

SIMPLIFIED EXPLANATIONS AND EXAMPLES OF COMPUTERIZED METHODS FOR CALCULATING CHEMICAL EQUILIBRIUM IN WATER

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Abstract—Simplified explanations and examples are provided for several methods for computing chemical equilibrium in water: Continuous-Fraction, Monotone-Sequences, Newton-Raphson, Secant, and Steffensens. The efficiencies of the methods are compared. Complexities caused by activity coefficients, precipitation-dissolution, variable pH, and variable pe (Eh) are discussed briefly.

Key Words: Aqueous speciation, Chemical equilibrium, Aqueous complexation.

INTRODUCTION

In the aqueous ion-pairing concept, computation of chemical equilibrium involves the calculation of concentrations of free ions, aqueous complexes, and ion pairs. Because of the large number of equations involved in the calculation, chemical equilibrium may be calculated by computer programs. There are many programs currently available for equilibrium calculations, as pointed out by Nordstrom and others (1979), however, these programs employ only a few specific methods for calculating equilibrium concentrations.

These methods can be categorized into three groups: (1) minimization of Gibb's Free Energy, (2) repetitive sequence of equations, and (3) solution of matrix equations. The first group is used rarely by hydrogeologists and low-temperature geochemists, and is not discussed in this paper; the remaining groups use equilibrium constants for the calculation of ion-pair and complex concentrations.

The methods briefly discussed here are presented in greater detail in the original references; however, one must spend much time with the abundance of superscripts, subscripts, and mathematics in the original references to gain a basic understanding. Also, some points discussed in this paper are not covered in the original references. Therefore, for hydrogeologists who wish to gain in a relatively short time a basic understanding of the methods and for those who wish a beginning point for the in-depth study of the methods, this paper presents simplified explanations and examples of general methods for the calculation of chemical species in water. In the examples, the simple aqueous system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 is analyzed. For the repetitive-sequence methods, a basic understanding of aqueous geochemistry and mathematics is

required; for the matrix-solvers, a basic understanding of partial derivatives and matrices also is required.

METHODS INVOLVING REPETITIVE SEQUENCES OF EQUATIONS

The two methods in this class are the Continuous-Fraction Method and the Monotone-Sequences Method.

Continuous-fraction method

This method is described in detail by Wigley (1977). The Continuous-Fraction Method involves a series of equations which a computer repetitively executes, that is performs iterations, until equilibrium is reached (Algorithm 1). Initially, trial concentrations for the master species (usually free ions such as Ca^{2+} and SO_4^{2-}) are assumed; in the simple system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , satisfactory initial assumptions are (Ca^{2+} = Total Calcium and (SO_4^{2-} = Total Sulfate (Algorithm 1). Then a trial concentration for CaSO_4^0 is calculated from the trial Ca^{2+} , the trial SO_4^{2-} , and the equilibrium constant for the reaction. Finally, trial total concentrations for Calcium and Sulfate are obtained by summing Ca^{2+} and CaSO_4^0 and by summing SO_4^{2-} and CaSO_4^0 , respectively.

The iterations through the equations then adjust the trial concentrations by multiplying the previous trial concentrations by the ratio of (actual total concentration of the element)/(trial total concentration of the element). For example, if the trial total concentration is larger than the actual total concentration, then (1) the trial concentration of the master species is reduced, (2) new trial concentrations of complexes are calculated, (3) a new trial total concentration is obtained by summing concentrations of the free species and the complexes, and finally (4) a new trial concentration of the master species again is calculated (Algorithm 1). This repetition is continued until the adjustment of the concentrations is less than a preselected error. The final result is the chemical-equilibrium concentrations of the free ions and complexes.

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The following "computer program" is a simplified algorithm employing the Continuous-Fraction Method. In the algorithm, activities ($[X]$) are assumed to be equal to concentrations ((X)), that is the ionic strength of the solution is assumed to be small; the use of activity coefficients when the ionic strength is significant is discussed later.

