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# Successive Substitution Augmented for Global Minimization of the Gibbs Free Energy

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## Abstract

The conventional approach to multiphase flash is the sequential usage of stability and flash calculations. It is a series of local minimizations of the Gibbs free energy, in which a false solution is obtained from fugacity equations for a fixed number of phases and corrected in the subsequent stability analysis. The robustness and efficiency of multiphase flash have been important issues to be resolved for compositional reservoir simulation with complex phase behavior.

This paper presents a new algorithm to solve the correct set of equations for global minimization of the Gibbs free energy for isothermal, isobaric, multiphase flash. The Peng-Robinson equation of state with the van der Waals mixing rules is used for thermodynamic properties.

The number of equilibrium phases is part of the solution in the new algorithm, in contrast to the sequential stability/flash approach. Therefore, false solutions are not necessary for multiphase flash with the new algorithm. The advantage of the new algorithm in terms of robustness and efficiency is more pronounced for more complex phase behavior, in which multiple local minima of the Gibbs free energy are present. It is straightforward to implement the algorithm because of the simple formulation, which also allows for an arbitrary number of initial compositions.

## Introduction

A multiphase equilibrium calculation requires global minimization of the Gibbs free energy subject to material balance. The conventional algorithms after Michelsen (1982a, 1982b) are based on the sequential usage of phase-stability and flash calculations. That is, a phase-stability calculation is performed for a composition, at which the tangent plane to the Gibbs free energy surface is defined. If it detects phase instability, a flash calculation is performed under the assumption that one more equilibrium phase is present.

This conventional approach has been successfully applied for various compositional flow problems in the literature (e.g., Mehra et al. 1983; Nghiem and Li 1984; Perschke 1988; Han and Rangaiah 1998). However, it is a series of local solutions for assumed numbers of phases, which requires obtaining and correcting false solutions for multiphase problems. Correction of false solutions in phase-stability analysis is highly sensitive to the initial guess used for the search for potential equilibrium phases. Also, it is not always possible to obtain reasonable initial K values for multiphase reservoir fluids.

For example, three different types of two equilibrium phases ($L_1 + V$, $L_1 + L_2$, and $L_2 + V$) exist in composition space that contains three equilibrium phases ($L_1 + L_2 + V$), where $L_1$ and $L_2$ and V stand for the oleic, solvent-rich liquid, and gaseous phases, respectively. When $L_1 + L_2$ or $L_2 + V$ is of the global minimum in the Gibbs free energy at the specified flash conditions, the conventional algorithms initiated with Wilson's correlation often fail to converge to the correct solution, or tend to be attracted by local minima before reaching it through negative flash.

One way to improve the robustness of multiphase flash is to use multiple initial guesses in phase-stability analysis as given in Michelsen (1982b), Perschke (1988), and Li and Firoozabadi (2012). However, it still requires obtaining and correcting false solutions, which are near local minima of the Gibbs free energy subject to material balance. Many stability calculations with different initial guesses can be required to obtain merely a false solution in multiphase flash.

Gupta et al. (1991) presented a novel methodology to perform phase-stability and flash calculations simultaneously. However, a few researchers (Abdel-Ghani 1995; Alsaifi and Englezos 2011) reported numerical issues associated with degenerate equations near phase boundaries on the basis of Gupta et al.' formulation. It has been also found that the initialization scheme proposed by Gupta (1990) and Gupta et al. (1991) often fails for multiphase problems. Even when it starts the iteration, the original algorithm of Gupta et al. is not robust since it does not check the feasibility of each Rachford-Rice (RR) solution.

This paper presents the correct set of equations and constraints that can be easily solved for minimization of the Gibbs free energy for isothermal isobaric flash. The main novelty lies in the unified usage of the tangent-plane distance function (Baker et al. 1982; Michelsen 1982a) for multiphase flash integrated with stability analysis for an arbitrary number of iterative compositions. A new algorithm is developed for minimization of the Gibbs free energy on the basis of successive substitution augmented with some important steps for robustness. Case studies are given to demonstrate the robustness of the developed algorithm.

## Algorithm

This section presents a new algorithm for global minimization of the Gibbs free energy as formulated in **Appendix A.** A step-wise description is presented along with key equations. The corresponding flow chart is given in **Appendix B.**

The developed algorithm uses the tangent plane distance equations

$$f_{ij} = \ln x_{ij}\varphi_{ij} - \ln x_{ir}\varphi_{ir} - \theta_j = 0 \tag{1}$$

to update all iterative compositions $x_{ij}$ ($i = 1, 2, \ldots, N_C$ and $j = 1, 2, \ldots, N_S$) through K values on the basis of successive substitution. $N_C$ is the number of components, and $N_S$ is the number of sampling compositions at which phase stability is measured during the iteration. The fugacity coefficient of component i at sampling composition j is denoted as $\varphi_{ij}$. A reference composition is expressed as $x_{ir}$ ($i = 1, 2, \ldots, N_C$). K values are defined as

$$K_{ij} = x_{ij}/\left(e^{\theta_j} x_{ir}\right) \tag{2}$$

for $i = 1, 2, \ldots, N_C$, and $j = 1, 2, \ldots, N_S$ except for r.

At an equilibrium state upon convergence, equation 1 becomes equation A-6; i.e., $\theta_j = D_j$ and the reference composition corresponds to one of equilibrium phases, which is denoted as $x_{iRef}$ in Appendix A. $N_P$ equilibrium phases satisfy $D_j = 0$ along with equations A-2, A-3, and A-4 for $j = 1, 2, \ldots, N_P$. $N_U$ unstable stationary points satisfy $D_j > 0$ and equation A-4 for $j = (N_P + 1), (N_P + 2) \ldots, N_S$, where $N_S = N_P + N_U$.

During the iterations, $N_S$ sampling compositions belong to either the equilibrium set P or the unstable set U. In set P, $\theta_j = 0$ and $\beta_j > 0$ for $j = 1, 2, \ldots, N_P$. In set U, $\theta_j > 0$ and $\beta_j = 0$ for $j = (N_P + 1)$,

$(N_P + 2)\ldots, N_S$. Successive substitution is performed to solve equation 1 together with equations A-2, A-3, and A-4 for K values. The reference composition is selected from set P adaptively, as described later.

