An Algorithm for Simultaneous Chemical and Phase Equilibrium Calculation

A new generalized algorithm has been developed for solving simultaneous chemical and phase equilibrium equations of two-phase systems. By rearranging convergence loops of the algorithm of Sanderson and Chien (1973), this new approach shows improved robustness and speed. Solutions to the material balance and chemical equilibrium equations are obtained with an improved Marquardt method (Zhan, 1976). An esterification reaction and dissociation reactions of electrolytes in phase equilibrium are presented as examples.

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Introduction

In chemical, petrochemical and metallurgical industries, more and more processes use operations with simultaneous chemical reaction and mass transfer in the same vessel, such as reactive distillation and chemical absorption, to meet energy conservation and environmental protection requirements. Chemical and phase equilibrium calculations are often necessary for designing these processes. Therefore, in flowsheeting systems, a simultaneous chemical and phase equilibrium module is usually considered to be essential.

Strong interactions among components, phases, and reactions have made the chemical and phase equilibrium computation very difficult. Not until the early 1970's, after the computer power became sufficient, did this probram attract interest. In 1972, Dluzniewski and Adler (1972) extended the minimum Gibb's free energy method for calculating the chemical equilibrium compositions of an ideal gas mixture by White et al. (1958) to vapor-liquid and liquid-liquid systems, thus creating a generalized method known as RAND. During the last decade, RAND has been much improved. It was enhanced to automatically determine phase regions (Gautam and Seider, 1979a) for electrolyte systems (Gautam and Seider, 1979b), for slow reactions (White III and Seider, 1981) and for alternative (i. e., other than temperature and pressure) specifications (Gautam and Wareck, 1986). Several other algorithms based on the minimum Gibb's free energy had been published (George et al., 1976; Gautam and Seider, 1979c; Casittilo and Grossmann, 1981; Zhou and Xu, 1987). Hitherto, methods of this kind have found broad applications and have been generally favored by metallurgists, chemists, and chemical engineers (Mather, 1986).

This problem can also be stated in an alternative formulation. The equilibrium compositions and phase numbers of a system can be obtained by solving a set of mass balance, phase and chemical equilibrium equations for specified components and reactions. This is called the k-value method. For those cases that only certain fast reactions reach equilibrium (Seider et al., 1980) or only the activity coefficient model is available for the phase equilibrium, the minimum energy method is not easy to apply but the k-value method remains effective.

In early 1973, Sanderson and Chien published a paper on a k-value method which was perhaps the first rigorous method for multiphase systems (henceforth referred to as the S-C algorithm). Electrolyte systems are invariably solved in a k-value formulation (Zemaitis and Rafal, 1975). This paper presents another k-value method based on "effective" chemical equilibrium constants, K_z's, for equivalent single-phase compositions, z_i's (henceforth referred to as the KZ algorithm). It reverses the order of chemical reaction and phase equilibrium calculation loops in the S-C algorithm. This strategy is analogous to the inside-out idea of Boston and Britt (1978) for flash calculations. For many problems, the new algorithm can be faster and yet more stable than that of Sanderson and Chien.

Combining the idea of Sanderson and Chien in calculating chemical equilibrium and that of Boston and Britt in calculating phase equilibrium, the KZ algorithm shows improved robustness and speed when compared to the S-C algorithm. The average number of k-value iterations is only one fourth to one tenth that of the S-C algorithm with little increase in iterations of extents.

The KZ algorithm is very flexible. It can easily be extended to

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solve problems with alternative specifications. With the final amounts of species being iteration variables, it can accurately calculate compositions of trace species.

Finally, it should be noted that the KZ algorithm has the same requirement as others that an accurate description of the thermodynamic characteristics of the system is critical for a valid solution.

Problem Formulation and the S-C Algorithm

For a two-phase system involving N components and M reactions:

$$\sum_{i=1}^{N} \nu_{ij} A_i = 0; \quad j = 1, \ldots, M \tag{1}$$

where i and j are the component and reaction indices, respectively, ν the stoichiometric coefficients, and A_i the chemical species. The reaction equilibrium constants are defined by:

$$\prod_{i=1}^{N} (\gamma_i x_i)^{\nu_{ij}} = \prod_{i=1}^{N} \left(\frac{p_i \hat{\phi}_i}{f_i^o}\right)^{\nu_{ij}} = K_j; \quad j = 1, \ldots, M \tag{2}$$

The equilibrium constants, K_j, may be determined experimentally or calculated by

$$K_j = \exp\left(\frac{-\Delta G_j^o}{RT}\right)$$

where

$$\Delta G_j^o = \sum_{i=1}^{N} \nu_{ij} G_i^o$$

Symbols are defined in the notation section. Equations 2 are valid for systems with a vapor phase and one stable liquid phase.

