New Efficient Algorithm for Solving Thermodynamic Chemistry

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Modeling thermodynamic equilibrium of complex nonlinear chemical systems with the most used Newton-Raphson method can lead to nonconvergence. From the mathematical properties of the set of equations, a chemically permitted interval is defined. By imposing this interval, the robustness of the Newton-Raphson method is increased at a low computing time cost. The new method, the positive continuous fraction, does not depend on the first derivative of the objective function to find the solution. A new algorithm is thus built by the association of this very robust method with the fast Newton-Raphson method and the definition of the chemically allowed interval. This combined algorithm is very impressive in terms of reliability, robustness, and speed.

Introduction

Chromatographic prediction and optimization involving multicomponent systems in chemical engineering or risk assessment in highly sensitive environmental domains such as heavy metal contamination (Chilakapati, 1999), nuclear waste disposal (White et al., 1984; Walsh et al., 1984), or nuclear testing (Bellot et al., 1999; Kersting et al., 1999) requires more and more calculation of reactive transport. The operator-splitting approach has mainly been used in reactive transport models by coupling mass transport equation and batch chemistry (Bryant et al., 1986; Krebs et al., 1987). In this case, the code solving the chemistry is called at least once per node and per time step.

In thermodynamic terms, a chemical equilibrium calculation, which attempts to find the minimum value for the Gibbs free energy, can be carried out in one of two ways: by minimizing a free energy function or by solving a set of nonlinear equations consisting of equilibrium constants and mass balance constraints. The two methods are thermodynamically equivalent, but the major disadvantage of using a free energy database is that these values are not nearly as reliable as directly measured equilibrium constants (Nordstrom and Ball, 1984). Many mathematical methods have been tested to solve the set of nonlinear algebraic equations describing thermodynamic equilibria. Zero-order methods such as the continuous fractions method (Wigley, 1977) and the Simplex method (Nelder and Mead, 1965; Wood, 1993) do not use the derivative of the objective function. The latter methods converge more slowly (Morin, 1985), but are sometimes considered more robust than first-order methods. The Simplex method is believed to be the most robust and may find the thermodynamic equilibrium when first-order methods are inefficient (Brassard and Bodurtha, 2000; Parkhurst and Appelo, 1999). First-order methods use the derivative of the objective function. The Newton-Raphson method is used the most to compute thermodynamic equilibrium in software such as MICROQL (Westall, 1979), IMPACT (Krebs et al., 1987), CHESS (van der Lee, 1998a,b), or PHREEQC (Parkhurst and Appelo, 1999a,b). Robustness (convergence for many cases), flexibility (easily modeling all chemical processes), and quickness (quadratic convergence (Morin, 1985)) are its great advantages. Nevertheless, the Newton-Raphson method is subject to nonconvergence for some ill-conditioned systems (van der Lee, 1998), and Brassard and Bodurtha (2000) have recently shown that this observation can be extended to other methods. Because of its frequent use, the Newton-Raphson method will be considered in this work as a reference method. Other methods such as the Gauss-Seidel, Gauss-Newton, or Levenberg-Marcard (Brassard and Bodurtha, 2000) can be used for calculating thermodynamic equilibrium. The Newton-Raphson method is sometimes associated with a relaxation technique (van der Lee, 1998) which controls the size of

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the method's down step and strengthens its robustness. This association can be done numerous ways with many relaxation techniques. Because of the high number of relaxation techniques or other methods applied to specific problems, these implementations will not be addressed in this work.

By assuming instantaneous equilibrium, it is known that chemistry computer codes are subject to nonconvergence (Walsh et al., 1984) which involves the loss of the computational effort or induce the wrong output. An accurate speciation code has to pursue the following criteria: reliability (exact solution), robustness (convergence certain), and quickness (computation time). The objective of this article is to present a new method, the Positive Continuous Fraction method, present a new constraint, respecting the chemically allowed interval (CAI), and propose a new algorithm, which respects these three criteria, to evaluate the thermodynamic equilibrium of nonlinear complex chemical systems. The principles reported here for examples of thermodynamic calculations are of great interest for every scientific domain that requires resolution of nonlinear algebraic systems.

Modeling

One very efficient formulation for the computation of thermodynamic equilibrium is based on the Tableau concept (referred to as Morel's Tableau) (Morel and Morgan, 1972; Morel, 1983). N_X components X_j are chosen among the N_C species C_i in order to write the formation of each species as a combination of the components. The mass action law for the formation of the C_i species is written with the equilibrium constant K_i and the stoichiometric coefficients $a_{i,k}$ for each component X_k

$$\{C_i\} = K_i \cdot \prod_{k=1}^{N_X} \{X_k\}^{a_{i,k}} \tag{1}$$

where $\{C_i\}$ and $\{X_k\}$ are the activities of species C_i and component X_k.

If N_{CP} precipitated species Cp_i are taken into account, the mass action law for the precipitation of Cp_i is written with the precipitation constant Kp_i such that $Kp_i = 1/Ks_i$, where Ks_i is the solubility product, and $ap_{i,k}$ is the stoichiometric coefficients. The saturation index (SI_i) of Cp_i is equal to its activity which is for a pure solid phase

$$SI_i = Kp_i \cdot \prod_{k=1}^{N_X} \{X_k\}^{ap_{i,k}} = 1 \tag{2}$$

The conservation of the total concentration $[T_j]$ of the jth component in the system is then written

$$[T_j] = \sum_{i=1}^{N_C} a_{i,j} \cdot [C_i] + \sum_{i=1}^{N_{CP}} ap_{i,j} \cdot [Cp_i] \tag{3}$$

where $[C_i]$ is the concentration of species C_i and $[Cp_i]$ is the amount of precipitated species Cp_i per liquid volume unit.

The activity of species C_i (respectively, component X_j) is calculated by the following relation

$$\{C_i\} = \gamma_i \cdot \frac{[C_i]}{[C^\circ]} \text{ and } \{X_j\} = \gamma_j \cdot \frac{[X_j]}{[C^\circ]} \tag{4}$$

where $_i$ (respectively, $_j$) is the activity coefficient of species C_i (respectively, component X_j) and $[C^\circ]$ is the reference concentration: one mol per liter.

By substituting the mass action law (Eq. 1) in the mass conservation equation (Eq. 3), the following relationship, which depends only on the components and the precipitated species concentrations, is thus obtained

$$[T_j] = \sum_{i=1}^{N_C} a_{i,j} \cdot \left(\frac{K_i}{\gamma_i} \cdot \prod_{k=1}^{N_X} (\gamma_k \cdot [X_k])^{a_{i,k}} \right) + \sum_{i=1}^{N_{CP}} ap_{i,j} \cdot [Cp_i] \tag{5}$$

There are two ways by which this set of equations can be solved. The most commonly used consists of changing the set of components by taking the precipitated species as a new component into account instead of the nonprecipitated species (Westall, 1979). This method implies new calculations of the stoichiometric matrix $a_{i,j}$ and $ap_{i,j}$ and total concentration $[T_j]$. In order to minimize calculation time, we prefer to add both an unknown, the precipitated species amount, and an equation, its saturation index which equals one. It is a set of $(N_X + N_{CP})$ nonlinear algebraic equations which can be numerically solved through iterative methods. The values of the component $[X_k]$ and the precipitated species $[Cp_i]$ concentrations at equilibrium are then found when the $(N_X + N_{CP})$ objective functions Y_j equal zero

$$Y_j = -[T_j] + \sum_{i=1}^{N_C} a_{i,j} \left(\frac{K_i}{\gamma_i} \cdot \prod_{k=1}^{N_X} (\gamma_k \cdot [X_k])^{a_{i,k}} \right) + \sum_{i=1}^{N_{CP}} ap_{i,j} \cdot [Cp_i] \quad \text{for } j = 1 \text{ to } N_X$$

$$Y_{j=N_X+i} = 1 - Kp_i \cdot \prod_{k=1}^{N_X} (\gamma_k \cdot [X_k])^{ap_{i,k}} \quad \text{for } i = 1 \text{ to } N_{CP} \tag{6}$$

If some species can precipitate, a first equilibrium, called transitory equilibrium, is searched without taking any precipitated species into account ($N_{CP} = 0$) in Eq. 5. The saturation index is then calculated. If all the SIs are smaller than one, all the precipitated species are undersaturated and the final equilibrium is obtained at a first stage. If some species (chemical forms) are supersaturated, the SIs are greater than one and the most supersaturated chemical form is then taken into account ($N_{CP} = N_{CP} + 1$) in Eq. 5 for searching a new equilibrium. This procedure is repeated until all the SIs are equal to or smaller than one.

