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# Minimization of Gibbs Free Energy in Geochemical Systems by Convex Programming

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**Abstract**—Calculation of complete and constrained chemical equilibrium in multicomponent multiphase and heterogeneous systems is reduced to the problem of convex programming. A set-theory system of notation is introduced for physicochemical models. Analytical expressions are provided for the chemical potentials of dependent components in symmetric and asymmetric reference states. Necessary and sufficient conditions are formulated for complete and metastable equilibrium using the Kuhn–Tucker conditions of the problem of convex programming, when one- and/or two-sided constraints can be set on part or all sought-for values of mole quantities of dependent components. The *prime solution* values of the convex programming problem are sought-for values of the molar quantities of dependent components, while the *dual solution* values are sought-for values of the chemical potentials of independent components of the system related to stoichiometric units. The use of the chemical potentials of independent components allows solving the problem of the determination of the Gibbs free energy of formation of compounds from their known contents in the systems and, vice versa, the concentrations of dependent components in solution phases from the known Gibbs free energies of formation and chemical potentials of independent components in representative subsystems. Dual solutions related to a balance constraint on the electric charge of the system permit explicit calculation of the redox potential of the system,  $Eh$  ( $pe$ ), without considering the partial pressure of oxygen or hydrogen and pH.

## INTRODUCTION

In this paper, the problems of Gibbs free energy minimization are considered in a convex programming formulation. These problems were either not discussed in previous publications [1, 2] or not covered in detail. However, details are often helpful in understanding and appreciating the constructive basis of the idea of a presentation of chemical thermodynamics in the mathematical objects of convex programming. The need for a sophisticated description of the basic formulation of the Gibbs free energy minimization problem is also related to the fact that, as was ingeniously remarked by Zeleznik and Gordon [3], it serves as a "cart" that is used to "convey" the formulations of the problems of the minimization of other thermodynamic potentials, which model various conditions of natural system state differing in the set of independent factors of equilibrium [4]. Moreover, the assembled formulation of the Gibbs energy minimization problem can be modified and extended to new promising applications, in particular, the study of adsorption–desorption processes involving aqueous electrolyte solutions and minerals [5].

## NOTATION SYSTEM

We will use set-theory notation. The advantage of the set-theory symbolism is that it makes clear and distinct the relationships between the elements of the formalized image of thermodynamic models. It is very important that the detailed character of the notation does not overcomplicate the presentation of formulas and equations. The symbolic loading is transferred to the identification of indexes with respect to their affiliation to sets and subsets, which define the properties of mathematical objects. This results in a compact and precise presentation of the detailed physicochemical structure of multicomponent multiphase heterogeneous thermodynamic systems. The language of set-theory notation significantly facilitates the formal presentation of chemical equilibrium problems of various kinds and the construction of algorithms for their solution. The traditional notation could also have been used, as is still common in the majority of geochemical publications related to the problems of chemical equilibrium [e.g., 6–11], but in that case, the tribute to scientific conservatism would result in an unjustified encumbering of mathematical expressions.

The basis of the formalized presentation of formulas and equations of chemical equilibrium in the mathematical programming language was borrowed from White *et al.* [12]. The experience of a generalized specification of multicomponent and multiphase systems by Brinkley [13, 14] and Prigogine and Defye [15] was also used.

The most important feature of the notation by White *et al.* [12] is the separation of prescribed and determined variables. The sought-for parameters are denoted by the last letters of the Latin alphabet. Other letters of the Latin alphabet and letters of the Greek alphabet are used for the initial parameters of a problem, constants, coefficients, and indexes. Symbols will be introduced and defined in the course of description. The general principle of the construction of a system of set-theory presentation of physicochemical models is discussed in Karpov's monograph [1].

### INITIAL SYSTEM OF EQUALITIES AND INEQUALITIES IN THE PROBLEM OF GIBBS FREE ENERGY MINIMIZATION

Let us consider the problem of Gibbs free energy minimization with the input empirical thermodynamic characteristics of individual substances that may have both symmetric (mineral solid solutions, melts, gas mixtures, nonelectrolyte solutions) and asymmetric reference systems (aqueous electrolyte solution). The necessary information on symmetric and asymmetric reference systems is given by Prigogine and Defay [15]. It is important to keep in mind that in using mathematical programming as a mathematical tool for the solution of chemical equilibrium problems, it is necessary to reduce the empirical thermodynamic characteristics of individual substances with different reference systems to a single reference state [1].

In the following discussion, Gibbs' explicit discrimination of components into independent and dependent is strictly followed. The term *component* will be used in place of the expression *dependent component*. However, an independent component will be always referred to as *independent component*. The definitions of dependent and independent components in the context of chemical equilibrium problems and rules for their selection are discussed in many publications (e.g., [1, 3, 10, 16, 17, and other]). We remind only that stoichiometrically identical components in different phases are thermodynamically different components.

Let us introduce the following designations:  $L$  is the set of dependent component indexes; hereafter,  $n(Z)$  is the number of elements of the finite set  $Z$ ;  $\Phi = \{1, 2, \dots, n(\Phi)\}$  is the set of indexes of the phases of a multisystem;  $l_\alpha$  is the set of dependent component indexes in phase  $\alpha$ ;  $\bigcup_{\alpha \in \Phi} l_\alpha = L$ ;  $S_w$  is the set of indexes corresponding to a phase, for which standard states of components are selected in an asymmetric reference

system (aqueous electrolyte solution);  $S_w^0 = S_w \setminus j_w$ ;  $j_w$  is the index referring to the solvent (water);  $S_g$  is the set of indexes of the components of a gas mixture, liquid nonelectrolyte solutions, solid solutions, and melts; and  $N$  is the set of independent component indexes.

We consider a heterogeneous multisystem of  $n(L)$  independent components, which may include simultaneously aqueous electrolyte solution with dissolved hydrocarbons, condensed single-component phases and solid solutions, gas mixture, and nonelectrolyte solutions including liquid hydrocarbons and melts.