For set P, equation 2 becomes $K_{ij} = x_{ij}/x_{ir}$. The conventional RR equations give the relationship between K values and mole fractions of apparent phases ($\beta_j$'s) as follows:

$$g_j = \sum_{i=1}^{N_C}(x_{ir} - x_{ij}) = \sum_{i=1}^{N_C}(1 - K_{ij})z_i/t_i = 0 \tag{3}$$

for sampling point $j \neq r$ within set P, where $t_i = 1 - \sum_{k=1,k\neq r}^{N_P}(1 - K_{ik})\beta_k$ for $i = 1, 2, \ldots, N_C$. Compositions are given as $x_{ir} = z_i/t_i$ and $x_{ij} = K_{ij}x_{ir}$ for sampling point $j \neq r$.

For set U, the summation constraint $\Sigma_i x_{ij} = 1.0$ gives

$$\theta_j = -\ln\left[\sum_{i=1}^{N_C} K_{ij}x_{ir}\right] \tag{4}$$

for sampling composition j within set U. Compositions for set U are given as $X_{ij} = e^{\theta j}K_{ij}X_{ij}$ for $i = 1, 2, \ldots, N_C$.

The fundamental structure of the current algorithm broadly follows the traditional successive substitution algorithms for flash and stability analysis. That is, each iteration first solves equations 3 for compositions for set P for a given set of K values and overall composition. Then, equation 4 is used to obtain compositions for set U for a given set of K values and reference composition. After that, K values are updated for sets P and U by use of equation 1, $\ln K_{ij} = \ln\varphi_{ir} - \ln\varphi_{ij}$.

The main difference from the conventional flash and stability analysis lies in the unified usage of the tangent plane distance equations (equation 1) for an arbitrary number of sampling compositions. This gives the flexibility in terms of robustness and efficiency that the algorithm offers; e.g., use of more sampling compositions increases the level of robustness at the expense of the increased number of equations, at least for the initial stage of iteration.

With the well-known convergence behavior of successive substitution (Mehra et al. 1983; Ammar and Renon 1987; Kaul 1992), sampling compositions converge to stationary points on the tangent plane distance function at an equilibrium state. As will be discussed later, sampling compositions naturally merge for a case in which $N_S$ is greater than the number of stationary points present upon convergence.

$N_S$ sampling compositions can be initialized by a biased or unbiased distribution in composition space. Biased initialization methods include use of a correlation suitable for the fluid of interest, such as Wilson's correlation, Li and Firoozabadi (2012), and Zhu and Okuno (2015b), and use of certain information from the previous time-step in flow simulation. Unbiased initialization methods include a random distribution and a distribution near vertices in composition space. The unbiased methods are useful when no reliable information is available for equilibrium phases of the fluid of interest.

A reference composition is also initialized to define equation 1. First, function D (equation A-5) is used for $N_S$ sampling compositions with the overall composition as the reference. Then, the initial reference composition is defined at which D is the minimum among the $N_S$ sampling compositions.

Other important steps for robustness include the feasibility check for each RR solution by use of the method of Okuno et al. (2010). Also, the constraints regarding $\beta_j$ and $\theta_j$ described previously are used for classification of sampling compositions for sets P and U.

The Peng-Robinson (PR) EOS (Peng and Robinson 1976a, 1976b) with the van der Waals mixing rules is used to calculate thermodynamic properties in this research. A stepwise description of the algorithm is given below.

Step 1. Set $N_S$ sampling compositions $\vec{x}_j^{(k)}$ for $j = 1, 2, \ldots, N_S$ by a certain initialization scheme as described previously. The number in the bracket represents the iteration-step number; $k = 1$ for the initial iteration.

Step 2. Calculate $D_j$ for $j = 1, 2, \ldots, N_S$ with $\vec{z}$ as the reference composition from equation A-5. Select the sampling composition with the minimum D value as the reference composition, $\vec{x}_r^{(1)}$ . Initialize K values, $\vec{K}_j^{(1)}$ , by use of $\ln K_{ij} = \ln\varphi_{ir} - \ln\varphi_{ij}$ for $j = 1, 2, \ldots, N_S$ except for r. Recalculate $D_j$ with $\vec{x}_r^{(1)}$ and set $N_U$ as the number of sampling compositions with positive D values. $N_P = N_S - N_U$. If $N_P = 1$, go to step 6. Otherwise, continue to step 3.

Step 3. Check the feasibility of the RR solution for set P. If feasible, go to step 5. Otherwise, continue to step 4.

Step 4. Exclude from set P as many sampling compositions as required until the feasibility is satisfied for the given RR problem. Update $N_P$. $N_U = N_S - N_P$. If $N_P = 1$, go to step 6. Otherwise, continue to step 5.

Step 5. Perform the convex minimization to obtain $\vec{x}_j^{(k)}$ and $\beta^{(k)}{}_j$ for set P that satisfy equation 3, as presented in Okuno et al. (2010). The convergence criterion is that $\|g_j\|_\infty < \varepsilon_g$ (e.g., $\varepsilon_g = 10^{-10}$).

Step 6. Obtain $\vec{x}_j^{(k)}$ and $\theta^{(k)}{}_j$ for set U by use of equation 4.

Step 7. Check to see if there is any $\theta^{(k)}{}_j$ that is negative in set U. If so, update $\vec{x}_r$ and $N_U$. $N_P = N_S - N_U$. Go to step 10. Otherwise, continue to step 8.

Step 8. Check to see if there is any $\beta^{(k)}{}_j$ that is negative in set P. If so, perform necessary updates for $\vec{x}_r$ and $N_U$. $N_P = N_S - N_U$. Go to step 10. Otherwise, continue to step 9.

Step 9. Check for convergence. Stop if $\|f_{ij}\|_\infty < \varepsilon_f$ (e.g., $\varepsilon_f = 10^{-12}$). Otherwise, continue to step 10.

