

## GENERAL RESEARCH

## Multiphase Equilibrium Calculations Using Gibbs Minimization Techniques

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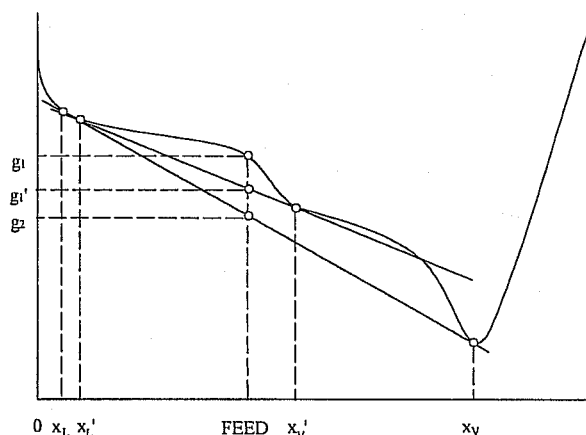
Three different algorithms combining the methodology of Gibbs energy minimization (GEM) and the iteration function method with an extended phase-check procedure have been developed. The computational strategies devised in this study attempt to balance algorithm reliability, simplicity, generalizability, and computational efficiency. As a result, different numerical methods and improved initialization procedures have been implemented. The efficacy of the three algorithms is highly dependent on the multiphase system encountered. Specifically, the reliability, versatility and computational efficiency of the different algorithms vary significantly. A number of challenging case studies were successfully used to demonstrate the viability of the proposed algorithms and the initialization procedures. The results of this study indicate that (a) the GEM algorithm should be applied in demanding process design tasks and (b) the accelerated GEM algorithms should prove effective in dealing with systems involving a large number of components.

## 1. Introduction

Multiphase equilibrium phenomena are encountered in many industrial applications, such as the production and processing of crude oil and natural gas, especially when such operations involve oils prone to wax deposition or fluid mixtures containing significant amounts of nitrogen, carbon dioxide, or water. In these applications and in many others, including food processing, heterogeneous extraction, and distillation,<sup>1,2</sup> proper characterization of the coexisting equilibrium phases is often critical in determining the economic and engineering feasibility of the process considered.

Multiphase equilibrium problems can be solved either by the conventional iteration function methods (IFMs) or by the Gibbs energy minimization (GEM) techniques. The IFMs, which are based on the conservation of mass and the equal-fugacity criterion, will produce a correct solution only if the number and types of phases present at a certain temperature, pressure, and composition can be determined in advance. Furthermore, good initial guesses for equilibrium constants or mole fractions are required. These methods always meet the conservation of mass and equal-fugacity requirements but do not always attain the minimum Gibbs free energy, as shown by Heidemann,<sup>2</sup> Evelein et al.,<sup>3</sup> and Sorensen et al.<sup>4</sup> This sometimes leads to trivial solutions (all phases present having the same properties) or incorrect phase distribution predictions.

In the GEM methods, in addition to mass conservation and the equal-fugacity requirement, the minimum Gibbs energy is also achieved; consequently, GEM methods are superior to IFM methods. Two subprob-



**Figure 1.** Tangent-plane criterion showing that two two-phase systems having different compositions ( $x_L'-x_V'$  and  $x_L-x_V$ ) satisfy the equal-fugacity criterion for equilibrium. However, the true solution is the two-phase system with composition  $x_L-x_V$ , which attains the minimum Gibbs energy.

lems, namely, phase stability and phase split, are solved to obtain a correct solution to the phase equilibrium problem. Both subproblems can be treated as minimization problems or as nonlinear systems of equations.

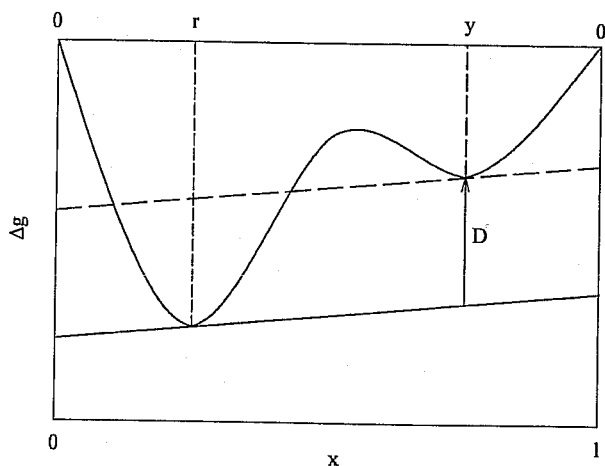
An important step in multiphase equilibrium calculations using the GEM methods is to determine the phase stability, which determines whether a mixture at a given operating condition will split into multiple phases. Baker et al.<sup>5</sup> showed that the phase stability could be ascertained by the tangent-plane criterion. Figure 1 shows that two two-phase systems having different compositions ( $x_L'-x_V'$  and  $x_L-x_V$ ) satisfy the equal-fugacity criterion for equilibrium. However, the true solution is the two-phase system with the composition  $x_L-x_V$ , which has the minimum Gibbs energy. The tangent line that intersects the Gibbs energy surface also indicates the unstable system. Therefore, the equal-

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**Figure 2.** Schematic of the tangent-plane criterion. The negativity of the tangent-plane distance ( $D$ ) is used to determine a stable phase. The points  $r$  and  $y$  designate a reference composition and an arbitrary composition, which can be thought of as the feed composition or the composition of the evaluated phase.

fugacity criterion is a necessary condition, but not a sufficient one for equilibrium. As described by Michelsen,<sup>6</sup> the stability can be inferred by seeking the minima of the tangent-plane distance ( $D$ ), as shown in Figure 2. Tangent-plane distances are determined by stationary points (extrema or saddle points in the Gibbs energy of the system), which are the results of solving a minimization problem or an equivalent system of nonlinear equations. If the tangent-plane distance has a negative value, then that tangent plane intersects the Gibbs free energy surface, and the phase is unstable.

The main problem in stability analysis is finding all of the stationary points with complete certainty. This difficulty triggered significant attempts by several researchers to develop a reliable method for solving phase-stability problems. For example, Michelsen<sup>6</sup> used multiple initial guesses to solve the system of nonlinear equations for stationary points. However, this method cannot guarantee that all of the stationary points have been found. A homotopy-continuation method was applied by Sun and Seider.<sup>7</sup> Two types of initial points for homotopy paths, which are easier than the initialization technique used by Michelsen,<sup>6</sup> were applied. The stationary points are obtained along the homotopy paths. The area method proposed by Eubank et al.<sup>8</sup> is based on integrating the Gibbs surface. The equilibrium-phase criterion is defined as the maximum area between the tangent plane and the Gibbs energy surface and is obtained by an exhaustive search over a defined grid. To find the approximate location of solutions, a coarse grid is first applied. The regions containing viable solutions are selected, and the regions that provide no solutions are eliminated. The search for solutions continues with a finer grid in the remaining regions. McDonald and Floudas<sup>9</sup> demonstrated solution of the phase-stability problem through the application of powerful global optimization techniques after they had reformulated the phase-stability problem for certain activity coefficient models. Their method does provide a mathematical guarantee that the global minimum of the tangent-plane distance will be found. Later, this work was extended by Harding and Floudas<sup>10</sup> to cubic equation of state models. Hua<sup>11</sup> and Hua et al.<sup>12</sup> offered the interval Newton/generalized bisection (IN/GB) method. This method is initialization-independent, and if properly implemented, it can produce the correct solution to the phase-stability problem because it pro-

vides a guarantee that all stationary points can be found. Lucia et al.<sup>13</sup> offered an algorithm that employs a combination of Gibbs energy minimization, binary tangent-plane analyses, and bubble-point calculations. A sequence of subproblems (liquid-vapor equilibrium, liquid-liquid equilibrium, etc.) is solved until the global minimum Gibbs energy is found. The initial guesses for a subproblem are generated by solving binary tangent plane and using previously solved subproblems.

In the present study, the regular Newton's method, because of its speed of convergence and simplicity, is chosen to solve a system of nonlinear equations for stationary points. A simple initialization scheme is devised to eliminate the initial guess problem. The only requirement for the initialization scheme to work is the knowledge of the upper and lower bounds of the variables. This information is used to generate nonuniform grid points that serve as the locations of initial guesses. The application of the regular Newton's method and the initialization scheme proposed in this work is relatively easier to program than the IN/GB method using the interval Newton approach. This technique is used to solve seven phase-stability problems consisting of binary, ternary, and quaternary systems under conditions that are in the vicinity of the critical region. The results show that this technique, with a generalized equation of state, is able to predict the stability of the system correctly, and they are in excellent agreement with those obtained by Hua et al.<sup>12</sup>

To determine the composition and fraction of each phase in equilibrium, a phase-split analysis is performed. Several researchers have attempted to solve the phase-split problem using various methods. For example, Michelsen<sup>14</sup> used the compositions of unstable phases found from phase-stability analysis as initial guesses and employed a second-order convergence method to obtain the solution. Sun and Seider<sup>7</sup> constructed a set of equations based on equal-fugacity and mass balance requirements. The stationary points obtained from the phase-stability analysis were employed as the initial guess, and Newton's method was used to solve the set of equations. Hua<sup>11</sup> combined the IN/GB method with successive quadratic programming (SQP) to locate the global minimum of the Gibbs energy. The stationary points found from the phase-stability analysis were used as the initial guesses for phase fractions in solving the minimization problem using SQP.

In this study, the phase-split analysis is performed by two methods. The first method is to minimize directly the molar sum of the Gibbs energy of mixing with the constraints of mass balance and equal fugacity. To ensure that the solutions attain the global minimum of the Gibbs free energy, the stability of each prospective phase found is tested. Then the equilibrium phase distribution is obtained if each phase is stable. The second method is to apply the IFM method with the extended phase-check procedure as suggested by Nelson<sup>15</sup> and Sofyan.<sup>16</sup> The second method is intended to improve the efficiency of the first method. The stationary points found from the phase-stability analysis are taken as the initial guesses for the mole fractions.

The reliability of these techniques is demonstrated by solving five test problems involving binary, ternary, and quaternary systems at several operating conditions where the system is in liquid-vapor or liquid-liquid-vapor equilibrium. The results obtained are comparable to those obtained by Hua<sup>11</sup> and Hua et al.,<sup>12</sup> as well as the published experimental data provided by Robinson et al.<sup>17</sup>

## 2. Phase-Stability Analysis

Determining the phase stability is a crucial step in phase equilibrium calculations. It is used to determine whether a mixture at certain temperature, pressure and compositions will split into multiple phases. For high-pressure phase equilibria, the phase-stability analysis is important, as even simple binary solutions can exhibit complex phase behavior.

