



Efficient and robust phase-split computations in the internal energy, volume, and moles (*UVN*) space

Ran Bi ^a, Abbas Firoozabadi ^{b, c, *}, Philip C. Myint ^d

^a Department of Petroleum Engineering, Texas A&M University, College Station, TX, 77843, USA

^b Reservoir Engineering Research Institute, Palo Alto, CA, 94301, USA

^c Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX, 77005, USA

^d Lawrence Livermore National Laboratory, Livermore, CA, 94550, USA

ARTICLE INFO

Article history:

Received 28 January 2020

Received in revised form

3 June 2020

Accepted 16 June 2020

Available online 3 July 2020

Keywords:

Phase-split

UVN Space

ABSTRACT

Phase-split computations in an isolated system, which in general may be defined as one where the total internal energy (U), volume (V), and the number of moles ($\mathbf{N} = N_1, N_2, \dots, N_n$) of the components are fixed at some specified set of values, involves the determination of the temperature (T), pressure (P), plus the amount and composition of the various phases that constitute the system. A simpler, but analogous problem is one where T , P , and \mathbf{N} are specified instead. In TPN space, one may first perform a stability analysis to determine whether the system is stable, meaning whether at equilibrium it will split up into multiple phases or remain in single phase. If the single-phase state is unstable, the stability analysis reliably provides a good set of initial guesses in the subsequent phase-split computations. In UVN space, however, we demonstrate that the stability analysis (which is the main subject of our earlier study [1]) may not in general provide good enough initial guesses; we offer alternative strategies for setting up good initial guesses. Furthermore, we show that a combination of successive substitution iteration (SSI) and Newton's method—two iterative methods that are prevalent in the literature in TPN space—facilitates a robust and efficient algorithm for phase-split computations in isolated systems. This combination has so far not been applied in UVN space.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Hydrodynamic simulations of materials in isolated vessels [2–7] may require efficient and robust phase-split computations of an n -component mixture with given internal energy (U), volume (V), and number of moles ($\mathbf{N} = N_1, N_2, \dots, N_n$). The specification of UVN fully defines the thermodynamic state of the system and corresponds to a microcanonical-ensemble description of an isolated system. All the other thermodynamic properties of the system, such as the temperature and pressure, should be computable in principle. Such computations are often challenging, partly because the stability analysis, which is used to determine the phase stability of the system (whether it will exist in multiple phases or in single phase), exhibits subtleties in UVN space that we explain in more detail later in this study. These subtleties are not present in the analogous, but

much more well-studied TPN space (isothermal–isobaric ensemble) [8–14] where the temperature (T), pressure (P), and moles (\mathbf{N}) are specified instead. In UVN space, the objective is to find not only the amounts and compositions of the phases that constitute the mixture (just like in TPN space), but the temperature and the pressure as well.

In a recent paper [1], we have presented an efficient and robust algorithm for stability analysis in isolated systems. That study illustrates the algorithm in mixtures that can either split up into two phases or remain as a single-phase mixture. If the single-phase state is deemed to be unstable relative to the two-phase state, which implies that the two-phase state has a higher entropy, one may perform the phase-split computations described in this study to find the equilibrium state of the two-phase mixture. The basic idea behind the stability analysis is to investigate if the introduction of an infinitesimal amount of a second phase increases the entropy of the total system compared to the single-phase scenario. If it does, then the equilibrium state for the given set of UVN is a two-phase state whose properties may be found by performing the phase-split computations, which entail iteratively solving for the

* Corresponding author. Reservoir Engineering Research Institute, Palo Alto, CA, 94301, USA.

E-mail address: abbas.firoozabadi@rice.edu (A. Firoozabadi).

temperature, pressure, and mole numbers of the two phases using an appropriate equation of state. The stability analysis is connected to the subsequent phase-split computations through the fact that the former may be used to seed the latter with a set of initial guesses.

As a brief aside, we note that a third commonly studied specification is *TVN* space, which corresponds to the canonical ensemble. It may be thought as being intermediate in complexity between the *TPN* and *UVN* spaces. Although *TVN* is generally simpler than *UVN* (temperature being easier to work with than internal energy), the two spaces do share a commonality: the initial guesses provided by the stability analysis for the *TVN* or *UVN* phase-split computations may not necessarily be reliable, which is unlike in *TPN*, where the initial guesses almost always guarantee convergence of the phase-split computations. This is an important distinction that we have alluded to above, and that we will explain in more detail later in this study. The reason why *TVN* or *UVN* space differs from *TPN* in this sense is because in *TPN*, the temperature and pressure remain fixed regardless of the phase amounts, and there are no constraints on V or U that must be satisfied. In contrast, in *TVN* or *UVN*, a good initial guess must be provided for the relative phase amounts since the phase amounts are used to satisfy the constraint on the total volume V . (In *UVN* space, the phase amounts are also used in the constraint on the total energy U .) The difficulty is that the stability analysis cannot provide information about phase amounts since it considers only infinitesimal perturbations, as we have explained above. Although there has been some discussion on initial guesses [15,16], this specific issue of the potential inadequacy of the stability analysis in providing suitable initial guesses for the phase-split computations has not been brought up in *TVN* space (nor in *UVN* space), to the best of our knowledge. Part of the reason may be because previous *TVN* studies focus on either the stability analysis [17,18] or the phase-split computations [19] without necessarily connecting these two parts together, or they may be more focused on the development of the underlying numerical methods [20–23]. One of the goals of our study is to make this contrast between *TPN* and *UVN* spaces more explicit, especially since this issue has not been discussed at length in the latter.

There is a limited number of published algorithms on the *UVN* space. Most authors rely on Newton's method or modifications along various constraints to facilitate convergence. Saha and Carroll in an early paper [4] have set the stage for later works on *UVN* phase-split computations. The authors set up the problem as the conventional *TPN* phase-split computation. The first step includes the estimation of mixture critical volume and pseudocritical temperature to obtain initial guesses for T and P . Then a *TPN* phase-split computation is implemented to find the total internal energy and volume of the split two-phase mixture. The temperature and pressure are updated using specific formulations until the total internal energy and volume of the two-phase mixture match the specified U and V , respectively. Three examples presented in Saha and Carroll reveal that a large number of phase-split computations (iterations) are required in the *TPN*-space loop.

In a later study, Michelsen [24] introduces a general framework to perform phase-split computations in various spaces, including the *UVN* space. He proposes two approaches: one is a nested optimization approach where a *TPN* phase-split computation is solved in the inner loop, and the outer loop updates T and P . The other one is based on a modified objective function without constraints. He states the second approach does not guarantee a maximum of entropy. Castier [25] has proposed a method for direct maximization of entropy. His approach involves adding or removing phases as needed during the computations. He reports negative pressures (and also imaginary numbers) in some computations. Because of these numerical deficiencies, he employs a

nested loop, in which the pressure and temperature are updated in the outer loop. In the inner loop, he uses a *TPN* phase-split computation to obtain phase amounts and compositions to compute the internal energies and volumes. In the computation of T and P , the step size is controlled by Newton's method. Castier emphasizes the maximization of entropy, but Newton's method and reduction of step size do not guarantee convergence. The unphysical behavior (negative pressures, imaginary numbers, and negative heat capacities) exhibited in some of the examples are interpreted to be related to convergence issues. His phase addition and removal procedures are computationally expensive. Quadratic convergence in Newton's method is expected to lead to convergence in few iterations [10]. More recently, Arendsen and Versteeg [26] have formulated the problem in terms of T , P , and individual phase compositions, and phase amounts. There is no report on the efficiency of the method and no rigorous validation is presented.