Monotone-Sequences Method is composed essentially of two simultaneous continuous-fraction iterations, which calculate a minimum and maximum concentration for each master species. The iteration process is stopped when the difference between the minimum and maximum values are less than a preselected error. The basic algorithm for Ca^{2+} , SO_4^{2-} , and CaSO_4^0 is:

**** INPUT VALUES AND INITIAL GUESSES (1)**

Total Ca

Total SO4

ERROR

$(\text{Ca}^{2+}) = \text{Total Ca}$

$(\text{SO}_4^{2-}) = \text{Total SO4}$

$K = \text{equilibrium constant for formation of } \text{CaSO}_4^0$

**** COMPUTATION**

100 $[\text{CaSO}_4^0] = K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}]$

$(\text{Ca}^{2+}) = (\text{Ca}^{2+}) * \{ \text{Total Ca} / ((\text{Ca}^{2+}) + (\text{CaSO}_4^0)) \}$

$(\text{SO}_4^{2-}) = (\text{SO}_4^{2-}) * \{ \text{Total SO4} / ((\text{SO}_4^{2-}) + (\text{CaSO}_4^0)) \}$

If CHANGE in species > ERROR go to 100

PRINT RESULTS

Stop

The computation section can be simplified to:

**** COMPUTATION (2)**

100 $(\text{Ca}^{2+}) = \text{Total Ca} / (1 + K * [\text{SO}_4^{2-}])$

$(\text{SO}_4^{2-}) = \text{Total SO4} / (1 + K * [\text{Ca}^{2+}])$

If CHANGE > ERROR go to 100

$[\text{CaSO}_4^0] = K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}]$

PRINT RESULTS

Stop

This simplification reduces the number of calculations in one iteration, but can only be used where there are no complexes or ion pairs containing more than one molecule of a master species. For example, if $\text{Ca}_2\text{SO}_4^{2+}$ existed instead of CaSO_4^0 , then the second term in the denominator of statement number 100 of Algorithm 2 would contain a $[\text{Ca}^{2+}]$ factor, thereby invalidating the simplification.

Monotone-sequences method

This method is a variation on the Continuous-Fraction Method and is described in detail by Wolery and Walters (1975) and Walters and Wolery (1975). The

**** INPUT VALUES AND INITIAL GUESSES (3)**

Total Ca

Total SO4

ERROR

$(\text{Max Ca}^{2+}) = \text{Total Ca}$

$(\text{Min Ca}^{2+}) = \text{Total Ca} * \text{very small value}$

$(\text{Max SO}_4^{2-}) = \text{Total SO4}$

$(\text{Min SO}_4^{2-}) = \text{Total SO4} * \text{very small value}$

$K = \text{equilibrium constant for } \text{CaSO}_4^0$

**** COMPUTATION**

100 $(\text{Min SO}_4^{2-}) = (\text{Min SO}_4^{2-}) * \{ \text{Total SO4} / ((\text{Min SO}_4^{2-}) + K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}]) \}$

$\{ \text{Total SO4} / ((\text{Min SO}_4^{2-}) + K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}]) \}$

$+ K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}] \}$

$(\text{Min Ca}^{2+}) = (\text{Min Ca}^{2+}) * \{ \text{Total Ca} / ((\text{Min Ca}^{2+}) + K * [\text{Min Ca}^{2+}] * [\text{Max SO}_4^{2-}]) \}$

$\{ \text{Total Ca} / ((\text{Min Ca}^{2+}) + K * [\text{Min Ca}^{2+}] * [\text{Max SO}_4^{2-}]) \}$

$+ K * [\text{Min Ca}^{2+}] * [\text{Max SO}_4^{2-}] \}$

$(\text{Max Ca}^{2+}) = (\text{Max Ca}^{2+}) * \{ \text{Total Ca} / ((\text{Max Ca}^{2+}) + K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}]) \}$

$$\left\{ \text{Total Ca} / ((\text{Max Ca}^{2+}) + K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}]) \right\}$$

$$(\text{Max SO}_4^{2-}) = (\text{Max SO}_4^{2-}) *$$

$$\left\{ \text{Total SO}_4 / ((\text{Max SO}_4^{2-}) + K * [\text{Min Ca}^{2+}] * [\text{Max SO}_4^{2-}]) \right\}$$