Step 10. Check to see if there are any compositions to be merged on the basis of the criterion that the max norm for two compositions is less than $\varepsilon_x$ (e.g., $\varepsilon_x = 10^{-3}$). If so, perform necessary updates for $N_S$ and $N_U$. $N_P = N_S - N_U$.

Step 11. Update K values by use of equations 1 and 2; i.e., $\ln K^{(k+1)}{}_{ij} = \ln\varphi^{(k)}{}_{ir} - \ln\varphi^{(k)}{}_{ij}$ for $i = 1, 2, \ldots, N_C$ and $j \neq r$. Increase the iteration-step index by one; $k = k + 1$. Go to step 6 if $N_P = 1$. Otherwise, go to step 3.

In step 4, the exclusion of sampling compositions from set P is performed on the basis of their $D_j$ values from equation A-5. That is, the sampling composition with the largest $D_j$ value among set P is first excluded. The subsequent exclusions, if necessary, are in the order of decreasing $D_j$. If step 4 is taken in the first iteration ($k = 1$), the $D_j$ values calculated in step 2 are directly used.

In step 7, the sampling composition with the minimum $\theta_j$ value is selected for updating $\vec{x}_r$ . In step 8, a sampling composition with $0 < \beta_j < 1$ is selected for updating $\vec{x}_r$.

The algorithm presented above is substantially different from that of Gupta et al. (1991). An important difference comes from the difference in formulation; that is, they introduced an additional set of equations, $\beta_j\theta_j = 0$, which were called "stability equations" in their papers. A similar set of equations, $\beta_j\theta_j/(\beta_j + \theta_j) = 0$, were then solved simultaneously with the RR equations in their algorithm. However, Appendix A clearly shows that the complete formulation does not require Gupta et al.'s stability equations. The correct set of equations in the current paper does not have the degeneracy issues that Gupta et al.'s algorithm exhibits near phase boundaries due to their stability equations, as reported by Alsaifi and Englezos (2011).

The robustness of the current algorithm also comes from the careful initialization and adaptive selection of the reference composition. The initialization scheme of Gupta (1990) eliminates the sampling compositions that have positive D values from equation A-5 with $\vec{z}$ as the reference composition. However, this often leads to a complete failure of the calculation. The improvements over Gupta et al. (1991) were developed by following the fundamental theory behind the formulation (see Appendix A) that the lowest Gibbs free energy should be searched for in composition space.

The simplicity of the formulation has led to the straightforward iteration steps, which are essentially the widely-used successive substitution. Unlike in other publications following Gupta et al. (1991), such as Abdel-Ghani (1995), Chaikunchuensakun et al. (2002), and Alsaifi and Englezos (2011), the robust solution of multiphase RR equations (Okuno et al. 2010) further enhances the robustness of the current algorithm.

## Case Studies

In this section, case studies are given to demonstrate the robustness and simplicity of the algorithm developed in this research, in comparison with the sequential method and the method of Gupta et al. (1991). The new algorithm can make multiphase flash problems straightforward by not having to solve for and correct false solutions.

In the sequential method used for this section, single-phase stability analysis is performed with two initial guesses, searching for a V-like phase first and a L-like phase next, on the basis of Wilson's K values (Michelsen 1982a). For stability analysis for one of multiple phases, initial guesses recommended by Firoozabadi (1999) are used in addition to the V-like and L-like guesses, in the following order: a V-like phase, a L-like phase, compositions near vertices in composition space, the midpoint of phase compositions, and $\varphi_i X_i$ for i = 1, 2,. . . , $N_C$. Stability analysis in this section uses only successive substitution for the fair comparison between the new and conventional algorithms in terms of robustness. The convergence criterion for stability analysis is that the max norm of stationarity equations is less than $10^{-8}$.

For flash calculations in the sequential method used for this section, two numerical schemes have been tested: use of only successive substitution, and the combination of successive substitution and Newton's minimization of the Gibbs free energy. The convergence criterion used is that the max norm of fugacity equations is less than $10^{-12}$. The switching criterion from successive substitution to the minimization algorithm is that the max norm of fugacity equations is less than $10^{-3}$. However, the two sets of numerical schemes have given the same solutions for the sequential method in the cases tested in this section.

For the new algorithm, initial sampling compositions are distributed near vertices of composition space for cases 1 and 4, but also randomly distributed for Cases 2 and 3 using a random-number generator. This flexibility in initialization is one of the advantages over the conventional algorithms, as discussed in the previous section.

### Case 1

This case uses ternary mixtures of $H_2O$, $C_3$, and n-$C_{16}$ to show a few important features of the new algorithm. The properties used for the components are given in **Table 1**. **Figure 1** shows the two- and three-phase regions in composition space at 430 K and 35 bars. In the figure, L, V, and W represent the oleic, gaseous, and aqueous phases, respectively.

**Table 1—Properties of the components for case 1**

| Component | $P_C$ (bar) | $T_C$ (K) | $\omega$ |
|---|---|---|---|
| **$H_2O$** | 220.89 | 647.3 | 0.344 |
| **$C_3$** | 42.46 | 369.8 | 0.152 |
| **n-$C_{16}$** | 14.19 | 717.0 | 0.742 |

**Binary Interaction Parameters**

| | **$H_2O$** | **$C_3$** | **n-$C_{16}$** |
|---|---|---|---|
| **$H_2O$** | 0.0000 | 0.6841 | 0.3583 |
| **$C_3$** | 0.6841 | 0.0000 | 0.0000 |
| **n-$C_{16}$** | 0.3583 | 0.0000 | 0.0000 |