In the case of an ideal system assumption, the activity coefficients γ equal one. If an activity correction is required, approximations such as the Davies can be used for calculating activity coefficients (Stumm and Morgan, 1995). The equa-

tions are

$$\ln(\gamma_i) = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1+\sqrt{I}} - b \cdot I \right) \tag{7}$$

with

$$I = \frac{1}{2} \cdot \sum_i [C_i] \cdot z_i^2 \tag{8}$$

and

$$A = 1.82 \cdot 10^6 (\epsilon_w T)^{-3/2} \tag{9}$$

I is the ionic strength and z_i is the charge of the species C_i. At $T = 298$ K and for water (dielectric constant $\epsilon_w = 78.5$), A 0.5. Davies has proposed $b = 0.3$ or 0.2 (Stumm and Morgan, 1995). In our calculation, we chose $b = 0.24$ (Morel, 1983).

Comparison of Methods

Newton-Raphson method

Equation 5 is solved with the Newton-Raphson method (Westall, 1979), at the nth iteration with the Jacobian matrix Z^n of the objective functions

$$Z^n_{j,k}\Big|_{\substack{j=1,N_X+N_{CP} \\ k=1,N_X}} = \frac{\partial Y_j^n}{\partial [X_k]^n}$$

$$Z^n_{j,k}\Big|_{\substack{j=1,N_X+N_{CP} \\ k=N_X+1,N_X+N_{CP}}} = \frac{\partial Y_j^n}{\partial [CP_{k-N_X}]^n} \tag{10}$$

Z^n can be calculated by two ways. (a) From an analytical computation, we obtain the $(N_X + N_{CP})^*(N_X + N_{CP})$ values of Z^n by

$$Z^n_{j,k}\Big|_{\substack{j=1,N_X \\ k=1,N_X}} = \sum_{i=1}^{N_C} a_{i,j} \cdot a_{i,k} \frac{[C_i]^n}{[X_k]^n}$$

$$Z^n_{j,k}\Big|_{\substack{j=1,N_X \\ k=N_X+1,N_X+N_{CP}}} = ap_{k-N_{X,j}}$$

$$Z^n_{j,k}\Big|_{\substack{j=N_X+1,N_X+N_{CP} \\ k=1,N_X}} = ap_{k-N_X,j} \cdot \frac{SI^n_{j-N_X}}{[X_k]^n}$$

$$Z^n_{j,k}\Big|_{\substack{j=N_X+1,N_X+N_{CP} \\ k=N_X+1,N_X+N_{CP}}} = 0 \tag{11}$$

Activity coefficients are assumed to be constant for the Jacobian calculation. (b) From the first-order approximation of Eq. 10, we obtain the relationship 12. The progress step of the method ΔX^n (Eq. 13) is obtained by assuming that the objective function Y^{n+1} in Eq. 13 has to equal zero at the $(n+1)^{\text{th}}$ iteration

$$Z^n = \frac{Y^{n+1} - Y^n}{\Delta X^n} \tag{12}$$

$$\Delta X^n = -(Z^n)^{-1} \cdot Y^n \tag{13}$$

The values of the component concentrations at the $(n+1)^{\text{th}}$ iteration are

$$[X]^{n+1} = [X]^n + \Delta X^n \tag{14}$$

The new component concentrations are used for calculating the activity coefficients, which will be assumed constant during all the $(n+1)^{\text{th}}$ iteration. Activity correction is then cal-

Table 1. Morel's Tableau for the Gallic Acid Test with pH Fixed to 5.8*

Species	H^+	Al^{3+}	H_3L	log K	Equilib. (M)
H^+	1	0	0	0	1.58×10^{-6}
Al^{3+}	0	1	0	0	2.03×10^{-5}
H_3L	0	0	1	0	2.59×10^{-7}
OH^-	−1	0	0	−14	6.31×10^{-9}
H_2L^-	−1	0	1	−4.15	1.16×10^{-5}
HL^{2-}	−2	0	1	−12.59	2.65×10^{-8}
L^{3-}	−3	0	1	−23.67	1.39×10^{-13}
$AlHL^+$	−2	1	1	−4.93	2.45×10^{-5}
AlL	−3	1	1	−9.43	4.90×10^{-4}
AlL_2^{3-}	−6	1	2	−21.98	8.97×10^{-6}
AlL_3^{6-}	−9	1	3	−37.69	1.14×10^{-10}
$Al_2(OH)_2(HL)_3^{2-}$	−8	2	3	−22.65	4.01×10^{-6}
$Al_2(OH)_2(HL)_2L^{3-}$	−9	2	3	−27.81	1.75×10^{-5}
$Al_2(OH)_2(HL)L_2^{4-}$	−10	2	3	−32.87	9.61×10^{-5}
$Al_2(OH)_2L_3^{5-}$	−11	2	3	−39.56	1.24×10^{-4}
$Al_4L_3^{3+}$	−9	4	3	−20.25	2.61×10^{-7}
$Al_3(OH)_4(H_2L)^{4+}$	−5	3	1	−12.52	6.51×10^{-5}
Total (M)	pH 5.8	10^{-3}	10^{-3}		
Initial (M)	1.58×10^{-6}	variable	variable		
Equilib. (M)	1.58×10^{-6}	2.03×10^{-5}	2.59×10^{-7}		

*Initial concentrations for Al^{3+} and H_3L component are variable.
†Thermodynamic values are from Brassard and Bodurtha (2000).

culated through Picard iterations using concentration values of the n^{th} iteration.

The iteration procedure is used until the convergence criteria for the mass balance (Eq. 15) and for the saturation index when precipitation occurs (Eq. 16) are reached for every component with $\epsilon = 10^{-9}$.

$$\left| \frac{-[T_j] + \sum_{i=1}^{N_C} a_{i,j} \cdot [C_i] + \sum_{i=1}^{N_{CP}} ap_{i,j} \cdot [Cp_i]}{[T_j] + \sum_{i=1}^{N_C} |a_{i,j}| \cdot [C_i] + \sum_{i=1}^{N_{CP}} |ap_{i,j} \cdot [Cp_i]} \right| \leq \epsilon \text{ for } j = 1 \text{ to } N_X \quad (15)$$

$$\left| 1 - Kp_i \prod_{k=1}^{N_{CP}} (\gamma_k \cdot [X_k])^{ap_{i,k}} \right| \leq \epsilon \text{ for } i = 1 \text{ to } N_{CP} \quad (16)$$

The criterion given by Eq. 15 ensures that the solution is obtained with the same precision for every component in the system, whatever are the low or very high concentrations.

A singular or near-singular Jacobian matrix of the objective functions (Reed, 1982) is unfortunately not the only condition for the nonconvergence of the Newton-Raphson method. Walsh et al. (1984) have reported that poor initial root guesses may cause convergence difficulties, and Brassard and Bodurtha (2000) have recently shown the high sensitivity of first- and second-order methods with respect to the initial vector of components for gallic acid (Table 1). For many starting points (Figure 1a), the Newton-Raphson method is blocked in a loop and turns infinitely (Figure 2a).