If DIFFERENCE between Max and Min >

ERROR go to 100

PRINT RESULTS

Stop

As with the Continuous-Fraction Method, routine (3) can be simplified if all complexes and ion pairs contain a maximum of one molecule of each master species. In this simplification, initial guesses for (Min Ca^{2+}) and (Min SO_4^{2-}) are not needed and the computation is:

** COMPUTATION

$$100 (\text{Min SO}_4^{2-}) = \text{Total SO}_4 / (1 + K * [\text{Max Ca}^{2+}])$$

$$(\text{Min Ca}^{2+}) = \text{Total Ca} / (1 + K * [\text{Max SO}_4^{2-}])$$

$$(\text{Max Ca}^{2+}) = \text{Total Ca} / (1 + K * [\text{Min SO}_4^{2-}])$$

$$(\text{Max SO}_4^{2-}) = \text{Total SO}_4 / (1 + K * [\text{Min Ca}^{2+}])$$

If DIFFERENCE > ERROR go to 100

$$[\text{CaSO}_4^0] = K * [\text{Max Ca}^{2+}] * [\text{Min SO}_4^{2-}]$$

PRINT RESULTS

Stop

METHODS INVOLVING SOLUTION OF MATRIX EQUATIONS

These methods solve matrix equations for the change in master species at each iteration. The matrix equations are derived from the Taylor's Series using $d(x)$ as the change in activities at one iteration:

$$f(x + d(x)) = f(x) + d(x) * f'(x) + (d(x)/2^2 * f''(x) + \dots \quad (5)$$

where $f'(x)$ is the first derivative of $f(x)$ and $f''(x)$ is the second derivative of $f(x)$. Assuming that only the first two terms on the right are important leads to:

$$f(x + d(x)) = f(x) + d(x) * f'(x). \quad (6)$$

If f is formulated so that it is equal to zero at equilibrium and if $d(x)$ is selected so that chemical equilibrium is attained, then $f(x + d(x)) = 0$ and

$$0 = f(x) + d(x) * f'(x). \quad (7)$$

Readjusting Equation 7 yields:

$$f'(x) * d(x) = -f(x). \quad (8)$$

Because f is nonlinear and because the series in Equation 5 is truncated to Equation 6, the proper value of $d(x)$ for equilibrium cannot be calculated readily; an iterative approach is required.

Because there are n number of master species and complexes present in a water, $f'(x)$ is matrix of size $n \times n$ and $f(x)$ and $d(x)$ are vectors of length n . If $f'(x)$ and $f(x)$ are constructed so that they contain only known values at an iteration, then $d(x)$ for an iteration can be calculated by techniques such as Gaussian Elimination and $d(x)$ can be added to the trial concentrations of the master species to produce new trial concentrations for the next iterations:

$$x_{(k+1)} = x_{(k)} + d(x)_{(k)} \quad (9)$$

where k = iteration number. Then $f'(x)$ and $f(x)$ are recalculated and a new $d(x)$ is obtained. This process is continued until $d(x)$ is less than a preselected error.

The equations that form $f'(x)$ and $f(x)$ now will be examined. At equilibrium, $d(x) = 0$ and thus, by Equation 8, $f(x) = 0$ at equilibrium. This is consistent with the formulation used in deriving Equation 7 from Equation 6. Function $f(x)$ has two different types of entries: one for complexes and ion pairs, and one for mass balance. As an example, the system containing Ca^{2+} , SO_4^{2-} , and CaSO_4^0 again is examined:

$$d(x_1) = d[\text{CaSO}_4^0], \quad d(x_2) = d[\text{Ca}^{2+}],$$

$$d(x_3) = d[\text{SO}_4^{2-}] \quad (10)$$

$$f(x_1) = [\text{CaSO}_4^0] - K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}] \quad (11)$$

$$f(x_2) = (\text{CaSO}_4^0) + (\text{Ca}^{2+}) - (\text{Total Ca})$$

$$f(x_3) = (\text{CaSO}_4^0) + (\text{SO}_4^{2-}) - (\text{Total SO}_4).$$

However, the exact form and approximations selected to represent the $f'(x)$ matrix produce the three methods examined in this group.