Mathematically, the tangent-plane distance  $D$  shown in Figure 2 can be expressed as

$$D(\bar{x}, v) = \Delta g_{\text{mix}}(\bar{x}, v)_y - \Delta g_{\text{mix}}(\bar{x}, v)_r - \sum_{j=1}^n \left( \frac{\partial \Delta g_{\text{mix}}}{\partial x_j} \right)_r (x_{j,y} - x_{j,r}) \quad (1)$$

where  $\Delta g_{\text{mix}}$  is the change of Gibbs energy of the mixture,  $\bar{x}$  is the mole fraction and  $v$  is molar volume of the phases, and  $n$  is the number of components in the mixture. The subscripts  $r$  and  $y$  indicate the evaluation at a reference composition and at an arbitrary composition, which can be thought of as the feed composition or the composition of the evaluated phase.

The van der Waals-type equations of state, such as the Soave-Redlich-Kwong<sup>18</sup> (SRK) and Peng and Robinson<sup>19</sup> (PR), are capable of representing the phase behavior of normal fluids. In this study, a generalized cubic equation of state (see, e.g., Reid et al.<sup>20</sup>) is used

$$P - \frac{RT}{v-b} + \frac{a}{v^2 + ubv + wb^2} = 0 \quad (2)$$

The PR and SRK equations of state (EOS) are obtained by assigning the values  $u = 2$ ,  $w = -1$  and  $u = 1$ ,  $w = 0$ , respectively.

To determine whether the minimum tangent-plane distance  $D$  is ever negative, the following minimization problem is undertaken

$$\begin{aligned} &\text{minimize } D(\bar{x}, v) = \\ &\quad \bar{x}, v \\ &\Delta g_{\text{mix}}(\bar{x}, v)_y - \Delta g_{\text{mix}}(\bar{x}, v)_r - \sum_{j=1}^n \left( \frac{\partial \Delta g_{\text{mix}}}{\partial x_j} \right)_r (x_{j,y} - \bar{x}_{j,r}) \end{aligned}$$

subject to

$$\begin{aligned} &1 - \sum_{j=1}^n x_j = 0 \\ &P - \frac{RT}{v-b} + \frac{a}{v^2 + ubv + wb^2} = 0 \end{aligned} \quad (3)$$

Hua<sup>11</sup> converted the minimization problem given by eq 3 into a system of nonlinear equations (where  $n$  is the number of components), as shown in eqs 4

$$\begin{cases} \left[ \left( \frac{\partial \Delta g_{\text{mix}}(\bar{x}, v)}{\partial x_j} \right) - \left( \frac{\partial \Delta g_{\text{mix}}(\bar{x}, v)}{\partial x_n} \right) \right] - \left[ \left( \frac{\partial \Delta g_{\text{mix}}(\bar{x}, v)}{\partial x_j} \right) - \left( \frac{\partial \Delta g_{\text{mix}}(\bar{x}, v)}{\partial x_n} \right) \right]_r = 0 \quad j = 1, \dots, n-1 \\ 1 - \sum_{j=1}^n x_j = 0 \\ P - \frac{RT}{v-b} + \frac{a}{v^2 + ubv + wb^2} = 0 \end{cases} \quad (4)$$

Using eq 2, the reduced molar Gibbs free energy of mixing is given by

$$\Delta g_{\text{mix}}(\bar{x}, v) = \frac{Pv}{RT} + \ln \left( \frac{RT}{v-b} \right) + \frac{a}{RTb\Delta} \ln \left( \frac{2v + ub - b\Delta}{2v + ub + b\Delta} \right) + \sum_{j=1}^n x_j \ln x_j - \sum_{j=1}^n x_j g_j^\circ \quad (5)$$

where  $g_i^\circ$  represents the pure-component reduced molar Gibbs free energy and  $\Delta = \sqrt{u^2 - 4w}$ . The pure-component reduced Gibbs free energy is expressed by

$$g_i^\circ = \frac{Pv_i}{RT} + \ln \left( \frac{RT}{v_i - b_i} \right) + \frac{a_i}{RTb_i\Delta} \ln \left( \frac{2v_i + ub_i - b_i\Delta}{2v_i + ub_i + b_i\Delta} \right) \quad (6)$$

and the derivative of the reduced Gibbs free energy with respect to the mole fraction is written as

$$\begin{aligned} \frac{\partial \Delta g_{\text{mix}}}{\partial x_j} &= \frac{b_j}{v-b} + \\ &\frac{a}{bRT\Delta} \left( \frac{2\bar{a}_j}{a} - \frac{b_j}{b} \right) \ln \left( \frac{2v + ub - b\Delta}{2v + ub + b\Delta} \right) - \\ &\frac{ab_j}{RTb} \left( \frac{v}{v^2 + uvb + wb^2} \right) + 1 + \ln x_j - g_j^\circ \end{aligned} \quad (7)$$

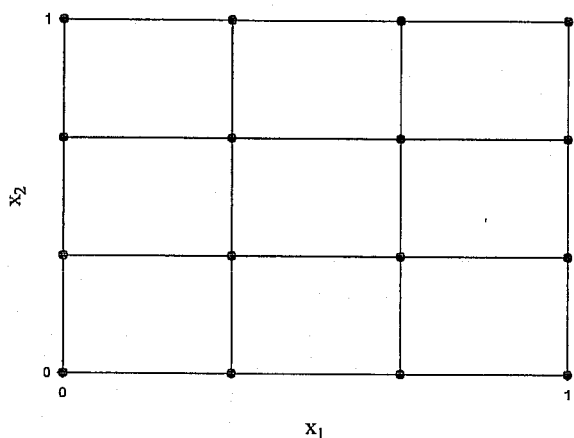
where

$$\bar{a}_j = \sum_{k=1}^n x_k a_{jk}$$

In this study, the phase-stability analysis is conducted by solving the system of nonlinear equations given by eqs 4 using the regular Newton's method. To obtain correct solutions, a proper initialization scheme for iteration variables is required. In this study, an initialization scheme is devised that is based on (a) finding a feasible domain of the iteration variables and (b) constructing several grid points as initial guesses in the physical domain.

## 3. Initialization Scheme

A careless choice for initial guesses might converge to a particular solution or a trivial solution, or it might generate physically meaningless parameters, such as negative mole fractions.<sup>21</sup> To eliminate the initial-guess-dependence problem, in this study, an initialization scheme is proposed. This scheme can be applied correctly only if the feasible domains of iteration variables are known in advance. Therefore, to solve the system of nonlinear equations given by eqs 4, the feasible domain (upper and lower bounds) of the mole fractions



**Figure 3.** Initial-guess locations. The uniform grid shown here is to illustrate the points of intersections used for initial guesses.

( $\bar{x}$ ) and molar volume ( $v$ ) need to be obtained. The lower bound of  $v$  is the smallest pure-component size parameter  $b$ , and the upper bound is the ideal-gas molar volume; the feasible domain of  $\bar{x}$  is  $[0, 1]$ .

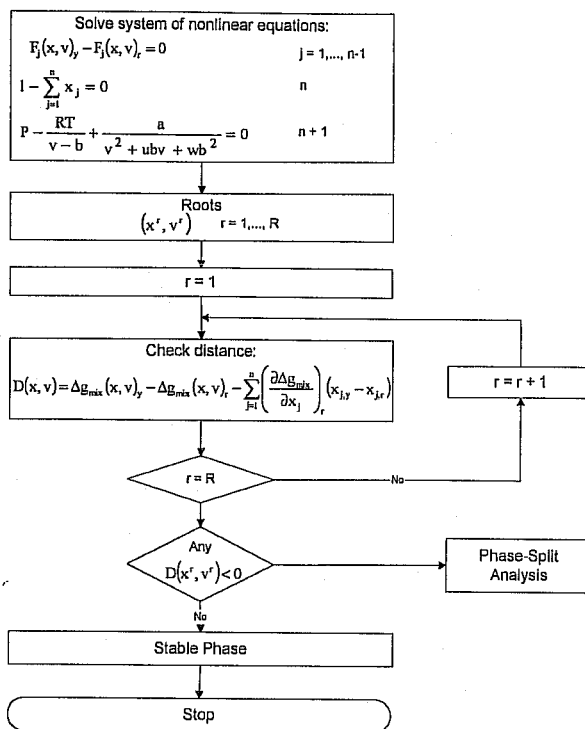
In this scheme, the physical domains of the iteration variables are divided into several regions. The initial guesses are chosen as the points of the intersecting lines. For example, if the variables are  $x_1$  and  $x_2$ , the initial guesses are the black circular points depicted in Figure 3.

It is possible that the solutions of the system of nonlinear equations are close to each other. With a coarse grid, all solutions might not be obtained. To eliminate this problem, the grid should be refined. However, such a procedure would produce more initial guesses and, consequently, would need extra computational time. In anticipation of this, a nonuniform grid, as proposed by Patankar,<sup>22</sup> is applied in this study. The grid is generated by applying the formula

$$\frac{x_k}{\kappa} = \left(\frac{k}{\vartheta}\right)^\tau \quad (8)$$

where  $x_k$  is the location of the  $k$ th grid point of variable  $x$ ,  $k$  is the index denoting the position of  $x$ ,  $\vartheta$  is the number of grid points in the domain  $x$ ,  $\tau$  is any positive number describing the shape of the nonuniformity, and  $\kappa$  is the range of variable  $x$ . When the exponent  $\tau$  in eq 8 is greater than 1, the grid is fine near the left end and becomes progressively coarser toward the right end. Near the right end, the grid tends to be coarse and uniform. When  $\tau < 1$ , the grid is coarse at the left end and becomes uniformly fine near the right end. In this study, both  $\tau > 1$  and  $\tau < 1$  are applied, so that fine grids at the left and right ends and relatively fine grids in the middle are constructed.

Because the initial guesses are generated by the initialization scheme of eq 8, the number of roots or stationary points obtained depends on the number of grid points ( $\vartheta$ ) and the nonuniformity shape ( $\tau$ ). Our graphical analysis of the Gibbs free energy curves reveals that the number of stationary points is always an odd number. To increase the efficiency of this method, based on our experience in solving the case studies, the grids are generated first by setting  $\vartheta$  equal to 12. These initial values are used to solve the set of nonlinear equations given by eq 4. If the initial values of the variables used in Newton's method produces infeasible values of the variables in the next iteration,



**Figure 4.** Flowchart of the phase-stability algorithm.

the next initial guess is used. If all stationary points cannot be found after all initial guesses have been used, the number of grid points is increased automatically. The number of grid points used in the scheme is not constant but varies depending on the complexity of the problem.

#### 4. Algorithm for Phase-Stability Analysis

Following is an outline for the phase-stability-analysis algorithm, as depicted in Figure 4:

1. Calculate the molar volume of each component.
2. Calculate the Gibbs energies for the pure components using eq 6.
3. Calculate the molar volume of the mixture using the equation of state. Note that, if multiple real roots for the volume exist at the feed composition, the molar volume at the feed composition ( $v_r$ ) must be the root yielding the minimum value of the reduced molar Gibbs energy of mixing as given by eq 5 at the feed  $[\Delta g_{\text{mix}}(\bar{x}, v)_r]$ .
4. Find all stationary points (roots) of the system of nonlinear equations given by eqs 4 by applying eq 7 and the regular Newton's method with the initialization scheme.
5. Calculate all of the tangent-plane distances ( $D$ ) using eq 1. If the  $D$  values are all greater than or equal to zero, the phase is stable. Otherwise, it is unstable, and we proceed with the phase-split analysis.