Nonconvergence of the Newton-Raphson method can occur in a field of great environmental importance. Pyrite (FeS_2), which is the most abundant metal sulfide on Earth, is involved in many processes such as formation of acid mine drainage, redox cycling of metals in sediments, oxic-anoxic boundaries of sediments or estuaries, flotation, and nuclear waste disposals (Singer and Stumm, 1970; Morse et al., 1987;

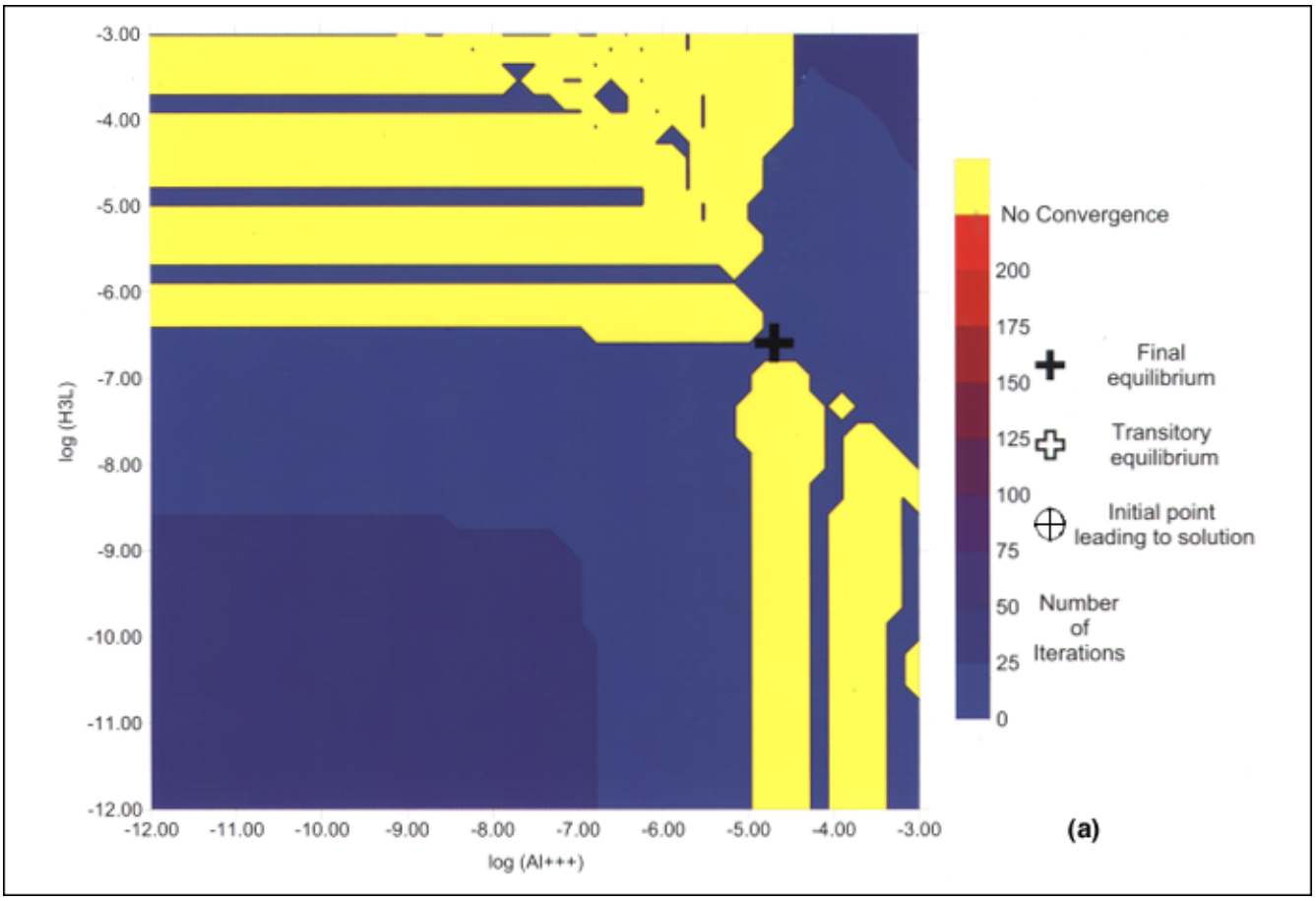

Figure 1. Convergence map.

They report if the solution is achieved and provide the number of iterations needed for convergence. X- and Y-axes correspond to the 50×50 initial component concentration vectors used to initiate the system's resolution. (a) Resolution of the gallic acid test with the Newton-Raphson method starting in nonconvergence zones (yellow) trapped in the infinite loop; (b) resolution of the FeS_2 test with the Newton-Raphson method (with initial concentrations of 0.1 μm for H^+ and 1 mM for O_2). Seven starting points only lead to the solution after around 250 iterations. Transitory equilibrium is calculated first. Final equilibrium is reached for the precipitation of FeS_2; (c) resolution of the FeS_2 test with the Newton-Raphson method on CAI (with initial concentrations of 0.1 μM for H^+ and 1 mM for O_2). Only some starting points induce nonconvergence; (d) resolution of the gallic acid test with the combined algorithm with convergence reaching starting points. Blue zones (before yellow) show the influence of the preconditioning method, red ones show the interest of the reconditioning method. (Figure continued on next page).

