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Convergence of the Equilibrium Code SOLGASMIX

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The procedure used to calculate chemical equilibrium in the code SOLGASMIX has been evaluated mathematically and applied to several examples in aqueous electrolyte chemistry. Matrix representation of the solution procedure allows convenient expression as a standard fixed-point iteration. Evaluation of sample problems illustrates the importance of certain free energy differences in theoretical convergence results. An interpolation scheme based on the oscillation of Gibbs energies yields legitimate equilibrium results in situations where the code would otherwise fail to converge properly.

Key Words: convergence; chemical equilibrium.

1. INTRODUCTION

The code SOLGASMIX and predecessors [1–4] have been prominent for more than two decades as a means of calculating the equilibrium in a chemical system. It is still widely used in such diverse applications as metallurgy, chemical engineering, and geoscience. Various versions serve as the basic component of several commercial products [5, 6]. The popularity of the code is due at least in part to the fact that it was initially distributed free of charge, and it is highly capable and dependable, although not mathematically sophisticated.

Its convergence properties are no better than first-order, but, in fact, it does converge in almost every circumstance, a valuable attribute. The original authors note circumstances in which the code fails to perform and propose a simple remedy [2]. However, their remedy involves perturbing the chemical system under consideration, which may produce an undesirable result; furthermore, it may not actually correct the problem. The purpose of this article is to examine the code with mathematical rigor, to note situations in which it

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fails to converge, and to propose remedies which do not alter the chemical system being considered. Of particular importance are applications to aqueous electrolytes since these systems depart strongly from ideal behavior.

2. BASIC MATHEMATICAL FORMULATION

The approach used in SOLGASMIX is that of the Gibbs-energy minimization, which can be formulated as an optimization problem,

$$\text{minimize: } G = \sum_{i=1}^{I} n_i \left(\mu_i^0 + \ln \hat{a}_i\right) \tag{1a}$$

$$\text{subject to: } \sum_{i=1}^{I} a_{ij} n_i = b_j, \quad j = 1, \ldots, J, \tag{1b}$$

$$n_i \geq 0, \quad i = 1, \ldots, I, \tag{1c}$$

where G is the reduced[2] Gibbs energy for the total system; μ_i^0, $\hat{a}_i$, n_i are, respectively, the reduced standard chemical potential, activity, and mole inventory of species i; b_j is the mole inventory of element j; and a_{ij} are the stoichiometric coefficients ($a_{ij} =$ moles of element j occurring in 1 mole of species i). The problem can be restated using the Lagrangian,

$$L = \sum_{i=1}^{I} n_i \left(\mu_i^0 + \ln \hat{a}_i\right) - \sum_{j=1}^{J} \pi_j \left(\sum_{i=1}^{I} a_{ij} n_i - b_j \right) - \sum_{i \in S_\mathrm{a}} \lambda_i n_i, \tag{2}$$

where π_j and λ_i are Lagrange multipliers and S_a is the "active set" containing indices of all species whose inventory is zero. (The terminology "active set" arises in mathematical optimization theory and operations research. For applications such as this, it may seem counterintuitive. We emphasize that a species is in the active set if equality holds in Eq. (1c), i.e., if the species is *not* present.) In practice, the proper identification of the active set is the most difficult aspect of the problem; one of the great strengths of SOLGASMIX is its highly effective capability in this regard.

Mathematically, the solution to problem (1) can be found by locating the critical points of the Lagrangian and maintaining the multipliers π_j and λ_i nonnegative. Thus, at equilibrium, the system satisfies the following conditions:

$$\frac{\partial L}{\partial n_i} = \mu_i^0 + \ln \hat{a}_i + \sum_{k=1}^{I} n_k \frac{\partial \ln \hat{a}_k}{\partial y_i} - \sum_{j=1}^{J} \pi_j a_{ij} = 0, \quad i \notin S_\mathrm{a}, \tag{3a}$$

$$\frac{\partial L}{\partial \pi_j} = \sum_{i=1}^{I} a_{ij} n_i - b_j = 0, \quad j = 1, \ldots, J, \tag{3b}$$

$$\frac{\partial L}{\partial \lambda_i} = n_i = 0, \quad i \in S_\mathrm{a}, \tag{3c}$$

$$\frac{\partial L}{\partial n_i} = \mu_i^0 + \ln \hat{a}_i + \sum_{k=1}^{I} n_k \frac{\partial \ln \hat{a}_k}{\partial n_i} - \sum_{j=1}^{J} \pi_j a_{ij} - \lambda_i = 0, \quad i \in S_\mathrm{a}. \tag{3d}$$

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[2] For a thermodynamic function X, the corresponding reduced quantity is X/RT. Use of reduced quantities is particularly convenient for computational purposes, since it renders the problem nondimensional and avoids a factor of RT in many expressions.

The sums in Eqs. (3a) and (3d) involving differentiation of ln $\hat{a}_k$ are zero, due to the Gibbs–Duhem equation.

The identification of the active set is accomplished by using Eqs. (3c) and (3d). If, during a given iteration, some species inventory is reduced to zero (or less than zero), its index enters the active set. To evaluate if a member should leave the active set, Eq. (3d) can be rearranged to get

$$\lambda_i = \mu_i^0 + \ln \hat{a}_i - \sum_{j=1}^{J} \pi_j a_{ij}, \quad i \in S_\mathrm{a}. \tag{4}$$

Since Lagrange multipliers must be positive, a negative value for λ_i in Eq. (4) is an indicator that species i should leave the active set. In a practical sense, this implies that the system Gibbs energy could be lowered if the inventory of species i was increased from zero.

With a given active set, the system equilibrium is obtained by solving Eqs. (3a) and (3b), revised as

$$\mu_i^0 + \ln \hat{a}_i - \sum_{j=1}^{J} \pi_j a_{ij} = 0, \quad i \notin S_\mathrm{a}, \tag{5}$$

$$\sum_{i=1}^{I} a_{ij} n_j = b_j, \quad j = 1, 2, \ldots, J. \tag{6}$$

These equations form the basis for the primary iteration in SOLGASMIX. They are approximated and simplified according to the following special cases:

1. *Gas phase.* This phase is assumed to be ideal so that Eq. (5) becomes

$$\mu_i^0 + \ln P + \ln \frac{n_i}{N_\mathrm{g}} - \sum_{j=1}^{J} \pi_j a_{ij} = 0, \tag{5a}$$

where $P =$ total system pressure and $N_\mathrm{g} =$ total moles in gas phase.