In recent studies, Paterson et al. [27] extend the modified RAND algorithm [14] to phase-split problems in *UVN* space by adapting their algorithm for *TPN* phase-split computations. Their modified RAND algorithm in *TPN* space involves solving a matrix equation to minimize the total Gibbs energy of a multiphase, multicomponent mixture subject to the constraints that the mole numbers cannot be negative. They state that an advantage of the algorithm is that they can achieve quadratic convergence as in the traditional Newton-based methods, but their matrix does not become singular when a phase amount or the moles of a particular component in a certain phase goes to zero. The computational-cost analysis suggests that modified RAND may be more expensive than traditional methods for two-phase mixtures, but may become more efficient for mixtures composed of four or more phases. In *UVN* space, they are able to largely follow the same approach as in the *TPN* phase-split computations, with one difference being that their matrix equation now seeks to maximize the entropy instead of minimizing the Gibbs energy. This involves the introduction of internal energy- and volume-balance constraints that increase the rank of the matrix equation by two compared to the *TPN* case. The two extra equations are used to solve for two additional unknowns: the temperature and the pressure. Some additional steps are taken to improve the robustness; most notably, if a certain number of iterations is exceeded, the nested optimization approach developed by Michelsen [24] is followed instead. It is reported that the phase-split computations in *UVN* space take on average about 1.5 times the number of iterations in the phase-split computations as in *TPN* space and that a few of the examples exceeded the iteration threshold to switch to the nested optimization approach mentioned above. Paterson et al. report that the number of iterations required for convergence is generally 10 or less for most conditions of the three examples in their study. It can take up to about 40 iterations for a particular example (a three-component mixture near the critical point).

Smejkal and Mikyška [28] present a comprehensive paper on the subject. The authors provide a systematic approach in which they first formulate the stability analysis and then the phase-split computations. They use a Newton-based method for the solution of the nonlinear algebraic equations. Both line search and a modified Cholesky decomposition are implemented to help convergence. The stability analysis is performed in energy-density and molar-density space, while the phase-split computations are in *UVN* space. To use the stability analysis results as initial guesses for the phase-split computations, Smejkal and Mikyška assume an initial volume for the trial phase. The initial volume must satisfy a condition that the initial two-phase mixture has higher entropy than the given single-phase. Starting with the total volume of the system, they keep halving this value until a volume that satisfies this requirement is found. This initial setup can be computationally

expensive because the stability analysis assumes the volume of the trial phase is negligible. Smejkal and Mikyška choose mole numbers as one of the independent variables. However, experience (Example 5.6 in Firoozabadi [29]) in the TPN space shows that this choice of variables may lead to numerical divergence for states that lie close to phase boundaries. This problem can be alleviated by using equilibrium ratios (partition coefficients) instead. Recently Smejkal and Mikyška [30] present a general formulation for phase-behavior computations in various spaces by direct minimization or maximization of thermodynamic functions. The algorithm in UVN space is the same as Smejkal and Mikyška [28]. They find that phase-split computations in TPN space require more iterations than those in UVN space, which does not agree with the conclusions drawn by Paterson et al. [27].

In this work, we present our algorithms for phase-split computations in UVN space. In various TPN examples, Li and Firoozabadi [10] have found that a sequential combination of two iterative techniques—successive substitution iteration (SSI) and Newton's method—are more robust and efficient than relying on Newton's method alone when the two-technique approach is supplied with a good set of initial guesses. In this approach, a soft (large) tolerance (e.g., 10^{-5}) is assigned to the SSI method to obtain approximate solutions, and these are then used as initial guesses for the subsequent Newton's method, which requires a much tighter tolerance (e.g., 10^{-8}) to achieve convergence. SSI allows one to get reasonably close to the final solution in a fairly robust manner, and it provides a good starting point for the more efficient, but less robust Newton's method to converge quickly (in a small number of iterations) to the final solution. We employ a similar combination of the SSI method followed by Newton's method to improve the efficiency and robustness of the computations in UVN space. Moreover, we formulate our phase-split computation in terms of equilibrium ratios (also called partition coefficients) to avoid numerical issues with division by vanishingly small mole numbers near phase boundaries. Perhaps equally as important, this work also introduces a general strategy for using the results of the stability analysis as initial guesses in the phase-split computations and possibly supplementing them with additional guesses if those from the stability analysis are not effective.

The rest of this paper is structured as follows. Section 2 presents the formulation of phase-split computations. Section 3 outlines a general strategy for setting up initial guesses for the phase-split computations that utilize results from the stability analysis, as well as an alternative prescription for setting up the initial guesses when the stability analysis results are not adequate for this purpose. We follow this with a description of the numerical procedure for the SSI and Newton's methods. Section 4 demonstrates our algorithm with the same examples presented in our earlier work on the stability analysis [1]. We conclude with a summary of our main findings.

2. Formulation of the phase-split computations

If the stability analysis [1] determines that the original single phase is unstable, we assume that the mixture will split into two phases. The phase-split computations that we discuss here represent a general numerical procedure for using the equation of state we have chosen to describe our system to find the thermodynamic state of the two split phases. This involves calculating the internal energy, volume, amount, and composition of each phase, plus the temperature and pressure corresponding to the given UVN .

As a starting point, we use the fact that the total internal energy, volume, and mole numbers are fixed at U^* , V^* , $\mathbf{N}^* = (N_1^*, N_2^*, \dots, N_n^*)$, respectively, where n is the number of components. The problem may be expressed in terms of the following $n + 2$ constraints:

$$U^* - U_1 - U_2 = 0, \quad (1)$$

$$V^* - V_1 - V_2 = 0, \quad (2)$$

$$N_i^* = N_{i1} + N_{i2} \quad (i = 1, 2, \dots, n), \quad (3)$$

in which the subscripts 1, 2 refer to the individual phases. Let us denote the entropy of phase 1 as $S_1 = S_1(U_1, V_1, \mathbf{N}_1)$, in which $\mathbf{N}_1 = (N_{11}, N_{21}, \dots, N_{n1})$. Similarly, we have $S_2 = S_2(U_2, V_2, \mathbf{N}_2)$, in which $\mathbf{N}_2 = (N_{12}, N_{22}, \dots, N_{n2})$ for phase 2. The objective of the phase-split computations is to find the equilibrium state of the two-phase mixture that satisfies the constraints in Eqs. (1)–(3) and maximizes the total entropy $S^* = S_1 + S_2$. It can be shown [31–33] that a set of necessary but not sufficient conditions for S^* to be a maximum are

$$T_1 - T_2 = 0, \quad (4)$$

$$P_1 - P_2 = 0, \quad (5)$$

$$\mu_{i1} = \mu_{i2} \quad (i = 1, 2, \dots, n), \quad (6)$$

where $\boldsymbol{\mu} = (\mu_1, \mu_2, \dots, \mu_n)$ are the chemical potentials. The $n + 2$ equations in (4)–(6) represent conditions for thermal, mechanical, and phase equilibrium, respectively. If all the three sets of conditions are satisfied, then the two-phase mixture is said to be in thermodynamic equilibrium. Equilibrium requires the chemical potential of each component i , as well as the temperature and pressure, to be the same across both phases. The $2n + 4$ equations in (1)–(6) comprise the basic set of equations that are solved in the phase-split computations to find the $2n + 4$ variables in U_1, V_1, \mathbf{N}_1 and U_2, V_2, \mathbf{N}_2 .