#### 5. Phase-Split Analysis

At a given temperature and pressure, for a system consisting of  $n$  components and  $m$  phases, the Gibbs free energy minimization requirement that would satisfy the material balance and the equal-fugacity criterion can

be formulated as

$$\text{minimize } \Delta G(\bar{x}, \bar{v}, \bar{\alpha}) = \sum_{i=1}^m \alpha_i \Delta g_{\text{mix}}^i(\bar{x}, \bar{v})$$

subject to

$$\text{EOS}^i = 0 \quad i = 1, \dots, m$$

$$\sum_{j=1}^m x_j^i = 1 \quad i = 1, \dots, m$$

$$\sum_{i=1}^m \alpha_i x_j^i = z_j \quad j = 1, \dots, n-1$$

$$\sum_{i=1}^m \alpha^i = 1 \quad (9)$$

where the superscript  $i$  represents the  $i$ th phase and  $\alpha$  is the corresponding phase fraction.

**5.1. Algorithms for Phase-Split Analysis Using Gibbs Energy Minimization.** The minimization problem given by eq 9 could be converted into an equivalent system of nonlinear equations. The resulting system could then be solved using the regular Newton's method as we did for the phase-stability analysis, but such a procedure requires a considerable computational effort. In the case of a three-component and three-phase problem, such a procedure would require the solution of a set of  $15 \times 15$  nonlinear equations. For computational efficiency, in this study, the minimization problem given by eq 9 is solved directly using the successive quadratic programming (SQP) method to locate a local minimum of the Gibbs free energy. The method transforms the nonlinear problem into a series of quadratic subproblems and solves the subproblems instead of the nonlinear problem. A quadratic problem is a problem with a quadratic objective function and linear or linearized constraints.

To obtain a correct solution to the minimization problem, the initial guesses for the iteration variables ( $\bar{x}$ ,  $\bar{v}$ , and  $\bar{\alpha}$ ) should be determined accurately. The stationary points found from the phase-stability analysis can be effectively used as initial estimates for  $\bar{x}$  and  $\bar{v}$ . However, initial guesses for  $\bar{\alpha}$  are required. In this study, the initial guesses for  $\bar{\alpha}$  are produced in two ways: (a) by applying the initialization scheme as we did to initialize the stability analysis and (b) by using the IFM method originating from the known initial guesses for  $\bar{x}$ .

To verify whether a global minimum has been reached, the phase-stability analysis is then used. Once a negative value for the tangent-plane distance is obtained, we can immediately conclude that the phase is unstable.

In this study, two algorithms using the Gibbs energy minimization method are devised. The first algorithm, called algorithm I, is constructed by generating  $\bar{\alpha}$  using the initialization scheme, and the second algorithm, called algorithm II, is developed using  $\bar{\alpha}$  values that are obtained from the simple IFM method. Both of the algorithms are included in the Phase Equilibrium Calculation (PEC) computer program.

**5.1.1. Algorithms I and II.** Following is an outline for phase-split algorithms I and II, as depicted in the Figures 5 and 6, respectively:

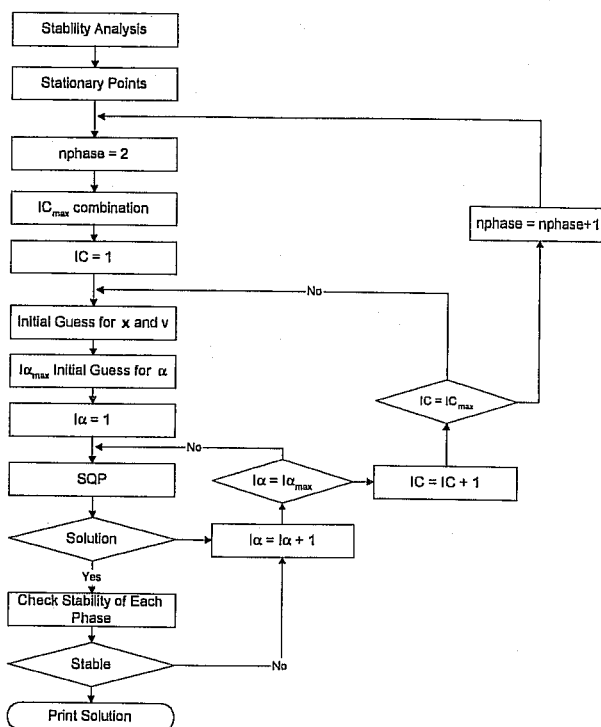


Figure 5. Flowchart of algorithm I for the phase-split analysis.

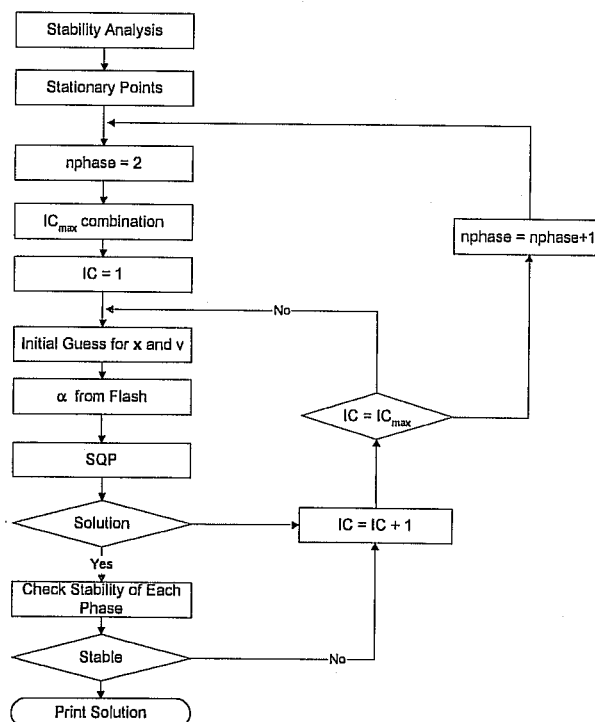


Figure 6. Flowchart of algorithm II for the phase-split analysis.

1. Take the stationary points found from the phase-stability analysis as initial guesses.
2. Assume the number of phases  $m = 2$ .
3. Generate a set of initial-guess combinations for  $\bar{x}$  and  $\bar{v}$  ( $IC_{\text{max}}$ ). Set the first combination as the initial guesses for  $\bar{x}$  and  $\bar{v}$ .
4. For algorithm I, generate  $IC_{\text{max}}$  initial guesses for  $\alpha$  for each combination found from step 3.

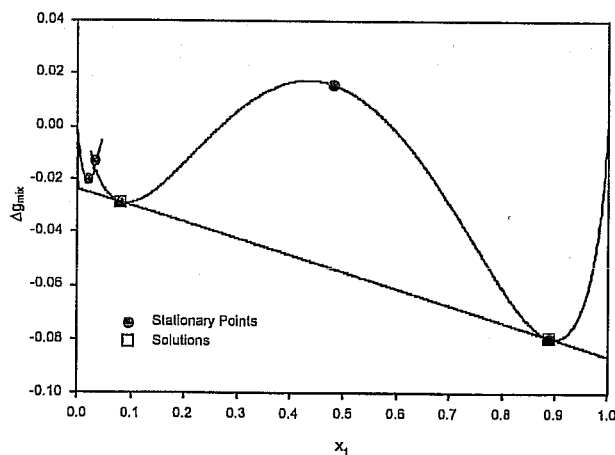


Figure 7. Location of some stationary points that are close to the equilibrium state.

For algorithm II, obtain  $\alpha$  using the regular IFM method.

5. Start the process with the initial guesses for  $\bar{x}$  and  $v$  along with the initial guess for  $\alpha$  (for algorithm I, use the first  $\alpha$ ).
6. Perform SQP.
  - a. If no solution is produced by the SQP
 

For algorithm I, use the next initial guess for  $\alpha$  and go back to step 5. If after  $IC_{max}$ , no equilibrium phase is obtained, go to step 7.

For algorithm II, go to step 7.
  - b. Otherwise, go to step 8.
7. For algorithms I and II, use the next combination for  $\bar{x}$  and  $v$ . For algorithm I, use the first initial guess for  $\alpha$ . For algorithm II, calculate  $\alpha$  using the new initial guesses for  $\bar{x}$  and  $v$  and go back to step 5.
8. Perform the phase-stability check for each phase.
  - a. If each phase is stable, the phases in equilibrium are obtained. Terminate the process.
  - b. Otherwise
 

For algorithm I, use the next initial guess for  $\alpha$  and go back to step 5.

For algorithm II, use the next combination for  $\bar{x}$  and  $v$ , obtain  $\alpha$  using the regular IFM method, and go back to step 5.
9. If no equilibrium phase is obtained after  $IC_{max}$  combinations and  $IC_{max}$  initial guesses for  $\alpha$  (algorithm I) have been used, then set  $m = m + 1$ . The value of  $m$  is restricted by the phase rule ( $m \leq n + 2$ ). Go back to step 4.

The phase-stability check in step 8 calculates the tangent-plane distance directly once the stationary point is located. If the tangent-plane distance is negative, we immediately continue the process using the next initial guess. This strategy might save some computation time.

**5.2. Algorithm for Phase-Split Analysis Using the IFM Method.** The IFM method is capable of producing accurate solutions in a relatively short time, provided that a good initial guess is made for  $\bar{x}$ . As shown in Figure 7, some of the stationary points produced by the phase-stability analysis are close to the equilibrium phase distribution. Therefore, the stationary points can be used as good initial guesses for the IFM method. Algorithm III, which is the combination of the phase-stability analysis and the IFM method, is

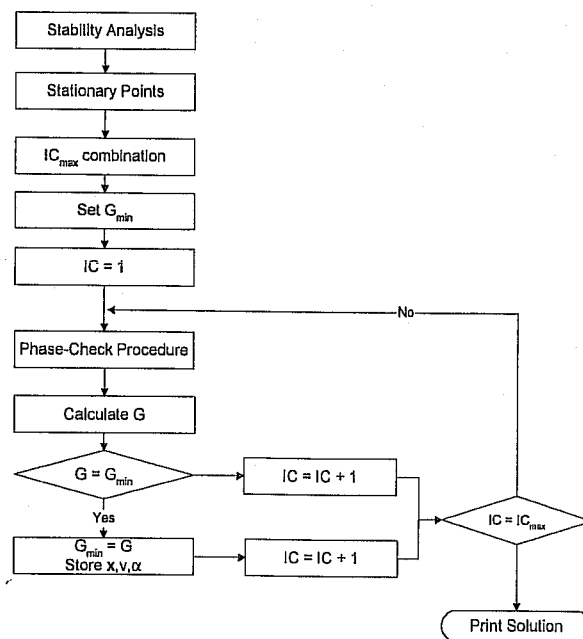


Figure 8. Flowchart of algorithm III for the phase-split analysis.

devised to incorporate the advantages of the IFM method. Further, to eliminate the unnecessary calculations for the higher number of phases, the IFM method is enhanced by the phase-check procedure suggested by Nelson<sup>15</sup> and Sofyan.<sup>16</sup> A summary of the liquid-liquid-vapor phase-check procedure is given in Appendix A.