Newton-Raphson Method

The Newton-Raphson Method is discussed in detail in Parkhurst, Thorstenson, and Plummer (1980) and Palmer (1983). In this method, the $f'(x)$ matrix for Ca^{2+} , SO_4^{2-} , and CaSO_4^0 is:

$$\frac{\partial f(x_1)}{\partial [\text{CaSO}_4^0]} \quad \frac{\partial f(x_1)}{\partial [\text{Ca}^{2+}]} \quad \frac{\partial f(x_1)}{\partial [\text{SO}_4^{2-}]}$$

$$\frac{\partial f(x_2)}{\partial [\text{CaSO}_4^0]} \quad \frac{\partial f(x_2)}{\partial [\text{Ca}^{2+}]} \quad \frac{\partial f(x_2)}{\partial [\text{SO}_4^{2-}]}$$

$$\frac{\partial f(x_3)}{\partial [\text{CaSO}_4^0]} \quad \frac{\partial f(x_3)}{\partial [\text{Ca}^{2+}]} \quad \frac{\partial f(x_3)}{\partial [\text{SO}_4^{2-}]} \quad (12)$$

Evaluating Matrix 12 through Equation 11 yields: where

$$\begin{bmatrix} 1 & -K \times [\text{SO}_4^{2-}] - K \times [\text{Ca}^{2+}] \\ \frac{1}{g_1} & \frac{1}{g_2} & \emptyset \\ \frac{1}{g_1} & \emptyset & \frac{1}{g_3} \end{bmatrix} \begin{bmatrix} d[\text{CaSO}_4^0] \\ d[\text{Ca}^{2+}] \\ d[\text{SO}_4^{2-}] \end{bmatrix}$$

g_1 = activity coefficient of CaSO_4^0

g_2 = activity coefficient of Ca^{2+}

g_3 = activity coefficient of SO_4^{2-}

(g_1, g_2, g_3 are assumed to equal 1 in these ex
The values of $d(x)$ now can be solved by stand
niques such as Gaussian Elimination; howev
mainframe-computer systems have efficient
stored in program libraries for solving this
The problem of activity coefficients which are
to 1 is discussed in the section on Addition
plexities in Chemical Equilibrium.

The simplified algorithm for Ca^{2+} , SO_4^{2-} ,
 CaSO_4^0 is as follows; minor variations of this
gorithm exist.

$$= \begin{bmatrix} -f(x_1) \\ -f(x_2) \\ -f(x_3) \end{bmatrix} \quad (13)$$

** INPUT VALUES AND INITIAL GUESSES

Total Ca

Total SO4

ERROR

Initial guess for $[\text{Ca}^{2+}]$

Initial guess for $[\text{SO}_4^{2-}]$

Initial guess for $[\text{CaSO}_4^0]$

K = equilibrium constant for CaSO_4^0

** COMPUTATION

$$100 \quad F(1) = [\text{CaSO}_4^0] - K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}]$$