2. *Mixture phase.* The chemical potential is represented using the rational system so activity is the product of mole fraction and the rational activity coefficient. For each species in the mixture, Eq. (5) then becomes

$$\mu_i^0 + \ln \frac{n_i}{N_\mathrm{m}} + \ln f_i - \sum_{j=1}^{J} \pi_j a_{ij} = 0, \tag{5b}$$

where N_m is the total number of moles in the mixture.

3. *Stoichiometric condensed solid.* In this case, $\hat{a}_i = 1$, so Eq. (5) becomes

$$\mu_i^0 - \sum_{j=1}^{J} \pi_j a_{ij} = 0. \tag{5c}$$

3. NUMERICAL PROCEDURE

The systems (5) (or (5a)–(5c)) and (6) are nonlinear, and hence, some type of iterative procedure is called for. The superscripts k and $k+1$ are used on variables to indicate which iteration produced them. When not necessary to distinguish between different iterations, the superscript is dropped. Thus, given an approximate solution, n_i^k, N_g^k, N_m^k, π_j^k, either from an initial guess ($k=0$) or previous iteration, a representation for a new solution y^{k+1} is found by manipulation of Eqs. (5) and (6). To begin, the logarithmic terms in Eqs. (5a) and (5b) are linearized as

$$\ln\frac{n_i^{k+1}}{N^{k+1}} = \ln\frac{n_i^{k+1}}{n_i^k} - \ln\frac{N^{k+1}}{N^k} + \ln\frac{n_i^k}{N^k} = \frac{n_i^{k+1}}{n_i^k} - \frac{N^{k+1}}{N^k} + \ln\frac{n_i^k}{N^k} + \epsilon^{k+1}, \tag{7}$$

where the error term ϵ^{k+1} is given by

$$\epsilon^{k+1} = \left(\frac{n_i^{k+1}}{n_i^k} - \frac{N^{k+1}}{N^k}\right)\left[1 - \frac{1}{2}\left(\frac{n_i^{k+1}}{n_i^k} + \frac{N_i^{k+1}}{N_i^k}\right)\right] + \cdots.$$

Depending on the chemical system and the values at the previous iteration, the error term may or may not be small. In the code itself, ϵ^{k+1} is assumed to be zero, and this may account for the slow convergence. Of course, $\epsilon^{k+1} \to 0$ as convergence progresses, so the final result should not be affected by the coarseness of this approximation.

Substituting Eq. (7) into Eq. (5a) or (5b) and rearranging yields,

$$n_i^{k+1} = -\phi_i^k + n_i^k\left(\frac{N^{k+1}}{N^k} + \sum_{j=1}^{J}\pi_j^{k+1}a_{ij}\right), \tag{8}$$

where ϕ_i^k depends only on quantities already known:

$$\phi_i^k = \begin{cases} \left(\mu_i^0 + \ln P + \ln\dfrac{n_i^k}{N_g^k}\right)n_i^k, & i \in \text{gas phase} \\ \left(\mu_i^0 + \ln f_i^k + \ln\dfrac{n_i^k}{N_m^k}\right)n_i^k, & i \in \text{mixture phase.} \end{cases}$$

Note that the activity coefficient at the new iteration is approximated, i.e.,

$$f_i^{k+1} \cong f_i^k. \tag{8a}$$

In practice, several mixture phases could be present; however, for simplicity, only one will henceforth be considered. Denoting S_g and S_m as the sets of gas and mixture species, Eq. (8) is summed over each in turn and simplified to get

$$\sum_{j=1}^{J}\pi_j^{k+1}\sum_{i\in S_g}n_i^k a_{ij} = \sum_{i\in S_g}\phi_i^k \tag{9a}$$

$$\sum_{j=1}^{J}\pi_j^{k+1}\sum_{i\in S_m}n_i^k a_{ij} = \sum_{i\in S_m}\phi_i^k. \tag{9b}$$

Finally, Eq. (8) is substituted into Eq. (3b); after considerable rearrangement, this yields

$$\begin{aligned}\sum_{n=1}^{J}\pi_n^{k+1}r_{jn} + \left(\frac{N_g^{k+1}}{N_g^k} - 1\right)\sum_{i\in S_g}n_i^k a_{ij} + \left(\frac{N_m^{k+1}}{N_m^k} - 1\right)\sum_{i\in S_m}n_i^k a_{ij} + \sum_{i\in S_S}a_{ij}n_i^{k+1} \\ = \sum_{i\in S_g+S_m}a_{ij}\left(\phi_i^k - n_i^k\right) + b_j, \quad j = 1, \ldots, J,\end{aligned} \tag{9c}$$

where $r_{jn} = \sum_{i \in S_g + S_m} n_i a_{ij} a_{in}$ and S_s is the set of solid species with nonzero inventory (i.e., not in the active set S_a). Revising Eq. (5c) yields

$$\sum_{j=1}^{J} \pi_j^{k+1} a_{ij} = \mu_i^0, \quad i \in S_s. \tag{9d}$$

If the number of solid species is N_s, then Eqs. (9a) through (9d) comprise $2 + J + N_s$ equations in the unknowns $\pi_j^{k+1} (j = 1, \ldots, J)$, $(N_g^{k+1}/N_g^k - 1)$, $(N_m^{k+1}/N_m^k - 1)$, and $n_i^{k+1} (i \in S_s)$. Due to the approximations (7) and (8a), the equations are linear in the unknowns. Thus, under favorable circumstances, the values at the new $(k + 1)$ iteration can be obtained by simply solving a linear system, after which the species distribution within each mixture is obtained from Eq. (8). However, two difficulties can arise which prevent the successful calculation of equilibrium conditions:

1. The set of linear equations at some iteration becomes singular, in which case no unique solution exists.
2. The sequence of iterates fails to converge.

4. MATRIX REPRESENTATION

In order to evaluate these two possibilities, it is useful to express the linear system at iteration $k + 1$ in matrix form. It is henceforth assumed that species in the active set (i.e. having zero inventories) are no longer under consideration; hence, all species have nonzero inventory. The stoichiometric coefficients are taken as elements of the stoichiometric matrix $\mathbf{A} = (a_{ij})$, which can be divided into submatrices representing the mixtures and solids.