To ascertain that the global minimum of Gibbs free energy is attained, the initial guesses generated from the combination of stationary points are all applied. For each initial guess, the Gibbs free energy is calculated and stored. The equilibrium phase distribution is then obtained as the solution having the lowest Gibbs free energy.

Following is an outline for algorithm III, as depicted in Figure 8:

1. Take the stationary points found from the phase-stability analysis as the initial guesses.
2. Generate  $IC_{max}$  combinations of the initial guesses.
3. Assign a large value for the minimum Gibbs energy.
4. Start with the first combination as the initial guess for  $\bar{x}$ .
5. Perform the phase-check procedure.
6. Calculate the total Gibbs energy.
7. If the calculated Gibbs energy is less than the assigned value of the Gibbs energy, then set the calculated Gibbs energy as the minimum Gibbs energy; store the calculated  $\bar{x}$ ,  $v$ , and  $\alpha$ ; use the next combination for  $\bar{x}$ ; and go back to step 5.
8. After  $IC_{max}$  combinations, print  $\bar{x}$ ,  $v$ , and  $\alpha$  and terminate the process.

## 6. Results of Implementing the Phase-Stability and Phase-Split Algorithms

A computer program written in Fortran 90 called Phase Equilibrium Calculation (PEC) that incorporates the phase-stability and phase-split algorithms discussed above has been developed. Eleven challenging case studies from the literature were selected to test the reliability of the PEC algorithm. These case studies involve phase-stability and phase-split problems for

Table 1. Critical Properties and Acentric Factors Used

	$T_c$ (K)	$P_c$ (bar)	$\omega$
hydrogen sulfide	373.2	89.4	0.1
nitrogen	126.2	33.9	0.04
carbon dioxide	304.2	73.8	0.225
water	647.3	220.5	0.344
methane	190.6	46	0.008
ethane	305.4	48.8	0.098
propane	369.8	42.5	0.152

vapor-liquid, liquid-liquid, and liquid-liquid-vapor systems consisting of two, three, or four components. In addition, some case studies reflect conditions that are close to the critical region and in the proximity of the three-phase region, where phase equilibrium calculations are known to be very demanding. It should be noted that the results of the phase-split analysis are given for some of the unstable systems identified by the phase-stability analysis.

The critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and acentric factor ( $\omega$ ) of each component evaluated are given in Table 1. Table 2 presents the binary interaction parameters for the evaluated case studies as compiled by Hua<sup>11</sup> and Trebble and Bishnoi.<sup>23</sup> The numbers in parentheses in Table 2 signify the case study numbers.

The entry function evaluation (FE) in Tables 3-9 signifies the number of times the system of nonlinear equations was visited using PEC to locate all of the stationary points. In the same tables, for the IN/GB method, the number of root inclusion tests (RIT) that were performed using constrained space plus monotonic interval extension (F<sup>CSM</sup>) to find all of the stationary points are also listed. The CPU times in the tables reflect the times required for the calculations on an AMD 400-MHz machine.

**Case Study 1.** Table 3a presents the phase-stability analysis for the binary system consisting of hydrogen sulfide (1) and methane (2) at 190 K and 40.53 bar using the SRK equation of state. As indicated, our stability-analysis results for several feed compositions are identical to those obtained by Hua et al.<sup>12</sup> using the IN/GB method.

The PEC algorithm using generated initial guesses predicts that the feed composition with  $z_1 = 0.0187$  is an unstable single phase with a global minimum at  $x_1 = 0.0767$ . This is in contrast to the stable single-phase prediction produced by the highly reliable LNGFLASH approach (based on Michelsen's<sup>6</sup> algorithm from the IVC-SEP package<sup>24</sup>). This indicates that, in this case, PEC is perhaps more reliable than LNGFLASH.

The unstable feeds of this case study are subjected to the phase-split analysis. The results of PEC along with

those of Hua<sup>11</sup> are presented in Table 3b, where  $\alpha$  is the phase fraction of the corresponding phase at equilibrium. As shown in Table 3b, PEC produces results similar to those of the INTFLASH algorithm of Hua.<sup>11</sup> Figures 9 and 10 depict the results of the split analysis. In Figure 9, the tangent line at the first equilibrium composition  $x_1 = 0.0173$  is also tangent at the second equilibrium composition  $x_1 = 0.0661$ , and similarly in Figure 10, the tangent line at the first equilibrium composition  $x_1 = 0.0797$  is also tangent at the second equilibrium composition  $x_1 = 0.8886$ . As expected, these tangent lines satisfy the equal-fugacity criterion.

**Case Study 2.** Table 4 presents a comparison for the phase-stability analysis of the binary system consisting of methane (1) and propane (2) at 277.6 K and pressures of 50 and 100 bar using the SRK equation of state. PEC predicts an unstable single phase at 100 bar for the feed compositions  $z_1 = 0.68$  and 0.73. These results are identical to those obtained by Hua et al.<sup>12</sup> In comparison, Michelsen's<sup>6</sup> algorithm incorrectly predicts a stable single phase under these conditions, which indicates that a good initialization strategy is required to predict the proper phase-stability conditions.

**Case Study 3.** The phase stability of the binary system consisting of nitrogen (1) and ethane (2) at 270 K and 76 bar was analyzed using the PR equation of state. The given temperature and pressure are near the critical region of the mixture. Several feed compositions were tested, and a comparison of the results is shown in Table 5a. The results we obtain with PEC agree very well with those of Hua et al.<sup>12</sup> Also, the phase predictions given by PEC are comparable to the results reported by Prausnitz et al.<sup>25</sup>

Table 5b presents the phase-split analysis for the unstable feed compositions identified by the phase-stability analysis. The PEC predictions are in excellent agreement with those of Hua.<sup>11</sup>

**Case Study 4.** The phase stability of the binary system consisting of carbon dioxide (1) and methane (2) at 220 K and 60.8 bar was analyzed using the PR equation of state. The results of our analysis for several feed compositions are shown in Table 6. The table indicates that PEC predictions are comparable to those generated by IN/GB.<sup>12</sup> Independently, these two sets of predictions reproduce the stability analysis given by Prausnitz et al.<sup>25</sup>

**Case Study 5.** Table 7 summarizes the phase-stability analysis for the ternary system consisting of nitrogen (1), methane (2), and ethane (3) at 270 K and 76 bar, which was analyzed using the PR equation of state. Results for the four feed compositions tested,

Table 2. Matrix for the Binary Interaction Parameters Used

	Peng-Robinson Equation of State					
	hydrogen sulfide	nitrogen	carbon dioxide	water	methane	ethane
hydrogen sulfide			0.0999 (6, 7)	0.04 (7)	0.0755 (6, 7)	
nitrogen					0.038 (5)	0.08 (3, 5)
carbon dioxide				0 (7)	0.095 (4)	
Soave-Redlich-Kwong Equation of State					0.1005 (6, 7)	
water					0.4928 (7)	
methane	0.08 (1)					0.021 (5)
propane					0.029 (2)	

Table 3. Case Study 1. Phase-Stability Analysis and Phase-Split Analysis for the Unstable Feed Compositions of the Binary System Hydrogen Sulfide (1) and Methane (2) at 190 K and 40.53 bar Using the SRK Equation of State

feed (z <sub>1</sub> , z <sub>2</sub> )	(a) Phase-Stability Analysis						PEC CPU time (s)
	roots (x <sub>1</sub> , x <sub>2</sub> , v)			distance			
	IN/GB	PEC	IN/GB	PEC	IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	
(0.0115, 0.9885)	(0.0115, 0.9885, 212.8)	(0.0115, 0.9885, 212.8)	0.0	0.0	1079	721	0.11
	(0.0237, 0.9763, 97.82)	(0.0237, 0.9763, 97.82)	0.0137	0.0137			
	(0.0326, 0.9674, 78.02)	(0.0326, 0.9674, 78.02)	0.0130	0.0130			
(0.0187, 0.9813)	(0.0187, 0.9813, 207.3)	(0.0187, 0.9813, 207.3)	0.0109	0.0109	1428	697	0.11
	(0.0187, 0.9813, 207.3)	(0.0187, 0.9813, 207.3)	0.0	0.0			
	(0.0313, 0.9687, 115.4)	(0.0313, 0.9687, 115.4)	0.0079	0.0079			
	(0.0767, 0.9233, 64.06)	(0.0767, 0.9233, 64.06)	-0.004	-0.004			
	(0.4905, 0.5095, 41.50)	(0.4905, 0.5095, 41.50)	0.0729	0.0729			
	(0.8743, 0.1257, 36.65)	(0.8743, 0.1257, 36.65)	0.0512	0.0512	1414	691	0.11
(0.07, 0.93)	(0.5228, 0.4772, 40.89)	(0.5228, 0.4772, 40.89)	0.0965	0.0965			
	(0.0178, 0.9822, 208.0)	(0.0178, 0.9822, 208.0)	0.0015	0.0015			
	(0.0304, 0.9696, 113.7)	(0.0304, 0.9696, 113.7)	0.0100	0.0100			
	(0.07, 0.93, 65.35)	(0.07, 0.93, 65.35)	0.0	0.0			
(0.50, 0.50)	(0.8819, 0.1181, 36.60)	(0.8819, 0.1181, 36.60)	-0.057	-0.057	1416	690	0.11
	(0.0184, 0.9816, 207.5)	(0.0184, 0.9816, 207.5)	-0.079	-0.079			
	(0.0311, 0.9689, 114.9)	(0.0311, 0.9689, 114.9)	-0.071	-0.071			
	(0.0746, 0.9254, 64.44)	(0.0746, 0.9254, 64.44)	-0.082	-0.082			
	(0.50, 0.50, 65.35)	(0.50, 0.50, 65.35)	0.0	0.0			
(0.888, 0.112)	(0.888, 0.112, 36.55)	(0.888, 0.112, 36.55)	0.0	0.0	1412	998	0.11
	(0.0190, 0.9810, 207.1)	(0.0190, 0.9810, 207.1)	0.0026	0.0026			
	(0.0316, 0.9684, 116.0)	(0.0316, 0.9684, 116.0)	0.0103	0.0103			
	(0.0792, 0.9208, 63.60)	(0.0792, 0.9208, 63.60)	-0.002	-0.002			
	(0.4795, 0.5205, 41.72)	(0.4795, 0.5205, 41.72)	0.0683	0.0683			
(0.89, 0.11)	(0.89, 0.11, 36.54)	(0.89, 0.11, 36.54)	0.0	0.0	1411	686	0.11
	(0.0192, 0.9818, 206.9)	(0.0192, 0.9818, 206.9)	0.0113	0.0113			
	(0.0319, 0.9681, 116.4)	(0.0319, 0.9681, 116.4)	0.0189	0.0189			
	(0.0809, 0.9191, 63.31)	(0.0809, 0.9191, 63.31)	0.0058	0.0058			
	(0.4725, 0.5275, 41.87)	(0.4725, 0.5275, 41.87)	0.0724	0.0724			