The material balance equations for the reactions are

$$F_{\text{out}\,i} = F_{\text{in}\,i} + \sum_{j=1}^{M} \nu_{ij} \xi_j; \quad i = 1, \ldots, N \tag{3}$$

The phase equilibrium equations and the flash equations are

$$z_i = \frac{F_{\text{out}\,i}}{\sum_{i=1}^{N} F_{\text{out}\,i}}; \quad i = 1, \ldots, N \tag{4}$$

$$z_i = \alpha y_i + (1 - \alpha) x_i; \quad i = 1, \ldots, N \tag{5}$$

$$y_i = \frac{f_i^o \gamma_i}{P \hat{\phi}_i} x_i = k_i x_i; \quad i = 1, \ldots, N \tag{6}$$

$$\sum_{i=1}^{N} (y_i - x_i) = 0 \tag{7}$$

The liquid activity coefficients, γ_i, may be correlated by any excess Gibbs energy model: e.g., Wilson, NRTL, or UNIQUAC. The vapor fugacity coefficients, $\hat{\phi}_i$, may be calculated using any equation of state: e.g., Soave-Redlich-Kwong or Peng-Robinson. An accurate description of the mixture nonideality is important for a valid solution to the problem. However, the numerical method described in this paper is independent of the correlation or the equation of state used.

For a system with fixed temperature, pressure and feed compositions, Eq. 2–7 are solved iteratively for the $4N + M + 1$ unknowns:

$$\begin{array}{ll} F_{\text{out}\,i} & i = 1, 2, \ldots, N \\ x_i, y_i, z_i & i = 1, 2, \ldots, N \\ \xi_i & j = 1, 2, \ldots, M \end{array}$$

and α

An algorithm using only extents as the iterative variables must search for a solution that satisfies the following set of linear constraints:

$$F_{\text{out}\,i} \geq 0; \quad i = 1, \ldots, N \tag{8}$$

or

$$\sum_{j=1}^{M} \nu_{ij} \xi_j \geq -F_{\text{in}\,i}; \quad i = 1, \ldots, N \tag{9}$$

Sanderson and Chien (1973) stated that generalized methods for constrained problems produced disappointing results when applied to this problem because of its nonlinearity. They developed an algorithm that searches for ξ_i's and $F_{\text{out}\,i}$'s to satisfy Eqs. 2 and 3 in its outer loop; x_i's, y_i's and α to satisfy Eqs. 5, 6 and 7 in its inner loop. Their approach allows constraint equations (Eqs. 9) to be violated during the search and thus avoids the typical complications for these problems when solutions are close to the constraints. It was shown to be effective in obtaining solutions for difficult problems.

The S-C algorithm is as follows:

1. Estimate ξ_i's and $F_{\text{out}\,i}$'s.
2. Perform flash calculation on $F_{\text{out}\,i}$'s to get x_i's and y_i's and α by solving Eqs. 5, 6 and 7.
3. Repeat above steps if Eqs. 2 and 3 are not satisfied.

The simultaneous chemical reaction and phase equilibrium calculations are done in two loops: the former is in the outer loop and the latter in the inner loop. Theoretically, the S-C algorithm should perform well for systems with simple phase equilibrium models but with complex reactions. If the phase equilibrium calculation in the inner loop is slow, however, this algorithm may consume too much CPU time. Chen (1981) suggested the use of this algorithm for constant k values that are updated in yet another outer loop for reduced k-value evaluations with improved speed and reliability.

0. Estimate k values.
1. Estimate ξ_i's and $F_{\text{out}\,i}$'s.
2. Perform flash with constant k values on $F_{\text{out}\,i}$'s to get x_i's and y_i's and α by solving Eqs. 5, 6 and 7.
3. Return to step 1 if Eqs. 2 and 3 are not satisfied.
4. Return to step 0 until k values are converged.

This idea was originally used by Boston and Britt (1978) for flash calculations. It reduces the number of k-value evaluations to improve speed and stabilizes the highly sensitive k values to improve reliability. However, moving the k-value calculations outside represents only a minor modification to the S-C algorithm. It is possible to move the entire flash loop to the outside as described in the following section.

In calculations involving phase equilibria, it has been reported that the computation of composition ratios, k_i's, requires as much as 80% of the total CPU time (Westerberg et al., 1980; Chimowitz et al., 1984). Therefore, it is efficient for an algorithm to reduce the number of k-value evaluations as much as possible. A different approach to reduce these evaluations is used by the new algorithm. The outer loop of this algorithm is used for phase equilibrium calculations with constant k values, and the inner loop is for chemical equilibrium computations. For systems with simple chemical reactions, the new method can be extremely effective.

A New Formulation

To present the KZ algorithm, Eqs. 2-7 are rearranged as follows.

From Eqs. 5 and 6, the liquid composition can be expressed as:

$$x_i = \frac{z_i}{(k_i - 1)\alpha + 1}; \quad i = 1, \ldots, N \tag{10}$$

Equations 7 can be rewritten as:

$$S_\alpha \equiv \sum_{i=1}^{N} \frac{(k_i - 1)z_i}{(k_i - 1)\alpha + 1} = 0 \tag{11}$$

When z_i's are given, solving Eqs. 6, 10, 11 is equivalent to the conventional isothermal flash calculation.