The reduced isobaric-isothermal potential of the system is written as

$$G(x) = \sum_{j \in L} c_j x_j + \sum_{j \in l_\alpha} x_j \ln \frac{x_j}{X_\alpha} - \sum_{j \in S_w^0} x_j \ln \frac{x_j}{X_\alpha}, \quad (1)$$

$$\alpha \in \Phi.$$

In Eq. 1,  $G(x) = G/RT$ , where  $G$  is the Gibbs free energy of the system (isobaric-isothermal potential);  $T$  is the temperature in K;  $R$  is the universal gas constant;  $x_j$  is the number of moles of dependent component  $j$ ; and  $X_\alpha = \sum_{j \in l_\alpha} x_j$  is the number of moles of dependent components in phase  $\alpha$ .

$$c_j = \begin{cases} \frac{g_j}{RT} + \ln \gamma_j, & j \in L \setminus (S_g \cap S_w^0) \\ \frac{g_j}{RT} + \ln \gamma_j + \ln P, & j \in S_g \\ \frac{g_j}{RT} + \ln \gamma_j + \ln 55.51 & (j \in S_w^0), \end{cases} \quad (2)$$

where  $g_j$  are empirical functions substituting for the unknown true values of the Gibbs free energy of components of the multisystem in a selected standard state and coordinate system normalized to a common level;  $\gamma_j$  is the coefficient of activity or fugacity of component  $j$  (in agreement with the accepted reference system for  $g_j$ ); and  $P$  is the pressure.

Hereafter, in addition to the index presentation of formulas and equations, we will use, when necessary, the equivalent concise matrix-vector forms, which can provide clearness, readability, simplicity, and space saving.

The system of mass balance equations, which includes, when necessary, the electric neutrality equation, is specified as

$$Ax = b, \quad (3)$$

where  $b$  is the  $n(N)$ -dimensional column vector, whose element  $b_i$  is the total number of moles of independent component  $i$  in the system;  $A$  is the  $n(N) \times n(L)$  matrix, whose element  $a_{ij}$  is the number of moles of independent component  $i$  in one mole of dependent component

$j$ ; and  $x$  is the  $n(L)$ -dimensional column vector, whose element  $x_j$  is the molar quantity of the dependent component with index  $j$ .

From physical considerations, the molar quantities of components cannot be negative. Thus,

$$x \geq 0. \quad (4)$$

Condition 4 excludes the appearance of the vector  $x$  with all elements simultaneously equal to zero; i.e., always,  $n(L) > 0$ .

Frequently, there is a need to introduce additional constraints into the formulation of the problem of Gibbs free energy minimization defining possible limits of the changes in the molar quantities of dependent components and phases of the system. Such constraints allow more sophisticated accounting for empirical information on the specific characteristics of processes occurring in the system. The introduction of additional constraints allows the formulation and solution of physicochemical problems with predetermined nonequilibrium states, which is of prime importance in the chemical thermodynamics of natural systems. In the physicochemical sense, additional constraints may be represented by kinetic limitations, retarded and metastable states, catalytic selectivity, retention of particular components and phases from decomposition, undersaturation and oversaturation of solutions, fixation of pH, managing of relationships between liquid and gas phases, etc. Because of this, in the general case, the trivial condition of nonnegativity of the molar quantities of dependent components Eq. (4) is replaced by the following system of inequalities:

$$\begin{aligned} x_j &\geq 0, & j \in D_0; \\ x_j &\leq x_j, & j \in D_1; \\ x_j &\leq \bar{x}_j, & j \in D_2; \\ x_j &\leq x_j \leq \bar{x}_j, & j \in D_3, \end{aligned} \quad (5)$$

where  $x_j$  and  $\bar{x}_j$  are the prescribed upper and lower bounds of the molar quantities of dependent component  $j$ .

Obviously,

$$x_j > 0, j \in D_1 \cup D_3, \quad \bar{x}_j > 0, \quad j \in D_2 \cup D_3$$

and, always,

$$L = D_0 \cup D_1 \cup D_2 \cup D_3.$$

The set  $D_0$  includes indexes of those dependent components, whose molar quantities are constrained only by the nonnegativity condition, i.e.,  $D_0 = L \setminus (D_1 \cup D_2 \cup D_3)$ . If  $D_1 = \emptyset$ ,  $D_2 = \emptyset$ , and  $D_3 = \emptyset$ , inequalities (5) are reduced to the simple condition of nonnegativity of the molar quantities of dependent components, i.e., condition (4).

In the following discussion, we distinguish the constraints of Eq. (3) from those of the  $x \in R$  form, referring to them as functional and direct constraints, respectively.

#### NECESSARY AND SUFFICIENT CONDITIONS FOR THE MINIMUM OF GIBBS FREE ENERGY OVER A SET OF BALANCE CONSTRAINTS AS A KUHN-TUCKER CONDITION OF THE CONVEX PROGRAMMING PROBLEM

Under isobaric and isothermal conditions, the equilibrium composition of the system (vector  $\hat{x}_j$ ) is determined by the minimization of the convex scalar continuous function of Gibbs free energy over a set of constraints defined by mass balance Eq. (3) and conditions (5).

Problem  $G_0$ :

$$\begin{aligned} &\text{minimize } G(x) \\ &\text{under constrains } Ax = b, \quad x \in R, \end{aligned} \quad (6)$$

where

$$R = \{x | x_j \geq 0, j \in D_0; x_j \leq x_j, j \in D_1; x_j \leq \bar{x}_j, j \in D_2; x_j \leq x_j \leq \bar{x}_j, j \in D_3\}. \quad (7)$$

Denoting the partial derivatives of the function  $G(x)$  with respect to  $x_j$  by  $v_j$ , we have

$$v_j = \frac{\partial G(x)}{\partial x_j} = \begin{cases} c_j + \ln(x_j/X_\alpha) & j \in l_\alpha^S, \quad \alpha \in \Phi \\ c_j + \ln(x_j/X_w) - \ln(x_{j_w}/X_w) - x_{j_w}/X_w + 1, & j \in l_w^{OS} \\ c_{j_w} + \ln(x_{j_w}/X_w) - X_w/x_{j_w} - x_{j_w}/X_w + 2, & j_w \in l_{j_w}^S. \end{cases} \quad (8)$$

$$(9)$$

$$(10)$$

In Eqs. (8)–(10),

$$l_\alpha^S = \{j | j \in l_\alpha \cap (L_S \setminus (S_w \cap L_S))\},$$

$$\alpha \in \Phi; \quad l_w^{OS} = \{j | j \in S_w^O \cap L_S\};$$

$$l_{j_w}^S = \{j_w | j_w \in L_S\}.$$

The set  $L_S$  is defined below in the section "L<sub>S</sub> Set"  
 $X_w = \sum_j x_j, j \in l_w^S$ , and  $l_w^S = \{j | j \in S_w \cap L_S\}$ . The par-

tial derivatives  $v_j, j \in L_S$  are the reduced chemical potentials of the dependent components of the system.