feed (z <sub>1</sub> , z <sub>2</sub> )	(b) Phase-Split Analysis for the Unstable Feed Compositions											
	phase I						phase II					
	min. Gibbs energy		α		composition (x <sub>1</sub> , x <sub>2</sub> , v)		min. Gibbs energy		α		composition (x <sub>1</sub> , x <sub>2</sub> , v)	
(0.0187, 0.9813)	Hua <sup>c</sup>	PEC	Hua	PEC	Hua	PEC	Hua <sup>c</sup>	PEC	Hua	PEC	Hua	PEC
(0.5, 0.5)	-0.0199	-0.0199	0.029	0.029	(0.0661, 0.9339, 0.0662)	(0.0662, 0.9339, 0.0662)	0.971	0.971	(0.0173, 0.9827, 208.5)	(0.0173, 0.9827, 208.5)	6.65	0.33
(0.888, 0.112)	-0.055	-0.055	0.480	0.480	(0.0797, 0.9203, 0.0635)	(0.0797, 0.9203, 0.0635)	0.520	0.520	(0.8886, 0.1114, 0.0365)	(0.8886, 0.1114, 0.0365)	14.88	5.05
	-0.0793	-0.0793	0.001	0.001	(0.0797, 0.9203, 0.0635)	(0.0797, 0.9203, 0.0635)	0.999	0.999	(0.8886, 0.1114, 0.0365)	(0.8886, 0.1114, 0.0365)	0.44	1.38

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation. <sup>c</sup> Hua<sup>1</sup> applied INTFLASH code.



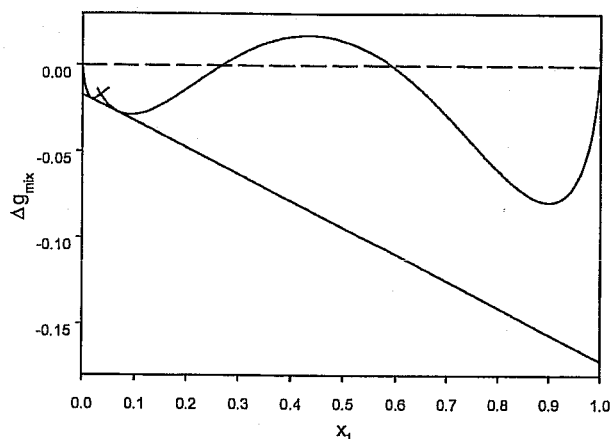


Figure 9. Results of the phase-split calculations for case study 1 depicting vapor-liquid equilibria.

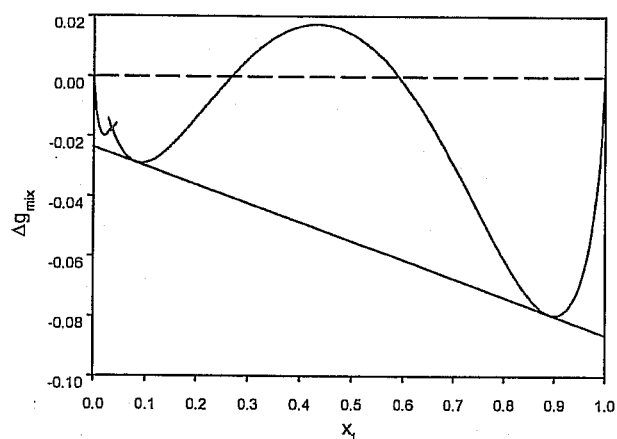


Figure 10. Results of the phase-split calculations for case study 1 depicting liquid-liquid equilibria.

along with those obtained by Hua et al.,<sup>12</sup> are presented, which indicate that the first two feed compositions are not stable. The phase predictions obtained using PEC are in agreement with the experimental data given by Prausnitz et al.<sup>25</sup> Although the second and the third feed compositions are in the proximity of the critical point of the system, PEC efficiently produced the correct solutions.

Table 4. Case Study 2: Phase-Stability Analysis for the Binary System of Methane (1) and Propane (2) at 277.6 K Using the SRK Equation of State ( $P$  in bar)

feed ( $P, z_1, z_2$ )	roots ( $x_1, x_2, v$ )		distance		IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	PEC CPU time (s)
	IN/GB	PEC	IN/GB	PEC			
(50, 0.10, 0.90)	(0.10, 0.90, 86.71)	(0.10, 0.90, 86.71)	0.0	0.0	587	637	0.11
(50, 0.40, 0.60)	(0.8654, 0.1346, 378.4)	(0.8655, 0.1345, 378.4)	-0.153	-0.153	1169	1010	0.11
	(0.5515, 0.4485, 115.3)	(0.5516, 0.4484, 115.3)	0.0106	0.0106			
	(0.40, 0.60, 89.46)	(0.40, 0.60, 89.45)	0.0	0.0			
(50, 0.60, 0.40)	(0.7058, 0.2942, 313.0)	(0.7061, 0.2940, 313.2)	-0.007	-0.007	1091	1001	0.17
	(0.60, 0.40, 216.5)	(0.60, 0.40, 216.4)	0.0	0.0			
	(0.1928, 0.8072, 86.07)	(0.1928, 0.8072, 86.07)	-0.223	-0.223			
(50, 0.9, 0.10)	(0.90, 0.10, 388.5)	(0.90, 0.10, 388.5)	0.0	0.0	878	813	0.11
(100, 0.40, 0.60)	(0.40, 0.60, 82.22)	(0.40, 0.60, 82.22)	0.0	0.0	680	710	0.11
(100, 0.68, 0.32)	(0.7721, 0.2279, 126.0)	(0.7724, 0.2276, 126.1)	$-3.3 \times 10^{-4}$	$-3.3 \times 10^{-4}$	3334	3754	0.22
	(0.6881, 0.3119, 103.0)	(0.6877, 0.3123, 102.9)	$4.10 \times 10^{-7}$	$3.49 \times 10^{-7}$			
	(0.68, 0.32, 101.4)	(0.68, 0.32, 101.4)	0.0	0.0			
	(0.7567, 0.2433, 121.1)	(0.7570, 0.2430, 121.2)	$-2.0 \times 10^{-5}$	$-2.1 \times 10^{-5}$	2693	1320	0.17
(100, 0.73, 0.27)	(0.73, 0.27, 113.2)	(0.73, 0.27, 113.2)	0.0	0.0			
	(0.6506, 0.3494, 96.38)	(0.6503, 0.3497, 96.33)	$-2.9 \times 10^{-4}$	$-2.9 \times 10^{-4}$			
	(0.90, 0.10, 165.2)	(0.90, 0.10, 165.2)	0.0	0.0	685	965	0.17

<sup>a</sup> RIT = root inclusion test; <sup>b</sup> FE = function evaluation.

**Case Study 6.** The phase stability of the ternary system consisting of methane (1), carbon dioxide (2), and hydrogen sulfide (3) was analyzed using the PR equation of state. The four feed compositions studied by Sun and Seider<sup>7</sup> using their HOMPEQ solver were considered. Our stability-analysis results, along with those obtained by Hua,<sup>11</sup> are presented in Table 8. The present predictions show a 5% maximum deviation from those obtained by Sun and Seider.<sup>7</sup> For the first feed composition at 208.5 K and 55.1 bar, five stationary points were located, three of which were very close to each other. Without a robust initialization strategy, those points would have been difficult to locate. In this study, the proposed initialization scheme with a nonuniform grid was successfully employed to differentiate the solutions that are close to each other.

**Case Study 7.** Table 9a presents the phase-stability analysis for the quaternary system consisting of methane (1), carbon dioxide (2), hydrogen sulfide (3), and water (4), which was analyzed using the PR equation of state. Four feed compositions were tested. Our predictions generated using PEC are in excellent agreement with those reported by Hua.<sup>11</sup> In addition, the determination that this system is unstable at each of the conditions given is in good agreement with the experimental data provided by Huang et al.<sup>26</sup>

Table 9b reports the phase-split analysis for the unstable feed compositions of this case. As shown, there is a little difference in the results predicted by PEC and by the IN/GB method of Hua.<sup>11</sup> This is probably due to the difference in the convergence criteria and the tolerances used. The results for the feed compositions yielding two-phase equilibrium are very close to the experimental data given by Huang et al.<sup>26</sup>

**Case Study 8.** PEC was used to analyze the phase split of the ternary system consisting of methane (1), carbon dioxide (2), and hydrogen sulfide (3) using the SRK equation of state. This problem was formulated from experimental data reported by Robinson et al.<sup>17</sup> The feed composition  $z = (0.50, 0.25, 0.25)$  was analyzed at different temperatures and pressures. The results, presented in Table 10, indicate that predictions of PEC are comparable to the experimental data.

**Case Study 9.** The phase split for the ternary system consisting of methane (1), carbon dioxide (2), and hydrogen sulfide (3) was analyzed using the PR equation of state. The binary interaction parameters, as given

Table 5. Case Study 3: Phase-Stability Analysis and Phase-Split Analysis for Unstable Feed Compositions for the Binary System Nitrogen (1) and Ethane (2) at 270 K and 76 bar Using the PR Equation of State

feed (z <sub>1</sub> , z <sub>2</sub> )	(a) Phase-Stability Analysis										(b) Phase-Split Analysis for Unstable Feed Composition											
	roots (x <sub>1</sub> , x <sub>2</sub> , v)					distance					phase I					phase II						
	IN/GB	PEC	IN/GB	PEC	IN/GB RIT <sup>c</sup>	PEC FE <sup>b</sup>	PEC	IN/GB	PEC	IN/GB	PEC	IN/GB	PEC	IN/GB	PEC	IN/GB	PEC	IN/GB	PEC	IN/GB	PEC	algorithm CPU time (s)
(0.10, 0.90)	(0.10, 0.90, 71.11)	(0.10, 0.90, 71.11)	0.0	0.0	604	632	0.0	0.0	0.0	0.0	604	632	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.11
(0.18, 0.82)	(0.4943, 0.5057, 198.3)	(0.4943, 0.5057, 199.8)	-0.010	-0.010	1312	942	-0.010	-0.010	0.0058	0.0058	1312	942	-0.010	-0.010	0.0058	0.0058	0.0058	0.0058	0.0058	0.0058	0.0058	0.17
(0.30, 0.70)	(0.18, 0.82, 78.61)	(0.18, 0.82, 78.61)	0.0	0.0	1316	941	0.0	0.0	0.0	0.0	1316	941	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.16
(0.44, 0.56)	(0.4893, 0.5107, 198.3)	(0.4893, 0.5107, 198.3)	-0.007	-0.007	1293	923	-0.007	-0.007	0.0026	0.0026	1293	923	-0.007	-0.007	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.11
(0.60, 0.40)	(0.30, 0.70, 112.3)	(0.30, 0.70, 112.3)	0.0	0.0	901	875	0.0	0.0	-0.016	-0.016	901	875	0.0	0.0	-0.016	-0.016	-0.016	-0.016	-0.016	-0.016	-0.016	0.11