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1J} \\ a_{21} & a_{22} & \cdots & a_{2J} \\ \vdots & \vdots & & \vdots \\ a_{I2} & a_{I2} & \cdots & a_{IJ} \end{bmatrix} = \begin{bmatrix} \mathbf{A}_g \\ \mathbf{A}_m \\ \mathbf{A}_s \end{bmatrix} = \begin{bmatrix} \mathbf{A}_0 \\ \mathbf{A}_s \end{bmatrix}.$$

Within the gas phase and the mixture phase, the vector of known inventories (from the previous iteration) are

$$\mathbf{n}_g = \left(n_1^k, n_2^k, \ldots, n_{N_g}^k\right)^T, \quad \mathbf{n}_m = \left(n_{N_g+1}^k, \ldots, n_{N_g+N_m}^k\right)^T.$$

Similarly, the vector of solid species is

$$\mathbf{n}_s = \left(n_{N_g+N_m+1}^k, \ldots, n_N^k\right)^T.$$

Also defined are vectors of reduced chemical potentials for the gas and mixture phases and solids:

$$\begin{aligned} \boldsymbol{\mu}_g &= \left(\mu_1, \mu_2 \ldots, \mu_{N_g}\right)^T, & \mu_i &= \mu_i^0 + \ln P + \ln \frac{n_i^k}{N_g^k}, \\ \boldsymbol{\mu}_m &= \left(\mu_{N_g+1}, \ldots, \mu_{N_g+N_m}\right)^T, & \mu_i &= \mu_i^0 + \ln f_i + \ln \frac{n_i^k}{N_m}, \\ \boldsymbol{\mu}_s &= \left(\mu_{N_g+N_m+1}, \ldots, \mu_N\right)^T, & \mu_i &= \mu_i^0, \end{aligned}$$

and vectors composed entirely of ones (with respective dimensions N_g and N_m):

$$\mathbf{e}_\mathrm{g} = (1, 1, \ldots, 1)^\mathrm{T}, \quad \mathbf{e}_\mathrm{m} = (1, 1, \ldots, 1)^\mathrm{T}.$$

Analogous to these vectors, we define the diagonal matrices

$$\mathbf{N}_\mathrm{g} = \mathrm{diag}(\mathbf{n}_\mathrm{g}) = \begin{bmatrix} n_1^k & & & & \mathbf{0} \\ & n_2^k & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \cdot \\ \mathbf{0} & & & & n_{N_\mathrm{g}}^k \end{bmatrix}, \quad \mathbf{N}_\mathrm{m} = \mathrm{diag}(\mathbf{n}_\mathrm{m}),$$

and the block diagonal matrices

$$\mathbf{N}_0 = \begin{bmatrix} \mathbf{N}_\mathrm{s} & \mathbf{0} \\ \mathbf{0} & \mathbf{N}_\mathrm{m} \end{bmatrix}, \quad \mathbf{N} = \begin{bmatrix} \mathbf{N}_\mathrm{g} & & \mathbf{0} \\ & \mathbf{N}_\mathrm{m} & \\ \mathbf{0} & & \mathbf{I}_\mathrm{s} \end{bmatrix},$$

where $\mathbf{I}_\mathrm{s}$ is an identity matrix with dimension N_s. It is also useful to group vectors into larger vectors:

$$\mathbf{n} = \begin{bmatrix} \mathbf{n}_\mathrm{s} \\ \mathbf{n}_\mathrm{m} \\ \mathbf{n}_\mathrm{s} \end{bmatrix}, \quad \boldsymbol{\mu}_0 = \begin{bmatrix} \boldsymbol{\mu}_\mathrm{g} \\ \boldsymbol{\mu}_\mathrm{m} \end{bmatrix}, \quad \boldsymbol{\mu} = \begin{bmatrix} \boldsymbol{\mu}_\mathrm{g} \\ \boldsymbol{\mu}_\mathrm{m} \\ \mathbf{0} \end{bmatrix}, \quad \mathbf{e}_0 = \begin{bmatrix} \mathbf{e}_\mathrm{g} \\ \mathbf{e}_\mathrm{m} \end{bmatrix}, \quad \mathbf{e} = \begin{bmatrix} \mathbf{e}_0 \\ \mathbf{0} \end{bmatrix},$$

where the zero vectors in $\boldsymbol{\mu}$ and $\mathbf{e}$ have dimensions N_s.

With these definitions, the linear system composed of Eqs. (9a) through (9d) can be expressed by the single matrix equation

$$\mathbf{R}\mathbf{x} = \mathbf{d}, \tag{10}$$

where

$$\mathbf{R} = \begin{bmatrix} \mathbf{A}_0^\mathrm{T}\mathbf{N}_0\mathbf{A}_0 & \mathbf{A}_\mathrm{g}^\mathrm{T}\mathbf{n}_\mathrm{g} & \mathbf{A}_\mathrm{m}^\mathrm{T}\mathbf{n}_\mathrm{m} & \mathbf{A}_\mathrm{s}^\mathrm{T} \\ \mathbf{n}_\mathrm{g}^\mathrm{T}\mathbf{A}_\mathrm{g} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{n}_\mathrm{m}^\mathrm{T}\mathbf{A}_\mathrm{m} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{A}_\mathrm{s} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{bmatrix}, \quad \mathbf{d} = \begin{bmatrix} \mathbf{d}_0 \\ \mathbf{n}_\mathrm{g}^\mathrm{T}\boldsymbol{\mu}_\mathrm{g} \\ \mathbf{n}_\mathrm{m}^\mathrm{T}\boldsymbol{\mu}_\mathrm{m} \\ \boldsymbol{\mu}_\mathrm{s} \end{bmatrix},$$

$$\mathbf{d}_0 = \mathbf{b} + \mathbf{A}_0^\mathrm{T}\mathbf{N}_0(\boldsymbol{\mu}_0 - \mathbf{e}_0),$$

and $\mathbf{x}$ is the vector of unknowns at iteration $k+1$:

$$\mathbf{x} = \left(\pi_1^{k+1}, \pi_2^{k+1}, \ldots, \pi_J^{k+1}, \frac{N_\mathrm{g}^{k+1}}{N_\mathrm{g}^k} - 1, \frac{N_\mathrm{m}^{k+1}}{N_m^k} - 1, n_{N_\mathrm{g}+N_\mathrm{m}+1}^{k+1}, \ldots, n_N^{k+1}\right)^\mathrm{T}. \tag{10a}$$