Before proceeding further, we transform the equations in (1)–(6) to an alternative but equivalent set that allows for a numerically robust formulation. It has been found from past experience [29,34] that working directly with the moles can cause numerical problems when a particular phase becomes very small with negligible amounts of some components. This issue can be overcome by formulating the algorithm in terms of a set of surrogate variables: a mole fraction β ($0 \leq \beta \leq 1$) and a set of equilibrium ratios K_i (also called partition coefficients) for which $i = 1, 2, \dots, n$. The former represents the mole fraction of phase 1, which is the ratio of the total moles N_1 of phase 1 to the total moles N^* of the two-phase mixture:

$$\beta = \frac{N_1}{N^*} = \frac{\sum_{i=1}^n N_{i1}}{\sum_{i=1}^n N_i^*}. \quad (7)$$

It follows that the mole fraction of phase 2 is equal to $1 - \beta = N_2/N^*$. The equilibrium ratio K_i of component i is defined as

$$K_i = \frac{x_{i1}}{x_{i2}} \quad (i = 1, 2, \dots, n), \quad (8)$$

where $x_{i1} = N_{i1}/N_1$ and $x_{i2} = N_{i2}/N_2$ represent the mole fraction of component i in phases 1 and 2, respectively. The overall mole fraction $z_i = N_i^*/\sum_{i=1}^n N_i^*$ of component i is known from the given set of overall mole numbers N^* , and it can be expressed in terms of β , x_{i1} , and x_{i2} as

$$z_i = \frac{N_1}{N^*} \frac{N_{i1}}{N_1} + \frac{N_2}{N^*} \frac{N_{i2}}{N_2} = \beta x_{i1} + (1 - \beta) x_{i2} \quad (i = 1, 2, \dots, n). \quad (9)$$

We may combine Eqs. (8) and (9) and rearrange to yield explicit

expressions for x_{i1} , and x_{i2} :

$$x_{i1} = \frac{K_i z_i}{1 + \beta(K_i - 1)} \quad (i = 1, 2, \dots, n), \quad (10)$$

$$x_{i2} = \frac{z_i}{1 + \beta(K_i - 1)} \quad (i = 1, 2, \dots, n), \quad (11)$$

from which one readily obtains $N_{i1} = N^* \beta x_{i1}$ and $N_{i2} = N^* (1 - \beta) x_{i2}$ for $i = 1, 2, \dots, n$. We can, therefore, determine the equilibrium values of the mole numbers $\mathbf{N}_1 = (N_{11}, N_{21}, \dots, N_{n1})$ and $\mathbf{N}_2 = (N_{12}, N_{22}, \dots, N_{n2})$ if we can find β and all K_i for the given $\mathbf{N}^* = (N_1^*, N_2^*, \dots, N_n^*)$.

Let us rewrite the equations in (6) in terms of the set of K_i . Recalling the definitions of fugacity f_i and fugacity coefficient ϕ_i (these are surrogate variables for the chemical potential and are prevalent in thermodynamic studies on mixtures [1,29,31,32]), the phase equilibrium conditions in Eq. (6) may be written as

$$\mu_{i1} - \mu_{i2} = RT \ln \frac{f_{i1}(T, V_1, \mathbf{N}_1)}{f_{i2}(T, V_2, \mathbf{N}_2)} = RT \ln \frac{\phi_{i1}(T_1, V_1, \mathbf{N}_1) x_{i1} P_1}{\phi_{i2}(T_2, V_2, \mathbf{N}_2) x_{i2} P_2} = 0 \quad (i = 1, 2, \dots, n). \quad (12)$$

Since constraints for equilibrium given by Eqs. (4) and (5) state that $T_1 = T_2$ and $P_1 = P_2$, substituting Eq. (8) into Eq. (12), the phase equilibrium conditions in Eq. (6) can be expressed in terms of the equilibrium ratios as

$$\ln K_i - \ln \frac{\phi_{i2}}{\phi_{i1}} = 0 \quad (i = 1, 2, \dots, n). \quad (13)$$

One can determine the mole fraction β by solving the Rachford–Rice equation in Eq. (14) below, which may be derived by summing both Eqs. (10) and (11) over all the components, noting that both of these sums equal 1, and subtracting them from each other:

$$\sum_{i=1}^n \frac{(K_i - 1) z_i}{1 + \beta(K_i - 1)} = 0. \quad (14)$$

We note that it is a simple matter to incorporate the thermal equilibrium condition in Eq. (4) and the volume constraint in Eq. (2) if we model our system with pressure-explicit equations of state (EOS's) since such EOS's, by definition, treat the temperature T and volume V as independent variables. By solving the set of $n + 3$ equations in (1), (5), (14), and (13), we can find the $n + 3$ unknowns T , V_2 , β , and the set of K_i in which $i = 1, 2, \dots, n$. The equilibrium state of the two-phase mixture is then completely specified once these unknowns have been determined. As we have stated above, the mole numbers \mathbf{N}_1 and \mathbf{N}_2 can be computed from the given \mathbf{N}^* , β , and all the equilibrium ratios K_i . In addition, we have $V_1 = V^* - V_2$, $U_1 = U_1(T, V_1, \mathbf{N}_1)$, and $U_2 = U_2(T, V_2, \mathbf{N}_2)$. An alternative option when an initial guess for V_2 is not available is to replace Eq. (5) with the volume constraint in Eq. (2) to solve for P and then solve for V_1 and V_2 with this newly found value of P . As stated in the Introduction, we solve the aforementioned equations with the same combination of the SSI and Newton's methods that we have used previously for the stability analysis [1]. The details behind these numerical techniques form the topic of the next section.