Substituting Eq. 10 into Eq. 2 yields:

$$\prod_{i=1}^{N} (z_i)^{\nu_{ij}} = K_{zj}; \quad j = 1, \ldots, M \tag{12}$$

where

$$K_{zj} \equiv K_j \prod_{i=1}^{N} \left(\frac{\gamma_i}{(k_i - 1)\alpha + 1} \right)^{-\nu_{ij}}; \quad j = 1, \ldots, M \tag{13}$$

In this formulation, effects of multiple phases and their nonideality on the reaction equilibria have been merged into a set of new parameters, K_{zj}; $j = 1, \ldots, M$. Given these parameters, solving Eqs. 3, 4 and 12 is equivalent to the chemical equilibrium calculation of a single-phase ideal mixture.

In order to avoid division by zero and the nonlinearity of division, Eqs. 12 are rewritten into a kinetic form:

$$S_j \equiv K_{zj} \left(\prod_{i=1}^{N} (z_i)^{-\nu_{ij}} \right)_{\nu_{ij}<0} - \left(\prod_{i=1}^{N} (z_i)^{\nu_{ij}} \right)_{\nu_{ij}>0}; \quad j = 1, \ldots, M \tag{14a}$$

for $K_{zj} \geq 1$ and

$$S_j \equiv \left(\prod_{i=1}^{N} (z_i)^{-\nu_{ij}} \right)_{\nu_{ij}<0} - \frac{1}{K_{zj}} \left(\prod_{i=1}^{N} (z_i)^{\nu_{ij}} \right)_{\nu_{ij}>0}; \quad j = 1, \ldots, M \tag{14b}$$

for $K_{zj} < 1$.

The material balance equations (Eqs. 3) are redefined to be:

$$S_{M+i} \equiv F_{\text{out}\,i} - F_{\text{in}\,i} - \sum_{j=1}^{M} \nu_{ij}\xi_j; \quad i = 1, \ldots, N \tag{15}$$

At the solution, the functions S_t; $t = 1, \ldots, N + M$, are to be forced to zero.

A New Algorithm

The overall "basic" algorithm proceeds as follows:

1. Estimate k_i; $i = 1, \ldots, N$.
2. Estimate α.
3. Calculate K_{zj}; $j = 1, \ldots, M$ with Eqs. 13.
4. Estimate ξ_j; $j = 1, \ldots, M$ and $F_{\text{out}\,i}$; $i = 1, \ldots, N$.
5. return to step 4 with new estimates from the modified Marquardt method until Eqs. 14 and 15 are satisfied.
6. Return to step 2 until Eq. 11 is satisfied.
7. Return to step 2 with new estimates of k_i until $E \equiv \Sigma(k_{i\,\text{new}}/k_i - 1)^2 < 10^{-6}$.

The phase equilibrium calculation (in steps 2 and 6) is performed in the outer loop by solving for α to satisfy Eq. 11 with a typical algorithm for isothermal flash. The k-value loop (in steps 1 and 7) is often enhanced with a bounded Wegstein method. In this work, however, we used a simple direct iteration method. The chemical equilibrium calculation of this algorithm (in steps 4 and 5) is described in detail in the next section.

In the fine tuning of this "basic" algorithm, we found that in the initial phase of the search when k values are not yet close to their final values, there is little justification to force convergence of the inner loops, i.e., the α and extents loops. By taking the extents loop out of the α loop, we saved many steps in the search of extents at the cost of extra k-value evaluations. This is accomplished by replacing step 6 with: calculate α to satisfy Eq. 11.

The recommended algorithm uses this "preliminary" algorithm when $E > 10^{-4}$ and switch to the "basic" algorithm afterwards. In example 1 of this paper, we show a comparison of these variations.

Chemical Equilibrium Calculation

When K_{zj}; $j = 1, \ldots, M$ are given, solving Eqs. 4, 14 and 15 (in steps 4 and 5) is equivalent to the chemical equilibrium calculation of a single-phase ideal mixture. This calculation is placed in the inner loop of the KZ algorithm.

In the S-C algorithm, $F_{\text{out}\,i}$'s are included as iterative variables in addition to the extents and Eqs. 15 as additional objective functions to eliminate linear constraints 8 or 9 in order to obtain consistent solutions in the presence of nonlinearity. Without the nonlinearity in the S-C approach, the new set of reaction equilibrium equations may be solved by using only extents as iterative variables. However, we found that Eqs. 3 are very susceptible to round-off errors in extents. When certain reactions are directed by equilibria to approach completion, the residue trace quantities of reactants cannot be accurately evaluated by the differences of extents expressed in finite digits. This problem can be solved by including $F_{\text{out}\,i}$'s as iterative variables.