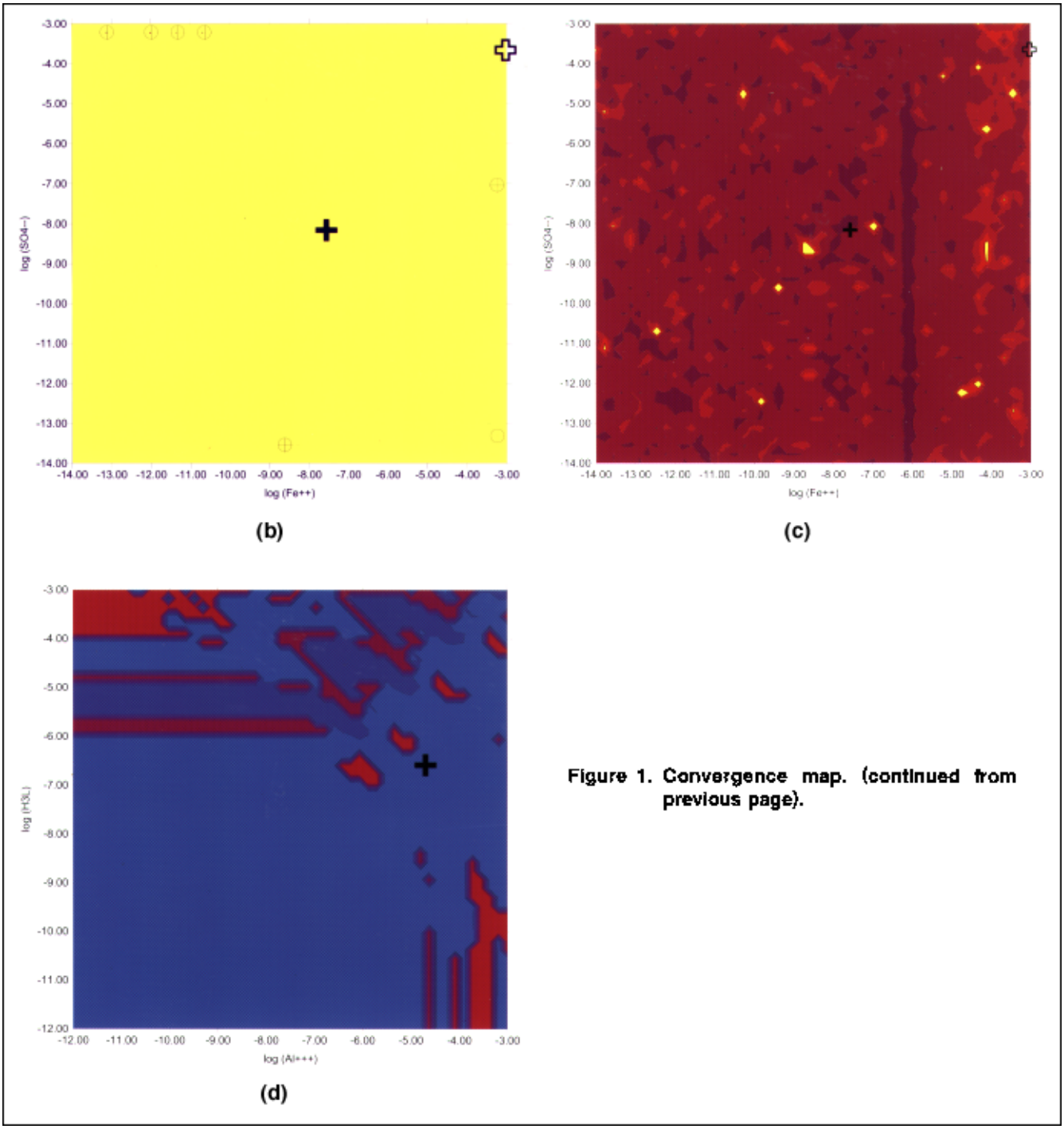

Figure 1. Convergence map. (continued from previous page).

Chilakapati, 1999; Lalvani et al., 1991; Bosch, 1999). It is therefore very important to calculate the FeS_2 oxidation without any convergence problem knowing the complexity of thermodynamic equilibria. The use of analytical solutions avoids a convergence problem but leads to severe simplifications of a chemical problem, as shown by comparing the three major reactions analytically used by Chilakapati (1999) and the complexity of the 52 species reported in Table 2. The system is nonideal and activity are corrected using Davies approximation (Eq. 7). Nevertheless, complexity induces convergence problems. The inefficiency of the Newton-Raphson method is mainly due to the initial dissolved oxygen concentration (Figure 1b). In such a case, the system is assumed to be closed without any contact with the atmosphere. The infiltrated meteoritic water is assumed to be in equilibrium with the atmospheric oxygen, that is, initial O_2 concentration = 1 mM. The total concentration of the component O_2 is negative to respect the mass balance for the formation of 1 mmol

FeS_2 in one liter with the chosen set of components

$$Fe^{2+} + 2SO_4^{2-} + 2H^+ - \frac{7}{2}O_2 \rightarrow FeS_2 + H_2O \qquad (17)$$

The component H_2O, which is the solvent, was omitted in Table 2, because its activity is constant and equal to one. As shown in Figure 2b, the Newton-Raphson method can give excessive concentrations, which are physically unacceptable.

Chemically allowed interval (CAI)

It has been proven (Weltin, 1990) that the objective function (Eq. 5) has a unique solution in the CAI, defined as $0 < [X_j] < T_j$. However, this definition is restricted to chemical systems where all stoichiometric coefficients are positive. For the most general chemical system, we define the CAI as $0 < [X_j] < Max_j$ and set a definition of the upper limit (Max_j) of the CAI based on the limiting reactive notion

$$\mathrm{Max}_j = [T_j] + \sum_{i=1}^{N_C} |a_{i,j}|_{a_{i,j}<0} \cdot (\min|a_{i,k}| \cdot [T_k]|_{a_{i,k}>0}) \qquad (18)$$

It can be seen in the FeS_2 test-case (Table 2) that the Newton-Raphson method can overstep the CAI and then can give

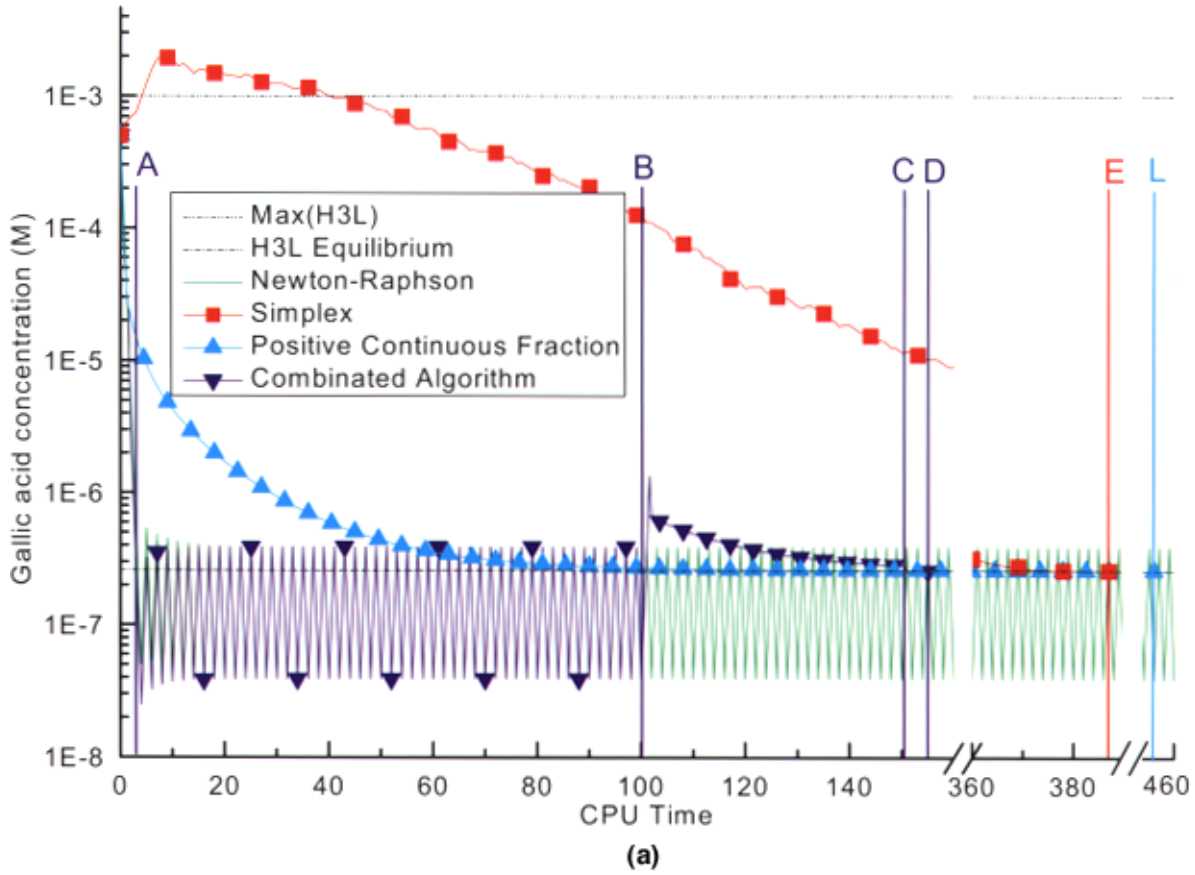

Figure 2. Newton-Raphson, Newton-Raphson on CAI, simplex, positive continuous fraction methods, and the combined algorithm.

