem be :

$$\text{minimize } K(n) \text{ subject to } \sum a_{ij}n_j = b_i, n_j \geq 0 \quad (i = 1 \dots m; j = 1 \dots k) \quad (.1)$$

where K is the Korzhinkii potential ; m is the number of inert components in the system ; k is the number of components ; a_{ij} are the stoichiometric coefficients expressing the compositions of components by the inert components ; b_i is the total mole quantities of the inert components ; n is the vector of the components (species) mole numbers. As the system is assumed to be open so set D of its valid compositions, determined by conditions (1), can be infinite. Mathematically it means that for every number M there exists a system composition n (vector) satisfied with conditions (1) such that $\sum n_j > M$. Physically it means that the system may absorb perfectly mobile components and increase its volume infinitely.

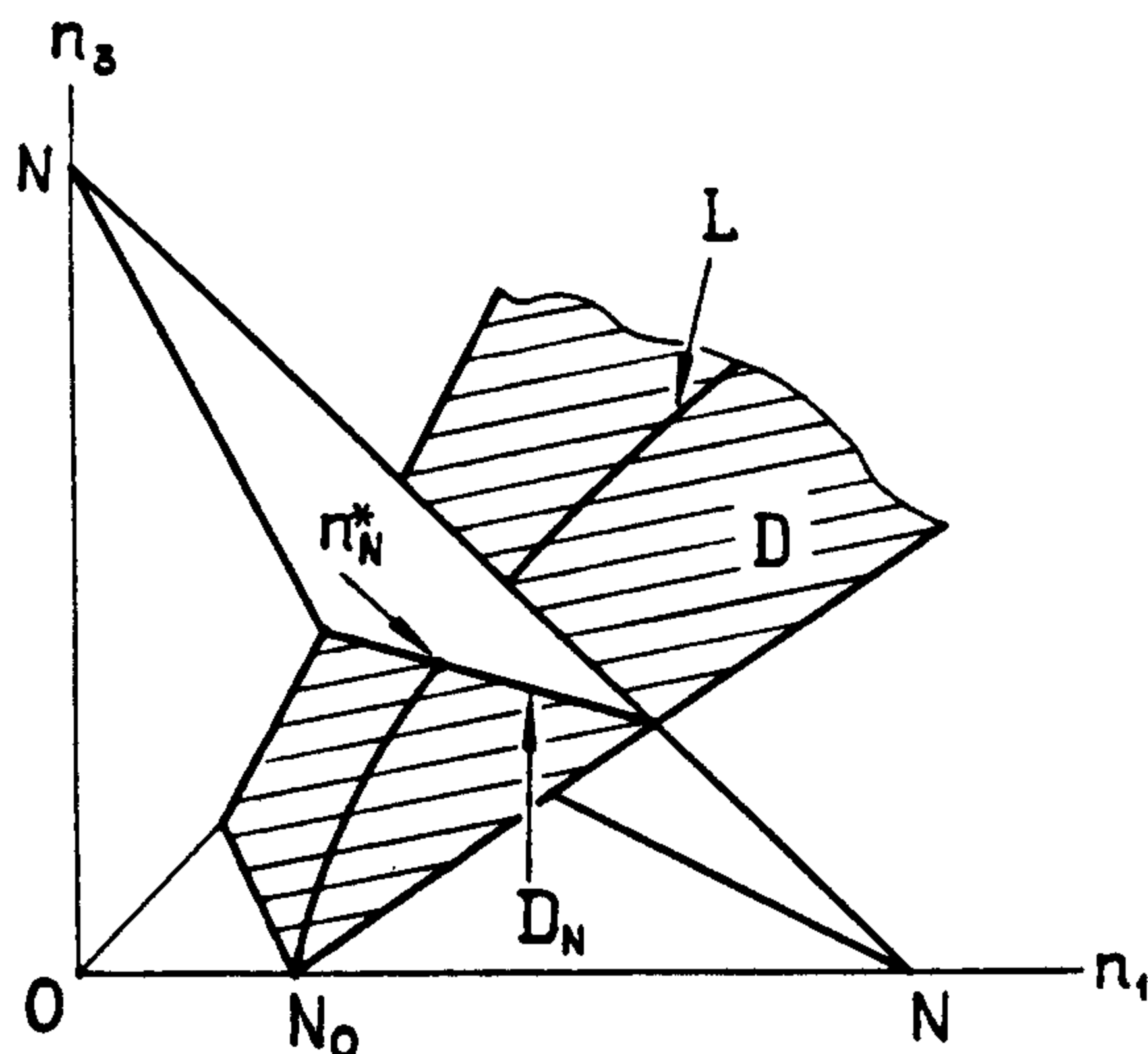
While constructing the criterion for existence of the solution to the problem (1) we shall use the convexity of potential K . This property follows from the fact that this potential is the sum of two convex functions — Gibbs free energy and a linear function*.