$$F(2) = (\text{CaSO}_4^0) + (\text{Ca}^{2+}) - (\text{Total Ca})$$

$$F(3) = (\text{CaSO}_4^0) + (\text{SO}_4^{2-}) - (\text{Total SO4})$$

$$\text{FPRIME}(1,1) = 1.0$$

$$\text{FPRIME}(1,2) = [\text{SO}_4^{2-}] * (-K)$$

$$\text{FPRIME}(1,3) = [\text{Ca}^{2+}] * (-K)$$

$$\text{FPRIME}(2,1) = 1/g_1$$

$$\text{FPRIME}(2,2) = 1/g_2$$

$$\text{FPRIME}(2,3) = 0.0$$

$$\text{FPRIME}(3,1) = 1/g_1$$

$$\text{FPRIME}(3,2) = 0.0$$

$$\text{FPRIME}(3,3) = 1/g_3$$

$$[\text{CaSO}_4^0] = K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}]$$

*SUB-PROGRAM to calculate dx

$$[\text{Ca}^{2+}] = [\text{Ca}^{2+}] + d[\text{Ca}^{2+}]$$

$$[\text{SO}_4^{2-}] = [\text{SO}_4^{2-}] + d[\text{SO}_4^{2-}]$$

If CHANGE in concentrations > ERROR go to 100

PRINT RESULTS

Stop

Beginning with an initial guess, $f'(x)$ and $f(x)$ can be calculated at each iteration and then $d(x)$ can be evaluated. Equation 9 then is used to change the activities of the master species (Ca^{2+} and SO_4^{2-}). Iterations continue until $d(x)$'s converge to values less than a preselected error.

Secant Method

In this method (e.g. Rice, 1983), $f'(x)$ is replaced by a finite-difference approximation using values from two previous iterations:

$$f'(x) = \frac{f_{(k)}(x) - f_{(k-1)}(x)}{x_{(k)} - x_{(k-1)}} \quad (15)$$

where k = iteration number. Again using the system with Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , the $f'(x)$ matrix for the Secant Method is:

$$\begin{array}{ccc} \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{CaSO}_4^0]_{(k)} - [\text{CaSO}_4^0]_{(k-1)}} & \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{Ca}^{2+}]_{(k)} - [\text{Ca}^{2+}]_{(k-1)}} & \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{SO}_4^{2-}]_{(k)} - [\text{SO}_4^{2-}]_{(k-1)}} \\ \frac{f_{(k)}(x_2) - f_{(k-1)}(x_2)}{[\text{CaSO}_4^0]_{(k)} - [\text{CaSO}_4^0]_{(k-1)}} & \frac{f_{(k)}(x_2) - f_{(k-1)}(x_2)}{[\text{Ca}^{2+}]_{(k)} - [\text{Ca}^{2+}]_{(k-1)}} & \frac{f_{(k)}(x_2) - f_{(k-1)}(x_2)}{[\text{SO}_4^{2-}]_{(k)} - [\text{SO}_4^{2-}]_{(k-1)}} \\ \frac{f_{(k)}(x_3) - f_{(k-1)}(x_3)}{[\text{CaSO}_4^0]_{(k)} - [\text{CaSO}_4^0]_{(k-1)}} & \frac{f_{(k)}(x_3) - f_{(k-1)}(x_3)}{[\text{Ca}^{2+}]_{(k)} - [\text{Ca}^{2+}]_{(k-1)}} & \frac{f_{(k)}(x_3) - f_{(k-1)}(x_3)}{[\text{SO}_4^{2-}]_{(k)} - [\text{SO}_4^{2-}]_{(k-1)}} \end{array} \quad (16)$$

where k = iteration number. Values for $f(x)$ are calculated from Equation 11 using $[\text{CaSO}_4^0]$, $[\text{Ca}^{2+}]$, and $[\text{SO}_4^{2-}]$ at the k iteration. However, the Secant Method requires two initial guesses for the concentrations of each species so that the $f'(x)$ matrix can be calculated initially, then $d(x)$ can be obtained by Gaussian Elimination or through other software routines. Equation 9 then provides new values and a new iteration is performed. Iterations continue until $d(x)$ is less than a preselected error. As will be shown later, the Secant Method is a poor method for calculating chemical equilibrium and should not be used in its basic form.

Steffensens' Method

In this method (e.g. Rice, 1983), $f'(x)$ is replaced by:

$$f'(x) = \frac{f(x + f(x)) - f(x)}{f(x)} \quad (17)$$

with Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , the $f'(x)$ matrix is:

$$\begin{array}{ccc} \frac{f\{x_1 + f(x_1)\} - f(x_1)}{f(x_1)} & \frac{f\{x_1 + f(x_2)\} - f(x_1)}{f(x_2)} & \frac{f\{x_1 + f(x_3)\} - f(x_1)}{f(x_3)} \\ \frac{f\{x_2 + f(x_1)\} - f(x_2)}{f(x_1)} & \frac{f\{x_2 + f(x_2)\} - f(x_2)}{f(x_2)} & \frac{f\{x_2 + f(x_3)\} - f(x_2)}{f(x_3)} \\ \frac{f\{x_3 + f(x_1)\} - f(x_3)}{f(x_1)} & \frac{f\{x_3 + f(x_2)\} - f(x_3)}{f(x_2)} & \frac{f\{x_3 + f(x_3)\} - f(x_3)}{f(x_3)} \end{array} \quad (18)$$