3. Numerical algorithms

3.1. Initial guess setup

This section presents our strategy for setting up the initial

guesses for the SSI method in a way that utilizes the results of the stability analysis. Moreover we describe how to supplement those results with additional guesses when the stability analysis does not provide good initial guesses. The inadequacy of the stability analysis in (sometimes) providing good initial guesses is a particular complication of UVN space that one does not encounter in TPN space. As explained in our previous work [1], the stability analysis determines whether the equilibrium state of a mixture at a given set of UVN (according to our notation in Section 2, these are fixed at values U^* , V^* , and \mathbf{N}^* , respectively) is a single-phase state or two-phase state or more. The procedure for the stability analysis is as follows: we first assume that the mixture will exist as a single phase and introduce an infinitesimal amount of a second phase, which is referred to as the trial phase, and examine if the introduction of the trial phase increases the entropy of the total system. If it does, then the equilibrium state for the given set of UVN is a two-phase state or more, and this equilibrium state may be found by solving the equations presented in Section 2 using a sequential combination of the SSI method followed by Newton's methods, as described in this section. The stability analysis provides the molar concentrations c' of all the components and the pressure P' of the trial phase (the prime is used to denote properties of this phase), as well as a temperature $T^{stability}$. These quantities may be used as described below to prepare initial guesses for the SSI method of the phase-split computations, which converges to within some relatively large tolerance. Subsequently, the Newton's method uses these approximate solutions from the SSI method as initial guesses to produce a set of final solutions that satisfy a much tighter tolerance criterion.

3.1.1. Initial guesses for equilibrium ratios $K^{initial}$ and $K^{new initial}$

The equilibrium ratios are defined in Eq. (8). For the initial guesses of these quantities, we compute the mole fractions of all the components in the trial phase using the molar concentrations (c'_i , which is defined as N'_i/V' and has units of moles per volume) obtained as part of the converged solution from the stability analysis:

$$x'_i = \frac{c'_i}{\sum_{i=1}^n c'_i} \quad (i = 1, 2, \dots, n). \quad (15)$$

We set the initial guess of the equilibrium ratios $K^{initial}$ as

$$K_i^{initial} = \frac{x'_i}{z_i} \quad (i = 1, 2, \dots, n). \quad (16)$$

Eq. (16) is a robust and widely used method to setup initial estimates for equilibrium ratios in phase-split computations in TPN space [10]. Based on our testing of various problems, the initial guesses described above for the equilibrium ratios work well for all the problems in Section 4 except Problem 1. In order to be able to perform phases-split computations on mixtures like those in Problem 1, we suggest an alternative set of initial guesses $K^{new initial}$ defined as

$$\begin{cases} K_i^{new initial} = \frac{0.99}{z_i}, \\ K_j^{new initial} = \frac{(0.01)}{z_j} \quad (j \neq i). \end{cases} \quad (17)$$

Equation (17) is motivated by the suggestion of Michelsen [9] that the trial phase composition can be initially assumed to be a pure species. The initial guesses $K^{new initial}$ implies that the mole

fraction of one component in the trial phase is 99%, while the other components equally share the remaining 1%. We suggest the phase-split computations should be first performed with $\mathbf{K}^{\text{initial}}$. If the $\mathbf{K}^{\text{initial}}$ does not lead to a converged solution, then $\mathbf{K}^{\text{new initial}}$ may be used.

3.1.2. Initial guess for mole fraction β^{initial}

Similar to phase-split computations in TPN space [10], an initial value β^{initial} of the mole fraction β may be computed from the Rachford–Rice equation in (14) using the bisection method once initial equilibrium ratios are known. Using the initial guess of the equilibrium ratios mentioned above in Section 3.1.1, β^{initial} will be very close to 0 because the stability analysis assumes that we have only an infinitesimal amount of the trial phase. In TPN space, β^{initial} computed from the Rachford–Rice equation most often results in convergence of the algorithm in a reasonable number of iterations. Convergence is not significantly affected by the choice of β^{initial} because properties that are strongly influenced by the mole fraction β (i.e., those that depend strongly on the amount of each phase present), such as the internal energy and volumes of the phases, do not need to be computed as part of the solution.

In contrast, determining a good initial guess for the mole fraction β^{initial} is a challenge for phase-split computations in UVN space. Unlike in TPN space, where T and P are specified in advance, T and P in UVN space are based on the solution of the energy constraint [Eq. (1)] and volume constraint [Eq. (2)] at each iteration. During the computations, both the internal energy and the volume of each split-phase must be computed to examine whether they satisfy those constraints. Therefore, T and P are strongly dependent on the value of the mole fraction β at each iteration since T and P are functions of the individual phase volumes and energies, which are in turn highly affected by the value of β . An improper initial value β^{initial} can thus easily lead to unphysical (negative) T and P , resulting in convergence issues.

It is important to develop a general strategy for evaluating β^{initial} , which we propose as follows. Because of the small amount of the trial phase in the stability analysis, we first use an initial guess of $\beta^{\text{initial}} = 0.1$. This initial guess works well for most of the cases we have tried. If $\beta^{\text{initial}} = 0.1$ leads to a negative value of T or P at the initial iteration, various guesses for β^{initial} are then tested in the range from 0 to 1 with a specified value of increment between each test. The first β^{initial} that leads to physical T and P will be used in the initial iteration. For problems where the equilibrium state is near a phase boundary (e.g., Problem 2 in Section 4), a small increment (0.0001) may be needed, while for other problems (e.g., Problems 1 and 5 in Section 4), we use an increment of 0.01. The value of β in the following iterations is then updated by solving the Rachford–Rice equation. If the β^k (where k denotes the iteration count) for $k > 1$ is not between 0 and 1, or if the β^k leads to unphysical T or P , then β^k at this iteration is set to be equal to the value from the previous iteration (i.e., we reset $\beta^k = \beta^{k-1}$).

3.1.3. Initial guesses for temperature T^{initial} and pressure P^{initial}

In Step 2 of the SSI algorithm, we compute T and P simultaneously using Newton's method by solving Eqs. (1) and (2). We set $T^{\text{initial}} = T^{\text{stability}}$ and $P^{\text{initial}} = P'$ as initial guesses for T and P in the phase-split computations. Based on our experience, this set of initial guesses will work in most cases. However, in some problems (e.g., Problems 1 and 5), all the combinations of initial equilibrium ratios ($\mathbf{K}^{\text{initial}}$ and $\mathbf{K}^{\text{new initial}}$) and initial mole fraction (β^{initial}) fail to find a positive P using the initial guesses T^{initial} and P^{initial} . In that case, we modify T^{initial} by multiplying it by 1.5, 2, or 2.5, computing the pressure that satisfies Eq. (2) for the corresponding T^{initial} , and setting this pressure as P^{initial} . For iterations $k > 1$, solutions from the previous iteration are used as initial guesses in the next iteration.

3.2. SSI

In the first iteration of SSI, we use the initial guesses for the unknowns as explained above in Section 3.1, with most of these guesses coming directly from the stability analysis. Our proposed algorithm for stability analysis [1] is formulated in terms of the energy density and molar density of the trial phase, and thus it cannot provide an initial guess for the total extensive volumes of the phases in the phase-split computations. Therefore, the SSI algorithm will solve Eqs. (1), (2), (13) and (14) [note that we solve (2) instead of (5); see our explanation for this choice near the end of Section 2] for the temperature T , pressure P , mole fraction β , and the set of equilibrium ratios K_i . The SSI method is carried out until convergence in the 2-norm of the equilibrium ratios is achieved to within a specified tolerance:

$$\Delta X^{(k)} = \left| K_i^{(k+1)} - K_i^{(k)} \right| < \varepsilon, \quad (18)$$

where $\Delta X^{(k)}$ denotes the convergence at iteration k and ε is the SSI switching tolerance. Once the norm falls below this tolerance, we assume that we are close to converging to the equilibrium state, and so we then switch to the more efficient Newton's method, whose initial guesses are seeded with the approximate solutions from the SSI method.