To illustrate this problem with an example, Xiao (1988) used the steam shift reaction of methane at 1,400 K and 1 atm with 1-mol methane and 5-mol steam in the feed. At such a high temperature, the reaction is in vapor phase and methane is almost completely converted. The residue methane (at $0.565 \cdot 10^{-7}$ mol) if calculated from the difference of the initial methane (at 1 mol) and the reaction extent (at 0.9999999435) would have required that the extent be accurate to 10 digits. If the final amount of methane is also a search variable, the error introduced to the objective function by the material balance equation

(Eq. 15) for methane would be very small when the extent is accurate only to 5 digits.

Equations 4, 14 and 15 are solved for extents and $F_{\text{out}i}$'s by a modified Marquardt method using the following Jacobian.

For $s = 1, \ldots, M$:

$$\frac{\partial S_s}{\partial \xi_j} = 0; \quad j = 1, \ldots, M \tag{16}$$

$$\frac{\partial S_s}{\partial F_{\text{out}i}} = \sum_{t=1}^{N} \frac{\partial S_s}{\partial z_t} \frac{\partial z_t}{\partial F_{\text{out}i}}; \quad i = 1, \ldots, N \tag{17}$$

For $s = M + 1, \ldots, M + N$:

$$\frac{\partial S_s}{\partial \xi_j} = -\nu_{s-M,j}; \quad j = 1, \ldots, M \tag{18}$$

$$\frac{\partial S_s}{\partial F_{\text{out}i}} = \delta_{s-M,i}; \quad i = 1, \ldots, N \tag{19}$$

For $K_{zj} \geq 1$:

$$\frac{\partial S_j}{\partial z_i} = -K_{zj} \frac{\nu_{ij}}{z_i} \left(\prod_{t=1}^{N} (z_t)^{-\nu_{tj}} \right)_{\nu_{tj}<0} \tag{20}$$

or

$$\frac{\partial S_j}{\partial z_i} = -\frac{\nu_{ij}}{z_i} \left(\prod_{t=1}^{N} (z_t)^{\nu_{tj}} \right)_{\nu_{tj}>0} \tag{21}$$

For $K_{zj} > 1$:

$$\frac{\partial S_j}{\partial z_i} = -\frac{\nu_{ij}}{z_i} \left(\prod_{t=1}^{N} (z_t)^{-\nu_{tj}} \right)_{\nu_{tj}<0} \tag{22}$$

or

$$\frac{\partial S_j}{\partial z_i} = -\frac{\nu_{ij}}{K_{zj} z_i} \left(\prod_{t=1}^{N} (z_t)^{\nu_{tj}} \right)_{\nu_{tj}>0} \tag{23}$$

Also,

$$\frac{\partial z_t}{\partial F_{\text{out}i}} = \frac{\delta_{ti} - z_t}{\sum_{s=1}^{N} F_{\text{out}s}}; \quad t = 1, \ldots, N; \quad i = 1, \ldots, N \tag{24}$$

The modified Marquardt method (Zhan, 1976) is used to minimize the objective function:

$$\sum_{t=1}^{M+N} S_t^2$$

It calculates the search vector with the following equation:

$$L(D + \lambda I)L^T \Delta x = -g \tag{25}$$

where

$$H = LDL^T = J^T J \tag{26}$$

$$g = J^T S \tag{27}$$

$$\Delta x = (\Delta \xi, \Delta F_{\text{out}}) \tag{28}$$

Equations 25 are valid in that the Hessian Matrix, H, is positive definite. This method was shown to be very efficient since it avoids the repeated operations on H and g. Moreover, it replaces the unity matrix, I, which in the classic Marquardt method (1963) improves only the diagonal elements of matrix H with a positive definite matrix, LL^T, to improve the entire H.

To enhance the performance of the Marquardt method, objective functions equations (Eqs. 14 and 15) are scaled by dividing each equation by the sum of the absolute values of all terms on its righthand side plus

$$\frac{1}{\sum_{i=1}^{N} F_{\text{out}i}}$$

These scale factors are updated at each new base point.

In the implementation of the modified Marquardt method, if the calculated new objective function is greater than that at the base point, the value of λ is increased by a factor of 4 and the calculation of a new objective function is repeated; if the new function is smaller, λ is decreased by a factor of 10 and the base point is updated. In either case, the iteration counter is advanced by one.

Comparisons between the KZ and the S-C Algorithm

Two systems have been included in this paper as examples to compare these two methods. One is the esterification reaction of ethanol and acetic acid, and the other is an electrolyte system with complex dissociation reactions. Both problems are initialized from:

$$\gamma_i = 1; \quad k_i = p_i^o/P; \quad i = 1, \ldots, N$$

$$\xi_j = 0; \quad j = 1, \ldots, M$$

$$F_{\text{out}i} = F_{\text{in}i}; \quad i = 1, \ldots, N$$

and

$$\alpha = 0$$

Convergence criteria are as follows.