This method requires one initial guess for Ca^{2+} , SO_4^{2-} , and CaSO_4^0 in order to obtain $f'(x)$ and $f(x)$,

then $d(x)$ is calculated and Equation 9 provides new values to recalculate $f'(x)$ and $f(x)$. Iterations continue until $d(x)$ is less than a preselected error. In its basic form, Steffensens' Method is a poor method for calculating chemical equilibrium, because of its divergent and unstable behavior.

COMPARISON AND LIMITATIONS OF THE METHODS

In the discussion of the methods, little was mentioned on how quickly the methods converge towards chemical equilibrium through a series of iterations or whether the methods converge at all. This section is concerned with these topics.

Assuming all the methods converge, the speed of convergence can be described by the "order of convergence":

$$\lim_{k \rightarrow \infty} \frac{|e_{(k+1)}|}{|e_{(k)}|^{(p)}} = \text{Constant} > 0 \quad (19)$$

where

k = iteration number
 $|e|$ = absolute value of (calculated concentration of a species)—(actual concentration at equilibrium)
 p = order of convergence.

Most of the methods discussed here have orders-of-convergence of either 1 or 2 (Table 1; Rice, 1983). As an example, assuming Constant = 0.5 and $|e(k)| = 0.01$, Equation 19 can be approximated by:

$$|e_{(k+1)}| = 0.5 * 0.01^{(p)} \quad (20)$$

If $p = 1$, then the error at the next iteration is about 0.005; if $p = 2$, the error at the next iteration is about 0.00005. At first, it would seem that methods with $p = 2$ are preferable, but the efficiency of a method determines which is preferable. Although Rice (1983) gives a specific mathematical definition

of efficiency, the more qualitative definition will be used here: efficiency of a method is a statement of

Table 1. Order-of-convergence (p) for methods

Method	p
Continuous-Fraction	1
Monotone-Sequences	1
Secant	1.6 (approx)†
Newton-Raphson	2
Steffensens	2†

† From Rice (1983).

the order of convergence as compared to the number of mathematical calculations performed during one iteration. For example, using the system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , the efficiency of the Continuous-Fraction Method ($p = 1$) is greater than the efficiency of the Newton-Raphson Method ($p = 2$), which has to perform many mathematical operations in order to calculate $f'(x)$, calculate $f(x)$, and to solve for $d(x)$. However, in larger systems, methods with $p = 2$ are more efficient.

The most important factors in determining which order-of-convergence is more efficient are, first, the combined number of master species and complexes and, second, the ratio of (complexes/master species).

$$\begin{array}{ccc}
 \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{CaSO}_4^0]_{(k)} - [\text{CaSO}_4^0]_{(k-1)}} & \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{Ca}^{2+}]_{(k)} - [\text{Ca}^{2+}]_{(k-1)}} & \frac{f_{(k)}(x_1) - f_{(k-1)}(x_1)}{[\text{SO}_4^{2-}]_{(k)} - [\text{SO}_4^{2-}]_{(k-1)}} \\
 \emptyset & \emptyset & \emptyset \\
 \emptyset & \emptyset & \emptyset
 \end{array} \quad (21)$$

However other factors such as the ratio of (the number of 1:1 complexes/the number of 1:2 complexes) also are important. The $p = 2$ methods are generally more efficient when the combined number of master species and complexes is about 40 to 150 and greater.