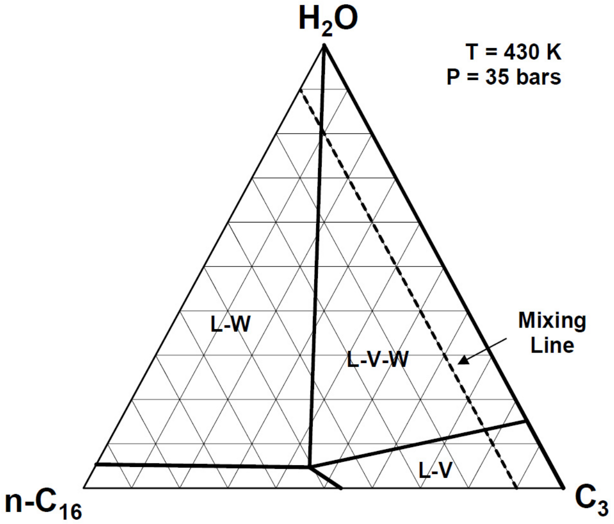

**Figure 1—Phase boundaries for the ternary system of $H_2O$, $C_3$, and n-$C_{16}$ at 430 K and 35 bars. L, V, and W stand for the oleic, gaseous, and aqueous phases, respectively. Properties of the components are given in Table 1**

Application of the algorithm along the mixing line between (0.0, 0.9, 0.1) and (0.9, 0.0, 0.1) results in the behavior of $\beta_j$ and $\theta_j$ shown in **Figure 2**. One unstable stationary point (in set U) is observed in the two-phase regions (L + V and L + W) along the mixing line. As mentioned in the algorithm section, the converged $\theta$values correspond to the dimensionless tangent plane distances at stationary points (see equation A-6). The converged $\theta$(or D) values qualitatively indicate the level of instability at the corresponding compositions. Hence, the new algorithm provides more global information about the Gibbs free energy than the conventional flash algorithms, when it converges with unstable stationary points. Unlike the current algorithm, the negative flash approach (Whitson and Michelsen 1989) may indicate phase instability by negative $\beta$values, when obtaining a false solution.

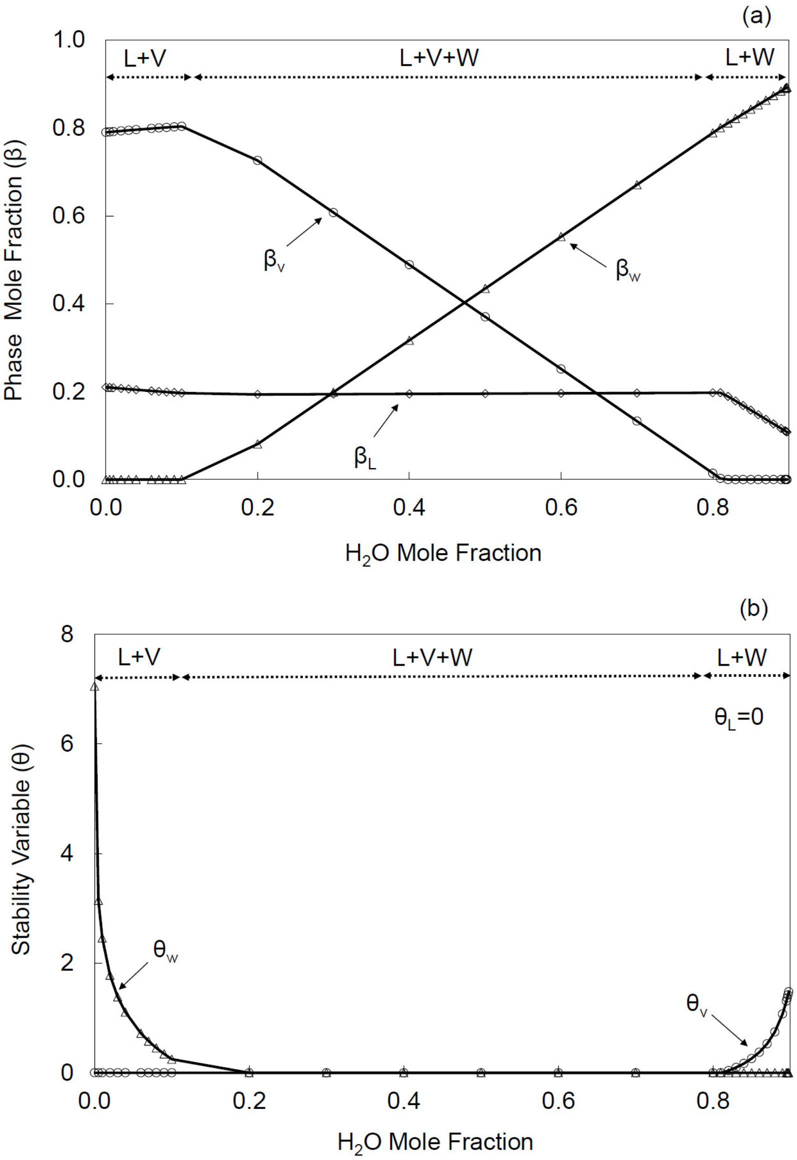

**Figure 2—Variation of parameters with the new algorithm applied along the mixing line given in Figure 1. (a) Phase mole fraction. (b) Stability variable**

**Figure 3** shows the Gibbs free energy and converged tangent planes for three overall compositions with the $H_2O$ concentrations of 0.10, 0.75, and 0.84 along the mixing line. The algorithm has successfully converged to the lowest Gibbs free energy subject to material balance for each overall composition. The D values at unstable stationary points in Figure 3 can be confirmed with Figure 2.

Figures 1, 2, and 3 clearly show that different sets of equilibrium phases can be easily calculated as thermodynamically stable stationary points by use of the unified algorithm that directly converges to the correct solution. It was observed that distributed sampling compositions (e.g., six compositions) naturally merge to three stationary points corresponding to the L, V, and W phases on the Gibbs free energy surface given in Figure 3. The convergence behavior is determined by the traditional successive substitution as described in the previous section. An illustrative figure for such a case is available upon request along with input data.