For the outer loop,

$$\sum_{i=1}^{N} \left(\frac{k_{i\,\text{new}}}{k_i} - 1 \right)^2 < 10^{-6}$$

For the inner loop,

$$\sum_{j=1}^{M} \left(\frac{1}{K_{zj}} \prod_{i=1}^{N} (z_i)^{\nu_{ij}} - 1 \right)^2 + \sum_{i=1}^{N} S_{M+i}^2 < 10^{-6}$$

and,

$$|S_\alpha| < 10^{-5}$$

Table 1. Antoine Constants for EtOH-HAC-EtAC-H_2O*

Comps	a	b	c
EtOH	9.95614	1,440.52	−60.44
HAC	9.6845	1,644.05	−39.63
EtAC	9.22298	1,238.71	−56.15
H_2O	10.09171	1,668.21	−45.14

$\mathrm{Log}_{10}\, p^s(\mathrm{N/m^2}) = a - b/(T, K + c)$

*Suzuki et al. (1970)

In both methods, direct iteration is used for the k-value convergence and the modified Marquardt method is used for the reaction extent.

Example 1

The esterification reaction of ethanol and acetic acid:

$$EtOH + HAC = EtAC + H_2O$$

approaches equilibrium in the presence of acid catalyst. It has often been used to check algorithms for simultaneous chemical and phase equilibria (Sanderson and Chien, 1973; George et al., 1976; Gautam and Seider, 1979c; Casittilo and Grossmann, 1981; Zhou and Xu, 1987). Since its chemical equilibrium can be explicitly solved as a quadratic equation, it is ideally suited for the KZ algorithm.

Its chemical equilibrium constant, based on vapor compositions, can be expressed as:

$$\ln (K_y) = -20.718 + 2518.399/T + 3.08 \ln (T) - 0.0031\, T + 1.2 \cdot 10^{-6}\, T^2$$

by correlating the data from Reid et al. (1976). The K in Eq. 2 is evaluated with

$$K = K_y \frac{p_1^s p_2^s}{p_3^s p_4^s}$$

The vapor pressures, p_i^s's, are calculated by the Antoine equation using constants in Table 1. For convenience, we also show K_y and K at different temperatures in Table 2.

The liquid activity coefficients for this system are computed by the UNIQUAC equation, with its parameters, which are shown in Table 3, generated by the UNIFAC model (Fredenslund et al., 1977). The vapor-phase mixture is assumed to be ideal, and the polymerization of acetic acid in the vapor phase has also been ignored.

Table 4 lists four cases to compare the KZ algorithm with the S-C algorithm using the system EtOH-HAC-EtAC-H_2O. The number of iterative calculations of k_i's of the S-C method is about four times that of the KZ method, and the number for extents of the KZ algorithm doubles that of S-C's.

Table 2. Chemical System Equilibrium Constants of EtOH + HAC = EtAC + H_2O

T, K	K_y	K
345	41.154	20.505
350	35.743	19.537
355	33.546	18.644
358	32.223	18.142

Table 3. UNIQUAC Parameters for System EtOH-HAC-EtAC-H_2O

Volume and Surface Area Parameters

Comps.	EtOH	HAC	EtAC	H_2O
q	1.972	2.092	3.116	1.400
R	2.1055	2.2024	3.4786	0.920

Binary Interaction Parameters: $(\tau_{ij} = A_{ij} + B_{ij}T)$

System	A_{12}	A_{21}	B_{12}	B_{21}
EtOH—HAC	−0.213	4.250	$1.37 \cdot 10^{-3}$	$-5.11 \cdot 10^{-3}$
EtOH—EtAC	1.340	0.289	$-4.05 \cdot 10^{-4}$	$5.57 \cdot 10^{-4}$
EtOH—H_2O	0.098	2.140	$9.61 \cdot 10^{-4}$	$-1.66 \cdot 10^{-3}$
HAC—EtAC	2.760	−0.076	$-2.64 \cdot 10^{-3}$	$1.07 \cdot 10^{-3}$
HAC—H_2O	3.140	−0.073	$-3.90 \cdot 10^{-3}$	$1.29 \cdot 10^{-3}$
EtAC—H_2O	0.223	1.040	$-1.03 \cdot 10^{-4}$	$2.08 \cdot 10^{-5}$

$$\ln \gamma_k = \ln \gamma_k^c + \ln \gamma_k^R$$

$$\ln \gamma_k^c = \ln \frac{\phi_k}{x_k} + \frac{Z}{2} q_k \ln \frac{\phi_k}{x_k} + l_k - \frac{\phi_k}{x_k} \sum_{1}^{N} x_i l_i$$

$$l_k = \frac{Z}{2}(R_k - q_k) - (R_k - 1); \qquad Z = 10$$

$$\theta_k = \frac{q_k x_k}{\Sigma\, q_i x_i}; \qquad \phi_k = \frac{R_k x_k}{\Sigma R_i x_i}$$

$$\ln \gamma_k^R = q_k \left(1 - \ln (\Sigma\, \theta_i \tau_{ij}) - \sum_{i=1}^{N} \frac{\theta_i \tau_{ik}}{\Sigma\, \theta_j \tau_{jk}}\right)$$