Let us introduce special designations for the latter terms of partial derivatives in Eqs. (9) and (10):

$$t_j = -x_{j_w}/X_w + 1, \quad j \in S_w^0 \cap L_S, \quad (11)$$

$$t_{j_w} = -X_w/x_{j_w} - x_{j_w}/X_w + 2, \quad j_w \in j \in l_{j_w}^S. \quad (12)$$

Since

$$\sum_j x_j t_j + x_{j_w} t_{j_w} = 0, \quad j \in l_w^{OS},$$

it is evident that

$$\sum_{j \in L_S} v_j x_j = G(x). \quad (13)$$

There are some remarks to be made here. Simple numeric estimates suggest that in low-concentration aqueous electrolyte solutions, the values  $t_j, j \in l_w^{OS}$  and  $t_{j_w}$  introduce a negligible contribution into the values of the chemical potentials of dependent components,  $v_j, j \in l_w^S$ . This contribution is significant in high-concentration solutions, and the rejection of the rightmost terms in Eqs. (9) and (10) can result in a failure of minimization algorithms. However, even if aqueous solution in the equilibrium model is low-concentration, the rejection of  $t_j, j \in l_w^{OS}$  and  $t_{j_w}$  is inadmissible. In fact, the initial approximation at the entry into the minimization algorithm includes all dependent components of all phases of the system in amounts no lower than some threshold values [2]. Such minimum values are assigned to those dependent components that did not appear in the nonzero solutions at the first step of the selection of the initial admissible approximation, which is carried out by the simplex method of linear programming [2]. However, the number of such nonzero solutions cannot be higher than the number of independent components plus additional lower constraints on the dependent components whose indexes belong to the sets  $D_1$  and  $D_2$  (Eq. (5)). Because of this, the initial admissible approximation can be selected in such a way that the nonzero solution will include some dependent components of aqueous solution, while solvent (water) will appear in the minimization algorithm with the minimum threshold content. Such a situation is rather common. In this case, the last terms  $t_j, j \in l_w^{OS}$  and  $t_{j_w}$  remove the disproportion in the relationship solvent-dissolved substances already at first iterations and "pushes out" dissolved water from the threshold value to a level corresponding to the common relationship of  $x_j, j \in l_w^{OS}$  and  $x_{j_w}, j_w \in l_{j_w}^S$  in aqueous solution, in

which, except for a concentrated solution,  $x_{j_w} \gg x_j, j \in l_w^{OS}$ . In any case, in all formulas and equations, partial derivatives must be taken in the complete analytical form of Eqs. (9) and (10). This remark concerns the formulas of the calculation of  $x_j, j \in l_w^S$  and  $g_j, j \in l_w^{OS}$  from dual solutions, which will be presented below Eqs. (51)–(53).

Under assumption of the convexity of the scalar continuous function  $G(x)$  and convexity of the close bounded set

$$M = \{x / Ax = b, x \in R\} \quad (14)$$

vector  $\hat{x}$  will be a solution to the problem  $G_0$  (Eq. (6)) if and only if there are such multipliers  $u_i, i \in N$  and  $p_j, j \in D_3$  that the following equations are realized:

$$\left. \begin{aligned} v_j - \sum_i a_{ij} u_i &\geq 0, \\ \left( v_j - \sum_i a_{ij} u_i \right) \hat{x}_j &= 0, \\ \hat{x}_j &\geq 0 \end{aligned} \right\}, \quad j = D_0 \cap L_S$$

$$\left. \begin{aligned} v_j - \sum_i a_{ij} u_i &\geq 0, \\ \left( v_j - \sum_i a_{ij} u_i \right) (\bar{x}_j - \hat{x}_j) &= 0, \end{aligned} \right\}, \quad j \in D_1 \cap L_S$$

$$\left. \begin{aligned} v_j - \sum_i a_{ij} u_i &\leq 0, \\ \left( v_j - \sum_i a_{ij} u_i \right) (\hat{x}_j - \bar{x}_j) &= 0, \end{aligned} \right\}, \quad j = D_2 \cap L_S$$

$$\left. \begin{aligned} v_j - \sum_i a_{ij} u_i + p_j &\geq 0, \\ \left( v_j - \sum_i a_{ij} u_i + p_j \right) (\bar{x}_j - \hat{x}_j) &= 0, \\ p_j &\geq 0, \\ p_j (\hat{x}_j - \bar{x}_j) &= 0, \end{aligned} \right\}, \quad j \in D_3 \cap L_S$$

$$\sum_i a_{ij} \hat{x}_j = b_i, \quad i \in N, \quad j \in L,$$

where  $u_i, i \in N$  are the dual solutions to the problem  $G_0$  interpreted as *reduced chemical potentials of independent components*;  $p_j, j \in D_3$  are the dual solutions to the problem  $G_0$  related to dependent components, whose molar quantities are constrained from both sides. The cap above  $\hat{x}_j, j \in L$  denotes an optimum solution.

Equalities and inequalities (15) are the necessary and sufficient Kuhn–Tucker conditions [18–20] of the convex programming problem, when all or part of the elements of  $x$  are constrained from one and/or two sides. They define the conditions of chemical equilibrium in the system with the solution vector  $\hat{x}$ . In an explicit analytical form with application to the problem of heterogeneous polyphase equilibrium without one-sided and two-sided constraints on  $x$ , they were first obtained by Karpov [1].

If  $D_1 = \emptyset, D_2 = \emptyset$ , and  $D_3 = \emptyset$ , constraints (5) are replaced by inequality (4) and the Kuhn–Tucker solution is written in the form

$$\begin{aligned} v - A^T u &\geq 0, \\ A\hat{x} &= b, \\ \hat{x} &\geq 0, \quad \hat{x}^T(v - A^T u) = 0. \end{aligned} \quad (16)$$

Here,  $v$  is the  $n(L)$ -dimensional column vector, whose element  $v_j$  is the reduced chemical potential of the dependent component with index  $j$ ;  $A^T$  is the transpose of  $A$ ;  $u$  is the  $n(N)$ -dimensional column vector, whose element  $u_i$  is the reduced chemical potential of the independent component with index  $i$ ; and  $\hat{x}^T$  is the transpose of  $\hat{x}$ . The upper cup denotes an optimum solution.

### $L_S$ SET

In program realizations, the following condition is checked:  $x \geq \varepsilon$ , where  $\varepsilon > 0$  is a sufficiently low value.