The vector $\mathbf{b} = (b_1, \ldots, b_J)^\mathrm{T}$ has components which are the elemental inventories appearing in Eq. (1b). Once Eq. (10) has been solved (provided, of course, that it is nonsingular), the components of $\mathbf{x}$ are known. The inventories of mixture species are obtained from Eq. (8), which can also be expressed in matrix form,

$$\mathbf{n}_{\mathrm{g}}^{k+1} = \mathbf{N}_{\mathrm{g}}^{k}\left(\mathbf{e}_{\mathrm{g}} - \boldsymbol{\mu}_{\mathrm{g}}^{k} + \mathbf{A}_{\mathrm{g}}^{\mathrm{T}}\boldsymbol{\pi}^{k+1}\right) + \mathbf{n}_{\mathrm{g}}^{k}\, x_{J+1}^{k+1}, \tag{11a}$$

$$\mathbf{n}_{\mathrm{m}}^{k+1} = \mathbf{N}_{\mathrm{m}}^{k}\left(\mathbf{e}_{\mathrm{m}} - \boldsymbol{\mu}_{\mathrm{m}}^{k} + \mathbf{A}_{\mathrm{m}}^{\mathrm{T}}\boldsymbol{\pi}^{k+1}\right) + \mathbf{n}_{\mathrm{m}}^{k}\, x_{J+2}^{k+1}, \tag{11b}$$

where $\boldsymbol{\pi} = (\pi_1, \ldots, \pi_J)^{\mathrm{T}}$.

An auxiliary matrix $\mathbf{P}$ is formed by concatenating the stoichiometric matrices $\mathbf{A}_{\mathrm{g}}$ and $\mathbf{A}_{\mathrm{m}}$ with the unity vectors $\mathbf{e}_{\mathrm{g}}$ and $\mathbf{e}_{\mathrm{m}}$ and an identity matrix $\mathbf{I}_{\mathrm{s}}$ of dimension N_{s}:

$$\mathbf{P} = \begin{bmatrix} \mathbf{A}_{\mathrm{g}} & \mathbf{0} & \mathbf{e}_{\mathrm{g}} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_{\mathrm{m}} & \mathbf{0} & \mathbf{e}_{\mathrm{m}} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{I}_{\mathrm{s}} \end{bmatrix}. \tag{11c}$$

This allows the entire iteration to be written in matrix form by combining Eqs. (10) through (11):

$$\mathbf{n}^{k+1} = \mathbf{N}^{k}(\mathbf{e} - \boldsymbol{\mu}^{k} + \mathbf{P}\mathbf{x}^{k+1}) = \mathbf{N}^{k}(\mathbf{e} - \boldsymbol{\mu}^{k} + \mathbf{P}(\mathbf{R}^{k})^{-1}\mathbf{d}^{k}). \tag{12}$$

The right-hand side of Eq. (12) depends only on problem inputs (stoichiometric coefficients and chemical potentials) and on the unknowns at the previous iteration. Thus Eq. (12) defines a fixed-point iteration of the form

$$\mathbf{n}^{k+1} = \mathbf{g}(\mathbf{n}^{k}), \tag{12a}$$

where $\mathbf{g}$ is a vector function $\mathbf{g} = (g_1, g_2, \ldots, g_N)^{\mathrm{T}}$. It is also helpful to define an additional matrix $\mathbf{Q} = \mathbf{P}\mathbf{R}^{-1}$, which simplifies the representation somewhat:

$$\mathbf{n}^{k+1} = \mathbf{N}^{k}(\mathbf{e} - \boldsymbol{\mu}^{k} + \mathbf{Q}^{k}\mathbf{d}^{k}).$$

In practice, $\mathbf{Q}$ can be calculated by solving the linear system $\mathbf{RQ} = \mathbf{P}$ using Gaussian elimination.

5. PRACTICAL EXAMPLE—AQUEOUS NaCl SOLUTION

When a strong electrolyte is dissolved in water, equilibrium is reached quickly, provided moderate mixing occurs. Often, the gas phase is not significant and will be neglected in this analysis for simplicity. There is thus a two-phase system involving water, aqueous ions Na^+, Cl^-, and crystalline solid NaCl. It should be noted that the aqueous solution departs strongly from ideality and may affect the numerical convergence.

For the present, the system is defined as having the three elements H_2O, Na^+, and Cl^-, whose total amounts b_1, b_2, and b_3 remain fixed. Obviously, H_2O is not a chemical element, but for the present it is defined as one for computational purposes. This selection will be discussed at greater length in the next section. In addition, there are four chemical species, $H_2O(\ell)$, $Na^+(aq)$, $Cl^-(aq)$, and $NaCl(s)$, whose respective inventories n_1, n_2, n_3, and n_4 may vary as equilibrium conditions are calculated. The chemical potentials μ_1, μ_2, μ_3, and μ_4 can be calculated from input free energies, the inventories n_i, and activity coefficients

f_i (which are presumed available). These variables are grouped in vectors **b** and **n**, which are related by the stoichiometric coefficients through Eq. (1b). Using the matrix notation of the previous section, this yields

$$\mathbf{A}_{\mathrm{g}} = \text{omitted}, \quad \mathbf{A}_{\mathrm{m}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{A}_{\mathrm{s}} = [0 \;\; 1 \;\; 1]$$

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_{\mathrm{m}} \\ \mathbf{A}_{\mathrm{s}} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix}, \quad \mathbf{R} = \begin{bmatrix} n_1 & 0 & 0 & n_1 & 0 \\ 0 & n_2 & 0 & n_2 & 1 \\ 0 & 0 & n_3 & n_3 & 1 \\ n_1 & n_2 & n_3 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{d} = \begin{bmatrix} b_1 + n_1(\mu_1 - 1) \\ b_2 + n_2(\mu_2 - 1) \\ b_3 + n_3(\mu_3 - 1) \\ n_1\mu_1 + n_2\mu_2 + n_3\mu_3 \\ \mu_4 \end{bmatrix}, \quad \mathbf{P} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 \end{bmatrix}.$$