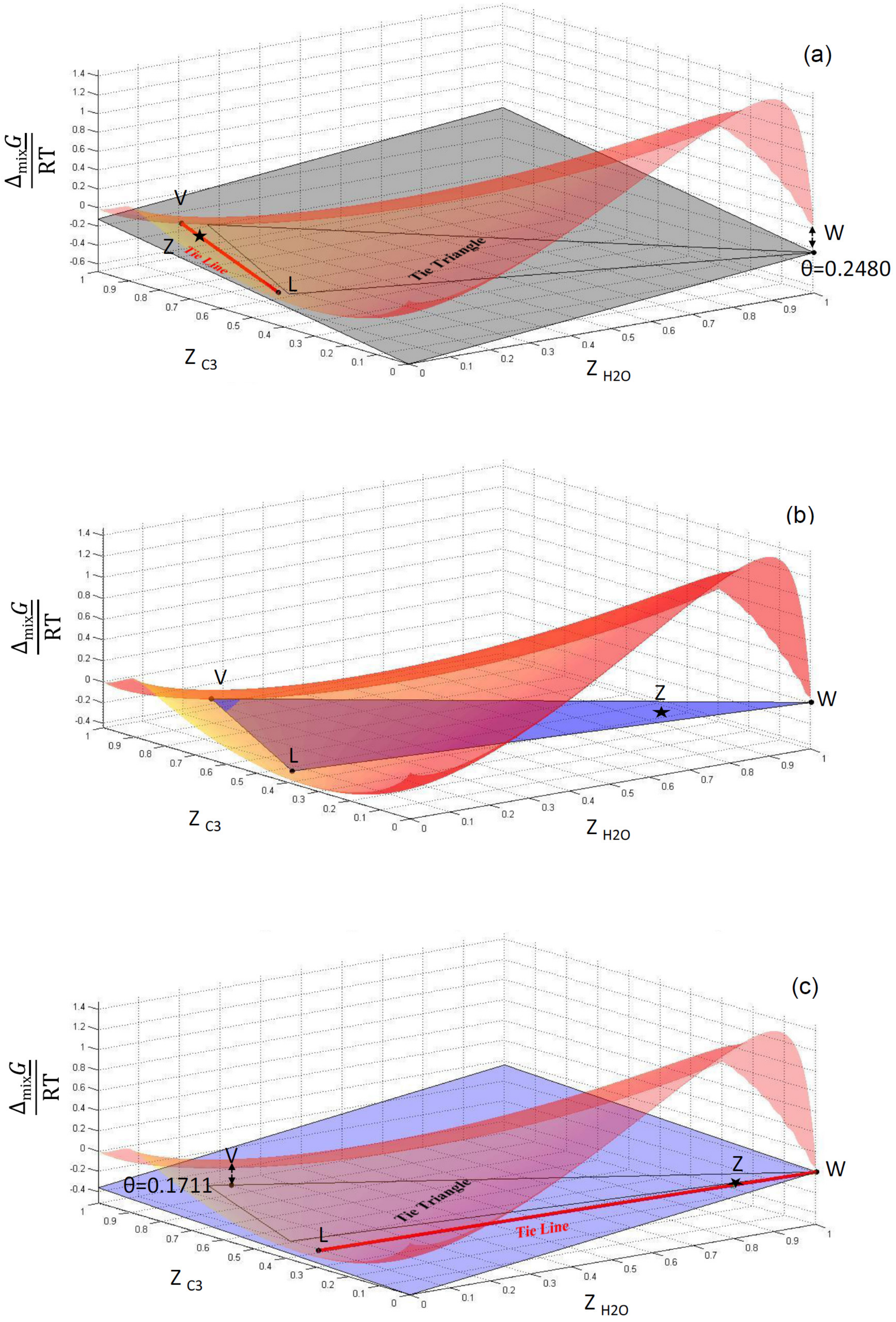

**Figure 3—Gibbs free energy surface and converged tangent plane along the mixing line given in Figure 1. (a) z$H_2O$ = 0.1. (b) z$H_2O$ = 0.75. (c) z$H_2O$ = 0.84**

## Case 2

The simplicity of the formulation and algorithm in this research yields the robustness in multiphase flash by not having to obtain false solutions. The advantage over the conventional sequential methods is pronounced when the correct solution in a multiphase calculation does not include either the $L_1$ or V phase, which can frequently occur in many gas and steam injection processes with multiple partially miscible phases.

This case uses the binary of $C_1$ and $H_2S$ at 190 K and 40.53 bars to show several issues of the sequential methods and the robustness of the new algorithm. **Table 2** gives the properties of the components. The Gibbs free energy surface in composition space exhibits three lobes corresponding to the $L_1$, $L_2$, and V phases in the order of increasing $C_1$ concentration ($z_{C1}$) (**Figure 4**). The new algorithm is initialized with three sampling compositions; two of them are distributed near vertices of composition space and the other is a randomly selected point. The sequential method fails to find the correct solutions with $L_2$ + V for $z_{C1}$ from 0.968 to 0.982.

**Table 2—Properties of the components for case 2**

| Component | $P_C$ (bar) | $T_C$ (K) | $\omega$ | BIP |
|---|---|---|---|---|
| $C_1$ | 46.0016 | 190.6 | 0.008 | 0.00 |
| $H_2S$ | 89.3686 | 373.2 | 0.1000 | 0.08 |

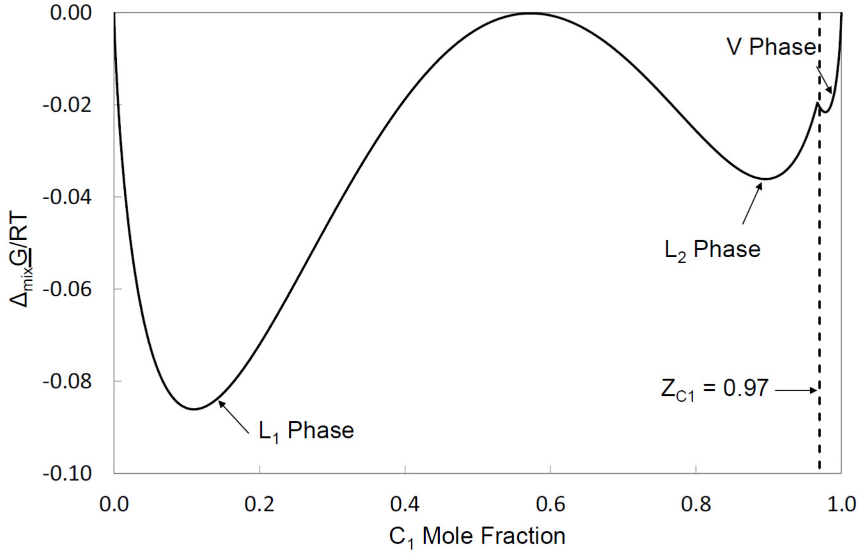

**Figure 4—Gibbs free energy surface in composition space for the binary system of $C_1$ and $H_2S$. Properties of the components are given in Table 2. The temperature and pressure are 190 K and 40.53 bar, respectively. The three lobes indicated correspond to the $L_1$, $L_2$, and V phases in the order of increasing $C_1$ mole fraction in composition space**