The Kuhn–Tucker conditions are considered over the set of indexes

$$\begin{aligned} L_S &= \{j/j \in l_\alpha, \alpha \in \Phi, n(l_\alpha) = 0 \\ Vn(l_\alpha) &= 1 \quad \forall n(l_\alpha) > 0 \quad \wedge x_j > \varepsilon\}. \end{aligned} \quad (17)$$

This point is rather important and must be additionally clarified [1, 21]. The set  $L_S$  is included into  $L$  and can be equal to it,  $L_S = L$ ; i.e., mathematically,  $L_S \subset L$ . By introducing  $L_S$ , we do not admit the appearance of partial derivatives  $v_j, j \in L_S$  equal to  $-\infty$ . The algorithms of  $G(x)$  optimization under  $L_S$  are organized in such a way that in the course of the computation procedure, the program automatically blocks the situation when  $x_j/X_\alpha = 0$ , and, consequently,  $\ln(x_j/X_\alpha) = -\infty$ . If, during computations,  $x_j$  becomes less than  $\varepsilon$  in phase  $\alpha$ , which is a solution phase with  $X_\alpha > \varepsilon$ , such a solution component is eliminated from the input list of dependent components potentially possible at equilibrium.

Therefore, at the beginning of computations,  $n(L_S) = n(L)$ , but as components with  $x_j < \varepsilon$  are omitted, the equality changes into the inequality  $n(L_S) < n(L)$ . In the program realizations,  $\varepsilon = 10^{-18}$  can be accepted. Sometimes, it is necessary to determine the apparent concentration of the omitted component with  $x_j < \varepsilon, j \in D_0 \cup D_2$ , for instance, in order to determine the oxygen partial pressure in a gas mixture, where it is practically absent. In such cases, the restoration of eliminated  $x_j < \varepsilon$  is carried out by the formula derived from the Kuhn–Tucker conditions (Eq. (16) and Eqs. (8) and (9)):

$$x_j = X_\alpha \exp\left(-\bar{c}_j + \sum_j a_{ij} u_i\right), \quad (18)$$

$$j \in (S_w^0 \cup S_g), \quad \alpha \in \Phi,$$

where

$$\bar{c}_j = \begin{cases} c_j, & j \in S_g, \\ c_j - \ln(x_{j_w}/X_w) - x_{j_w}/X_w + 1, & j \in S_w^0. \end{cases} \quad (19)$$

As is seen from Eqs. (18) and (19), the determination of the eliminated  $x_j < \varepsilon, j \in D_0 \cup D_2$  is performed for solution phases. In aqueous solution,  $x_j < \varepsilon, j \in S_w^0$  is restored for dissolved components.

### PHASE CRITERION $f_\alpha, \alpha \in \Phi$

The separation of the constraints of the convex programming problem into *functional* (3) and *direct* (4) and (5) is conventional. For example, in the problem  $G_0$ , direct inequality constraints (5) can be transformed into functional equality constraints using additional nonnegative variables:

$$x_j^- \geq 0, \quad j \in D_1; \quad x_j^+ \geq 0, \quad j \in D_2; \quad (20)$$

$$x_k^- \geq 0, \quad k \in D_3^-; \quad x_l^+ \geq 0, \quad l \in D_3^+. \quad (21)$$

In (21),

$$n(D_3^-) = n(D_3^+) = n(D_3).$$

Thus, the additional single- and two-sided constraints can be written as the equalities

$$x_j - x_j^- = x_j, \quad j \in D_1; \quad (22)$$

$$x_j + x_j^+ = \bar{x}_j, \quad j \in D_2; \quad (23)$$

$$x_j - x_k^- = x_k, \quad j \in D_3, \quad k \in D_3^-; \quad (24)$$

$$x_j + x_l^+ = \bar{x}_l, \quad j \in D_3, \quad l \in D_3^+. \quad (25)$$

A particular presentation of the convex programming problem depends on the aims of the study and specific features of numeric algorithms. The conversion of direct constraints into functional ones allows a more

detailed investigation of the properties of the chemical equilibrium problem. In particular, in our case, the specification of the problem  $G_0$  with constraints given by Eqs. (22)–(25) allows the unification of the presentation of Kuhn–Tucker phase criteria in the canonical form independent of the presence of one-sided and two-sided constraints in the formulation.

Adding Eqs. (22)–(25) to the system of Eq. (3), we obtain a system of balance equality constraints. They take into account in a functional form one-sided and two-sided bounds on the molar quantities of dependent components. Applying the Kuhn–Tucker theorem to the minimization problem  $G(x)$  on the set of functional equality constraints (Eqs. (3), (22)–(25)) at  $x_j \geq 0, j \in D_0$ , we obtain the following relationships between the direct and dual solutions characterizing the conditions of complementary slackness [18, 20] of the convex programming problem.<sup>1</sup>

If  $x_j > 0$ ,

$$v_j - \sum_i a_{ji} u_i - z_j = 0, \quad i = N, \quad j \in L_S. \quad (26)$$

If  $x_j = 0$ ,

$$v_j - \sum_i a_{ji} u_i - z_j \geq 0, \quad i = N, \quad j \in L_S. \quad (27)$$

In Eqs. (26) and (27),  $z_j, j \in L_S$  are the dual variables related to the functional constraints given by Eqs. (22)–(25). Their values depend on the structure of  $\hat{x}_j, j \in L$  relative to upper and lower constraints:

$$z_j = 0, \quad j \in D_0 \cap L_S; \quad (28)$$

$$\left. \begin{aligned} z_j &= 0, \text{ if } \hat{x}_j \geq \bar{x}_j, \quad x_j^- > 0, \\ z_j &\geq 0, \text{ if } \hat{x}_j = \bar{x}_j, \quad x_j^- = 0, \quad j \in D_1 \cap L_S; \end{aligned} \right\} \quad (29)$$

$$\left. \begin{aligned} z_j &= 0, \text{ if } \hat{x}_j < \underline{x}_j, \quad x_j^+ > 0, \\ z_j &\leq 0, \text{ if } \hat{x}_j = \underline{x}_j, \quad x_j^+ = 0, \quad j \in D_2 \cap L_S; \end{aligned} \right\} \quad (30)$$

$$\left. \begin{aligned} z_j &= \bar{z}_k + z_l^+, \quad j \in D_3, \quad k \in D_3^-, \quad j \in D_3^+, \\ z_j &= 0, \text{ if } \underline{x}_j < \hat{x}_j < \bar{x}_j, \quad x_j^+ > 0, \quad j \in D_3^+, \\ z_j &\geq 0, \text{ if } \hat{x}_j = \underline{x}_j, \quad j \in D_3, \\ z_j &\leq 0, \text{ if } \hat{x}_j = \bar{x}_j, \quad j \in D_3. \end{aligned} \right\} \quad (31)$$

The presentation of direct constraints (5) in the functional form of Eqs. (22)–(25) is inappropriate in a working minimization algorithm. Such an operation could significantly increase the dimensionality of the balance equation of Eq. (3) type. Therefore, the algorithm of the interior point method [2] takes into account

all additional one- and two-sided constraints introducing a single additional balance equation, which adds only one dimension to the system of balance equations. The values of  $z_j, j \in L_S$  are calculated from Eqs. (26)–(27) in the course of the iterative procedure.