X-axis gives the CPU time; unity is the time needed for one Newton-Raphson iteration. Line A corresponds to iteration when the combined algorithm leaves preconditioning with positive continuous fraction method for searching the solution with the Newton-Raphson method. Line D represents the end point of the combined algorithm with the Newton-Raphson method: (a) gallic acid test (from pH 5.8, 0.01 nM Al^{3+} and 0.5 mM H_3L). Line A, iteration 2; Line B, iteration 101, where the combined algorithm overruns maximum iterations allowed for the Newton-Raphson, and reconditioning by positive continuous fraction method; Line C, iteration 151, where the combined algorithm is close enough to the solution and leaves reconditioning by positive continuous fraction method for searching the solution with the Newton-Raphson method; Line D, iteration 155; Line E, iteration 392 corresponds to convergence with the Simplex method; Line L, iteration 457; convergence of the positive continuous fraction method. The Newton-Raphson method does not converge. (b) FeS_2 test (from pH 7, 1 mM O_2, 1 mM Fe^{2+} and 2 mM SO_4^{2-}). Line A, iteration 7; Line D, iteration 48; Line F, iteration 16 corresponds to the convergence to the transitory equilibrium of the combined algorithm with the Newton-Raphson method. Line G, iteration 193, where convergence to the transitory equilibrium of the Newton-Raphson method. Line H, iteration 225, where the Newton-Raphson method finally converges; Line I, iteration 108, where the Newton-Raphson method with respect of the CAI converges to the transitory equilibrium; Line J, iteration 140, where the Newton-Raphson method with respect of the CAI finally converges; Line K, iteration 300, where convergence to the transitory equilibrium of the positive continuous fraction method; iteration of 2 millions corresponds to convergence of the positive continuous fraction method. The Newton-Raphson method does not converge. The Simplex method does not converge and then stays blocked at the point: 0.132 μM H^+, 1.2 mM O^2, 1.22 mM Fe^{2+} and 0.995 mM SO_4^{2-}. Convergence with the Newton Raphson method is obtained if the starting point is: pH 7, 1 mM O_2, 596.4 μM Fe^{2+}, and 91.03 nM SO_4^{2-}.

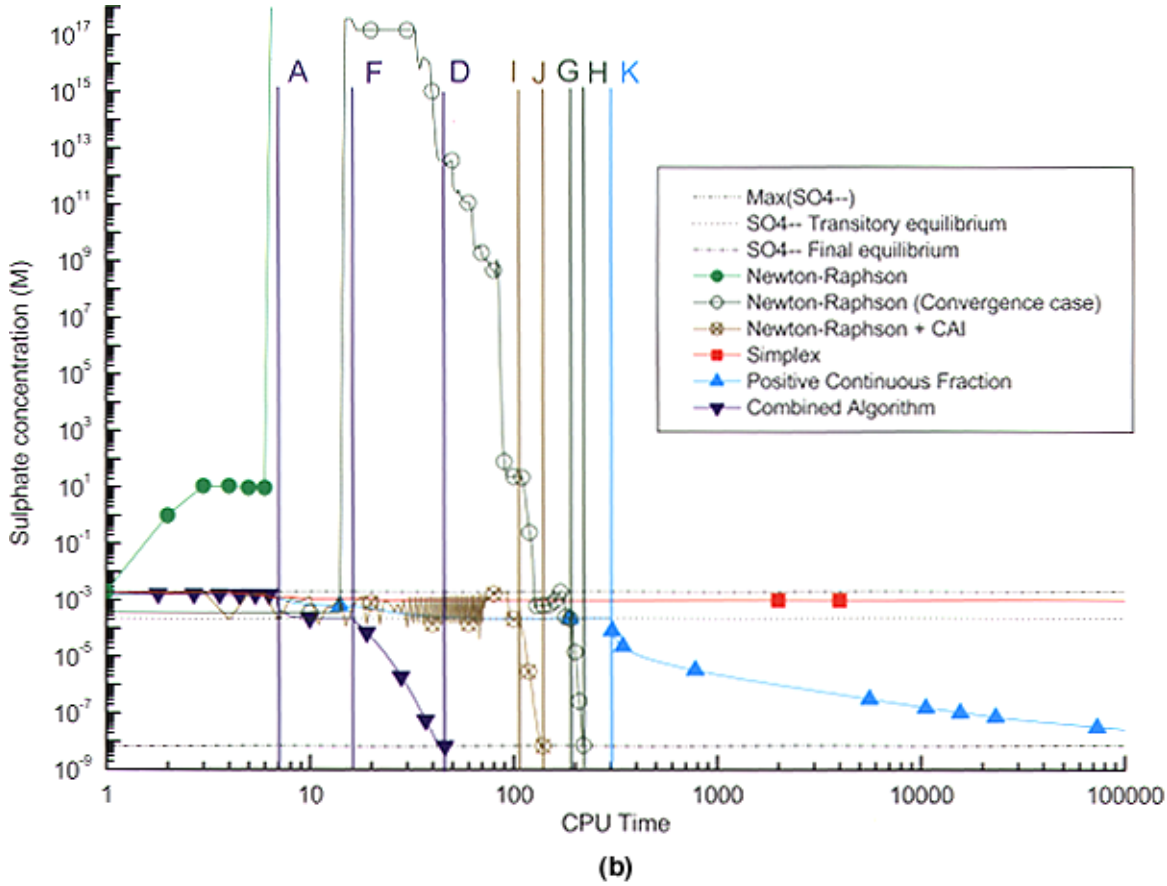

Figure 2. Newton-Raphson, Newton-Raphson on CAI, Simplex, positive continuous fraction methods, and the combined algorithm. (Continued from previous page).

concentrations which are much too high (see Figure 2b). Imposing a CAI appears thus as an important condition in a robust algorithm. The lowest limit of this interval, zero, is intuitive and has been taken into account by many computer codes. Morel and Morgan (1972) have proposed the following rule which has been used by Westall (1979) for the computer code MICROQL

$$\text{if } \left[X_j\right]^n + \Delta X_j^n < 0 \text{ then } \left[X_j\right]^{n+1} = \frac{\left[X_j\right]^n}{10} \qquad (19)$$

We propose the new rule to impose the upper limit of the CAI

$$\text{if } \left(\left[X_j\right]^n + \Delta X_j^n > \text{Max}_j\right) \text{ then } \left(\log\left(\left[X_j\right]^{n+1}\right) = \frac{\log\left(\text{max}_j\right) + \log\left(\left[X_j\right]^n\right)}{2}\right) \qquad (20)$$

For the H^+ component, to impose the pH in the usual domain, the lowest limit of the CAI is 10^{-14} and the upper limit is the smallest value 1 or Max_{H^+} as computed from Eq. 18. From these definitions, the CAI for the FeS_2 test case is between 10^{-14} and 32.5 mM, 0 and 286.3 mM, 0 and 1 mM, and 0 and 2 mM for components H^+, O_2, Fe^{2+}, and SO_4^{2-}, respectively.

By imposing the CAI in the Newton-Raphson algorithm, we avoid the risk of major overestimation in the FeS_2 test case (Figure 2b). The solution is then reached for a majority of starting points (see Figure 1c). This improvement is easy to introduce and very inexpensive in terms of computing time. Although very efficient for some cases, no improvement of convergence can be observed if the loop phenomena belongs to the CAI as, for example, the gallic acid test (Figure 2a).

Continuous fraction method

The continuous fraction method has been used to solve thermodynamic equilibrium in the computer code WATSPEC (Wigley, 1977), or for pre-conditioning the Newton-Raphson method for the major species in the PHREEQC code (Parkhurst and Appelo, 1999). This method, which only needs one computation of the approximate thermodynamic equilibrium per iteration, is the cheapest zero-order method. The iteration procedure is