Although the previous paragraph discussed the selection of $p = 1$ or $p = 2$ methods, it did not include the selection of a method after the p value has been decided. This selection is based on both the efficiency of the methods and whether the method converges at all. For the $p = 1$ methods, a quick inspection of Algorithms 1 and 3 show that the Continuous-Fraction Method is more efficient. For the $p = 1.6$ to 2 methods, general efficiency usually shows the decreasing trend of Secant > Newton-Raphson (Rice, 1983). However, in their basic forms, both the Secant and Steffensens' Methods display erratic and divergent behavior when solving for chemical equilibrium and, thus, should not be used in their basic forms. The causes of nonconvergence now will be discussed.

All methods examined in this paper will display nonconvergent or extremely slow convergent behavior if the proper master species (free ion or complex) for the elements are not selected. The requirement for the master species is that it has to be one of the dominant species for the element. For most elements, a proper master species is the free ion, such as Ca^{2+} and SO_4^{2-} . In low-pH waters, H_2CO_3^0 or HCO_3^- rather than

CO_3^{2-} should be the master species for carbonate. Also, Morin (1983) determined that, in low-pH seepage from uranium-tailings impoundments, Al-F and Al- SO_4 complexes may dominate aluminum behavior and using Al^{3+} as the aluminum master species could produce erroneous results. The precise reasons for nonconvergence by trace-concentration master species are (1) round-off errors in computer arithmetic (e.g. Rice, 1983) and (2) the large change in concentrations of dominant complexes containing more than one molecule of a master species when the concentration of the trace master species is changed slightly.

With properly selected master species, the $p = 1$ methods will converge as long as a reasonable initial guess is made (e.g. (master species) = total concentration of element). For the $p = 2$ methods, a "good" initial guess is required for convergence; however, the definition of "good" is not defined easily for a complex system. Even with good initial guesses, the Secant and Steffensens' Methods may not converge for chemical equilibrium because of their unsatisfactory approximations to $f'(x)$. For the Secant Method, its basic approximation to $f'(x)$ (Matrix 16) can be simplified by a technique similar to Gaussian Elimination to:

where k = iteration number. Matrix 21 indicates that $d(x)$ cannot be evaluated.

One technique of stabilizing a method to ensure convergence is to combine two methods into a "hybrid method". For example, the computer model PHREEQE (Parkhurst and others, 1980) combines the Continuous-Fraction and Newton-Raphson Methods; the Continuous-Fraction routine provides the good initial guess for the Newton-Raphson routine. Other hybrid methods simply involve changing or manipulating a few variables to increase efficiency and convergence of a basic method. For example, one such hybrid for the Newton-Raphson Method is the Discrete Newton Method (Rice, 1983), which is not examined here.

ADDITIONAL COMPLEXITIES IN CHEMICAL EQUILIBRIUM

There are four major complexities in calculating chemical equilibrium: (1) activity coefficients, (2) exchange with other phases (solids and gases), (3) variable pH, and (4) variable pe (or Eh). The first complexity must be accounted for by all aqueous chemical models; complexities 3 and sometimes 4 also must be accounted for by models allowing phase exchange. These topics are discussed briefly in this section.

Up to this point, activities have been set equal to concentrations, although activities have been distin-

guished from concentrations in the examples so that adding a routine for calculating activities is a minor task. Activity is related to concentration through activity coefficients:

$$[X] = g \cdot (X) \quad (21)$$

where g = activity coefficient. There are many equations for calculating the coefficients: Debye-Huckel Equation, Davies Equation, Mean-Salt Method, etc.; these equations are discussed in detail in texts on aqueous chemistry. Once an equation is selected, it is used at the beginning of an iteration to calculate new activity coefficients for the iteration.

The second complexity is phase exchange; the only phase exchange discussed here is precipitation-dissolution of compounds. There are three basic techniques by which precipitation-dissolution can be simulated. The first technique is an empirical approach in which particular amounts of ions are removed from or added to solution, the solution then is respecified by any of the Methods, then more precipitation-dissolution may be allowed if desired. This technique was combined with the Continuous-Fraction Method to simulate neutralization of uranium-tailings seepage (Morin, 1983). The second and third techniques are similar in that they involve the construction of a matrix, similar to Equation 8 for equilibrium speciation. The second technique combines the chemical-equilibrium matrix and the precipitation-dissolution matrix into one large matrix (Parkhurst and others, 1980) and the changes ($d(x)$) in activities and changes in amounts of compounds are solved. The third technique keeps the precipitation-dissolution matrix separate from the equilibrium matrix; this technique is less costly at times to use than the second technique (Palmer, 1983).