For $0.968 \leq z_{C1} < 0.980$, the sequential algorithm only finds an L phase in the single-phase stability analysis, and the subsequent two-phase flash results in a local minimum with $L_1$ + V. Then, the stability analysis for one of the two phases finds an $L_2$ phase. However, three-phase flash is not feasible for a binary mixture, due to the degree of freedom of one. Hence, the final result from the sequential algorithm is the $L_1$ + V phases that have been obtained. **Table 3** shows the correct solution from the new algorithm and the incorrect solution from the sequential method at $z_{C1}$ of 0.970. The new algorithm does not need to perform three-phase flash to reach the correct two-phase solution ($L_2$ + V). The converged Gibbs free energy from the new algorithm, -0.539476213, is confirmed to be lower than the value, -0.537697750, from the sequential method.

Table 3—Results for case 2 with the new and conventional algorithms. Properties of the components are given in Table 2. The overall composition is 97% $C_1$ and 3% $H_2S$. The specified temperature and pressure are 190 K and 40.53 bar

| | New Algorithm | | | Conventional Algorithm | |
|---|---|---|---|---|---|
| Component | $L_1$ | V | $L_2$ | $L_1$ | V |
| $C_1$ | 0.18634266482 | 0.98268738632 | 0.93604368336 | 0.12587785433 | 0.97953528887 |
| $H_2S$ | 0.81365733518 | 0.01731261368 | 0.06395631664 | 0.87412214567 | 0.02046471113 |
| $\beta$ | 0 | 0.7280 | 0.2720 | 0.0112 | 0.9888 |
| $\theta$ | 0.1323 | 0 | 0 | - | - |
| $\underline{G}_R/RT$ | | -0.53947621262 | | -0.5376977504 | |

For $0.980 \leq z_{C1} \leq 0.982$, the sequential algorithm fails to find phase instability in single-phase stability analysis. However, the new algorithm properly converges to the $L_2$ and V phases. **Table 4** shows the solution for $z_{C1}$ of 0.980. The Gibbs free energy at the solution, -0.492028012, is confirmed to be lower than the single-phase Gibbs free energy -0.491838307.

Table 4—Solution for case 2 with the new algorithm. Properties of the components are given in Table 2. The overall composition is 98% $C_1$ and 2% $H_2S$. The specified temperature and pressure are 190 K and 40.53 bar. The correct set of three phase compositions is identical to the one presented in Table 3. The conventional algorithm fails to find phase instability in single-phase stability analysis for this flash calculation

| Component | $L_1$ | V | $L_2$ |
|---|---|---|---|
| $\beta$ | 0 | 0.9424 | 0.0576 |
| $\theta$ | 0.1323 | 0 | 0 |
| $\underline{G}_R/RT$ | | -0.492028012 | |

Even if the degree of freedom is more than one for the sequential method, it has been observed that the sequential method initiated with Wilson's K values tends to fail to find the correct solution that does not involve the $L_1$ or V phase. An example is the ternary mixture of 60 mol% $CO_2$, 12 mol% $C_1$, and 28 mol% n-$C_{20}$ at 250 K and 38 bars. Three phases of $L_1$, $L_2$, and V are present in composition space, and the overall composition in the $L_1$-$L_2$ region is located in the vicinity of the tie triangle. The sequential method cannot find phase instability in the two-sided stability analysis with the V and L estimates from Wilson's correlation.

## Case 3

This case presents the complex phase behavior calculated for $H_2O$, n-$C_4$, and bitumen at 417 K and 35 bars. The components' properties are given in **Table 5.** Two different types of three-phase equilibria are present in composition space; one is $L_1 + L_2 + V$ and the other is $W + L_1 + V$. Each of the two-phase edges of the tie triangles forms a two-phase region. Therefore, a flash calculation within this composition space may experience several local minima before reaching the correct solution. The difficulty depends on the quality of the initial estimates used for phase compositions, or K values. However, no established correlations are available for K values involving the $L_2$ phase (Zhu and Okuno 2015a).

Table 5—Properties of the components for case 3

| Component | $P_C$ (bar) | $T_C$ (K) | $\omega$ |
|---|---|---|---|
| **$H_2O$** | 277.15 | 672.48 | 0.2699 |
| **n-$C_4$** | 36.01 | 421.56 | 0.2127 |
| **Bitumen** | 10.64 | 847.17 | 1.0406 |
| **Binary Interaction Parameters** | | | |
| | **$H_2O$** | **n-$C_4$** | **Bitumen** |
| **$H_2O$** | 0.000 | 0.560 | 0.110 |
| **n-$C_4$** | 0.560 | 0.000 | 0.075 |
| **Bitumen** | 0.110 | 0.075 | 0.000 |

The overall composition of 2 mol% $H_2O$, 95 mol% n-$C_4$, and 3 mol% bitumen yields $L_1 + L_2 + V$. The new algorithm was initiated with randomly-selected three sampling compositions and three compositions near the vertices of composition space. It converged to the correct solution **(Table 6)** after 136 iterations. The converged tangent plane gives four stationary points, out of which one unstable composition near 100% $H_2O$ has the $\theta$(or D) value of 0.6272.