Equalities and inequalities (15) refer to every dependent component of the system. However, in minimization algorithms, it is desirable to have a mathematically strict criterion for the presence or absence of a phase from a given list in the equilibrium solution. The initial array of potentially possible equilibrium phases can exceed significantly the number of independent components plus the number of additional balance constraints imposed upon the minimum molar quantities of one, part, or all dependent components in individual phases. The set of indexes  $j$ , which will be used in the discussion further,

$$l_\alpha^S = \{j/j \in l_\alpha \cap (L_S \setminus (S_w \cap L_S))\}, \quad \alpha \in \Phi$$

was already defined (see Eq. (8)).

Let us designate

$$w_j = c_j + \ln(x_j/X_\alpha) - \sum_i a_{ji} u_i - z_j, \quad (32)$$

$$i \in N, \quad j \in l_w^S, \quad \alpha \in \Phi,$$

where the set  $l_w^S$  was defined above, Eqs. (9) and (10);

$$w_j = c_j + \ln(x_j/X_w) - \ln(x_{j_w}/X_w) + t_j - \sum_i a_{ji} u_i - z_j, \quad (33)$$

$$i \in N, \quad j \in S_w^0 \cap L_S;$$

$$w_j = c_j + \ln(x_{j_w}/X_w) + t_{j_w} - \sum_i a_{ji} u_i - z_{j_w}, \quad (34)$$

$$j = j_w.$$

Equations (32)–(34) are expanded expressions of the left-hand side of the first inequality in the Kuhn–Tucker conditions (16) rewritten in such a way that direct inequality constraints (5) are transformed into functional equality constraints, Eqs. (22)–(25).

According to the conditions of supplementary slackness in Eq. (16),

$$w_j x_j = 0, \quad j \in L, \quad (35)$$

From this expression, it follows that, if

$$x_j > 0, \quad \text{then } w_j = 0, \quad j \in L_S, \quad (36)$$

and, if

$$x_j = 0, \quad \text{then } w_j > 0, \quad j \in L_S. \quad (37)$$

It should be noted that the product in Eq. (35) is defined also in the cases when  $x_j = 0$  and  $X_\alpha > 0, j \in l_\alpha$ .

<sup>1</sup> Intermediate calculations are omitted.

$\alpha \in \Phi$ , which is demonstrated by the differentiation of Eq. (35) with respect to  $x_j, j \in L$ .

Let us designate

$$s_j = w_j - \ln \frac{x_j}{X_\alpha}, \quad j \in l_\alpha \cap L_S, \quad \alpha \in \Phi \quad (38)$$

and transform  $w_j, j \in l_\alpha \cap L_S, \alpha \in \Phi$  changing the sign of  $w_j$  and applying the exponentiating operation:

$$f_j = \exp(-s_j) - x_j/X_\alpha \leq 0, \quad j \in l_\alpha, \quad \alpha \in \Phi, \quad (39)$$

$$f_j = \exp(-s_j) - x_j/X_w \leq 0, \quad j \in S_w \cap L_S, \quad \alpha = w, \quad (40)$$

$$f_{j_w} = \exp(-s_{j_w}) - x_{j_w}/X_w \leq 0, \quad j = j_w, \quad \alpha = w. \quad (41)$$

The summation of Eqs. (39)–(41) over  $j \in l_\alpha \cap L_S, \alpha \in \Phi$  yields

$$\sum_j f_j = \sum_j [\exp(-s_j)] - 1 \leq 0, \quad j = l_\alpha^S, \quad \alpha \in \Phi, \quad (42)$$

$$\sum_j f_j = \sum_j [\exp(-s_j)] + \exp(-s_{j_w}) - 1 \leq 0, \quad j \in S_w^0 \cap L_S, \quad j = l_{j_w}^S, \quad (43)$$

Let us designate

$$f_\alpha = \sum_j f_j, \quad j \in l_\alpha \cap L_S, \quad \alpha \in \Phi.$$

In Eqs. (42) and (43), all terms are of the same sign. Thus, in the summation operation, the situation is excluded when  $x_k = 0$  and  $f_k < 0$  but  $x_j > 0$  and  $f_j = 0, j \neq k$  and  $j, k \in l_\alpha, \alpha \in \Phi$ . This follows from the definition of the set  $L_S$ . Thus, the phase criterion

$$f_\alpha < 0, \quad X_\alpha = 0 \quad \text{and} \quad f_\alpha = 0, \quad X_\alpha \geq 0, \quad \alpha \in \Phi \quad (44)$$

can be used as a condition equivalent to the conditions of supplementary slackness relative to dependent components, Eqs. (35)–(37).

Equilibrium at  $f_\alpha = 0$  and  $X_\alpha = 0$  is permitted by Eq. (44) but is theoretically unlikely. However, such a situation is rather common in the practice of modeling. In any case, such a possibility must be kept in mind. The following is the simplest example. Let an isobaric and isothermal equilibrium state be calculated in a water–mineral system. The determined equilibrium state includes aqueous solution and two minerals. Let us take the vector  $b$  of the bulk chemical composition of the aqueous solution and calculate again the equilib-

rium composition of solution using  $b$  and the same isobaric–isothermal conditions. If in the second case, the two minerals occurring in the first solution were not rejected from the list of potentially possible equilibrium phases, then in the second solution, the conditions

$$f_\alpha = 0 \quad \text{and} \quad X_\alpha = 0$$

must be theoretically met for these two minerals.