In TPN space problems, the equilibrium ratios K_i are updated according to Eq. (13). But in UVN space, we have found that updating them in this manner may sometimes cause the SSI method to diverge. To facilitate the convergence, we introduce a damping parameter m in the update of K_i so that

$$K_i^{(k+1)} = \frac{mK_i^{(k)} + \phi_{i2}/\phi_{i1}}{m+1} \quad (i = 1, 2, \dots, n). \quad (19)$$

If the SSI method converges ($\Delta X^{(k)} < \Delta X^{(k-1)}$), we set m to zero, in which case Eq. (19) is equivalent to Eq. (13). If the SSI method diverges ($\Delta X^{(k)} > \Delta X^{(k-1)}$), we instead update the equilibrium ratios with (19) by first trying $m = 1$ and continuing to double the value of m until we find a value such that $\Delta X^{(k)}$ is found to be smaller than $\Delta X^{(k-1)}$. Below is a brief outline of our algorithm:

Determine the initial guesses for the equilibrium ratios K_i , the phase mole fraction β , the temperature T , and the pressure P following the strategy in Section 3.1. We then perform the following steps until Eq. (18) is satisfied:

1. Solve the Rachford–Rice equation in (14) for β by the bisection method. Update \mathbf{N}_1 and \mathbf{N}_2 .
2. Find T and P by solving the energy and the volume constraints simultaneously using Newton's method with the initial guesses T^{initial} and P^{initial} . This means that we find T and P such that $U^* - U_1 - U_2 = 0$ and $V^* - V_1 - V_2 = 0$. We compute the derivatives of V_1 and V_2 in terms of T and P numerically in this step, e.g., $dV_1/dT = (V_1(T+\Delta T) - V_1(T))/\Delta T$ and $dV_1/dP = (V_1(P+\Delta P) - V_1(P))/\Delta P$.
3. Update the set of K_i by evaluating the right side of the phase-equilibrium conditions in (19).
4. Check for convergence by evaluating (18). If not converged, return to step 1. Once a specified switching tolerance is met, proceed to Newton's method scheme described below.

3.3. Newton's method

A general approach for Newton's method is given in this section. In Newton's method, the initial guesses at the first iteration use the

solutions from the SSI method. As an initial guess for volume is available (unlike the case when forming initial guesses for the SSI method), we solve Eqs. ((1), (5), (13) and (14) for the variables $\ln K_i$, β , T , and V_2 . This set of $n + 3$ variables (unknowns) are consolidated into the solution vector \mathbf{X} defined as

$$\mathbf{X} = \begin{bmatrix} \ln K_1 \\ \ln K_2 \\ \vdots \\ \ln K_n \\ \beta \\ T \\ V_2 \end{bmatrix}. \quad (20)$$

The unknowns are iteratively updated using Newton's method

$$\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} - \mathbf{J}^{-1} \mathbf{R}, \quad (21)$$

where k denotes the iteration count. The unknowns $\mathbf{X}^{(k)}$ at $k = 1$ are the initial guesses from the solution of the SSI method. The vector \mathbf{R} represents the residuals of Eqs. ((1), (5), (13) and (14) and is defined as

$$\mathbf{R} = \begin{bmatrix} R_1 \\ R_2 \\ \vdots \\ R_n \\ R_{n+1} \\ R_{n+2} \\ R_{n+3} \end{bmatrix} = \begin{bmatrix} \ln K_1 - \ln \phi_{12} + \ln \phi_{11} \\ \ln K_2 - \ln \phi_{22} + \ln \phi_{21} \\ \vdots \\ \ln K_n - \ln \phi_{n2} + \ln \phi_{n1} \\ \sum_{i=1}^n \frac{z_i(K_i - 1)}{1 + \beta(K_i - 1)} \\ U^* - U_1 - U_2 \\ P_1 - P_2 \end{bmatrix} \quad (22)$$

The Jacobian \mathbf{J} is a square matrix of size $n + 3$ and is given by

$$\mathbf{J} = \begin{bmatrix} \frac{\partial R_1}{\partial \ln K_1} & \frac{\partial R_1}{\partial \ln K_2} & \cdots & \frac{\partial R_1}{\partial \ln K_n} & \frac{\partial R_1}{\partial \beta} & \frac{\partial R_1}{\partial T} & \frac{\partial R_1}{\partial V_2} \\ \frac{\partial R_2}{\partial \ln K_1} & \frac{\partial R_2}{\partial \ln K_2} & \cdots & \frac{\partial R_2}{\partial \ln K_n} & \frac{\partial R_2}{\partial \beta} & \frac{\partial R_2}{\partial T} & \frac{\partial R_2}{\partial V_2} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial R_{n+3}}{\partial \ln K_1} & \frac{\partial R_{n+3}}{\partial \ln K_2} & \cdots & \frac{\partial R_{n+3}}{\partial \ln K_n} & \frac{\partial R_{n+3}}{\partial \beta} & \frac{\partial R_{n+3}}{\partial T} & \frac{\partial R_{n+3}}{\partial V_2} \end{bmatrix}. \quad (23)$$

Newton's method is carried out until convergence in the 2-norm of the unknowns \mathbf{X} falls below a given tolerance. The tolerance for Newton's method is necessarily much tighter than that for the SSI method.

Below is a schematic outline of Newton's method algorithm that follows Step 4 in the SSI algorithm.

- Let k denote the iteration count of Newton's method. At $k = 1$, $\mathbf{X}^{(k)}$ is the solution from the SSI method.
- Evaluate Eqs. (22) and (23) to obtain $\mathbf{R}^{(k)}$ and $\mathbf{J}^{(k)}$ and update $\mathbf{X}^{(k+1)}$ by solving Eq. (21).
- Stop the iterations once the convergence criterion is met (the 2-norm of $\mathbf{X}^{(k+1)} - \mathbf{X}^{(k)}$ falls below some chosen threshold).

Table 1

Specifications for Problems 1–4. The given internal energy and volume are denoted by U and V , respectively. The given total number of moles of component i is labeled as N_i .

Specifications	Problem 1	Problem 2	Problem 3	Problem 4
U (J)	−756500.8	−1511407.6	−331083.7	−636468
V (cm ³)	52869	4268.1	80258.1	9926.71
N_{C_1} (mol)	10	0.95	15.1	10
N_{H_2S} (mol)	90	99.05	84.9	90

4. Results

In this work, we demonstrate the phase-split computations in the same mixtures featured in Problems 1–6 of our study on the stability analysis [1]. The mixtures in those problems cover a wide range of diversity in terms of phase-equilibria complexity, chemical species, and the number of moles. All of the mixtures are modeled with the well-known Peng–Robinson EOS [35], with the EOS parameters of all the species—including the critical temperature, critical pressure, acentric factor, correlation coefficients for computing heat capacities, and binary interaction coefficients—being the same as those used in the stability analysis paper [1]. We will not repeat them here for the sake of brevity.