The third complexity is the change in pH as precipitation-dissolution occurs. In this situation, three new variables are introduced ($[H^+]$, $[OH^-]$, and $[H_2O]$), which require three new equations. The value for $[H_2O]$ usually is assumed equal to 1 or is calculated independently as a function of the sum of concentrations of species; up to ionic strengths of 0.5, little error is involved in assuming $[H_2O] = 1.0$. The form of the remaining two equations are determined by the type of method used (repetitive equations or matrix-solver).

The matrix-solver equations are examined first. For $[OH^-]$, the corresponding $f(x)$ equation is $f(x) = [OH^-] - K \cdot [H_2O]/[H^+]$; thus $d(OH^-)$ is entered simply into the $d(x)$ vector and $f(OH^-)$ and $f'(OH^-)$ are entered in appropriate locations in $f(x)$ and $f'(x)$. The remaining variable, $[H^+]$, is accounted for by the charge-balance equation, which states that the sum of negatively charged ions times their charge and positive charged ions times their charge is zero. (For this approach to work, the initial solution must be charge balanced.) Also, at each iteration, the sum of the change ($d(x)$) in positively charged ions times their charge and the change in negatively charged ions times their charge must be zero. These are the forms of $f(H^+)$ and $f'(H^+)$,

respectively, which are added to $f(x)$ and $f'(x)$, and $d(H^+)$ is added to the $d(x)$ vector.

For repetitive equations, the equation $[OH^-] = K \cdot [H_2O]/[H^+]$ is added to the stack of equations. To account for $[H^+]$, the charge-balance equation again is used, but because the value for $[H^+]$ at the current iteration usually is not correct, the sum of the charge balance will not equal zero. However, the resulting sum does give an indication of how $[H^+]$ must be changed: if the sum is negative, $[H^+]$ must be increased; if the sum is positive, $[H^+]$ must be decreased. The magnitude of the sum is not equal to the required magnitude of the change in $[H^+]$ because H-complexes and OH-complexes consume or release H^+ as the pH changes. Morin (1983) determined that the optimum approach is to increment $[H^+]$ and respeciate until zero charge balance is obtained.

The final complexity is a change in pe (or Eh), the redox state of the solution. Because electrons do not exist in the free state in large quantities, changes in pe cannot be calculated along the same lines as changes in pH. For matrix-solvers, changes in pe are calculated by assigning "redox values" for every ion capable of undergoing oxidation-reduction, and equations ($f(x)$ and $f'(x)$) then can be written for the change in redox conditions (Parkhurst and others, 1980; Palmer, 1983). For repetitive equations, changes in redox conditions are more difficult to simulate and are limited to a few redox couples. For example, the redox couples can be grouped into one equation and the equilibrium constant for this combination is calculated from the published constants for each couple. Then concentrations in the numerator and denominator are incremented until the calculated value is equal to the actual K for the equation. If many redox couples are involved, a routine similar to that for matrix-solvers must be used.

SUMMARY

This paper has presented simplified explanations and examples for several methods of computing chemical equilibrium in water: Continuous-Fraction, Monotone-Sequences, Newton-Raphson, Secant, and Steffensens. The examples allow an easier understanding of the methods than does the standard mathematical notation used for the methods. The efficiencies of the methods are compared and, for systems with few master species, complexes, and ion pairs, the Continuous-Fraction Method is most efficient; in large systems, the Newton-Raphson Method is most efficient.

Four complexities in solving for chemical equilibrium were discussed briefly: activity coefficients, precipitation-dissolution, variable pH, and variable pe. Brief discussions have shown how the methods can incorporate these complexities.

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