feed (z <sub>1</sub> , z <sub>2</sub> )	min. Gibbs energy										α										
	phase I					phase II					α					α					
	Hua <sup>c</sup>	PEC	composition (x <sub>1</sub> , x <sub>2</sub> , v)	Hua	PEC	Hua <sup>c</sup>	PEC	composition (x <sub>1</sub> , x <sub>2</sub> , v)	Hua	PEC	Hua <sup>c</sup>	PEC	composition (x <sub>1</sub> , x <sub>2</sub> , v)	Hua	PEC	Hua <sup>c</sup>	PEC	composition (x <sub>1</sub> , x <sub>2</sub> , v)	Hua	PEC	algorithm CPU time (s)
(0.18, 0.82)	-0.212	0.035	(0.476, 0.524, 194.1)	0.035	0.035	(0.476, 0.524, 194.1)	0.035	0.035	0.965	0.965	(0.169, 0.831, 77.3)	0.965	0.965	(0.169, 0.831, 77.3)	0.965	0.965	(0.169, 0.831, 77.3)	0.965	0.965	22.47	1.42
(0.30, 0.70)	-0.260	0.426	(0.476, 0.524, 194.1)	0.426	0.426	(0.476, 0.524, 194.1)	0.426	0.426	0.574	0.574	(0.169, 0.831, 77.3)	0.574	0.574	(0.169, 0.831, 77.3)	0.574	0.574	(0.169, 0.831, 77.3)	0.574	0.574	1.65	1.37
(0.44, 0.56)	-0.315	0.882	(0.476, 0.524, 194.1)	0.882	0.882	(0.476, 0.524, 194.1)	0.882	0.882	0.118	0.118	(0.169, 0.831, 77.3)	0.118	0.118	(0.169, 0.831, 77.3)	0.118	0.118	(0.169, 0.831, 77.3)	0.118	0.118	1.04	0.27

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation. <sup>c</sup> Hua<sup>1</sup> applied INTFLASH code.

**Table 6. Case Study 4: Phase-Stability Analysis for the Binary System Carbon Dioxide (1) and Methane (2) at 220 K and 60.8 bar Using the PR Equation of State**

feed ( $z_1, z_2$ )	roots ( $x_1, x_2, v$ )		distance		IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	PEC CPU time (s)
	IN/GB	PEC	IN/GB	PEC			
(0.10, 0.90)	(0.10, 0.90, 168.5)	(0.10, 0.90, 168.5)	0.0	0.0	762	1096	0.16
(0.20, 0.80)	(0.20, 0.80, 141.6)	(0.20, 0.80, 134.3)	0.0	0.0	2141	1125	0.22
	(0.2589, 0.7411, 88.51)	(0.2589, 0.7411, 88.51)	0.0022	0.0022			
	(0.4972, 0.5028, 47.98)	(0.4972, 0.5028, 47.99)	-0.007	-0.007			
(0.30, 0.70)	(0.1848, 0.8152, 141.6)	(0.1848, 0.8152, 141.6)	-0.007	0.007	2478	1199	0.22
	(0.30, 0.70, 69.79)	(0.30, 0.70, 69.79)	0.0	0.0			
	(0.3579, 0.6421, 59.13)	(0.3579, 0.6421, 59.13)	$-1.9 \times 10^{-4}$	$-1.9 \times 10^{-4}$			
(0.43, 0.57)	(0.1912, 0.8088, 138.7)	(0.1912, 0.8088, 138.7)	-0.001	-0.001	2276	1167	0.22
	(0.2732, 0.7268, 79.62)	(0.2732, 0.7268, 79.62)	0.0032	0.0032			
	(0.43, 0.57, 52.14)	(0.43, 0.57, 52.14)	0.0	0.0			
(0.60, 0.40)	(0.60, 0.40, 43.69)	(0.60, 0.40, 43.69)	0.0	0.0	1880	2489	0.44

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation.

**Table 7. Case Study 5: Phase-Stability Analysis for the Ternary System Nitrogen (1), Methane (2), and Ethane (3) at 270 K and 76 bar Using the PR Equation of State**

feed ( $z_1, z_2, z_3$ )	roots ( $x_1, x_2, x_3, v$ )		distance		IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	PEC CPU time (s)
	IN/GB	PEC	IN/GB	PEC			
(0.30, 0.10, 0.60)	(0.312, 0.102, 0.587, 153)	(0.312, 0.102, 0.587, 153)	$-5.8 \times 10^{-6}$	$-5.8 \times 10^{-6}$	5498	4973	4.28
	(0.300, 0.100, 0.600, 147)	(0.300, 0.100, 0.600, 147)	0.0	0.0			
	(0.133, 0.068, 0.799, 77.5)	(0.133, 0.068, 0.799, 77.5)	-0.0148	-0.0148			
(0.15, 0.30, 0.55)	(0.150, 0.300, 0.550, 132)	(0.150, 0.300, 0.550, 132)	0.0	0.0	13421	6312	5.94
	(0.147, 0.297, 0.556, 130)	(0.147, 0.297, 0.556, 130)	$3.55 \times 10^{-7}$	$3.61 \times 10^{-7}$			
	(0.097, 0.245, 0.658, 90.3)	(0.097, 0.245, 0.658, 90.2)	-0.0012	-0.0012			
(0.08, 0.38, 0.54)	(0.080, 0.380, 0.540, 120)	(0.080, 0.380, 0.540, 120)	0.0	0.0	10207	5891	6.15
(0.05, 0.05, 0.90)	(0.050, 0.050, 0.900, 69.6)	(0.050, 0.050, 0.900, 69.6)	0.0	0.0	2514	2579	3.24

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation.

**Table 8. Case Study 6: Phase-Stability Analysis for the Ternary System Methane (1), Carbon Dioxide (2), and Hydrogen Sulfide (3) Using the PR Equation of State ( $T$  in K and  $P$  in bar)**

feed ( $P, T, z_1, z_2, z_3$ )	roots ( $x_1, x_2, x_3, v$ )		distance		IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	PEC CPU time (s)
	IN/GB	PEC	IN/GB	PEC			
(55.1, 208.5, 0.4989, 0.0988, 0.4023)	(0.919, 0.034, 0.047, 154)	(0.919, 0.034, 0.046, 143)	$-1.5 \times 10^{-2}$	$-1.5 \times 10^{-2}$	16328	3997	4.39
	(0.859, 0.051, 0.090, 75.1)	(0.859, 0.051, 0.090, 75.1)	$-9.4 \times 10^{-3}$	$-9.5 \times 10^{-3}$			
	(0.817, 0.060, 0.123, 61.8)	(0.817, 0.060, 0.123, 61.8)	$-9.7 \times 10^{-3}$	$-9.7 \times 10^{-3}$			
	(0.245, 0.091, 0.664, 35.3)	(0.245, 0.091, 0.664, 35.3)	$-6.8 \times 10^{-3}$	$-6.8 \times 10^{-3}$			
	(0.499, 0.099, 0.402, 40.0)	(0.499, 0.099, 0.402, 40.0)	0.0	0.0			
(57.5, 210.5, 0.4989, 0.0988, 0.4023)	(0.911, 0.037, 0.052, 134)	(0.911, 0.037, 0.052, 134)	-0.013	-0.013	16954	4411	4.94
	(0.255, 0.092, 0.653, 35.6)	(0.255, 0.092, 0.653, 35.6)	$-5.7 \times 10^{-3}$	$-5.7 \times 10^{-3}$			
	(0.499, 0.099, 0.402, 40.4)	(0.499, 0.099, 0.402, 40.4)	0.0	0.0			
(57.5, 210.5, 0.48, 0.12, 0.40)	(0.903, 0.045, 0.052, 129)	(0.903, 0.045, 0.053, 129)	$-5.5 \times 10^{-3}$	$-5.5 \times 10^{-3}$	20046	4363	5.06
	(0.862, 0.057, 0.081, 84.1)	(0.862, 0.057, 0.081, 84.1)	$-3.7 \times 10^{-3}$	$-3.7 \times 10^{-3}$			
	(0.767, 0.081, 0.152, 56.1)	(0.767, 0.081, 0.152, 56.1)	$-5.5 \times 10^{-3}$	$-5.5 \times 10^{-3}$			
	(0.290, 0.117, 0.593, 36.2)	(0.290, 0.117, 0.594, 36.2)	$-2.2 \times 10^{-3}$	$-2.2 \times 10^{-3}$			
	(0.48, 0.12, 0.40, 40.1)	(0.48, 0.12, 0.40, 40.1)	0.0	0.0			
(48.6, 227.55, 0.4989, 0.0988, 0.4023)	(0.900, 0.041, 0.059, 271)	(0.900, 0.041, 0.059, 271)	-0.185	-0.185	8695	3847	4.34
	(0.278, 0.094, 0.628, 38.0)	(0.278, 0.094, 0.628, 38.0)	$3.55 \times 10^{-7}$	$-5.2 \times 10^{-3}$			
	(0.499, 0.099, 0.402, 40.4)	(0.499, 0.099, 0.402, 45.1)	0.0	0.0			

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation.

by Oellrich et al.,<sup>27</sup> are  $k_{12} = 0.12$ ,  $k_{13} = 0.08$ , and  $k_{23} = 0.12$ . This problem was formulated from the experimental data given by Robinson et al.<sup>17</sup> The feed composition  $z = (0.4989, 0.0988, 0.4023)$  was analyzed at the listed temperatures and pressures. For the above feed condition, only two equilibrium phases were obtained, instead of the three phases indicated by the experimental data. To reconcile this difference, we had to either lower the pressure or adjust the binary interaction parameters. Specifically, three phases in equilibrium were located using an adjusted set of binary interaction parameters (i.e.,  $k_{12} = 0.13$ ,  $k_{13} = 0.095$ , and  $k_{23} = 0.097$ ). This indicates that the binary interaction parameters generated from vapor-liquid equilibrium data, at times, produce incorrect phase splits and/or poor phase compositions for liquid-liquid-vapor and other phase

combinations. The results of applying the adjusted binary interaction parameters are shown in Table 11.

## 7. Discussion of Results

The ability to find all stationary points or roots of a system of nonlinear equations is vital in determining the phase stability. In this study, the regular Newton's method with a proposed initialization scheme was utilized.