That is, the phase criterion must indicate the presence of phases in the equilibrium state, but, because of the exhaustion of balance relations in Eq. (3), the two minerals cannot precipitate from liquid. The precipitation is impossible without a violation of the mass balance and an increase in the free energy of the system. But this is a theoretical situation. In practice, both the mass balance Eq. (3) and the criterion of phase presence or absence in the algorithms of numeric minimization are always constructed with a prescribed finite threshold accuracy. Such threshold values are set within  $10^{-10}$ – $10^{-6}$  mol for the mass balance ( $\epsilon_2$ ) and  $10^{-12}$ – $10^{-6}$  mol for the presence of a phase ( $DS$  criterion in the program Selector-S [22]). Because of this, in spite of the fact that the accuracy of the solution is very high with respect to the mass balance, it could be lower than the accuracy with respect to  $DS$ , and, consequently, the theoretically expected relationships  $f_\alpha = 0$  and  $X_\alpha = 0$  are changed in the real solution by

$$|f_\alpha| < \epsilon_3, \quad 0 < X_\alpha \leq DS,$$

where

$$10^{-5} \leq \epsilon_3 \leq 10^{-3} \quad \text{and} \quad 10^{-12} \leq DS \leq 10^{-6}.$$

In other words, the minerals again precipitate in trace amounts as if from nothing. The only reason is the computational disagreement between the mass balance threshold criteria and the critical value of the molar quantity of a phase, above which it is assumed that it physically occurs in the equilibrium solution. However, these specific computational features are not unjustified obstacles in practical situations. If there is a need for a more accurate mass balance result, it can be improved by three–six orders of magnitude using special correction procedures. For instance, in Selector-S, there is a high-accuracy mode of equilibrium calculations, when the threshold value of residuals in mass balance calculations ( $\epsilon_2$ ) is set in the range  $10^{-17}$ – $10^{-21}$  mol. The necessity for a high-accuracy mode arises in problems involving independent components with molar quantities no higher than  $10^{-15}$ – $10^{-19}$  mol, for instance, rare earth elements.

## CALCULATION OF Eh

The formulation and solution of the chemical equilibrium problem as a convex programming problem allows direct determination of the redox potential of the system from the dual solution related to a balance constraint on the charge of the system. It is usually assumed



that the system is electrically neutral; i.e.,  $b_e = 0$ , where  $b_e$  is the independent component of the vector  $b$  related to the electric neutrality equation in the system of Eq. (3). However, the reasonable requirement of electric neutrality is not necessary. In the general case, equilibrium can be calculated in systems with fixed charge, i.e., at  $b_e \neq 0$ .

Let the chemical potential of electron as a dependent component be always zero under reference conditions  $T_r = T$  and  $P_r = 1$  bar ( $T_r$  and  $P_r$  are the reference temperature and pressure),

$$RTv_e^0 \equiv 0,$$

where  $v_e^0$  is the chemical potential of electron as a dependent component under reference conditions.

The chemical potential of electron as a dependent component in a system with a predefined vector  $b$ , which includes the charge of the system,  $b_e$ , temperature  $T$ , and pressure  $P$ , is equal to the chemical potential of the independent electron component determined as a dual solution related to the balance constraint on the charge of the system with the factor  $RT$ ,

$$RTv_e = RTu_e,$$

where  $v_e$  is the chemical potential of electron as a dependent component, and  $u_e$  is the dual solution related to the electric neutrality equation.

The free energy change of electron at the transition from the standard state with  $T_r$  and  $P_r$  to the conditions of system occurrence with prescribed  $T$ ,  $P$ , and vector  $b$  is

$$RTu_e - RTv_e^0 = RTu_e - 0 = RTu_e.$$

The latter value can be recast into the dimension of the redox potential,

$$RTu_e = EhF,$$

where  $Eh$  is the redox potential of the system;  $F$  is the faraday,  $F = 23062$  cal/(g mol); and  $R = 1.9872$  cal/(K mol). Thus,

$$Eh = 0.000086Tu_e \text{ (V)}. \quad (45)$$

By analogy with  $\text{pH} = -\log a_{\text{H}^+}$ , where  $a_{\text{H}^+}$  is the activity of  $\text{H}^+$ , the redox potential can be expressed in the activity units of the dependent component  $e$  (electron) in water,  $pe = -\log a_e$ , where  $a_e$  is the activity of electron. The values  $Eh$  and  $pe$  are related by the equation

$$pe = \frac{F}{2.3025RT} Eh \quad \text{or} \quad pe = 0.4343u_e. \quad (46)$$

Equations (45) and (46) allow direct calculation of the redox potential of the system without applying more complex relationships relating  $Eh$  and  $pe$  with  $\text{pH}$  and oxygen or hydrogen fugacity.

### CALCULATION OF $g_j$ FROM $x_j$ , $j \in J_2$

Geochemists and petrologists often face a need to calculate the unknown values of the Gibbs free energy of formation of compounds from their known contents in the system. For instance, let the composition of aqueous solution be analyzed in equilibrium with a mineral assemblage under given temperature and pressure. The problem is to determine the Gibbs free energies of formation of minerals of the assemblage. It is assumed that the stoichiometric compositions of the minerals are known. If the initial thermodynamic data are available, the method of Gibbs free energy minimization allows us to calculate the equilibrium composition of aqueous solution. In such a case, the problem of determining the Gibbs free energy of formation of minerals can be also solved. Initially, the equilibrium of aqueous solution is calculated. Then, using the numeric values of the chemical potentials of independent components, we can determine the Gibbs free energies of formation of minerals in equilibrium with the aqueous solutions. The same procedure is valid for a determination of the free energy of formation of dependent components of a silicate melt in equilibrium with gas phase, which contains all the independent components that make up the silicate melt.

In order to present a formal statement of such problems, let us introduce the following designations, which will be used below:

$$J_g = \{j/j \in L/S_w, x_j > \varepsilon\},$$

$$J_w^0 = \{j/j \in L/S_w^0, x_j > \varepsilon\},$$

$$J_w = \{j/j \in L/S_w, x_j > \varepsilon\}.$$

The thermodynamic system is divided into two subsystems. The first subsystem is referred to as a base subsystem, and the second one, as a nonbase subsystem. The sets of indexes of dependent components in the base and nonbase subsystems with  $x_j > \varepsilon$ ,  $j \in J$  are denoted as  $J_1$  and  $J_2$ , respectively, such that

$$J = J_1 \cup J_2.$$

Let us impose the following necessary condition: the base subsystem must contain all independent components of the whole system in physically significant amounts. Because of this, aqueous solution or a high-temperature gas phase in equilibrium with melt and minerals is usually selected as a base subsystem. However, in the general case, the base subsystem can include solid phases or various combinations of solid phases, gas mixture, and aqueous solution. The partition into base and nonbase subsystems depends on the goals of the study and conditions of system occurrence.