This example is simple enough that the elements of the fixed-point vector can be obtained from straightforward (but laborious!) algebra,

$$g_1 = b_1, \tag{13a}$$

$$g_2 = g_3 = \frac{2n_2n_3b_1 + n_2n_3n_T(\mu_4 - \mu_2 - \mu_3)}{n_1(n_2 + n_3)}, \tag{13b}$$

$$g_4 = \frac{n_2n_3}{n_1(n_2 + n_3)} \left[-2(b_1 + b_2 + b_3) + n_T\left(\frac{b_2}{n_2} + \frac{b_3}{n_3}\right) + n_T(\mu_2 + \mu_3 - \mu_4) \right], \tag{13c}$$

where $n_T = n_1 + n_2 + n_3$. Use of the charge balance ($n_2 = n_3$ and $b_2 = b_3$) has simplified the above expressions considerably. Thus with these representations, the fixed-point iteration (12a) is identical to the SOLGASMIX iteration (9).

6. FAILURE DUE TO MATRIX SINGULARITY

The entire iterative procedure is based on the assumption that the matrix **R** in Eq. (10) is nonsingular. This may not be the case in many practical applications. However, this difficulty is most commonly encountered through poor problem definition, a situation which can easily be corrected.

Consider the aqueous salt solution from the previous section. If the system is redefined with the chemical elements H, O, Na, and Cl, then the stoichiometric and computational matrices become

$$\mathbf{A} = \begin{bmatrix} 2 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 \end{bmatrix}, \quad \mathbf{R} = \begin{bmatrix} 4n_1 & 2n_1 & 0 & 0 & 2n_1 & 0 \\ 2n_1 & n_1 & 0 & 0 & n_1 & 0 \\ 0 & 0 & n_2 & 0 & n_2 & 1 \\ 0 & 0 & 0 & n_3 & n_3 & 1 \\ 2n_1 & n_1 & n_2 & n_3 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \end{bmatrix}.$$

The first and second rows of **R** are now linearly dependent; hence, **R** is singular and no solution exists. In practice, SOLGASMIX may actually compute a solution under these circumstances, since numerical round-off error could alter the entries sufficiently so that rows no longer appear dependent. Of course, the results of such computations should not be trusted.

The situation can be avoided by ensuring that the number of elements $b_1, \ldots, b_J$ are the minimum possible to adequately represent the problem. In mathematical terms, this implies rank $(\mathbf{A}) = J$. Thus the choice of computational "elements" may involve compounds or other groupings in addition to single chemical elements.

Even with a judicious choice of computational elements, it is still possible that **R** may be singular because of chance assignments of the species inventories n_i. This circumstance is extremely rare unless there is an assignment of zero to some n_i. In the example of the previous section, either $n_1 = 0$ or $n_2 = n_3 = 0$ will produce a singular **R**. In the former case, this could only happen if $n_1 = b_1 = 0$ was specified initially and is properly described as an input error (in practical terms, an aqueous solution with no water). The latter case might arise if the initial input specified water and solid NaCl. Some versions of SOLGASMIX have safeguarded against both of these possibilities by internally specifying a minimum initial value for all mixture species, say $n_i \geq 10^{-8}$, regardless of user input, and by eliminating from the calculation rows and columns associated with zero inventories of elements.

7. FAILURE DUE TO NONCONVERGENCE

The basic solution procedure in Eq. (12) represents a fixed-point iteration. There is a wide body of mathematical knowledge concerning the behavior of such systems that leads to both convergence and nonconvergence. While a detailed look at dynamical systems is beyond the scope of this work, it is helpful to use certain results in order to characterize the convergence patterns of Eq. (12) in practical situations.

7.1. *Salt Solution Example*

To perform meaningful calculations for the example introduced in Section 5, parameter values are specified for the NaCl system as shown in Table I. Activity coefficients are

TABLE I
Input Parameters at 25°C for Salt Solution Examples

Species	Parameter	Nominal value	Reference
H_2O	μ^0	−95.667	8
Na^+	μ^0	−105.695	8
Cl^-	μ^0	−52.928	8
NaCl	μ^0	−154.998	9
Na-Cl	$\beta^{(0)}$	0.0765	7
Na-Cl	$\beta^{(1)}$	0.2664	7
Na-Cl	C^{φ}	0.00127	7
K^+	μ^0	−113.965	8
KCl	μ^0	−164.813	8
K-Cl	$\beta^{(0)}$	0.04835	7
K-Cl	$\beta^{(1)}$	0.2122	7
K-Cl	C^{φ}	−0.00084	7

calculated using the ion-interaction approach of Pitzer [7], and Gibbs energies of formation are taken primarily from Ref. [8]. With this approach, the rational activity system is replaced by the practical system, in which the reduced chemical potential is

$$\mu_i = \mu_i^0 + \ln m_i \gamma_i,$$

where m_i is molality and the practical activity coefficients γ_i are functions of the empirical parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} (See Ref. [7] for details).

If initial species values are such that the total salt concentration is below the solubility limit of approximately 6.1 m, then the code calculation returns this result. That is, all sodium and chloride are predicted to be in solution. However, if the solubility limit is exceeded, then, depending on the initial species distribution, the code returns soluble species values of 7.11 or 4.53, or terminates with an error.

If instead a solution of KCl is modeled, then certain input parameters are changed (see Table I), but the computational matrices **A** and **R** remain the same. In this case, the code successfully calculates the solubility of KCl regardless of initial species amounts. That is, for total amounts less than 4.8 m, all salt is in solution. As additional salt is added, any excess over 4.8 m is predicted as condensed solid.

It thus appears that variations in input variables alone can cause radical changes in the convergence properties of the code. Because the legitimate (from a chemical-thermodynamic perspective) parameter values for NaCl can yield totally spurious results, it is essential that this problem be addressed.