Phase-stability-analysis results of some challenging problems indicate that our technique was able to predict accurately the stability of the mixtures at selected temperatures, pressures, and compositions as shown in Tables 3-11. From these tables, we can see that the results obtained using PEC are identical to those

Table 9. Case Study 7: Phase-Stability Analysis and Phase-Split Analysis for Unstable Feed Compositions for the Quaternary System Methane (1), Carbon Dioxide (2), Hydrogen Sulfide (3), and Water (4) Using the PR Equation of State ( $T$  in K and  $P$  in bar)

feed ( $P, T, z_1, z_2, z_3, z_4$ )	(a) Phase-Stability Analysis						IN/GB RIT <sup>a</sup>	PEC FE <sup>b</sup>	PEC CPU time (s)
	roots ( $x_1, x_2, x_3, x_4$ )			distance					
	IN/GB	PEC	PEC	IN/GB	PEC	PEC			
(76.0, 310.95, 0.1488, 0.2991, 0.0494, 0.5027)	(0.965, 0.033, 0.002, $2.2 \times 10^{-4}$ ) (0.149, 0.299, 0.049, 0.502) ( $2.7 \times 10^{-6}$ , $7.2 \times 10^{-4}$ , $2.4 \times 10^{-4}$ , 0.999)	(0.964, 0.033, 0.002, $2.2 \times 10^{-4}$ ) (0.149, 0.299, 0.049, 0.503) ( $2.7 \times 10^{-6}$ , $7.2 \times 10^{-4}$ , $2.4 \times 10^{-4}$ , 0.999)	-0.0271 0.0 -0.0117	-0.0271 0.0 -0.0117	-0.0271 0.0 -0.0117	180376	68598	22.26	
(129.3, 389.35, 0.1496, 0.3009, 0.0498, 0.4997)	( $3.3 \times 10^{-5}$ , 0.003, 0.001, 0.996) (0.150, 0.300, 0.050, 0.500) ( $3.6 \times 10^{-4}$ , 0.004, 0.045, 0.950)	(0.812, 0.163, 0.015, 0.010) ( $3.3 \times 10^{-5}$ , 0.003, 0.001, 0.996) (0.150, 0.300, 0.050, 0.500)	-1.201 -0.8308 0.0	-1.201 -0.8308 0.0	-1.201 -0.8308 0.0	29159	22626	29.06	
(181.7, 449.85, 0.0496, 0.0494, 0.4000, 0.5000)	(0.399, 0.097, 0.417, 0.087) (0.050, 0.050, 0.400, 0.500) (0.961, 0.014, 0.025, $3.7 \times 10^{-4}$ )	(0.398, 0.097, 0.416, 0.087) (0.050, 0.050, 0.400, 0.500) (0.961, 0.014, 0.025, $3.7 \times 10^{-4}$ )	-0.2948 0.0 - $2.7 \times 10^{-2}$	-0.1759 0.0 - $2.7 \times 10^{-2}$	-0.1745 0.0 - $2.7 \times 10^{-2}$	29956	30949	25.60	
(62.6, 310.95, 0.0504, 0.0503, 0.3986, 0.5008)	(0.0504, 0.0503, 0.3986, 0.5008) ( $4.3 \times 10^{-6}$ , 0.001, 0.004, 0.995)	(0.0504, 0.0503, 0.3986, 0.5008) ( $4.3 \times 10^{-6}$ , 0.001, 0.004, 0.995)	0.0 -0.6372	0.0 -0.6372	0.0 -0.6372	386029	50069	21.51	

feed ( $T, P, z_1, z_2, z_3, z_4$ )	(b) Phase-Split Analysis for the Unstable Feed Compositions													
	min. Gibbs energy				phase I				phase II					
	Hua <sup>c</sup>	PEC	Hua	$\alpha$	Hua	PEC	Hua	$\alpha$	Hua	PEC	Hua	algorithm CPU time (s)		
(310.95, 76.0, 0.1488, 0.2991, 0.0494, 0.5027)	-0.3956	-0.3961	0.4952	0.4959	0.3005, 0.6012, 0.0978, 0.0005, 235.9)	(0.3001, 0.6005, 0.0975, 0.0019, 235.9)	0.5048	0.5041	0.5048	0.5041	(0.0000, 0.0027, 0.0019, 0.9954, 21.47)	46.74	48.89	15.00
(380.35, 129.3, 0.1496, 0.3009, 0.0498, 0.4997)	-0.4388	-0.4399	0.4985	0.4988	(0.0000, 0.0079, 0.0036, 0.9885, 22.77)	(0.0000, 0.0069, 0.0044, 0.9887, 22.77)	0.5015	0.5062	0.5015	0.5062	(0.2955, 0.5921, 0.0957, 0.0139, 192.4)	196.9	47.35	19.39
(449.85, 181.7, 0.0496, 0.0494, 0.4000, 0.5000)	-0.3983	-0.4008	0.5325	0.5349	(0.0936, 0.0893, 0.6861, 0.1309, 126.3)	(0.0926, 0.0886, 0.6777, 0.1401, 124.5)	0.4675	0.4651	0.4675	0.4651	(0.0000, 0.0038, 0.0729, 0.9233, 25.84)	92.71	40.81	26.97

<sup>a</sup> RIT = root inclusion test. <sup>b</sup> FE = function evaluation. <sup>c</sup> Hua<sup>II</sup> applied INTPFLASH code.

**Table 10. Case Study 8: Phase-Split Analysis Results for the Ternary System Methane (1), Carbon Dioxide (2), and Hydrogen Sulfide (3) Using the SRK Equation of State for  $z = (0.5, 0.25, 0.25)$  ( $T$  in °F and  $P$  in psia)**

$(P, T)$	phase I (liquid)		phase II (vapor)		algorithm CPU time (s)		
	PEC	data	PEC	data	I	II	III
(1114.0, 39.2)	(0.1818, 0.2596, 0.5586)	(0.1792, 0.27460, 0.5462)	(0.5218, 0.2493, 0.2288)	(0.5213, 0.2499, 0.2288)	8.46	7.08	1.86
(1380.0, 39.38)	(0.2967, 0.2771, 0.4261)	(0.2764, 0.2861, 0.4375)	(0.5143, 0.2481, 0.2377)	(0.5156, 0.2503, 0.2341)	9.62	11.15	1.59
(511.1, -0.4)	(0.0657, 0.2075, 0.7267)	(0.0645, 0.2388, 0.6967)	(0.5560, 0.2555, 0.1885)	(0.5622, 0.2505, 0.1873)	7.74	6.82	2.19
(895.0, 0.94)	(0.1892, 0.3096, 0.5012)	(0.1864, 0.3198, 0.4938)	(0.6436, 0.2225, 0.1839)	(0.6506, 0.2163, 0.1831)	9.94	4.34	1.48
(1233.0, -0.4)	(0.3659, 0.2890, 0.3451)	(0.3637, 0.2939, 0.3424)	(0.6476, 0.2070, 0.1454)	(0.6539, 0.2054, 0.1407)	23.35	19.01	1.76
(251.1, -50.8)	(0.0394, 0.2378, 0.7228)	(0.0408, 0.2841, 0.6751)	(0.6319, 0.2535, 0.1146)	(0.6593, 0.2353, 0.1054)	8.19	7.91	2.53
(596.0, -51.3)	(0.1716, 0.3597, 0.4687)	(0.1677, 0.3692, 0.4631)	(0.7842, 0.1550, 0.0607)	(0.7817, 0.1515, 0.0668)	8.24	8.35	1.32
(822.0, -51.5)	(0.3092, 0.3235, 0.3673)	(0.3140, 0.3217, 0.3643)	(0.8112, 0.1300, 0.0588)	(0.8141, 0.1258, 0.0601)	13.18	13.67	1.43
(134.1, -101.2)	(0.0353, 0.3622, 0.6025)	(0.0357, 0.3879, 0.5764)	(0.7674, 0.1854, 0.0472)	(0.8015, 0.1584, 0.0401)	7.74	6.92	2.80
(346.4, -100.6)	(0.1363, 0.4027, 0.4610)	(0.1314, 0.4128, 0.4558)	(0.8905, 0.0861, 0.0235)	(0.8761, 0.0901, 0.0338)	13.78	2.36	1.26
(510.4, -100.5)	(0.2683, 0.3533, 0.3784)	(0.2691, 0.3562, 0.3747)	(0.9139, 0.0654, 0.0206)	(0.8980, 0.0700, 0.0320)	12.20	5.82	1.21

**Table 11. Case Study 9: Phase-Split Analysis for  $z = (0.4989, 0.0988, 0.4023)$  of the Ternary System Methane (1), Carbon Dioxide (2), and Hydrogen Sulfide (3) Using the PR Equation of State ( $T$  in °F and  $P$  in psia)**

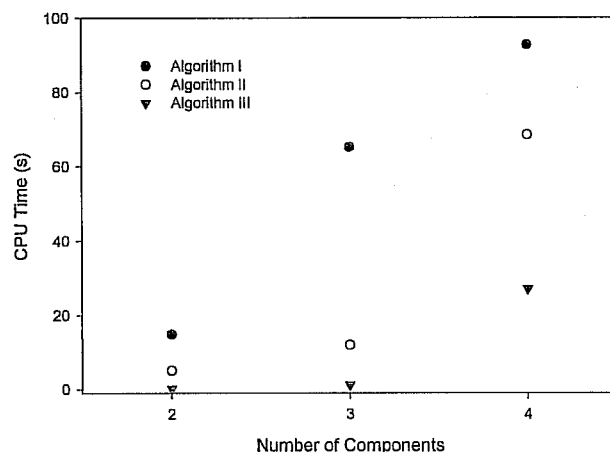
$(P, T)$	phase I (H <sub>2</sub> S liquid)		phase II (CH <sub>4</sub> liquid)		phase III (vapor)		algorithm CPU time (s)		
	PEC	data	PEC	data	PEC	data	I	II	III
(534.0, -117.38)	(0.1507, 0.1511, 0.6982)	(0.1901, 0.1395, 0.6704)	(0.8154, 0.0832, 0.1013)	(0.8175, 0.0806, 0.1019)	(0.9553, 0.0281, 0.0165)	(0.9383, 0.0287, 0.0330)	21.98	4.99	1.32
(730.0, -94.9)	(0.1796, 0.1339, 0.6864)	(0.2564, 0.1383, 0.6053)	(0.8191, 0.0755, 0.1054)	(0.7188, 0.0890, 0.1922)	(0.9252, 0.0399, 0.0348)	(0.9225, 0.0399, 0.0376)	70.47	5.17	1.37

obtained by Hua.<sup>11</sup> As revealed by the first composition of case 6 in Table 8, stationary roots that are very close to each other, and that often represent challenging phase conditions (such as feed compositions in the proximity of phase boundaries), are successfully obtained using PEC without any difficulty. Michelsen's<sup>6</sup> algorithm failed to detect the instability for the problems that appeared in the case studies 1 and 2, whereas PEC is capable of predicting the instability of those cases. The results indicate that PEC matches well the capability of the IN/GB method of Hua et al.,<sup>12</sup> which is considered to be an extremely reliable technique.