As the function K is continuous, it reaches its minimum value for every finite set, so if set D is restricted and not empty, the problem (1) always has a solution. If set D is unrestricted then K function minimum may not be reached due to continuous decreasing of the potential when vector n goes to infinity.

Let set D of the valid system compositions be unrestricted (fig. 1). Then the additional equation $\sum n_j = N$ (where N is a large number) cuts D set. The resulting section D_N is the subset of the system compositions, the mole sum of which is fixed and equal to N . It is obvious that there exists such number N_0 that D_N is not empty for all $N \geq N_0$. As all subsets D_N are restricted, every considered section contains a point n^*_N , which is the argument of the solution to the corresponding problem :

$$\text{minimize } K(n) \text{ subject to } \sum a_{ij}n_j = b_i, \sum n_j = N, n_j \geq 0 \quad (.2)$$

Let us name set of points n^*_N for all $N \geq N_0$ as L (see fig. 1). The line L consists of the points, in which the minimum of potential K is reached for every section, so this line L may be called as the « minimum potentials



— Figure 1 —

Illustration of the minimum potentials line constructing.

D : set of points satisfied with conditions of (1) problem (valid compositions set) ; D_N : D set section by restriction $\sum n_j = N$; n^*_N : point of minimum potential for D_N section ; L : minimum potentials line (consists of n^*_N points for all $N \geq N_0$).

Construction de la courbe des potentiels minimums.

D : multitude des points correspondants aux conditions (1) (multitude des compositions admissibles) ; D_N : coupe de la multitude D par la restriction $\sum n_j = N$; n^*_N : point correspondant au potentiel minimum pour la coupe D_N ; L : courbe des potentiels minimums (se compose des points n^*_N pour tous $N \geq N_0$).

* DE CAPITANI and BROWN (1987) mentioned that $\Delta_f G$ of a single non-ideal solution phase may be non-convex. However the Gibbs free energy of a system (even involving such phases) is always convex due to exsolving phenomenon. This is why the term « non-unique equilibria » used in that article is inexact.

line ». Let us define $K^*(N)$ as the minimum potential value corresponding to every N value. Then it may be shown that the convexity of the function $K^*(N)$ determined on the line L follows the convexity of potential K . The investigation of the system potential variance along the line L allows to obtain the conditions for existence of the solution to the problem (1). The reply to this question depends on potential K behaviour on the line L when sum of the mole numbers of the system components increases absolutely (or, that is the same, which is the limit of the function $K^*(N)$ when $N \rightarrow \infty$).

It follows from homogeneity of potential K that :

$$K(n) = \sum n_j \mu_j = N \cdot \sum \frac{n_j}{N} \mu_j = N \cdot \sum x_j \mu_j = N \cdot K(x)$$

where $\mu_j = \partial K / \partial n_j$ and $x_j = n_j / N$. Then dividing all equations (2) by N constant, the « specific » potential for n^*_N composition can be found as the solution to the minimization problem :

$$\text{minimize } K(x) \text{ subject to } \sum a_{ij} x_j = b_i / n, \sum x_j = 1, x_j \geq 0 \quad (.3)$$