Returning to the NaCl example, it is interesting to examine the convergence pattern as the reduced chemical potential of NaCl is varied from its nominal value of $\mu_4 = \mu_4^0 = -155.00$. (In order to perform this analysis, the internal code limit on the number of iterations was overridden.) For choice of $\mu_4 < -155.40$, SOLGASMIX successfully calculates an equilibrium distribution between solid and aqueous phases. The number of iterations (for convergence to six significant figures) is only a few dozen for values far from this point, but rises as μ_4 approaches -155.40, as shown in Fig. 1. As μ_4 continues to increase, the number of iterations declines, but the solution does not converge to a single value. Instead, it converges to an oscillation between two different values. As μ_4 continues to increase, these two values separate further from each other, and as μ_4 increases beyond -154.61, the solution converges to an oscillatory pattern of four different values. This behavior is illustrated in Fig. 2 where additional doubling steps are shown as well. The points at which the solution doubling occurs are known as bifurcation points and the oscillatory pattern is known as a limit cycle. Figure 2 is an illustration of a well-known phenomenon in the study of dynamical systems—the period-doubling route to chaos. Such behavior is commonly encountered with fixed-point iterations, and numerical results suggest the same thing here: at $\mu_4 = -154.304$, convergence to a limit cycle of 64 occurs in 238 iterations; however, for $\mu_4 = -154.303$ no convergence was evident in 10,000 iterations. As μ_4 is increased further, the chaotic pattern is disturbed at other points, where convergence to limit cycles of 12, 32, and 40 are observed; doubtless others also exist. Regardless of the intriguing nature of these phenomena, our situation is concerned not so much with chaotic dynamics as with the extraction of meaningful equilibrium information despite it.

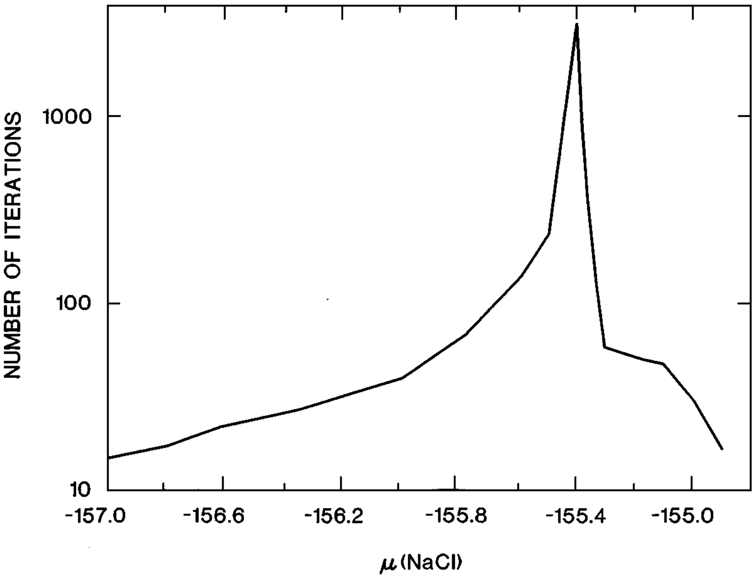

FIG. 1. Iterations for convergence to six significant figures.

7.2. *Fixed-Point Convergence*

Returning to the general case (12a), the Jacobian of the fixed-point vector is the matrix of partial derivatives:

$$\mathbf{F} = (f_{ij}), \quad f_{ij} = \frac{\partial g_i}{\partial n_j}. \tag{14}$$

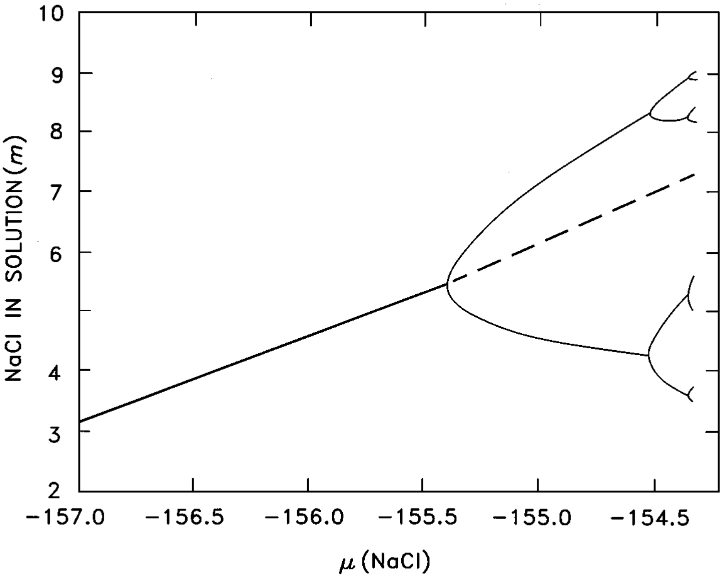

FIG. 2. Salt equilibrium determined by SOLGASMIX.

It can be shown [10] that a sufficient condition to ensure convergence to a single point (i.e., limit cycle of 1) is that all eigenvalues λ_i of $\mathbf{F}$ satisfy

$$|\lambda_i| < 1. \tag{15}$$

This condition is especially stringent, and convergence can occur (and often does) when it is violated. As will be shown later, the salt solution example does not satisfy (15) consistently, even where it does converge to a unique value. But inequality (15) is important since it helps to identify those quantities which influence limiting behavior.

The general case (12) is far too complicated to attempt analytical results. Thus we again turn to simpler situations, which will hopefully illustrate deficiencies and suggest possible remedies. Applying Eqs. (14) and (15) to the salt solution example is straightforward but tedious. The analysis is expedited by use of the symbolic processing tool MACSYMA [11]. Differentiation of Eq. (12a) with respect to n_i, $i = 1, 2, 3, 4$, yields the matrix $\mathbf{F}$, whose eigenvalues are zero (with multiplicity 3) and

$$\lambda = 1 + \left(2\frac{n_2}{n_1} + \frac{1}{2}\right)(\mu_4 - \mu_2 - \mu_3). \tag{16}$$

In order to ensure convergence to a single solution, it is necessary to maintain

$$\mu_4 - \mu_2 - \mu_3 < 0. \tag{17}$$

The quantity on the left-hand side of Eq. (17), $\Delta\mu = \mu_4 - \mu_2 - \mu_3$ is actually the difference in reduced chemical potentials of the solid salt (μ_4) and the ions in solution ($\mu_2 + \mu_3$); it should be zero at equilibrium.