As stated before, the extent for this system can be easily calculated using the explicit solution of a quadratic equation (in steps 4 and 5). This is possible since Eqs. 14 are identical to those for a single-phase ideal-solution problem. Inasmuch as the quadratic solution requires almost zero time and produces results reliably, it is preferred over any search method. The S-C algorithm, with its flash loop inside the reaction loop, invariably must use a search method for the reaction calculation even for the simplest of reactions. The number of extents trials for the KZ method as shown in Table 4 reflects only the use of a generalized approach.

Table 5 and 6 summarize the iterative steps of these two algorithms for the case at 355 K. Note that the S-C method moved very slowly at the beginning. The movements in the extent were generated by the Marquardt method. These changes were large enough to have required large numbers of updates of k values in the inner loop. In the KZ algorithm, the chemical equilibrium is

Table 4. Comparison Between Two Algorithms with System EtOH-HAC-EtAC-H_2O

		No. of k_i's		No. of ξ_j's	
Temp. K	α	S-C	KZ	S-C	KZ
358	1,000	35	10	7	9
355	0.877	42	9	10	23
350	0.413	23	6	10	21
345	0.000	5	3	5	11

Table 5. Iteration Summary at 355 K and 1 atm of the S-C Method

Outer Loop Counter	k Values Inner Loop	α	K_z	Reaction Extent	Objective Function
0	2	0.000	4.958	0.000	1.537
1	1	0.000	4.958	$2.3 \cdot 10^{-4}$	1.537
2	2	0.000	4.856	0.953	0.983
3	4	0.334	8.006	5.369	0.128
4	5	0.652	14.524	7.052	$3.66 \cdot 10^{-2}$
5	6	0.790	19.725	7.819	$6.68 \cdot 10^{-3}$
6	7	0.846	22.692	8.141	$9.29 \cdot 10^{-4}$
7	6	0.867	23.962	8.262	$1.08 \cdot 10^{-4}$
8	5	0.874	24.421	8.303	$1.16 \cdot 10^{-5}$
9	3	0.874	24.543	8.317	$1.18 \cdot 10^{-6}$
10	1	0.877	24.583	8.321	$1.14 \cdot 10^{-7}$
Total	42				

solved in the inner loop. Consequently, the reaction extent moved very quickly to the solution.

Using the "basic" algorithm, i.e., forcing convergence of extents inside the α loop, this problem took 35 calculations of extents and seven sets of k values. Using the S-C algorithm as modified by Chen, i.e., moving k values to the outer most loop, this problem took 40 extents calculations and seven sets of k values. As described earlier, not forcing convergence in the inner loop of the recommended algorithm reduced the number of extents calculations but increased the number of k values calculated slightly.

Table 7 gives results of the equilibrium calculation at 355 K and 1 atm. Initially, the system contains 10 kg · mol of ethanol and 10 kg · mol of acetic acid. The calculated extent of reaction is 8.321 kg · mol, and the flash ratio is 0.877.

Example 2

In processes for purifying plant effluent streams, one often encounters aqueous volatile weak electrolyte systems, such as NH_3-CO_2-H_2O. There have been many articles about its thermodynamics (Edwards et al., 1975, 1978; Beutier and Renon, 1978; Chen et al., 1979; Zhou and Zu, 1983) and equilibrium calculations (Zemaitis and Rafal, 1975; Gautam and Seider, 1979b). This paper uses it as an example for comparing the KZ algorithm with the S-C algorithm. The results should be of general interest due to its complex reactions and strong nonideality.

Table 6. Iteration Summary at 355 K and 1 atm by the KZ Method

Outer Loop Counter	Iterations Inner Loop	α	K_z	Reaction Extent
0	6	0.000	18.644	8.120
1	5	0.888	21.350	8.221
2	4	0.884	24.201	8.311
3	2	0.879	23.858	8.301
4	1	0.875	24.023	8.306
5	2	0.876	24.224	8.311
6	1	0.876	24.378	8.315
7	1	0.877	24.472	8.320
8	1	0.877	24.538	8.321
9	0	0.877	24.581	8.321
Total	23			

Table 7. Numerical Results of Esterification Equilibrium*

	mol %		
Comps.	Feed Stream	Liquid Stream	Vapor Stream
EtOH	50.0	6.86	8.62
HAc	50.0	23.76	6.24
EtAc	0.0	13.73	45.51
H_2O	0.0	55.65	39.63

*Conditions: Temperature, 355 K; pressure, 1 atm; conversion, 83.21%; flash ratio 87.7%