Table 6—Solution for case 3 with the new algorithm. Properties of the components are given in Table 5. The overall composition is 2% $H_2O$, 95% n-$C_4$, and 3% bitumen. The specified temperature and pressure are 417 K and 35 bar. The conventional algorithm converges to the same solution at the expense of a large number of iterations in sequential stability and flash calculations

| Component | W | $L_1$ | $L_2$ | V |
|---|---|---|---|---|
| **$H_2O$** | 9.99E-01 | 0.02757144227 | 0.01722624506 | 0.03886906998 |
| **n-$C_4$** | 2.21E-11 | 0.77654778633 | 0.96351359109 | 0.96099473155 |
| **Bitumen** | 0 | 0.19588077141 | 0.01926016386 | 0.00013619847 |
| **$\beta$** | 0 | 0.0710 | 0.8348 | 0.0942 |
| **$\theta$** | 0.6272 | 0 | 0 | 0 |
| **$\underline{G}_R/RT$** | | -0.95634664 | | |

The sequential method results in the same solution through a false solution in two-phase flash. The two-sided stability analysis for the overall composition takes 304 iterations. Then, two-phase flash requires 123 iterations with successive substitution alone, or 28 iterations with the combination of successive substitution and Newton's minimization. After that, one of the two phases is tested for phase stability. Phase instability is detected with the initial guess of $\varphi_i X_i$. The two-phase stability calculations with five different initial guesses take 446 iterations in total. Finally, three-phase flash requires 120 iterations with successive substitution alone, or 19 iterations with the combination of successive substitution and Newton's minimization. As shown in this case, the simplicity of the new algorithm is advantageous for complex phase behavior.

## Case 4

This case is to show the importance of the initialization scheme and checking the feasibility in multiphase RR solution. Mixtures of $H_2O$, $C_3$, and n-$C_{16}$ are used, for which Table 1 shows the components' properties.

First, the mixture of 80 mol% $H_2O$, 19 mol% $C_3$, and 1 mol% n-$C_{16}$ is considered at 566 K and 130 bars, near a critical endpoint. The algorithm of Gupta et al. (1991) results in non-convergence for this case because the RR solution during the iteration diverges with the following K values: ($6.48974 \times 10^{-1}$, $3.01954 \times 10^{3}$, $4.08377 \times 10^{10}$) for V + W, and ($4.85708 \times 10^{-1}$, $2.64248 \times 10^{3}$, $2.27912 \times 10^{11}$) for L + W. Such divergence occurs when the RR equations are nearly degenerate near a critical endpoint

(Zhu and Okuno 2015b). It is crucial to control Newton's step size to keep the feasibility in RR solution, as in Okuno et al. (2010). The new algorithm converges to the correct solution shown in **Table 7** in 8 iterations with no difficulty.

**Table 7—Solution for the first mixture of case 4 with the new algorithm. Properties of the components are given in Table 1. The overall composition is 80% $H_2O$, 19% $C_3$, and 1% n-$C_{16}$. The specified temperature and pressure are 566 K and 130 bar. The algorithm of Gupta et al. (1991) results in non-convergence because the Rachford-Rice solution during the iteration diverges**

| Component | V | W |
|---|---|---|
| $H_2O$ | 0.667919405 | 0.999888865 |
| $C_3$ | 0.315472893 | 0.000111135 |
| n-$C_{16}$ | 0.016607701 | 0 |
| $\beta$ | 0.6021 | 0.3979 |
| $\theta$ | 0 | 0 |
| $\underline{G}_R/RT$ | -0.823421643 | |

A second example is the mixture of 87 mol% $H_2O$, 3 mol% $C_3$, and 10 mol% n-$C_{16}$ at 574.5 K and 125 bars. The new algorithm converges to the correct solution given in **Table 8** in 6 iterations. However, it requires the proper initialization of RR solution (see Okuno et al. 2010) when K values are as follows: ($1.21887, 9.31203 \times 10^{-4}, 3.40328 \times 10^{-10}$) for V + W, and ($6.31210 \times 10^{-1}, 1.45442, 1.16067 \times 10^{1}$) for L + W. If the simplistic selection is made for initial $\beta$values, 1/3, for the three phases, the RR solution results in divergence. However, Gupta et al. (1991) did not discuss how to initialize a RR solution.

**Table 8—Solution for the second mixture of case 4 with the new algorithm. Properties of the components are given in Table 1. The overall composition is 87% $H_2O$, 3% $C_3$, and 10% n-$C_{16}$. The specified temperature and pressure are 574.5 K and 125 bar**

| Component | $L_1$ | W |
|---|---|---|
| $H_2O$ | 0.501407818 | 0.999929554 |
| $C_3$ | 0.114906006 | 7.04E-05 |
| n-$C_{16}$ | 0.383686176 | 1.11E-11 |
| $\beta$ | 0.2606 | 0.7394 |
| $\theta$ | 0 | 0 |
| $\underline{G}_R/RT$ | -0.550358484 | |

A third example is the mixture of 75 mol% $H_2O$, 15 mol% $C_3$, and 10 mol% n-$C_{16}$ at 560 K and 65 bars. For this mixture, the initialization scheme proposed by Gupta (1990) results in a RR problem with an open feasible domain, resulting in the failure in initialization. The new algorithm initialized with sampling compositions distributed near the vertices of composition space converges to the solution given in **Table 9** in 32 iterations. Two of the three sampling compositions that are initially present merge into the V phase at the 12th iteration. Unlike in Gupta et al. (1991), the RR routine embedded in the new flash algorithm is guaranteed to converge to the correct solution. It is important to confirm the existence of the unique solution for a given multiphase RR problem prior to the iteration as shown in Okuno et al. (2010).