4.1. Binary mixtures of methane (C₁) and hydrogen sulfide (H₂S)

The first four problems all involve binary, two-phase vapor–liquid mixtures of methane (C₁) and hydrogen sulfide (H₂S) at different UVN specifications. The mixture in Problem 1 is not close to a phase boundary nor is in the critical region, meaning that it lies clearly in the two-phase region. Problems 2 and 3 also involve two-phase mixtures but in both cases, they are in state that lies close to the phase boundary between the liquid and vapor phases. Finally, the mixture in Problem 4 is in the near-critical region. The specifications and stability analysis results of Problems 1 to 4 are presented in Tables 1 and 2, respectively. We prepare the initial guesses for each problem following the procedure in Section 3.1; these values are listed in Table 3.

The equilibrium solutions (the results of the phase-split computations) for each of the two phases for all four problems are presented in Table 4. We label the number of iterations required to achieve convergence in the form “ $a + b$ ”, where a is the number of iterations required by the SSI method to achieve convergence to within a tolerance of 10^{-5} , and b is the number of iterations required by Newton's method to achieve convergence to within a tolerance of 10^{-10} . Smejkal and Mikyška [28] report 9, 3, 3, and 5 Newton iterations for their algorithm to converge in Problems 1–4, respectively. Note that the initial guesses and stopping criteria that they use are different from ours, and so a direct comparison between the numerical efficiency of their algorithm and ours cannot be made. The algorithm by Smejkal and Mikyška relies solely on stability analysis and adjustment of phase mole fractions. In our algorithm we may change equilibrium ratios as well as phase mole fractions as discussed above.

The phase-split computations determine the compositions of the two phases, as well as the temperature and pressure at equilibrium. Our results are consistent with Castier [25] and Smejkal and Mikyška [25,28] in that we converge to the same equilibrium state as in those studies. Mass densities of the two phases presented in Table 4 help to indicate which phase is liquid and which is vapor. The initial guesses for the equilibrium ratios of Problems 2–4 use the set $\mathbf{K}^{initial}$ described in Section 3.1 (Eq. (16)), which is obtained directly from the properties of the trial phase as determined by the stability analysis. Initial guesses for other parameters are

Table 2

Results of stability analysis for Problems 1–4. The temperature of the system is T , the pressure of the trial phase is P' , and the concentration of component i in the trial phase is c_i' .

Stability analysis	Problem 1	Problem 2	Problem 3	Problem 4
T (K)	151.83	291.91	297.84	361.80
P' (MPa)	0.60	1.84	2.65	10.10
c_{C_1}' (mol/m ³)	104.12	146.18	13.22	1000.68
c_{H_2S}' (mol/m ³)	564.35	736.58	1413.64	8459.77

Table 3

Initial guesses for the SSI method of the phase-split computations in Problems 1–4. Initial guesses for the temperature and pressure are denoted as $T^{initial}$ and $p^{initial}$, respectively. The initial guess for the mole fraction of the trial phase is $\beta^{initial}$, and the initial guess for the equilibrium ratio K_i of component i is defined as the mole fraction of i in the trial phase divided by that in the overall system (Eqs. (16) and (17)).

Initial guesses	Problem 1	Problem 2	Problem 3	Problem 4
$T^{initial}$ (K)	303.66	291.91	297.84	361.80
$p^{initial}$ (MPa)	2.51	1.84	2.65	10.10
$\beta^{initial}$	0.38	0.0011	0.1	0.1
$K_{C_1}^{initial}$	0.1	17.4309	0.0613	1.0578
$K_{H_2S}^{initial}$	1.1	0.8424	1.1670	0.9936

also established following the strategy mentioned in that section. We have explained in Section 3.1 that the stability analysis does not provide a guess for the amount of the trial phase, but that this is of no consequence in TPN space since T , P , and the K_i values are independent of the amount of the trial phase in TPN problems. In UVN space, when the amount of one phase is small (Problems 2 and 3) or the mixture is close to the critical region (properties of the vapor and liquid phases become very similar; see Problem 4), the set $K^{initial}$ also works well. This is reasonable since the mixture virtually behaves almost like a single-phase system in such situations. However, the algorithm fails to converge if we use $K^{initial}$ as initial guesses for Problem 1, which as stated above, involves a mixture that lies well within the two-phase region. In such cases, the two phases are both present in non-negligible amounts so that the issue of setting up good initial guesses becomes more complicated. For Problem 1, we use the equilibrium ratios $K^{new\ initial}$ (defined in Eq. (17)) and the modified temperatures (see Section 3.1.3) to set up the initial guesses. Furthermore, we note that in this example, the temperature and pressure from the stability analysis (which we have presented in Table 2) are very far from the

equilibrium solutions in Table 4, while this is not the case in Problems 2–4. This is because the equilibrium state does not lie close to a phase boundary in Problem 1, while it does in the last three examples. Problem 1 thus illustrates the fact that the stability analysis may not necessarily provide good initial guesses for the phase-split computations. As we have alluded to earlier, this is one of the complexities of UVN space that one does not encounter in TPN space.

Similar to the behavior that we have observed in our stability analysis [1], the number of iterations depends on the switching and stopping criteria. Table 5 presents the number of iterations required for convergence for different choices of tolerance in Problem 3. Depending on the chosen tolerance, our algorithm needs four or less Newton iterations to converge. Just like for the stability analysis [1], the SSI method dramatically improves the robustness of our phase-split algorithm. We do not obtain a converged solution in Problem 3 unless we employ the SSI method with a tolerance of 10^{-5} or tighter. Among the 6 problems presented in this work (4 problems in Section 4.1 and 2 problems in Section 4.2), we are able to achieve convergence for only 2 of them—Problems 4 and 6, both of which feature mixtures that are in the near-critical region—by relying solely on Newton’s method. Only for these two problems are the initial guesses using the solutions of the stability analysis good enough to allow Newton’s method to converge. The remaining four problems require the SSI method as part of the numerical formulation so that it can seed Newton’s method with good initial guesses.

4.2. Liquefied petroleum gas (LPG) mixtures

Table 6 and Table 7 present the UVN specifications and stability analysis results, respectively, of two different 6-component LPG mixtures that we examine in Problems 5 and 6. Both of these are two-phase, vapor–liquid mixtures. In the equilibrium state of Problem 5, the liquid phase has a higher mole fraction, while the vapor phase has a higher volume fraction. Like Problem 4, Problem 6 is close to the critical region. Table 8 lists the initial guesses for phase-split computations, and Table 9 summarizes the equilibrium phase-split solutions for both problems.