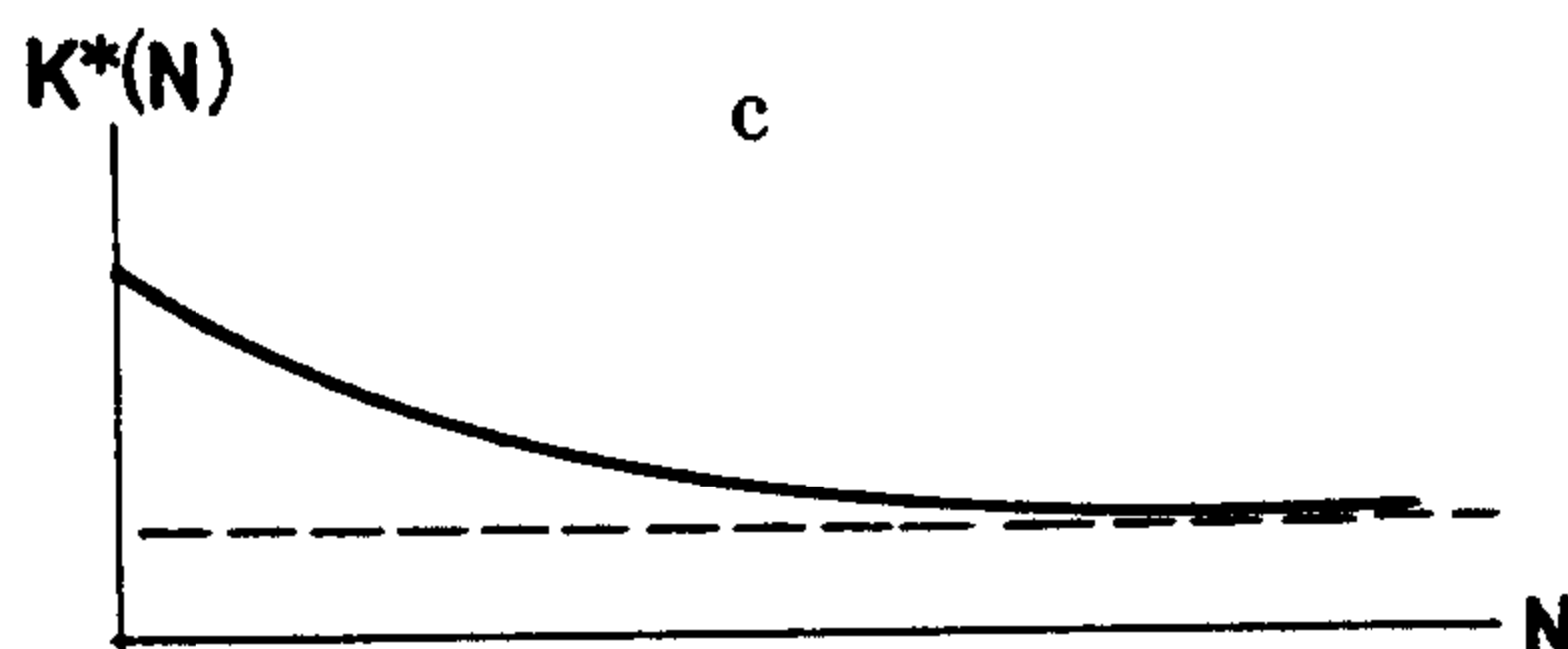
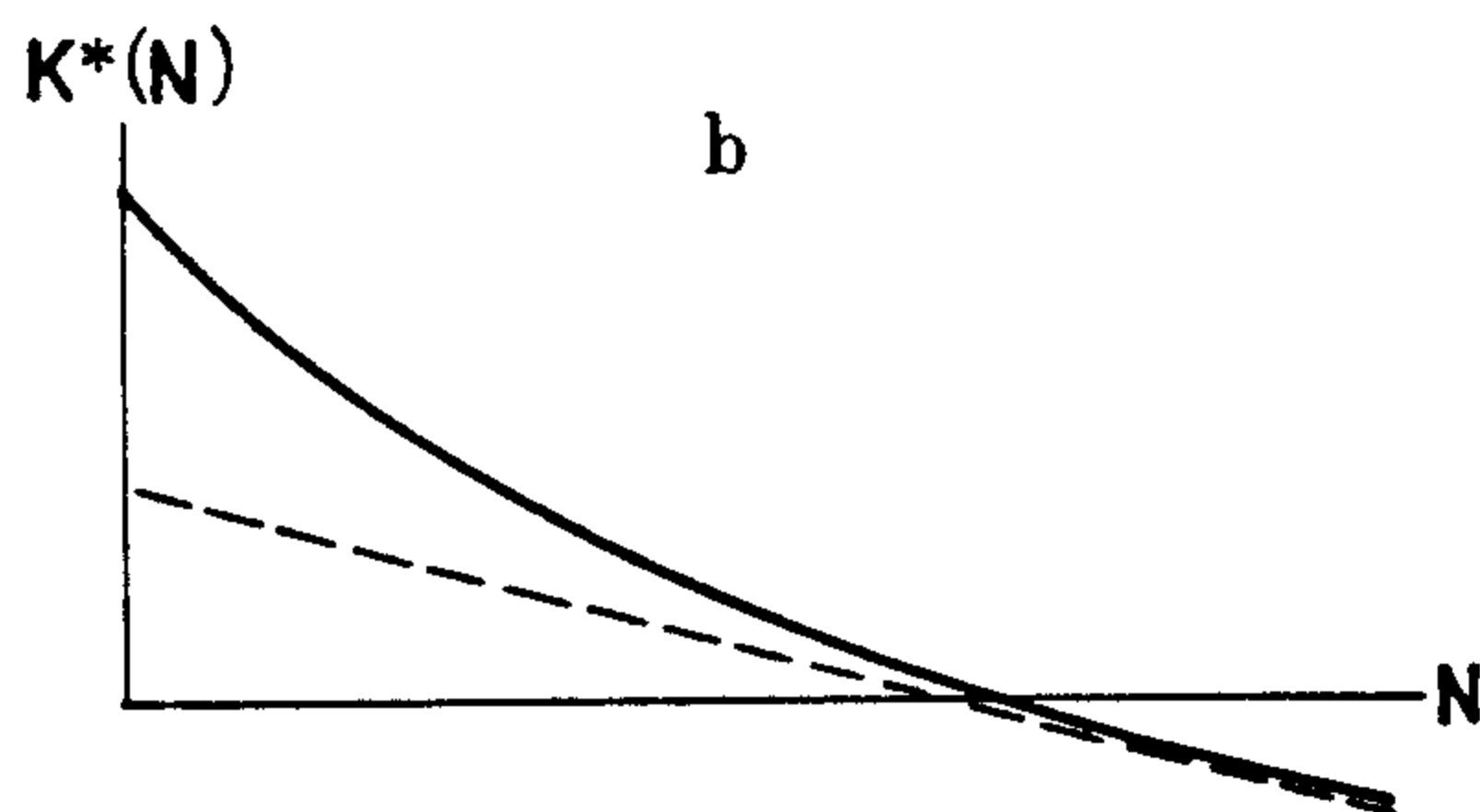
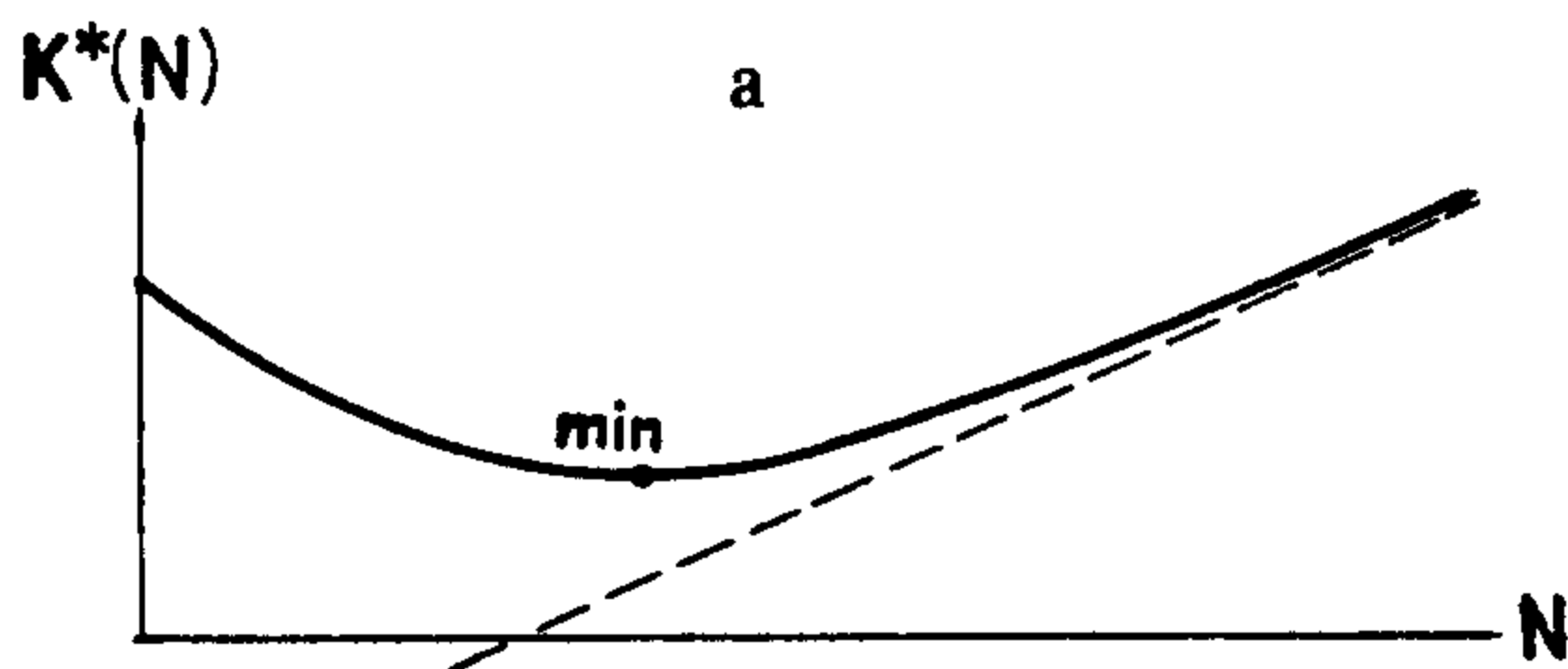
The $K(x^*_N)$ potential determined by this way is connected with $K^*(N)$ function in corresponding point n^*_N by the obvious relation :