A number of other aqueous systems have also been examined, with results shown in Table II. These involve additional complications not present in the NaCl example, but are still amenable to evaluation using MACSYMA. Each case includes one or two equilibrium relationships of the form

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C}. \tag{18}$$

TABLE II

Summary of Sample Problems

Aqueous species	Solid species	Nonzero eigenvalues[a]	Comments
H_2O, Na^+, Cl^-	NaCl	$\lambda = 1 + A\Delta\mu$	$\Delta\mu = \mu(\mathrm{NaCl}) - \mu(\mathrm{Na}^+) - \mu(\mathrm{Cl}^-)$
H_2O, Ca^{2+}, Cl^-	$CaCl_2$	$\lambda = 1 + A\Delta\mu$	$\Delta\mu = \mu(\mathrm{CaCl_2}) - \mu(\mathrm{Ca}^{2+}) - 2\mu(\mathrm{Cl}^-)$
H_2O, Na^+, Cl^-, NO_3^-	NaCl	$\lambda = 1 + A\Delta\mu$	$\Delta\mu = \mu(\mathrm{NaCl}) - \mu(\mathrm{Na}^+) - \mu(\mathrm{Cl}^-)$
H_2O, H^+, NO_3^-, HNO_3 (aq)	—	$\lambda = 1 + A\Delta\mu$	$\Delta\mu = \mu(\mathrm{HNO_3}) - \mu(\mathrm{H}^+) - \mu(\mathrm{NO_3^-})$
H_2O, H^+, Ca^{2+}, OH^-	$Ca(OH)_2$	$\lambda_\pm = 1 + \frac{A\Delta\mu_1 + B\Delta\mu_2 \pm \sqrt{C}}{D}$	$\Delta\mu_1 = \mu(\mathrm{Ca(OH)_2}) - \mu(\mathrm{Ca}^{2+}) - 2\mu(\mathrm{OH}^-)$ $\Delta\mu_2 = \mu(\mathrm{H_2O}) - \mu(\mathrm{H}^+) - \mu(\mathrm{OH}^-)$
H_2O, H^+, Na^+, Cl^-, OH^-	NaCl	$\lambda_\pm = 1 + \frac{A\Delta\mu_1 + B\Delta\mu_2 \pm \sqrt{C}}{D}$	$\Delta\mu_1 = \mu(\mathrm{NaCl}) - \mu(\mathrm{Na}^+) - \mu(\mathrm{Cl}^-)$ $\Delta\mu_2 = \mu(\mathrm{H_2O}) - \mu(\mathrm{H}^+) - \mu(\mathrm{OH}^-)$
H_2O, Na^+, K^+, Cl^-	NaCl, KCl	$\lambda_\pm = 1 + \frac{A\Delta\mu_1 + B\Delta\mu_2 \pm \sqrt{C}}{D}$	$\Delta\mu_1 = \mu(\mathrm{NaCl}) - \mu(\mathrm{Na}^+) - \mu(\mathrm{Cl}^-)$ $\Delta\mu_2 = \mu(\mathrm{KCl}) - \mu(\mathrm{K}^+) - \mu(\mathrm{Cl}^-)$

[a] Eigenvalues of Jacobian Matrix, Eq. (14). In each example, there were zero eigenvalues of multiplicity 3 or 4. The coefficients A, B, C, D depend on species inventories (cf. Eq. (16)) and are usually (but not always) positive. The discriminants C also depend on $\Delta\mu_1$ and $\Delta\mu_2$, and $C = 0$ when $\Delta\mu_1 = \Delta\mu_2 = 0$. If C is negative, the double roots are complex conjugates. The denominators D are always nonzero, unless all species inventories are zero.

In every case, the inequality in Eq. (15) holds if relationships analogous to Eq. (17) are maintained. Note, however, that in some cases the inequality in (17) should be reversed.

Examination of the convergence patterns in the actual code calculations for the NaCl example indicates that inequality (17) is rarely maintained but usually oscillates about zero. If desired convergence does occur, then the favorable instances with $\Delta\mu < 0$ evidently outweigh unfavorable circumstances when $\Delta\mu > 0$. (That is, the favorable steps cause faster convergence than the unfavorable ones do divergence.) It is shown in the Appendix that if convergence to a single equilibrium point does not occur, then $\Delta\mu$ always oscillates about zero.

7.3. *A Simple Remedy*

Thus far, two different attributes of equilibria have been discussed. The first is the minimization of Gibbs energy, upon which the fixed-point iteration (12) is based. However, because this iteration does not always find the equilibrium, we now focus on the second attribute—the equality of chemical potentials in different phases.

As mentioned above, the difference function $\Delta\mu$ oscillates between positive and negative values in the NaCl example. This usually happens when convergence to a single point is occurring, and always happens when it is not. Given two successive iterations with values $\Delta\mu^+ > 0$ and $\Delta\mu^- < 0$, the true equilibrium $\Delta\mu^* = 0$ lies between them. If we denote the corresponding species inventories as n_i^+ and n_i^-, it is reasonable to assume that the equilibrium values n_i^* should lie between n_i^+ and n_i^-. A good estimate can be obtained by linear interpolation:

$$n_i^* \cong n_i^- - \frac{\Delta\mu^-}{(\Delta\mu^+ - \Delta\mu^-)}(n_i^+ - n_i^-), \quad i = 1, 2, \ldots, I. \tag{19}$$

Actual code statements implementing this idea have been inserted into SOLGASMIX. That is, whenever $\Delta\mu$ changes sign, the most recent values of each species inventory are replaced by n_i^* calculated from Eq. (19).

When the revised code was applied to the NaCl example, convergence to a single equilibrium point occurred rapidly regardless of the value of μ_4. Even in the region where legitimate convergence did occur previously ($\mu_4 \leq -155.4$), the revised coding took only 5–10 iterations to converge (cf. Fig. 1). In the region where convergence to limit cycles of 2, 4, 8, ... occurred, or where chaotic behavior ensued, the revised coding yielded rapid convergence to a single equilibrium value. This is shown in Fig. 2 by the dashed line proceeding from the first fork (bifurcation). At $\mu_4 = -155.00$ (the original value from Ref. [9]), the calculated species in solution are $n_{\mathrm{Na}^+} = n_{\mathrm{Cl}^-} = 6.1$, in good agreement with experimental values for NaCl solubility.

The revision (19) was proven to work for the NaCl example (see Appendix), and it is reasonable (but not rigorously proven) to apply it to all systems. Even for those that would otherwise converge, convergence will probably occur more rapidly.