Smejkal and Mikyška [28] report that their algorithm requires 10 and 5 Newton iterations to converge in Problems 5 and 6, respectively. We again note that like the case for Problems 1–4, the initial guesses and stopping criteria in their work are different from ours. Both Problems 5 and 6 use the $K^{initial}$ that are computed from Eq. (16) as initial guesses for equilibrium ratios in the phase-split

Table 4

Results of phase-split computations for Problems 1–4. The equilibrium temperature, pressure, equilibrium ratio of component i , and mole fraction of the vapor phase are denoted by T , P , K_i , and β_v , respectively. K_i is defined as the mole fraction of component i in the vapor phase divided by the mole fraction of the same component in the liquid phase. In addition, the internal energy (U), volume (V), moles of component (N_i), and density of each phase are also presented for completeness.

Phase-split results	Problem 1		Problem 2		Problem 3		Problem 4	
T (K)	298.00		298.00		298.00		362.00	
P (MPa)	2.5		2.5		2.5		10.13	
K_{C_1}	16.2084		16.2072		16.2087		1.0738	
K_{H_2S}	0.8569		0.8569		0.8569		0.9922	
β_v	0.6398		0.0013		0.9996		0.6284	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
U (J)	–544956.2	–211544.6	–1510985.8	–421.8	–566.8	–330516.9	–245802.7	–390665.3
V (cm ³)	1502.36	51366.64	4165.67	102.43	1.56	80256.54	3512.56	6414.15
N_{C_1} (mol)	0.3357	9.6643	0.9307	0.0193	0.00035	15.0997	3.5514	6.4486
N_{H_2S} (mol)	35.6840	54.3160	98.9417	0.1083	0.0371	84.8629	33.6088	56.3912
Density (g/cm ³)	0.8135	0.0391	0.8135	0.0391	0.8135	0.0391	0.3425	0.3159
Iterations	14 + 6		12 + 5		343 + 4		321 + 5	

Table 5
The number of iterations required to achieve convergence as a function of the tolerance for the SSI method (the first number in each entry) and Newton's method (the second number in each entry) in Problem 3. As mentioned in Section 3.3, the algorithm requires the tolerance for Newton's method to be tighter than that for the SSI method; the cases that do not satisfy the requirement are left blank in this table.

SSI Switching Tolerance	Newton 10^{-2}	Newton 10^{-4}	Newton 10^{-6}	Newton 10^{-8}	Newton 10^{-10}
Newton only	failure	Failure	failure	failure	Failure
10^{-1}	failure	Failure	failure	failure	Failure
10^{-3}		Failure	failure	failure	Failure
10^{-5}			343 + 4	343 + 4	343 + 4
10^{-7}				356 + 2	356 + 3
10^{-9}					623 + 2

Table 6
Specifications for Problems 5 and 6. The internal energy and volume are denoted by U and V , respectively. The total number of moles of component i is labeled as N_i .

Specifications	Problem 5	Problem 6
U (J)	-16272506.4	24858.2
V (cm ³)	479845	289380.3
N_{C_2} (mol)	10.8	10.8
$N_{C_3H_6}$ (mol)	360.8	360.8
N_{C_3} (mol)	146.5	146.5
N_{iC_4} (mol)	233	233
N_{nC_4} (mol)	233	233
N_{nC_5} (mol)	15.9	15.9

Table 7
Results of stability analysis for Problems 5 and 6. The temperature of the system is T , the pressure of the trial phase is P' , and the concentration of component i in the trial phase is c'_i .

Stability analysis	Problem 5	Problem 6
T (K)	122.97	394.54
P' (MPa)	5.10×10^{-3}	4.22
c'_{C_2} (mol/m ⁻³)	0.33	46.40
$c'_{C_3H_6}$ (mol/m ⁻³)	3.10	1738.54
c'_{C_3} (mol/m ⁻³)	0.91	718.80
c'_{iC_4} (mol/m ⁻³)	0.39	1261.61
c'_{nC_4} (mol/m ⁻³)	0.29	1304.72
c'_{nC_5} (mol/m ⁻³)	0.0038	101.01

computations. In terms of the initial guesses for temperature $T^{initial}$ and pressure $p^{initial}$, Problem 6 uses solutions that come directly from the stability analysis (it sets $T^{initial} = T^{stability}$ and $p^{initial} = P'$), while the initial temperature for Problem 5 is modified following the procedure mentioned in Section 3.1.3. Problem 5 is an example where the temperature modification may be necessary even when the equilibrium ratios from the stability analysis appear to provide a sufficiently good guess for the composition. We report the number of iterations for Problem 6 in Table 10. Note that Newton's method alone works for this problem. However, a smaller number of iterations in Newton's method is needed (there may also be a potential improvement in the robustness) if it is complemented with the SSI method. Overall, our algorithm requires 5 or less iterations in Newton's method to converge to the final equilibrium solutions.

5. Conclusions

We have presented a general strategy for two-phase split computations in UVN space (i.e., for isolated systems). The phase-split computations are a series of numerical calculations whose

Table 8
Initial guesses of phase-split computations in Problems 5 and 6. The initial temperature of the system is $T^{initial}$, the initial pressure of the system is $p^{initial}$, the initial mole fraction of the trial phase is $\beta^{initial}$, and $K_i^{initial}$ is the initial value of the equilibrium ratio of component i .

Initial guesses	Problem 5	Problem 6
$T^{initial}$ (K)	307.42	394.54
$p^{initial}$ (MPa)	0.72	4.22
$\beta^{initial}$	0.12	0.1
$K_{C_2}^{initial}$	0.1646	0.8309
$K_{C_3H_6}^{initial}$	0.5841	0.9318
$K_{C_3}^{initial}$	0.8112	0.9488
$K_{iC_4}^{initial}$	3.0302	1.0471
$K_{nC_4}^{initial}$	3.9866	1.0829
$K_{nC_5}^{initial}$	20.8498	1.2285

objective is to find the equilibrium state of the system that corresponds to the given UVN . Using an appropriate EOS to calculate the relevant thermodynamic quantities, the phase-split computations determine the amounts and compositions of the phases as well as the temperature and the pressure at equilibrium. By testing our algorithm in six different mixtures of varying degrees of complexity, we have found that the stability analysis, which is a separate series of calculations that precedes the phase-split computations and is described in our earlier work [1], usually provides reliable initial guesses for the phase-split computations when the problems are near the critical region or near a phase boundary. In problems that are not near the critical point or close to a phase boundary, the initial guesses from the stability analysis may not necessarily work; we present alternative suggestions for initial guesses in such cases. Surprisingly this crucial point regarding the potential shortcoming of the stability analysis in providing good initial guesses in UVN space has not been brought up in the literature. Our algorithm is inspired by an approach that has been demonstrated to work well in TPN space [10], and it involves a two-technique procedure in which the SSI method and Newton's method are applied in tandem. Similar to what we have found for the stability analysis, the sequential combination of these two iterative techniques is far more robust than relying solely on Newton's method. By using the approximate solutions of the SSI method to seed the initial guesses for Newton's method, the latter converges to within a tight tolerance and requires no more than 6 iterations for all six problems that we have tested. We are currently working on an extension of this work, which is limited to two-phase mixtures, to model three-phase systems. Such multiphase mixtures are ubiquitous in the petrochemical industries [29,34,36], as well as in other types of systems, such as alloys and eutectic or peritectic mixtures of large, organic energetic materials [5–7].