Table 2. Morel's Tableau for the FeS_2 Test*

Species	H^+	O_2	Fe^{2+}	SO_4^{2-}	log K	Equilibrium (M)	Activity Coefficient
Aqueous							
H^+	1	0	0	0	0	9.24×10^{-8}	0.9998
OH^-	−1	0	0	0	−14	1.08×10^{-7}	0.9998
O_2	0	1	0	0	0	0.0	1
Fe^{2+}	0	0	1	0	0	2.73×10^{-8}	0.9991
$Fe(OH)_2$	−2	0	1	0	−20.6	8.03×10^{-15}	1
$Fe(OH)_3^-$	−3	0	1	0	−31	3.46×10^{-18}	0.9998
$FeOH^+$	−1	0	1	0	−9.5	9.35×10^{-11}	0.9998
$FeSO_4$	0	0	1	1	2.2	2.96×10^{-14}	1
Fe^{3+}	1	0.25	1	0	8.49	0.0	0.9980
$Fe(OH)_2^+$	−1	0.25	1	0	2.82	1.12×10^{-16}	0.9998
$Fe(OH)_3$	−2	0.25	1	0	−3.5	5.68×10^{16}	1
$Fe(OH)_4^-$	−3	0.25	1	0	−13.11	1.55×10^{-18}	0.9998
$FeOH^{2+}$	0	0.25	1	0	6.3	3.14×10^{-20}	0.9991
$Fe_2(OH)_2^{4+}$	0	0.5	2	0	14.03	0.0	0.9965
$Fe_3(OH)_4^{5+}$	−1	0.75	3	0	19.17	0.0	0.9946
$Fe(SO_4)_2^-$	1	0.25	1	2	11.7	0.0	0.9998
$FeSO_4^+$	1	0.25	1	1	10.4	0.0	0.9998
SO_4^{2-}	0	0	0	1	0	6.86×10^{-9}	0.9991
HSO_4^-	1	0	0	1	1.98	6.05×10^{-14}	0.9998
H_2SO_4	2	0	0	1	−1.02	0.0	1
SO_3^{2-}	0	−0.5	0	1	−46.62	4.97×10^{-19}	0.9991
HSO_3^-	1	−0.5	0	1	−39.42	7.27×10^{-19}	0.9998
H_2SO_3	2	−0.5	0	1	−37.41	0.0	1
SO_2	2	−0.5	0	1	−37.56	0.0	1
$HS_2O_3^-$	3	−2	0	2	−132.52	0.0	0.9998
$S_2O_3^{2-}$	2	−2	0	2	−133.54	9.64×10^{-19}	0.9991
H_2S	2	−2	0	1	−131.33	2.28×10^{-8}	1
HS^-	1	−2	0	1	−138.32	2.52×10^{-8}	0.9998
S^{2-}	0	−2	0	1	−151.25	3.21×10^{-14}	0.9991
S_2^{2-}	2	−3.5	0	2	−243.37	3.93×10^{-19}	0.9991
S_3^{2-}	4	−5	0	3	−335.56	0.0	0.9991
S_4^{2-}	6	−6.5	0	4	−427.97	0.0	0.9991
S_5^{2-}	8	−8	0	5	−520.60	0.0	0.9991
$S_2O_4^{2-}$	2	−1.5	0	2	−118.46	0.0	0.9991
$S_2O_5^{2-}$	2	1	0	2	−83.65	0.0	0.9991
$S_2O_6^{2-}$	2	−0.5	0	2	−51.42	0.0	0.9991
$S_2O_8^{2-}$	2	0.5	0	2	−22.5	0.0	0.9991
$S_3O_6^{2-}$	4	−2	0	3	−146.1	0.0	0.9991
$S_4O_6^{2-}$	6	−0.35	0	4	−22.88	0.0	0.9991
$S_5O_6^{2-}$	8	−5	0	5	−332.54	0.0	0.9991
Mineral							
Fe(s)	−2	−0.5	1	0	−59.03	0.0	
S(s)	2	−1.5	0	1	−93.22	0.0	
$Fe(OH)_2$	−2	0	1	0	−13.90	0.0	
$Fe(OH)_3$	−2	0.25	1	0	2.83	0.0	
$Fe(SO_4)_3$	2	0.5	2	3	13.77	0.0	
FeO	−2	0	1	0	−13.53	0.0	
$FeSO_4$	0	0	1	2	−2.66	0.0	
Goethite	−2	0.25	1	0	7.95	0.0	
Hematite	−4	0.5	2	0	16.87	0.0	
Melanterite	0	0	1	1	2.35	0.0	
Pyrite	2	−3.5	1		−217.40	9.9997×10^{-4}	
Pyrrhotite	0	−2	1	1	−134.6	0.0	
Wustite	−1.894	0.0265	0.947	0	−11.51	0.0	
Total (M)	2×10^{-3}	-3.5×10^{-3}	1×10^{-3}	2×10^{-3}			
Initial (M)	1×10^{-7}	1×10^{-3}	variable	variable			
Transitory equilib. (M)	1.93×10^{-8}	3.35×10^{-74}	9.58×10^{-4}	2.23×10^{-4}			
Equilib. (M)	9.24×10^{-8}	1.10×10^{-73}	2.73×10^{-8}	6.86×10^{-9}			

*Total concentrations correspond to 1 mmol FeS_2 dissolution in 1 L pure water. Equilibrium is obtained after precipitation of pyrite. Activity is corrected using Davies approximation. Thermodynamic values are from CHESS data base (van der Lee, 1998); Ionic strength $I = 1.81\times10^{-7}$ at $T = 298$ K. Activity of pure mineral = 1.

$$[X_j]^{n+1} = [X_j]^n \cdot \frac{[T_j]}{\sum_{i=1}^{N_C} a_{i,j} \cdot [C_i]^n} \quad (21)$$

However, the method is inoperative for systems in which a component has a zero total concentration $[T_j]$, as can be seen in relationship 21. The method can also diverge if some stoichiometric coefficients are negative. Often, the component H^+ has a zero total concentration and is associated with negative stoichiometric coefficients. In the code WATSPEC (Wigley, 1977), the pH value must be imposed to find the thermodynamic equilibrium. Hydrogen and oxygen are excluded from the continuous fraction pre-conditioning in the code PHREEQC (Parkhurst and Appelo, 1999). Moreover, it has never been used for nonideal system.

Positive continuous fraction method

We define two new values to take into account a component with zero (H^+ case) or negative (ion-exchange) total concentration, and to be more efficient with negative stoichiometric coefficients. The *reactive sum* is defined by Eq. 22 or 24 and the *product sum* by Eq. 23 or 25. The *reactive* (respectively, *product*) adjective refers to the C_i species where the component X_j is a reactive, that is, $a_{i,j} > 0$ (respectively, product, that is, $a_{i,j} < 0$).

If $[T_j] \geq 0$

$$\mathrm{Sum}_j^{\mathrm{reac}} = \sum_{a_{i,i} > 0} a_{i,j} \cdot [C_i] \quad (22)$$

$$\mathrm{Sum}_j^{\mathrm{prod}} = [T_j] + \sum_{a_{i,i} < 0} |a_{i,j}| \cdot [C_i] \quad (23)$$

If $[T_j] < 0$

$$\mathrm{Sum}_j^{\mathrm{reac}} = |[T_i]| + \sum_{a_{i,i} > 0} a_{i,j} \cdot [C_i] \quad (24)$$

$$\mathrm{Sum}_j^{\mathrm{prod}} = \sum_{a_{i,j} < 0} |a_{i,i}| \cdot [C_i] \quad (25)$$

Using these two new values, the mass balance Eq. 3 is written, without precipitation, at equilibrium

$$\mathrm{Sum}_j^{\mathrm{reac}} = \mathrm{Sum}_j^{\mathrm{prod}} \quad (26)$$

We choose a species C_{i0}, for which the stoichiometric coefficient $a_{i0,j}$ for component X_j is not zero. Very often, C_{i0} can be chosen equal to X_j. For other cases, we propose to take $a_{i0,j}$ as the smallest value of the strictly positive stoichiometric coefficient. The mass action laws are written for the reactive sum if $a_{i0,j}$ is positive (respectively, for the product sum if $a_{i0,j}$ is negative) by using component concentrations at iterations n and $(n+1)$

$$\left(\gamma_j [X_j]^{n+1}\right)^{a_{i0,j}} \cdot \left[\sum_{a_{i,j} > 0} a_{i,j} \cdot K_i \prod_{k \neq j} \left(\gamma_k [X_k]^n\right)^{a_{i,k}} \cdot \left(\gamma_j [X_j]^n\right)^{a_{i,j} - a_{i0,j}} \right] = [T_j] + \sum_{a_{i,j} < 0} |a_{i,j}| \cdot [C_i]^n \quad (27)$$