There are five reactions in the system NH_3-CO_2-H_2O:

$$NH_3 + H_2O = NH_4^+ + OH^- \tag{29}$$

$$CO_2 + H_2O = HCO_3^- + H^+ \tag{30}$$

$$HCO_3^- = CO_3^= + H^+ \tag{31}$$

$$H^+ + OH^- = H_2O \tag{32}$$

$$NH_3 + HCO_3^- = NH_2COO^- + H_2O \tag{33}$$

At 373 K, the equilibrium constants (defined in Eqs. 2) for the five reactions are $1.45 \cdot 10^{-5}$, $3.96 \cdot 10^{-7}$, $7.08 \cdot 10^{-11}$, $1.79 \cdot 10^{12}$ and 0.44, respectively (Edwards et al., 1978). The liquid activity coefficients of the system are also based on the

Table 8. Iteration Summary of the S-C Algorithm for System NH_3-CO_2-H_2O*

Outer Loop Counter	k Value Calc.	K_z (Eq. 25)	Ionic Strength	Objective Function
0	1	24.407	$2.507 \cdot 10^{-8}$	0.9945
1	2	25.403	$4.964 \cdot 10^{-3}$	$1.32 \cdot 10^{7}$
2	1	27.960	$4.440 \cdot 10^{-3}$	$1.95 \cdot 10^{6}$
3	1	26.006	$5.640 \cdot 10^{-3}$	$6.61 \cdot 10^{4}$
4	1	24.604	$1.126 \cdot 10^{-2}$	$2.18 \cdot 10^{3}$
5	1	24.230	$2.302 \cdot 10^{-2}$	$4.36 \cdot 10^{1}$
6	1	23.903	$4.036 \cdot 10^{-2}$	0.2657
7	1	23.717	$5.265 \cdot 10^{-2}$	0.9944
8	1	23.710	$5.251 \cdot 10^{-2}$	$3.23 \cdot 10^{-2}$
9	1	23.694	$5.157 \cdot 10^{-2}$	$8.54 \cdot 10^{-3}$
10	1	23.759	$4.995 \cdot 10^{-2}$	$1.23 \cdot 10^{-4}$
11	1	23.779	$4.850 \cdot 10^{-2}$	$2.31 \cdot 10^{-5}$
12	1	23.784	$4.809 \cdot 10^{-2}$	$4.57 \cdot 10^{-6}$
13	1	23.784	$4.808 \cdot 10^{-2}$	$1.11 \cdot 10^{-8}$
Total	15			

*Conditions: $T = 373$ K; $P = 10$ atm; F_{in}, $H_2O = 1$ kg; $NH_3 = 0.05$ mol; $CO_2 = 0.1$ mol

Table 9. Iteration Summary of the KZ Algorithm for System NH_3-CO_2-H_2O Conditions*

Outer Loop Counter	Iterations Inner Loop	K_z (Eq. 25)	Ionic Strength
0	14	0.5058	$3.330 \cdot 10^{-2}$
1	6	19.886	$4.778 \cdot 10^{-2}$
2	4	23.787	$4.807 \cdot 10^{-2}$
3	2	23.784	$4.808 \cdot 10^{-2}$
Total	26		

*See Table 8

Table 10. Iteration Summary of the S-C Algorithm for System NH_3-CO_2-H_2O*

Outer Loop Counter	Iterations Inner Loop	K_z (Eq. 25)	Ionic Strength	Objective Function
0	1	19.0125	$2.79 \cdot 10^{-8}$	0.8624
1	2	30.1505	$4.70 \cdot 10^{-3}$	$1.606 \cdot 10^{7}$
2	1	38.8530	$3.50 \cdot 10^{-3}$	$2.451 \cdot 10^{6}$
4	2	31.0743	$2.03 \cdot 10^{-2}$	$8.168 \cdot 10^{2}$
5	1	29.2720	0.2162	$2.534 \cdot 10^{3}$
8	5	14.0150	1.5370	$4.930 \cdot 10^{1}$
9	2	18.2190	0.7887	$9.900 \cdot 10^{1}$
12	4	17.4550	1.0030	$1.263 \cdot 10^{2}$
13	1	16.8970	1.0300	$1.074 \cdot 10^{2}$
18	9	12.4000	1.6642	$5.210 \cdot 10^{-5}$
27	9	12.3674	1.7613	$8.579 \cdot 10^{-7}$
36	10	12.3595	1.7855	$8.076 \cdot 10^{-8}$
38	2	12.3587	1.7878	$5.142 \cdot 10^{-8}$
Total	47			

*Conditions: T 373 K; P = 10 atm; F_{in}, H_2O = 1 kg; NH_3 = 2.9 mol; CO_2 = 1.45 mol

equations and parameters developed by them. Their equations, which are best suited for aqueous volatile weak electrolyte systems are based on work published by Zhou and Xu (1983) and can be applied to systems with high ionic strength comparable to equations developed by Chen et al. (1979). Vapor fugacity coefficients of the system are computed with the equation of state published by Nakamura et al. (1976).