**Table 9—Solution for the third mixture of case 4 with the new algorithm. Properties of the components are given in Table 1. The overall composition is 75% $H_2O$, 15% $C_3$, and 10% n-$C_{16}$. The specified temperature and pressure are 560 K and 65 bar. The algorithm of Gupta et al. (1991) fails for this case due to an open feasible domain in the initial RR problem based on their initialization scheme**

| Component | $L_1$ | V |
|---|---|---|
| $H_2O$ | 0.324593359 | 0.795746207 |
| $C_3$ | 0.095516095 | 0.15585894 |
| n-$C_{16}$ | 0.579890546 | 0.048394853 |
| $\beta$ | 0.0971 | 0.9029 |
| $\theta$ | 0 | 0 |
| $\underline{G}_R/RT$ | -0.967879426 | |

## Conclusions

This paper presented a new algorithm for global minimization of the Gibbs free energy for isothermal, isobaric flash. The correct set of equations is solved with successive substitution for stationary points of the tangent plane distance defined at a reference composition. Conclusions are as follows:

1. The number of equilibrium phases is part of the solution in the new algorithm, in contrast to the sequential stability/flash approach. Therefore, false solutions are not necessary for multiphase flash with the new algorithm. The advantage of the new algorithm in terms of robustness and efficiency is more pronounced for more complex phase behavior, in which multiple local minima of the Gibbs free energy are present.
2. The new algorithm can be initialized with either a biased or unbiased scheme because it can handle an arbitrary number of sampling compositions. This also yields the flexibility that the algorithm offers in terms of robustness and efficiency. For example, one can initialize the algorithm with more sampling compositions for enhanced robustness by capturing more information regarding the Gibbs free energy during the iteration. If reasonable estimates are available for equilibrium phases, one can use the biased initialization to reduce the number of equations to be solved.
3. The new algorithm does not use the stability equations of Gupta et al. (1991) because they are not necessary with the correct formulation presented in this research.

## Nomenclature

### Roman Symbols

D= Tangent plane distance
$f_{ij}$ = Residual of the tangent plane equations defined in Eq. 1
$g_j$ = Residuals of the material balance equations
$\underline{G}$ = Molar Gibbs free energy
$K_{ij}$ = K value for component i in phase j
$\vec{K}$ = Vector consisting of $N_C$ K values
$L_1$ = Oleic phase
$L_2$ = Solvent-rich liquid phase
$N_C$ = Number of components
$N_P$ = Number of phases
$N_S$ = Number of sampling compositions
$N_U$ = Number of sampling compositions in set U
P = Equilibrium set or pressure
$P_C$ = Critical pressure
r = Reference composition

R = Universal gas constant
T = Temperature
$T_C$ = Critical temperature
U = Unstable set
V = Vapor or gaseous phase
W = Aqueous phase
$\vec{x}_j$ = Vector consisting of $N_C$ concentrations
$x_{ij}$ = Mole fraction of component i in phase j
$z_i$ = Overall mole fraction of component i

**Greek Symbols**

$\beta_j$ = Mole fraction of phase j
$\varepsilon$ = Small number used for convergence test (e.g., $10^{-12}$)
$\varphi_{ij}$ = Fugacity coefficient of component i in phase j
$\omega$ = Acentric factor
$\theta$ = Stability variable

**Subscripts**

C = Critical property
i = Component index
j = Phase index
L = Oleic phase
mix = Mixing
P = Phase
r = Reference composition
R = Reduced property
Ref = Reference phase
S = Sampling composition
U = Unstable
V = Vapor phase
W = Aqueous phase

**Superscripts**

k = Index for iteration steps
R = Reduced property

**Abbreviation**

BIP = Binary interaction parameter
EOS = Equation of state
PR = Peng-Robinson
RR = Rachford-Rice

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## Appendix A

## Formulation for Global Minimization of the Gibbs Free Energy

The correct phase equilibrium for a given P, T, and $z_i$ (i = 1, 2, . . ., $N_C$) is defined by $x_{ij}$ (i = 1, 2, . . ., $N_C$ and j =1, 2, . . ., $N_P$) that gives the global minimum of

$$\underline{G}_R = \sum_{j=1}^{N_P} \sum_{i=1}^{N_C} \beta_j x_{ij} \ln\left(x_{ij}\varphi_{ij}\right), \tag{A-1}$$

where P is pressure, T is temperature, $z_i$ is the overall mole fraction of component i, $x_{ij}$ is the mole fraction of component i in phase j, $\beta_j$ is the mole fraction of phase j, $N_C$ is the number of components, and $N_P$ is the number of equilibrium phases. The following constraints are to be satisfied:

$$z_i = \sum_{j=1}^{N_P} \beta_j x_{ij} \tag{A-2}$$

$$\sum_{j=1}^{N_P} \beta_j = 1.0 \tag{A-3}$$

$$\sum_{i=1}^{N_C} x_{ij} = 1.0 \tag{A-4}$$

where $\beta_j \geq 0$ and $x_{ij} \geq 0$ for i = 1, 2, . . ., $N_C$ and j =1, 2, . . ., $N_P$.

The tangent plane to the Gibbs free energy surface at a stable equilibrium state cannot lie above the Gibbs free energy surface at any composition (Baker et al., 1982; Michelsen, 1982a). Therefore,

$$D_j = \sum_{i=1}^{N_C} x_{ij}\left(\ln x_{ij}\varphi_{ij} - \ln x_{iRef}\varphi_{iRef}\right) \geq 0 \tag{A-5}$$

for j = 1, 2, . . ., $N_S$ at a specified T and P. $N_S$ is the number of stationary points of the dimensionless tangent plane distance function, D, defined with a reference equilibrium-phase composition ($x_{iRef}$, where i = 1, 2, . . ., $N_C$). Note that $N_S = N_P + N_U$, where $N_U \geq 0$ and is the number of unstable stationary points of D. Equation (A-5) can be also written as

$$D_j = \ln x_{ij}\varphi_{ij} - \ln x_{iRef}\varphi_{iRef} \geq 0 \tag{A-6}$$

because the gradients of D in composition space are zero at a stationary point.

The unified formulation for phase-stability and flash calculations in the current paper is to find a set of $x_{ij}$ (i = 1, 2, . . ., $N_C$, and j =1, 2, . . ., $N_S$) such that $D_j = 0$ subject to equations A-2, A-3, and A-4 for equilibrium phases j = 1, 2, . . ., $N_P$, and $D_j > 0$ subject to equation A-4 for unstable stationary points j = ($N_P$ + 1), ($N_P$ + 2). . ., $N_S$. The algorithm presented in the current paper uses the tangent plane distance function, D, with adaptive selection of the reference composition for an arbitrary number of iterative compositions, which converge to stationary points with tangent plane distances $D_j$.

## Appendix B

## Flow Chart for the Augmented Successive Substitution