After reordering, it becomes

$$\left(\gamma_j [X_j]^{n+1}\right)^{a_{i0,j}} = \frac{\left(\gamma_j [X_j]^n\right)^{a_{i0,j}}}{\left(\gamma_j [X_j]^n\right)^{a_{i0,j}}} \times \frac{[T_j] + \sum_{a_{i,j} < 0} |a_{i,j}| \cdot [C_i]^n}{\sum_{a_{i,j} > 0} a_{i,j} \cdot K_i \prod_{k \neq j} \left(\gamma_k [X_k]^n\right)^{a_{i,k}} \cdot \left(\gamma_j [X_j]^n\right)^{a_{i,j} - a_{i0,j}}} \quad (28)$$

Since the product and reactive sums appear in Eq. 28, we obtain the relationship 29 giving $[X_j]$ at the $(n+1)^{\mathrm{th}}$ iteration

$$[X_j]^{n+1} = [X_j]^n \cdot \left(\frac{\mathrm{Sum}_j^{\mathrm{prod},n}}{\mathrm{Sum}_j^{\mathrm{reac},n}} \right)^{1/a_{i0,j}} \quad (29)$$

In relationship 29, the impact of the modification of the concentration $[X_k]$ over the Y_j function, as with all the zero-order methods, is not taken into account. The simultaneous modification of all component concentrations can induce unfavorable oscillations. In the positive continuous fraction method, the weighted mean given in relationship 30 is then used to calculate the Nx component concentrations at the $(n+1)^{\mathrm{th}}$ iteration, with θ between 0 and 1. This ensures convergence for certain

$$[X_j]^{n+1} = \theta \cdot [X_j]^n \cdot \left(\frac{\mathrm{Sum}_j^{\mathrm{prod},n}}{\mathrm{Sum}_j^{\mathrm{reac},n}} \right)^{1/a_{i0,j}} + (1-\theta) \cdot [X_j]^n \quad (30)$$

For a high θ value, such as $\theta = 0.9$, the near solution is reached quickly. Indeed, this corresponds to dividing (respectively, multiplying) the $[X_j]$ value per 10 if this value is much higher (respectively, lower) than the equilibrium value. Close to the solution, a small θ value ($\theta = 0.1$) avoids oscillations and ensures convergence. θ is thus calculated as an adaptive parameter

$$\text{if } \left(\mathrm{Sum}_j^{\mathrm{reac}} > \mathrm{Sum}_j^{\mathrm{prod}}\right) \text{ then } \left(\theta_j = 0.9 - \frac{\mathrm{Sum}_j^{\mathrm{prod}}}{\mathrm{Sum}_j^{\mathrm{reac}}} \cdot 0.8 \right)$$

$$\text{if } \left(\mathrm{Sum}_j^{\mathrm{reac}} < \mathrm{Sum}_j^{\mathrm{prod}}\right) \text{ then } \left(\theta_j = 0.9 - \frac{\mathrm{Sum}_j^{\mathrm{reac}}}{Sum_j^{\mathrm{prod}}} \cdot 0.8 \right) \quad (31)$$

If there is some precipitated species, the procedure is the same as presented in the modeling part, that is, research of the transitory equilibrium without precipitation, calculation of the *SI*, precipitation of the more supersaturated species Cp_i, and research of a new equilibrium.

We choose a component X_j which is reactive ($ap_{i,j}$ positive) for the precipitation of Cp_i. The precipitated species Cp_i controls the mass balance relationship for the component X_j

$$[Cp_i]^{n+1} = [T_j] - \frac{1}{a_{i,j}} \left(\sum_{k=1}^{N_C} a_{k,j}[C_k]^n - \sum_{\substack{k=1 \\ k \neq i}}^{N_{CP}} ap_{k,j}[Cp_k]^n \right) \tag{32}$$

The component X_j controls the saturation index of species Cp_i through the new definition of the *product sum*

$$\mathrm{Sum}_j^{\mathrm{prod}} = 1 \tag{33}$$

and the *reactive sum*

$$\mathrm{Sum}_j^{\mathrm{reac}} = \left(Kp_i \prod_{k=1}^{N_X} \left(\gamma_k [X_k]^n \right)^{ap_{i,k}} \right)^{1/ap_{i,j}} \tag{34}$$

Equations 22 to 25 are used for the other components. The iteration procedure to find the current equilibrium is first Eq. 32 for all the precipitated species, and then Eq. 30 for all the components with θ calculated with Eq. 31. Convergence is obtained if

$$\frac{|\mathrm{Sum}_j^{\mathrm{reac}} - \mathrm{Sum}_j^{\mathrm{prod}}|}{\mathrm{Sum}_j^{\mathrm{reac}} + \mathrm{Sum}_j^{\mathrm{prod}}} \leq \epsilon \tag{35}$$

for all the components.

Since the positive continuous fraction method does not need computation and inversion of the Jacobian of objective functions, one iteration is much faster with this new method than with the Newton-Raphson or other first-order methods, such as twice for the gallic acid test and 10 times faster for the FeS_2 test. Moreover, the positive continuous fraction method very quickly reaches close solution, but it takes some time to get a precise convergence (Figure 2a), whereas the Simplex method takes a long time far from the solution before finding the right way and quickly converging. This method appears to be very attractive for approximating the solution. Moreover, the solution of the FeS_2 test can be obtained with the positive continuous fraction method when other methods cannot (Figure 2b). The Simplex or Newton-Raphson methods are based on the slope of the objective function to search the solution. For initial value of the O_2 component concentration close to 1 mM, both methods cannot converge due to high iron and sulfate values. On the contrary, the positive continuous fraction method, which does not depend on the slope of the objective function, is thus insensitive to local minima and infinite loop phenomena (Figure 2) and gives the solution of the gallic and the FeS_2 tests with whatever initial point is used.

A New Efficient Combined Algorithm

The positive continuous fraction method is a new, very robust and fast zero-order numerical method to approach thermodynamic equilibrium of complex chemical systems. By coupling this method with a first-order method which quickly converges near the solution, a combined algorithm, impressive with respect to the criteria of reliability, robustness, and quickness, is then obtained. In order to be close to the solution and use the Newton-Raphson method in the best conditions, a first step to the solution with the positive continuous fractions method (pre-conditioning) is performed under the assumption of an ideal system. When the error is less than 50%, the accurate solution is searched with the Newton-Raphson method (see Figure 2b) associated with the respect of the CAI for the real system. Some nonconvergence areas can be very close to the solution (Figure 1a), and the pre-conditioning is thus inefficient, as shown in Figures 1d and 2a. If the Newton-Raphson method does not converge after the maximum allowed number of iterations, the solution research continues with the positive continuous fraction method (re-conditioning) for the real system. For a relative error less than 5%, the final solution is then found with the fast Newton-Raphson method. For the FeS_2 test during the pre-conditioning, the O_2 value, which is responsible for the nonconvergence, quickly decreases. In this case, the solution for every initial values reported in Figure 1b is found with the combined algorithm. Moreover, the CPU time is five times faster (48 iterations) than with the Newton-Raphson method (250 iterations) for the seven initial values where convergence is observed (Figure 2b). The efficiency of the re-conditioning is shown from the gallic acid test for which the solution is found for every starting point (Figure 1d).

This new algorithm, which makes the resolution of highly nonlinear algebraic chemical system more robust, rapid, and without any constraint about the initial values, should also be useful for the resolution of all nonlinear algebraic systems.

Conclusion

In this article, we thus propose to associate a new method, the positive continuous fraction, a new constraint, respecting the chemically allowed interval (CAI) and the Newton-Raphson method, for solving nonlinear algebraic systems which cannot be solved using the classical Newton-Raphson method. Efficiency of the positive continuous fractions method for pre- or re-conditioning and of the CAI for robustness are shown in their association with the simplest Newton-Raphson method in the combined algorithm. For each specific problem, an adapted relaxation technique can be implemented in the Newton-Raphson method. The new combined algorithm will thus be strengthened and accelerated by the use of the efficient Positive Continuous Fraction pre- or re-conditioning, by imposing the CAI and by the specific relaxation technique.