Let us calculate separately the equilibrium state of the base subsystems. If the whole system is in equilibrium, the chemical potentials of independent components in the two subsystems are identical. Thus, using dual solutions for the base subsystem, it is possible to calculate the functions  $g_j$ ,  $j \in J_2$  for the dependent com-

ponents of the second, nonbase subsystem, if their stoichiometric compositions are known. The functions  $g_j$ ,  $j \in J_2$  are calculated by formulas derived from Eqs. (2), (8)–(12), and (26)–(31)

$$g_j = RT \left[ \sum_i \alpha_{ji} \hat{u}_i^1 - \ln \gamma_j - \ln P - \ln \frac{x_j}{X_\alpha} \right], \quad (47)$$

$$i \in N, \quad j \in J_\alpha \cap J_g \cap J_2, \quad \alpha \in \Phi;$$

$$g_j = RT \left[ \sum_i a_{ji} \hat{u}_i^1 - \ln \gamma_j - \ln 55.51 - \ln \frac{x_j}{X_w} + \ln \frac{x_{j_w}}{X_w} - t_j \right], \quad (48)$$

$$i \in N, \quad j \in J_w^0 \cap J_2;$$

$$g_j = RT \left[ \sum_i a_{ji} \hat{u}_i^1 - \ln \gamma_j - \ln \frac{x_j}{X_w} - t_j \right], \quad (49)$$

$$i \in N, \quad j = j_w \cap J_2.$$

In Eqs. (47)–(49),  $\hat{u}_i^1$  is the reduced chemical potential of the independent component with index  $i$  calculated by Gibbs free energy minimization in the base subsystem.

Depending on which equilibrium (complete or metastable) is attained in the base subsystem and which equilibrium occurs between the two subsystems, the calculated values of  $g_j$  characterize either the equilibrium or metastable state of the nonbase subsystem. In other words, it is necessary to take into account the particular thermodynamic conditions of system occurrence. Kulik *et al.* [5] reported interesting results along this line from a study of the bottom deposits of the Baltic Sea.

#### CALCULATION OF $g_k$ , $k \in J_w^0$

Of particular interest is the determination of  $g_k$ ,  $k \in J_w^0$  in aqueous solutions from the known molar quantities  $x_k^0$ ,  $k \in J_w^0$ . The formula for the calculation is derived from Eqs. (2), (8)–(12), and (26)–(31):

$$g_k = RT \left[ \sum_i a_{ki} \hat{u}_i^1 - \ln \gamma_k - \ln 55.51 - \ln \frac{x_k^0}{X_w} + \frac{x_{j_w}}{X_w} - t_j \right], \quad (50)$$

$$i \in N, \quad k \in J_w^0, \quad X_w = \sum_j x_j + x_k^0, \quad j \in J_w, \quad k \neq j.$$

Initially, equilibrium is calculated for a system without the dependent component with index  $k$ . This is a preliminary step;  $r = 0$ . The value  $g_k^{r=0}$  is estimated from Eq. (50) using the obtained values  $\hat{u}_i^1$ ,  $i \in N$ ,  $x_{j_w}$ ,  $X_w$ , and activity coefficient  $g_k$  calculated from a certain modification of the Debye–Hückel equation, e.g., [23]. Then, the Gibbs free energy is again minimized in a system including the dependent component  $k$  and its  $g_k^{r=0}$ . This is the first step;  $r = 1$ . The minimization yields a new value of  $x_k^{r=1} = f(g_k^{r=0})$ . The general recursive scheme is represented by the operator

$$x_k^r = f(g_k^{r-1}),$$

where  $f(g_k^{r-1})$  is the operator symbolizing the problem of Gibbs free energy minimization for the system with  $g_k^{r-1}$ .

Let us introduce the criterion function

$$f_g = \frac{|x_k^0 - x_k^r|}{x_k^r} \geq \varepsilon_g$$

and minimize it by the bisection (or golden section) procedure over the interval

$$g_k^r \in [\underline{g}_k, \bar{g}_k],$$

where  $\underline{g}_k$  and  $\bar{g}_k$  are the lower and upper limits of possible  $g^r$  values;  $\varepsilon_g$  is the threshold value of the minimum  $f_g$ . The minimization procedure is terminated when  $f_g \leq \varepsilon_g$ . The numerical values of  $\varepsilon_g$  are defined empirically within

$$10^{-2} \leq \varepsilon_g \leq 10^{-1}.$$

Thus, it can be written that

$$\hat{g}_k = \operatorname{argmin} f_g,$$

where  $\hat{g}_k$  is the sought-for value of  $g_k$ ,  $k \in J_w^0$  corresponding to the known value of  $x_k^0$ ,  $k \in J_w^0$ .

The above-described scheme of  $\hat{g}_k$  determination can be significantly simplified. Such a possibility is inherent in the problem of  $G(x)$  minimization with additional constraints on the molar quantities of dependent components. After the preliminary and first steps, instead of a stepwise  $f_g$  minimization, we set upper or lower bounds on the value  $x_k^{r=2}$  using the following rule: if  $x_k^{r=1} > x_k^0$ , then the upper bound is used,  $x_k^{r=2} \leq x_k^0$ ;

and if  $x_k^{r=1} < x_k^0$ , the lower bound is used,  $x_k^{r=2} \geq x_k^0$ . Then, the minimization problem with additional lower or upper constraints on  $x_k^{r=2}$  is solved, and  $g_k$  is directly determined from Eq. (50). Such a procedure was applied for the estimation of the standard Gibbs free energy of formation of nitrate ion from the chemical composition of Lake Baikal water [24].

It should be pointed out once more that the application of Eq. (50), as well as Eqs. (47)–(49), implies a strict identification of the conditions of system occurrence with respect to the realization of complete or metastable equilibrium between the base and nonbase subsystems. In the case of Eq. (50), the dependent component with index  $k$  can be considered as a nonbase subsystem, which is included into the base subsystem of aqueous solution.

DETERMINATION OF  $x_j, j \in J_2$  FROM  $g_j, j \in J_2$

In particular cases, the evaluation of chemical equilibrium in a convex programming formulation allows the determination of the possible concentrations of dependent components in solution phases from the known values of their Gibbs free energies of formation. For this purpose, Eqs. (47)–(49) are rewritten in such a way that  $x_j, j \in J_2$  depends functionally on  $g_j, j \in J_2$ . Let  $X_\alpha = 1, \alpha \in \Phi_2$ , where  $\Phi_2$  is the set of phases of the nonbase subsystem. In addition,  $n(l_\alpha) \geq 2, \alpha \in \Phi_2$ . The dependency of  $x_j$  on  $g_j, j \in J_2$  is as follows:

$$x_j = \exp \left[ -\frac{g_j}{RT} - \ln \gamma_j - \ln P + \sum_i a_{ji} \hat{u}_i^1 \right], \quad (51)$$

$$i \in N, \quad j \in l_\alpha \cap J_g \cap J_2, \quad \alpha \in \Phi_2;$$

$$x_j = \exp \left[ -\frac{g_j}{RT} - \ln \gamma_j - \ln 55.51 + \ln x_{j_w} + x_{j_w} - 1 + \sum_i a_{ji} \hat{u}_i^1 \right], \quad (52)$$

$$i \in N, \quad j \in j_w \cap J_2;$$

$$x_{j_w} = \exp \left[ -\frac{g_{j_w}}{RT} - \ln \gamma_{j_w} + 1/x_{j_w} + x_{j_w} - 2 + \sum_i a_{ji} \hat{u}_i^1 \right], \quad (53)$$

$$i \in N, \quad j_w \in J_w.$$

In Eq. (53),  $x_{j_w}$  is calculated by the method of successive approximations. At the preliminary step, it is accepted that  $x_{j_w} = X_w$ , which is equivalent to  $t_{j_w} = 0$ .