The phase-stability algorithm developed in this study is relatively simple to program. However, this simplicity does not sacrifice reliability, as revealed by the results obtained thus far. The number of function evaluations performed using the PEC method is highly dependent on the complexity and number of components of the multiphase system encountered. The number of the root inclusion tests of the IN/GB method also shows the same trend.

In this study, three algorithms (algorithms I, II, and III) were developed to solve phase-split problems. Algorithm I uses stationary points as the initial guess for mole fractions and the initialization scheme for the phase fraction ( $\alpha$ ). The minimization problem was solved by SQP. Algorithm II is the same as algorithm I, but the IFM method is employed to identify the initial guesses for the phase fraction. Algorithm III used the IFM method initialized by the stationary-point mole fractions and enhanced with a phase-check procedure. The results of those algorithms are in excellent agreement with those of Hua<sup>11</sup> and are comparable with experimental data, as shown in Tables 3b, 5b, 7, 10 and 11.

The results of many challenging case studies obtained from the phase-split analysis indicate that the algorithms developed in this study are reliable for solving phase equilibrium problems. This is accomplished in algorithms I and II by (a) providing viable initial guesses using the proposed initialization scheme, (b) implementing Newton's method in the convergence neighborhoods

**Figure 11. CPU time comparison of algorithms I, II, and III.**

generated by good initial guesses, (c) checking the stability of the prospective phases in the equilibrium produced by SQP, and (d) applying the equal-fugacity criterion to verify that the compositions of the phases in equilibrium are definitely located at the tangent points. In algorithm III, the global minimum of Gibbs energy is obtained by taking the lowest Gibbs energy from several solutions resulting from several initial guesses constructed from stationary points. Some of the above measures have also enhanced the computational efficiency of the PEC algorithm. Algorithm I can be accelerated by using the IFM method to find phase fractions (leading to algorithm II). Further acceleration is applied in algorithm III, where the final compositions are obtained from the enhanced IFM method. This acceleration is illustrated in Figure 11. This figure shows that, as the number of components increases, the accelerated methods are much faster than the original method, where initial guesses for phase fraction(s) were generated by the initialization scheme.

The effect of acceleration is more pronounced in the solution of three-phase systems. As shown in Table 11, for the second feed composition, algorithm I required 70.47 s to produce the solutions, whereas algorithm II

needed only 5.7 s. As discussed before, the phase-split analysis began with the assumption that the feed is split into two phases. Each of the phases was checked for its stability. If there are two combinations of initial guesses for mole fractions, then, for each combination, 10 initial guesses for  $\alpha$  are generated to be applied in algorithm I. When the two-phase checks failed, algorithm I used 20 initial guesses (10 initial guesses for  $\alpha$  for each combination) to complete the check, whereas algorithm II employed only two initial guesses (one initial guess for  $\alpha$  for each combination). Therefore, it is obvious that algorithm I requires a much larger CPU time than algorithm II. For the same case 9, algorithm III took only 1.37 s. Although the number of initial guesses used in algorithm III is the same as those utilized in algorithm II, the stability check was conducted in algorithm III through a phase-check procedure, which is faster than the stability analysis performed in algorithm II.

The results of the phase-split algorithms established in this study are similar to those of the IN/GB method. This indicates that our proposed method is reliable in producing accurate results when the recommended initialization scheme is applied properly.

Often, the use of binary interaction parameters ( $k_{ij}$ ) generated from vapor-liquid equilibrium data leads to unsatisfactory results for liquid-liquid-vapor and solid-liquid-vapor systems. This indicates that a careful use of  $k_{ij}$ 's is required. In this study, such parameters were regressed from experimental data to ensure accurate representations of the systems considered. Sample results of this strategy are given in Table 11 for the methane/carbon dioxide/hydrogen sulfide system, where experimental data were used to generate  $k_{ij}$ 's for the full phase diagram.

In designing a new separation process, reliable solutions are mandatory, while computational efficiency is desirable. Therefore, algorithm I can be used for this purpose. Algorithms II and III are offered to improve the efficiency of algorithm I. They are well-suited for the evaluation and development of thermodynamic models where the phase conditions are known. In such cases, the efficiency of the computation is the point of emphasis. However, algorithms II and III require additional extensive testing to ascertain their reliability.

## 8. Conclusions

The reliability, versatility, and computational efficiency of the different algorithms vary significantly. Ten challenging case studies were successfully used to demonstrate the viability of the proposed algorithms and the initialization procedures. Further, the proposed initialization strategy applied in algorithms I, II, and III proved successful for the case studies considered.

In general, our multiphase predictions are identical to those obtained by Hua<sup>11</sup> using the IN/GB method, and they compare well with reliable experimental data. For quaternary systems, the results generated by the IN/GB method are slightly different from our results. The difference might be due to the convergence criteria and tolerances used in the calculations. The results of several tests reveal that the present method is as reliable as the IN/GB method. However, additional tests involving complex systems need to be conducted to determine the reliability and efficiency of our method.

The present evaluations indicate that (a) the GEM algorithm (algorithm I) should be applied in demanding

process design tasks and (b) the accelerated GEM algorithms (algorithms II and III) should prove effective in dealing with systems involving a large number of components.

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## Nomenclature

$g$  = reduced Gibbs free energy  
 $i$  = phase  $i$   
 $j$  = component  $j$   
 $K$  = equilibrium constant  
 $k$  = index denoting the position of  $x$ , binary interaction parameter  
 $n$  = number of components  
 $P$  = pressure  
 $T$  = temperature  
 $v$  = molar volume  
 $\bar{x}$  = mole fraction  
 $x$  = mole fraction of the liquid phase  
 $y$  = mole fraction of the vapor phase  
 $z$  = feed mole fraction

### Subscripts

$c$  = critical  
 mix = mixture  
 $r$  = reference composition  
 $y$  = arbitrary composition

### Superscript

$o$  = pure component

### Greek Symbols

$\alpha$  = phase fraction  
 $\Delta$  = change  
 $\kappa$  = range of variable  $x$   
 $\vartheta$  = number of grid points  
 $\tau$  = any positive number describing the shape of nonuniformity  
 $\omega$  = acentric factor

## Appendix A. Liquid-Liquid-Vapor Phase-Check Procedure

For liquid-liquid-vapor systems, the iteration functions can be expressed as

$$F_1(\alpha_1, \alpha_2) = \sum_j \frac{z_j K_j^2 (1 - K_j^1)}{K_j^1 K_j^2 + \alpha_1 K_j^2 (1 - K_j^1) + \alpha_2 K_j^1 (1 - K_j^2)}$$

$$F_2(\alpha_1, \alpha_2) = \sum_j \frac{z_j K_j^1 (1 - K_j^2)}{K_j^1 K_j^2 + \alpha_1 K_j^2 (1 - K_j^1) + \alpha_2 K_j^1 (1 - K_j^2)}$$

where  $K_j^1$  and  $K_j^2$  are the liquid<sup>1</sup>-vapor and liquid<sup>2</sup>-vapor equilibrium constants for component  $j$  and  $z_j$  is feed mole fraction of component  $j$ .  $\alpha_1$  and  $\alpha_2$  are the phase fractions of liquid<sup>1</sup> and liquid<sup>2</sup>, respectively.

The three phase-check procedures can be stated as follows:

## 1. Single phase exists

(i) only vapor phase

$$\sum_j \frac{z_j}{K_j^1} < 1 \quad \text{and} \quad \sum_j \frac{z_j}{K_j^2} < 1$$

(ii) only liquid<sup>1</sup> phase

$$\sum_j z_j K_j^1 < 1 \quad \text{and} \quad \sum_j z_j \frac{K_j^1}{K_j^2} < 1$$

(iii) only liquid<sup>2</sup> phase

$$\sum_j z_j K_j^2 < 1 \quad \text{and} \quad \sum_j z_j \frac{K_j^2}{K_j^1} < 1$$

## 2. Two phases exist

(i) liquid<sup>1</sup> and vapor

$$\sum_j \frac{z_j}{K_j^1} > 1, \quad \sum_j z_j K_j^1 > 1$$

and  $F_2(\alpha_1, 0) < 0$  at the root of  $F_1(\alpha_1, 0) = 0$ (ii) liquid<sup>2</sup> and vapor

$$\sum_j \frac{z_j}{K_j^2} > 1, \quad \sum_j z_j K_j^2 > 1$$

and  $F_1(\alpha_1, 0) < 0$  at the root of  $F_2(\alpha_1, 0) = 0$ (iii) liquid<sup>1</sup> and liquid<sup>2</sup>

$$\sum_j z_j \frac{K_j^1}{K_j^2} > 1, \quad \sum_j z_j \frac{K_j^2}{K_j^1} > 1$$

and  $F_2(\alpha_1, 1 - \alpha_1) > 0$  at the root of  $F_1(\alpha_1, 1 - \alpha_2) - F_2(\alpha_1, 1 - \alpha_2) = 0$ 

## 3. Three phases exist

(i) liquid<sup>1</sup>-liquid<sup>2</sup>, bubble-point prediction

$$\sum_j z_j \frac{K_j^1}{K_j^2} > 1, \quad \sum_j z_j \frac{K_j^2}{K_j^1} > 1$$

and  $F_2(\alpha_1, 1 - \alpha_1) = 0$  at the root of  $F_1(\alpha_1, 1 - \alpha_2) - F_2(\alpha_1, 1 - \alpha_2) = 0$ (ii) liquid<sup>1</sup>-vapor, dew point of liquid<sup>2</sup>

$$\sum_j \frac{z_j}{K_j^1} > 1, \quad \sum_j z_j K_j^1 > 1$$

and  $F_2(\alpha_1, 0) = 0$  at the root of  $F_1(\alpha_1, 0) = 0$ (iii) liquid<sup>2</sup>-vapor, dew point of liquid<sup>1</sup>

$$\sum_j \frac{z_j}{K_j^2} > 1, \quad \sum_j z_j K_j^2 > 1$$

and  $F_1(\alpha_1, 0) = 0$  at the root of  $F_2(\alpha_1, 0) = 0$ 

Once it has been determined that three phases exist (liquid<sup>1</sup>, liquid<sup>2</sup>, and vapor), the two iteration functions

above are solved simultaneously for  $\alpha_1$  and  $\alpha_2$ . The new mole fractions of component  $j$  in the vapor, liquid<sup>1</sup>, and liquid<sup>2</sup> phases are calculated, respectively, as

$$y_j = \frac{z_j K_j^1 K_j^2}{K_j^1 K_j^2 + \alpha_1 K_j^2 (1 - K_j^1) + \alpha_2 K_j^1 (1 - K_j^2)}$$

$$y_j^1 = \frac{z_j K_j^2}{K_j^1 K_j^2 + \alpha_1 K_j^2 (1 - K_j^1) + \alpha_2 K_j^1 (1 - K_j^2)}$$

$$y_j^2 = \frac{z_j K_j^1}{K_j^1 K_j^2 + \alpha_1 K_j^2 (1 - K_j^1) + \alpha_2 K_j^1 (1 - K_j^2)}$$

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