An iteration summary of the S-C algorithm for a system with total molalities of NH_3 and CO_2 at 0.05 and 0.1, respectively, is given in Table 8. Because of the low electrolyte concentrations, the liquid nonideality is minimal and the number of k value updates in the inner loop is small. Yet the total number by the S-C algorithm is 15 in contrast to only three iterations of k values required by the KZ algorithm as shown in Table 9. There is at least one k value update for each iteration of extents. For very dilute systems, this is apparently not efficient.

When the total molalities of NH_3 and CO_2 reach 2.9 and 1.45, respectively, the nonideality becomes strong. The S-C algorithm, as shown in Table 10, did not reach the solution smoothly. Instead, the "objective function" increased many times, at first, 5th, 9th and 12th iterations, indicating frequent increases of λ in the Marquardt method. This phenomenon is certainly attributable to the strong nonideality. Yet, the path by the KZ algorithm, which is shown in Table 11, was very stable and fast. The numbers of k-value evaluations by the two algorithms are 47 and 5, respectively, and those of extents are both 38.

Table 11. Iteration Summary of the KZ Algorithm for System NH_3-CO_2-H_2O Conditions*

Outer Loop Counter	Iterations Inner Loop	K_z (Eq. 25)	Ionic Strength
0	16	0.4925	0.9879
1	12	12.2968	1.5530
2	4	12.6277	1.7224
3	3	12.4392	1.7723
4	2	12.3653	1.7852
5	1	12.3578	1.7880
Total	38		

*See Table 10

Table 12. Calculated Results of System NH_3-CO_2-H_2O-CH_4-C_2H_6*

Species	Molalities (mol/kg)	Activity Coeff.	Partial Pres.	Fugacity Coeff.
NH_3	0.6151	1.010	0.1543	0.9761
CO_2	0.0183	1.014	1.8080	0.9793
CH_4			3.5457	0.9937
C_2H_6			3.5457	0.9691
H_2O	55.555	1.035	0.9462	0.9651
NH_4^+	2.2256	0.188		
HCO_3^-	1.6712	0.162		
$CO_3^=$	0.1780	0.004		
NH_2COO^-	0.1984	0.392		
H^+	$5.34 \cdot 10^{-8}$	0.483		
OH^-	$4.61 \cdot 10^{-5}$	0.445		

*Conditions: T = 373 K; P = 10 atm; F_{in}, H_2O = 1 kg; NH_3 = 3 mol; CO_2 = 3 mol; CH_4 = 2 mol; C_2H_6 = 2 mol

Table 12 gives the results of equilibrium calculation for the system NH_3-CO_2-H_2O-CH_4-C_2H_6, in which CH_4 and C_2H_6 are inert with respect to the chemical equilibrium and assumed to be insoluble in water. All ions are assigned small k values, e.g., 10^{-10}, and CH_4 and C_2H_6 large k values, e.g., 10^{10}. The calculated fractions of NH_3 and CO_2 absorbed in water are 97.10% and 66.00%, respectively. The ionic strength is 2.404 M.

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Notation

A_i = chemical species i
D = decomposed diagonal matrix of H (Eq. 25)
f_i = fugacity of species i, atm
$F_{in\,i}$ = initial amount of species i, mol
$F_{out\,i}$ = final amount of species i (or estimate), mol
G_i^o = standard Gibb's free energy of formation of species i, J
ΔG_j^o = standard Gibb's free energy of reaction for reaction j, J
g = gradient vector of equation (Eq. 27)
H = Hessian matrix of equation (Eq. 26)
I = unity matrix
J = Jacobian matrix
K_j = chemical equilibrium constant for reaction j (Eq. 2)
K_{zj} = constant for reaction j defined by Eq. 13
k_i = phase equilibrium ratio for species $i (= y_i/x_i)$
L = decomposed lower triangle matrix of H (Eq. 26)
M = number of reactions
N = number of components
P = system pressure, atm
p_i = partial pressure of species i, atm
R = universal gas constant
S_i = error in i, described in Eqs. 14-15
S_α = error in flash equation (Eq. 11)
T = system temperature, K
x_i = mole fraction of species i in liquid phase
y_i = mole fraction of species i in vapor phase
z_i = mole fraction of species i in total system including liquid and vapor

Greek letters

α = vapor to liquid mole ratio
δ = Kronecker delta
γ_i = activity coefficient of species i
λ = Marquardt parameter
ν_{ij} = stoichiometric coefficient of species i in reaction j
ξ_j = extent of reaction j, mol
ϕ_i = fugacity coefficient of species i in the mixture

Subscripts

i = species number
j = reaction number

Superscripts

o = standard state (at 1 atm and system temperature)
s = saturation
T = transpose

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