In many applications, more than one relation of the form (18) exists (i.e., there are several difference functions, $\Delta\mu_k$ (see Table II)). Numerical experiments indicate that all of them tend to oscillate in the SOLGASMIX iteration scheme. Thus it should suffice to apply Eq. (19) to one or more of them. In fact, this has proven to be the case in examples where 2, 3, 4, or more difference functions were present.

8. SUMMARY AND CONCLUSION

The code SOLGASMIX has been useful in many applications where the calculation of chemical equilibrium is necessary. Its strength is its ability to adequately determine what chemical species should actually be present. However, the refinement of quantitative species inventories is based on first-order (at best) approximations and usually converges slowly. In certain cases, the convergence yields spurious values or does not occur, due to behavior commonly found in fixed-point iterations.

Theoretical evaluation of the iteration scheme indicates that differences in chemical potential of different phases are important in convergence. An interpolation scheme based on this analysis vastly improves the convergence properties. In situations where convergence to equilibrium conditions did not occur due to numerical artifacts in the standard SOLGASMIX procedure, the revised procedure converges quickly and accurately. Where convergence was previously occurring, the revised procedure produces much more rapid convergence, usually reducing the number of iterations by an order of magnitude or more. Applications to aqueous electrolyte examples demonstrate the usefulness of the modifications. In practice, the modified code has also been applied to problems involving as many as 18 elements and dozens of reactions, with excellent results.

APPENDIX A

Consider a single step of the fixed-point iteration for the salt solution example, given by Eqs. (13). Note that n_1 (water) stays constant and the solid inventory n_4 does not enter the calculations (i.e., **g** is a function only of n_1, n_2, and n_3). Also, the cation and anion inventories are equal: $n_2 = n_3 \equiv n$, and notation is simplified by following only this quantity without subscripts. After rearrangement, Eq. (13b) can be expressed as

$$n^{k+1} = n^k + n^k\left(\frac{1}{2} + \frac{n^k}{b_1}\right)\Delta\mu^k, \tag{A.1}$$

where

$$\Delta\mu^k = \mu_4^k - \left(\mu_3^k + \mu_2^k\right) = \mu_4^0 - \left(\mu_3^0 + \ln\hat{a}_3^k + \mu_2^0 + \ln\hat{a}_2^k\right) = \Delta\mu^0 - 2\ln\hat{a}^k,$$

and $\hat{a}^k = \sqrt{\hat{a}_2^k\hat{a}_3^k}$. Now, at equilibrium, $\hat{a} = \hat{a}^*$, $n = n^*$, and $\Delta\mu = 0$, so that $\Delta\mu^0 = 2\ln\hat{a}^*$. Thus, Eq. (A.1) can be rewritten as

$$n^{k+1} = n^k + n^k\left(1 + \frac{2n^k}{b_1}\right)\ln\frac{\hat{a}^*}{\hat{a}^k}. \tag{A.2}$$

It is a virtual certainty that chemical activity is an increasing function of the mole amount. Otherwise, addition of a small amount of substance would lower its chemical influence. This is true even when activity coefficients themselves are decreasing. In the present example, this situation arises in the Debye–Hückel region of dilute salt solution,

$$\hat{a} = m\gamma = n\gamma/M_1, \quad \ln\gamma = -0.51\sqrt{m},$$

where $M_1 =$ mass of water (kg). Now, $\mathrm{d}\hat{a}/\mathrm{d}n = (\gamma/M_1)(1 + \frac{1}{2}\ln\gamma)$, which is positive for small m (i.e., small n). Hence, $\hat{a}$ is increasing even where γ is most strongly decreasing.

Now, if $n^k < n^*$ then $\hat{a}^k < \hat{a}^*$, and Eq. (A.2) implies that $n^{k+1} - n^* > n^k - n^*$. This implies either that $|n^{k+1} - n^*| < |n^k - n^*|$ or that $n^{k+1} > n^*$ (in fact, both may be true). Similarly, if $n^k > n^*$, then either $|n^{k+1} - n^*| < |n^k - n^*|$ or $n^{k+1} < n^*$. In either case, if $|n^{k+1} - n^*| < |n^k - n^*|$, then the step is a convergent one. Thus, if the iteration does not move toward convergence, it must oscillate about the equilibrium point. From Eq. (A.1) it is clear that any oscillation of n^{k+1} about n^* must be caused by oscillation of $\Delta\mu^k$ about zero. These observations are summarized by the statement:

For any sequence of iterates $\{\boldsymbol{n^k}\}$ which does not converge to the single equilibrium point $\boldsymbol{n^*}$, then both $\{\boldsymbol{n^k - n^*}\}$ and $\{\boldsymbol{\Delta\mu^k}\}$ must be alternating sequences.

APPENDIX B: NOMENCLATURE

$\hat{a}$	Chemical activity
$\mathbf{A} = (a_{ij})$	Stoichiometric matrix (Eq. (1b))
$\mathbf{A}_\mathrm{g}, \mathbf{A}_\mathrm{m}, \mathbf{A}_\mathrm{s}$	Partial stoich. matrices for gas, mixture, solid phases
b	Elemental inventory
$\mathbf{d}$	Auxiliary vector (Eq. (10))
$\mathbf{e}$	Unity vector
f	Rational activity coefficient
$\mathbf{F} = (f_{ij})$	Jacobian (Eq. (14))
$\mathbf{g}$	Fixed point vector (Eq. (12a))
G	Reduced chemical potential
i, j, k	Indices: species, elements, time step
I, J	Number of species, elements
n	Mole inventory
$N_\mathrm{g}, N_\mathrm{m}$	Total moles in gas, mixture phases
P	Pressure
$\mathbf{P}$	Auxiliary matrix (Eq. (11c))
$\mathbf{R} = (r_{jn})$	Solution matrix (Eqs. (9c), (10))
S_a	Active set (Eq. (2))
$S_\mathrm{g}, S_\mathrm{m}, S_\mathrm{s}$	Index sets for gas, mixture, solid species
$\mathbf{x}$	Unknown vector (Eq. (10a))
ϵ	Truncation error
λ_i	Eigenvalues of Jacobian (Section 7)
λ_i, π_j	Lagrange multipliers (Section 2)
μ	Reduced chemical potential
μ^0	Reduced standard chemical potential
$\Delta\mu$	Chemical potential difference (Table II)
ϕ_i^k	Coefficient (Eq. (8))

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