$$K^*(N) = N \cdot K(x^*_N), \text{ or } K(x^*_N) = K^*(N) / N \quad (.4)$$

As the value of specific potential continuously depends on the right parts of restrictions (3), the limit of $K(x^*_N)$ when $N \rightarrow \infty$ is the solution to the following problem obtained from (3) by limit transition :

$$\text{minimize } K(x) \text{ subject to } \sum a_{ij} x_j = 0, \sum x_j = 1, x_j \geq 0 \quad (.5)$$

Let us design the solution to the problem (5) as K^* . This value is the limit of $K(x^*_N)$ function when $N \rightarrow \infty$, so it may be named as « specific potential in infinity ». If this value is positive then from (4) $K^*(N) \rightarrow +\infty$ when $N \rightarrow \infty$. As L is the minimum potentials line then, moving towards infinity along any other line in D area, the



— Figure 2 —

Possible variance of $K^*(N)$ function on the line L .

Minimum exists when $K^* > 0$ (a) and is absent when $K^* < 0$ (b) or $K^* = 0$ (c). K^* is the $K^*(N)$ asymptote gradient.

Variations possibles de la fonction $K^*(N)$ sur la courbe L .

Le minimum existe à la condition que K^* soit supérieur à 0 (a) ; il n'existe pas si l'on a $K^* < 0$ (b) ou $K^* = 0$ (c).

$K(n)$ value increases more rapidly. It follows from this that potential K reaches a minimum value in a finite area of D set (fig. 2a). If $K^* < 0$ then $K^*(N) \rightarrow -\infty$ with $N \rightarrow \infty$ as it follows from (4). In this case the system potential (on the line L) decreases infinitely, that means the absence of the initial problem solution (fig. 2b). When $K^* = 0$ the situation is the same, as may be shown by careful consideration of figure 2c.

CONCLUSIONS

The criterion for existence of the equilibrium composition of an open system may be formulated as follows. Consider the auxiliary problem (5) to verify the existence of the problem (1) solution. If the restrictions of the problem (5) are incompatible then the initial problem solution exists (incompatibility of the auxiliary problem restrictions means the limitation of D set). If the restrictions (5) are compatible, there exists the minimum value K^* which is the solution to this problem. Then the solution to the initial problem exists if $K^* > 0$ and not if $K^* \leq 0$.

The problem (5) does not principally differ from initial equilibrium problem, but is, as a rule, much easier because it contains fewer variables and restrictions. So it may be solved by the same algorithm used for solving the main problem. However the algorithm used must identify « unnecessary » variables (because of zeroes in the right parts of the mass balance equations), block them from consideration and also delete the resulting linear-dependent restrictions.

The above criterion is realized in Gibbs program for the wide use in the field of chemical equilibrium calculations. The criterion is used for forecasting the equilibrium existence in open chemical systems and for verifying compatibility of the constant composition phases in the current phase assemblage in open and closed systems. The verifying is executed when any new constant composition phase appears in the system. If the incompatibility of the new phase assemblage is spotted by means of the criterion, the solution to the auxiliary problem (5) allows to determine and block the phase which is the reason for such unfavourable situation for the computing. A more elaborate consideration of the realized algorithm is given by SHVAROV (1988).

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