The use of Eqs. (51)–(53) allows the determination of the probable composition of aqueous solution or high-temperature fluid in equilibrium with the mineral assemblage whose dependent components contain volatile substances  $H_2O, CO_2, F, Cl, B, S,$  and  $N$ . The mineral assemblage is considered as a base subsystem. Under preset  $T$  and  $P$  conditions,  $G(x)$  minimization in the base subsystem allows us to determine  $\hat{u}_i^1$  and the composition of aqueous solution or fluid in equilibrium with the given mineral assemblage from known  $g_j, \gamma_j, j \in J_2$ .

CALCULATION OF METASTABLE GIBBS FREE ENERGIES AND ACTIVITY COEFFICIENTS OF DEPENDENT COMPONENTS IN PROBLEMS OF GIBBS FREE ENERGY MINIMIZATION WITH ADDITIONAL CONSTRAINTS

By means of the dual variables  $z_j, j \in L_S$  related to the additional constraints on the dependent components of the system (Eqs. (26) and (27)), metastable values can be calculated for the Gibbs free energies and activity coefficients of independent components.

Let a solution be obtained for the problem  $G_0$  of Gibbs free energy minimization (Eqs. (6) and (7)). Then, according to Eqs. (26) and (27),

$$\sum_j a_{ij} u_i - v_j = z_j, \quad i \in N, \quad j \in L_S, \quad (54)$$

where  $z_j$  are the dual variables related to the functional constraints (22)–(25).

In equilibrium solutions,  $z_j = 0$ , and, in nonequilibrium solutions,  $z_j \neq 0$ . We will need the values

$$\Delta g_j = v_j - \frac{g_j}{RT}, \quad j \in L,$$

where  $\Delta g_j$  are determined by the following expressions depending on the reference frame:

$$\Delta g = \begin{cases} \ln \gamma_j + \ln P + \ln(x_j/X_\alpha), & j \in L \setminus S_w, \quad \alpha \in \Phi; \\ \ln \gamma_j + \ln 55.51 + \ln(x_j/X_\alpha) \\ - \ln(x_{j_w}/X_w) - (x_{j_w}/X_w) + 1, & j \in S_w^0; \\ \ln \gamma_j + \ln(x_{j_w}/X_w) - (X_w/x_{j_w}) \\ - (x_{j_w}/X_w) + 2, & j = j_w. \end{cases}$$

Let us designate  $g_j^M = g_j + RTz_j$ ,  $j \in L$ , where  $g_j^M$  is the metastable Gibbs free energy of the component with index  $j$ . Using the relation

$$\sum_i a_{ij}u_i - \frac{g_j}{RT} - \Delta g_j = z_j, \quad i \in N, \quad j \in L$$

we obtain an explicit analytical expression for the metastable Gibbs free energy of the dependent component with index  $j$

$$g_j^M = RT \left[ \sum_i a_{ij}u_i - \Delta g_j \right], \quad i \in N, \quad j \in L. \quad (55)$$

The solutions of the problem of Gibbs free energy minimization with  $g_j$ ,  $j \in L$  with additional constraints and the solution of the same problem with  $g_j^M$ ,  $j \in L$  without additional constraints will be fully identical within computation uncertainties. The substitution of  $g_j$  for  $g_j^M$  in the initial data appears to be equivalent to an elimination of additional constraints. Such a substitution allows a statement and solution in the framework of the physicochemical model studied and a number of other problems of Gibbs free energy minimization in a metastable formulation.

In order to calculate the activity coefficient, it is necessary to determine the excess partial molar Gibbs free energy

$$g_j^{\text{ex}} = RT \left[ \sum_i a_{ij}u_i - \Delta g_j^0 \right] - g_j, \quad i \in N, \quad j \in L, \quad (56)$$

where

$$\Delta g_j^0 = \Delta g_j - \ln \gamma_j, \quad j \in L,$$

and

$$\ln \gamma_j = \frac{g_j^{\text{ex}}}{RT}, \quad j \in L. \quad (57)$$

Solving the problem  $G_0$  with known  $T$  and  $P$ , we determine then the activity coefficients of dependent components using Eqs. (56) and (57). We emphasize that the problem  $G_0$  is solved in an ideal statement. Nonideality is retained by additional constraints. The departure from ideality is fixed by the dual solutions  $z_j$ ,  $j \in L$  related to constraints set by Eqs. (22)–(25). Thus,  $\gamma_j$  is directly calculated without the preliminary choice of an appropriate solution model. Such a choice is possible after accumulating and processing an array of  $\gamma_j$ ,  $j \in L$ . Such a scheme of  $\gamma_j$  calculation was successfully used in a study of the determination of activity coefficients in carbonate solid solutions from analytical data in the system pore solution–authigenic mineral phases in the bottom deposits of the Baltic Sea [5].

## CONCLUSION

The formulation of the Gibbs free energy minimization problem as a convex programming problem with additional one- and two-sided constraints on the molar quantities of dependent components provides new opportunities for the thermodynamic modeling of geochemical processes. The duality relation of convex programming is of crucial importance. The prime variables of the convex programming problem are the sought-for molar quantities of the dependent components, while the dual variables are the sought-for chemical potentials of the independent components.

The presence or absence of particular phases in the solution is determined by the phase criterion, which is derived from the Kuhn–Tucker condition accounting for the additional one- and (or) two-sided constraints on the molar quantities of the dependent components.

The redox potential of a system containing charged dependent components is calculated from the dual solutions in the problem of the determination of the equilibrium composition by Gibbs free energy minimization. Thus,  $E_h$  is a simple function of temperature, pressure, and the chemical potentials of the independent component—electron, which is a dual solution related to the balance constraint on the charge of the system.

The duality relation extends considerably the possibilities of problem formulation and solution for the identification of the physicochemical potentials of natural systems. Among such problems are the calculations of the Gibbs free energy, fluid constituent contents in a phase, and activity coefficients and determination of the mineral assemblage that could be in complete or metastable equilibrium with the aqueous solution.

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