The implementation of this combined algorithm in reactive transport code instead of the classical ones shall highly increase the robustness of the chemical module. This algorithm converges even if initial conditions are far from equilibrium. This allows greater transport time steps and the modeling of very sharp concentration fronts. Some subsequent computing time reduction shall be induced: each thermodynamic equilibrium is computed faster, and the increase in the transport time steps should reduce their number. Finally, the reactive transport code which includes this combined algorithm shall be able to induce new predictions which are more detailed

and, over a longer period, in sensible domains such as contaminant migration or nuclear waste disposal assessment.

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Notation

$a_{i,j}$ = stoichiometric coefficient of component X_j for the formation of species C_i
$ap_{i,j}$ = stoichiometric coefficient of component X_j for the formation of precipitated species Cp_i
A = parameter for Davies activity correction ($A \approx 0.5$ at 298 k)
b = parameter for Davies activity correction ($b = 0.24$ at 298 k)
C_i = species
Cp_i = precipitated species
$[Cp_i]$ = amount of precipitated species Cp_i per liquid volume unit, M
$[C^\circ]$ = reference concentration $[C^\circ] = 1$ M
I = ionic strength
K_i = equilibrium constant for the formation of species C_i
Kp_i = precipitation constant for the formation of precipitated species Cp_i
Ks_i = solubility product of precipitated species Cp_i
Max_j = upper limit of the chemically allowed interval for component X_j, M
N_C = number of species
N_{CP} = number of precipitated species
N_X = number of components
SI_i = saturation index of precipitated species Cp_i
$\mathrm{Sum}_j^{\mathrm{prod}}$ = product sum for component X_j, M
$\mathrm{Sum}_j^{\mathrm{reac}}$ = reactive sum for component X_j, M
T = temperature ($T = 298$ K)
$[T_j]$ = total concentration of component X_j, M
X_j = component
Y_j = objective function for component X_j, M
$T_{j=N_X+i}$ = objective function for precipitated species Cp_i
z_i = electric charge of species C_i
Z^n = Jacobian matrix of the objective functions at iteration n
$Z^n_{j,k}$ = Jacobian matrix coefficient at iteration n
γ_i = activity coefficient of species C_i
ΔX^n = progress step of the Newton-Raphson method at iteration n (M)
ϵ = precision criterion of the methods ($\epsilon = 10^{-9}$)
ϵ_w = dielectric constant of water ($\epsilon_w = 78.5$)
θ = weighted mean coefficient for the Positive Continuous Fraction method
i = subscript of species
j,k = subscript of component
n = superscript of iteration
[ ] = concentration, M
{ } = activity

Literature Cited

Bellot, J. C., R. V. Tarantino, and J. S. Condoret, "Thermodynamic Modeling of Multicomponent Ion-Exchange Equilibria of Amino Acids," *AIChE J.*, **45**, 1326 (1999).

Bosch, X., "Doñana Clean-up 'Left Half the Soil Still Contaminated'," *Nature*, **398**, 178 (1999).

Brassard, P., and P. Bodurtha, "A Feasible Set for Chemical Speciation Problems," *Comput. Geosci.*, **26**, 277 (2000).

Bryant, S. L., R. S. Schechter, and L. W. Lake, "Interactions of Precipitation/Dissolution Waves and Ion Exchange in Flow through Permeable Media," *AIChE J.*, **32**, 751 (1986).

Chilakapati, A., "Optimal Design of a Subsurface Redox Barrier," *AIChE J.*, **45**, 1342 (1999).

Kersting, A. B., D. W. Efud, D. L. Finnegan, D. J. Rokop, D. K. Smith, and J. L. Thompson, "Migration of Plutonium in Ground Water at the Nevada Test Site," *Nature*, **397**, 56 (1999).

Krebs, R., M. Sardin, and D. Schweich, "Mineral Dissolution, Precipitation and Ion Exchange in Surfactant Flooding," *AIChE J.*, **33**, 1371 (1987).

Lalvani, S. B., B. A. DeNeve, and A. Weston, "Prevention of Pyrite Dissolution in Acidic Media," *Corrosion*, **47**, 55 (1991).

Morel, F. M. M., and J. J. Morgan, "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems," *Environ. Sci. Technol.*, **6**, 58 (1972).

Morel, F. M. M., *Principles of Aquatic Chemistry*, Wiley Interscience, New York, 446 pp. (1983).

Morin, K. A., "Simplified Explanations and Examples of Computerized Methods for Calculating Chemical Equilibrium in Water," *Comput. Geosci.*, **11**, 409 (1985).

Morse, J. W., F. J. Millero, J. C. Cornwall, and D. Rickard, "The Chemistry of the Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters," *Earth Sci. Rev.*, **24**, 1 (1987).

Nelder, J. A., and R. Mead, "A Simplex Method for Function Minimization," *Comput. J.*, **7**, 308 (1965).

Nordstrom, D. K., and J. W. Ball, "Chemical Models, Computer Programs and Metal Complexation in Natural Waters," *Complexation of Trace Metals in Natural Waters*, C. J. M. Kramer and J. C. Duinker, eds., M. Nijhoff and W. Junk (Publishers), The Hague, The Netherlands (1984).

Parkhurst, D. L., and C. A. J. Appelo, "User's Guide to PHREEQC (version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations," Water-Resour. Invest. Rep. 99-4259, U.S. Geological Survey, Denver, CO (1999a).

Partehurst, D. L., and C. A. J. Appelo, "PHREEQC: http://water.usge.gov/software/phreege.htlm (1999b).

Reed, M. H., "Calculation of Multicomponent Chemical Equilibria and Reaction Processes in Systems Involving Minerals, Gases and an Aqueous Phase," *Geochem. Cosmochem. Acta*, **46**, 513 (1982).

Singer, P. C., and W. Stumm, "Acid Mine Drainage: The Rate Limiting Step," *Sci.*, **167**, 1121 (1970).

Stumm, W., and J. J. Morgan, *Aquatic Chemistry*, 3rd ed., Wiley-Interscience, New York, 1,040 pp. (1995).

Syed, F. H., R. Datta, and K. L. Jensen, "Thermodynamically Consistent Modeling of a Liquid-Phase Nonisothermal Packed-Bed Reactor," *AIChE J.*, **46**, 380 (2000).

van der Lee, J., "Thermodynamic and Mathematical Concepts of CHESS," Technical Report Nr. LHM/RD/98/39, Ecole Nationale Supérieure des Mines de Paris, Fontainebleau, France (1998a).

van der Lee, J., "CHESS: http://chess.ensmp.fr" (1998b).

Walsh, M. P., S. L. Bryant, R. S. Schechter, and L. W. Lake, "Precipitation and Dissolution of Solids Attending Flow through Porous Media," *AIChE J.*, **30**, 317 (1984).

Weltin, E., "Are the Equilibrium Concentrations for a Chemical Reaction Always Uniquely Determined by the Initial Concentrations?" *J. Chem. Educ.*, **67**, 548 (1990).

Westall, J. C., "MICROQL: a Chemical Equilibrium Program in BASIC. Computation of Adsorption Equilibria in BASIC," Swiss Federal Institute of Technology EAWAG, Dübendorf, Switzerland (1979).

White, A. F., J. M. Delany, T. N. Narasimhan, and A. Smith, "Groundwater Contamination from an Inactive Uranium Mill Tailings Pile: 1. Application of a Chemical Mixing Model," *Water Resour. Res.*, **20**, 1743 (1984).

Wigley, T. M. L., "WATSPEC: A Computer Program for Determining the Equilibrium Speciation of Aqueous Solutions," Brit. Geomorphol. Res. Group Tech. Bull. 20 (1977).

Wood, J. R., "Calculation of Fluid-Mineral Equilibria Using the Simplex Algorithm," *Comput. Geosci.*, **19**, 23 (1993).

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