Table 9

Results of phase-split computations for Problems 5 and 6. The temperature, pressure, equilibrium ratio of component i , and mole fraction of the vapor phase are denoted by T , P , K_i , and β_v , respectively. The table presents details of each phase at equilibrium, including the internal energy (U), volume (V), moles of each component (N_i), and density. The number of iterations presented here is in the form “ $a + b$ ”, where a is the number of iterations required by the SSI method to achieve convergence to within a tolerance of 10^{-5} , and b is the number of iterations required by Newton’s method to achieve convergence to within a tolerance of 10^{-10} .

Phase-split results	Problem 5		Problem 6	
T (K)	300.00		395.00	
P (MPa)	0.70		4.23	
K_{C_2}	4.2801		1.1858	
$K_{C_3H_6}$	1.5663		1.0672	
K_{C_3}	1.3434		1.0491	
K_{iC_4}	0.5803		0.9573	
K_{nC_4}	0.4257		0.9286	
K_{nC_5}	0.1404		0.8263	
β_v	0.1296		0.9203	
	Liquid	Vapor	Liquid	Vapor
U (J)	−15892619.41	−379886.99	−150016.51	174874.71
V (cm ³)	78647.6	401197.4	16233.23	273147.07
N_{C_2} (mol)	6.5966	4.2034	0.7353	10.0647
$N_{C_3H_6}$ (mol)	292.5742	68.2258	27.0890	333.7110
N_{C_3} (mol)	122.0830	24.4170	11.1742	135.3258
N_{iC_4} (mol)	214.4708	18.5292	19.3343	213.6657
N_{nC_4} (mol)	219.1146	13.8854	19.8809	213.1191
N_{nC_5} (mol)	15.5744	0.3256	1.5088	14.3912
Density (g/ cm ³)	0.5621	0.0149	0.2490	0.1689
Iterations	6 + 5		7 + 3	

Table 10

The number of iterations required to achieve convergence as a function of the tolerance in the SSI method (the first number in each entry) and Newton’s method (the second number in each entry) for Problem 6.

SSI Switching Tolerance	Newton 10 ^{−2}	Newton 10 ^{−4}	Newton 10 ^{−6}	Newton 10 ^{−8}	Newton 10 ^{−10}
Newton only	0 + 3	0 + 4	0 + 4	0 + 5	0 + 5
10 ^{−1}	1 + 2	1 + 3	1 + 4	1 + 4	1 + 5
10 ^{−3}		2 + 2	2 + 3	2 + 3	2 + 3
10 ^{−5}			7 + 2	7 + 2	7 + 3
10 ^{−7}				14 + 2	14 + 2
10 ^{−9}					22 + 2

Credit author statement

Ran Bi: Completed the formulated and developed the algorithm. Wrote the first draft.

Abbas Firoozabadi. Suggested the formulation and gave the general idea. Examined the issues throughout the work. Finalized the paper.

Philip Myint. Secured the funding and was involved in the work. Help with writing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Financial support has been provided by the WSC RCC LEARN Program under Subcontract B630279.

Nomenclature

EOS	Equation of state
SSI	Successive substitution iteration
c_i	Molar concentration of component i in the trial phase from the stability analysis
f_i	Fugacity of component i
J	Jacobian matrix in Newton’s method
k	Number of iterations
K_i	Equilibrium ratio of component i
$K_i^{initial}$	Initial guess for the equilibrium ratio of component i
$K_i^{new\ initial}$	Additional initial guess for the equilibrium ratio of component i
m	Damping parameter in the update of the equilibrium ratios K_i
n	Number of components
N_i	Number of moles of component i
P	Pressure
P'	Pressure of the trial phase from the stability analysis
$p^{initial}$	Initial guess for the pressure
R	Gas constant
R	Residual vector in Newton’s method
S	Entropy
T	Temperature
$T^{initial}$	Initial guess for the temperature in the SSI method
$T^{stability}$	Temperature from the stability analysis

U	Internal energy
V	Volume
x_i	Mole fraction of component i in a phase
\mathbf{X}	Solution vector in Newton's method
z_i	Overall mole fraction of component i
β	Mole fraction of the trial phase
β_v	Mole fraction of the vapor phase
β^{initial}	Initial guess for the mole fraction of the trial phase
ε	Tolerance
μ_i	Chemical potential of component i
ϕ_i	Fugacity coefficient of component i
ΔX	Convergence of the 2-norm of the equilibrium ratios

References

- [1] R. Bi, A. Zidane, A. Firoozabadi, Efficient and robust stability analysis in the internal energy, volume, and moles (UVN) space, *Fluid Phase Equil.* (2020), <https://doi.org/10.1016/j.fluid.2020.112468>.
- [2] M. Castier, Dynamic simulation of fluids in vessels via entropy maximization, *J. Ind. Eng. Chem.* (2010), <https://doi.org/10.1016/j.jiec.2010.01.007>.
- [3] L. Qiu, Y. Wang, R.D. Reitz, Multiphase dynamic flash simulations using entropy maximization and application to compressible flow with phase change, *AIChE J.* (2014), <https://doi.org/10.1002/aic.14519>.
- [4] S. Saha, J.J. Carroll, The isoenergetic-isochoric flash, *Fluid Phase Equil.* (1997), [https://doi.org/10.1016/s0378-3812\(97\)00151-9](https://doi.org/10.1016/s0378-3812(97)00151-9).
- [5] P.C. Myint, M.A. McClelland, A.L. Nichols, Application of the Peng-Robinson equation of state to energetic materials RDX and TNT: pure components, liquid mixtures, and solid mixtures, *Ind. Eng. Chem. Res.* (2016), <https://doi.org/10.1021/acs.iecr.5b04808>.
- [6] P.C. Myint, A.L. Nichols, Thermodynamics of HMX polymorphs and HMX/RDX mixtures, *Ind. Eng. Chem. Res.* (2017), <https://doi.org/10.1021/acs.iecr.6b03697>.
- [7] P.C. Myint, B.T. Gersten, M.A. McClelland, A.L. Nichols, H.K. Springer, Entropy maximization and free energy minimization of multiphase mixtures using particle swarm optimization, *AIP Conf. Proc.* (2018), <https://doi.org/10.1063/1.5044776>.
- [8] A. Firoozabadi, H. Pan, Fast and robust algorithm for compositional modeling: Part I - stability analysis testing, *SPE J.* (2007), <https://doi.org/10.2118/77299-pa>.
- [9] M.L. Michelsen, The isothermal flash problem. Part I. Stability, *Fluid Phase Equil.* (1982), [https://doi.org/10.1016/0378-3812\(82\)85001-2](https://doi.org/10.1016/0378-3812(82)85001-2).
- [10] Z. Li, A. Firoozabadi, General strategy for stability testing and phase-split calculation in two and three phases, *SPE J.* (2013), <https://doi.org/10.2118/129844-pa>.
- [11] H. Pan, A. Firoozabadi, Fast and robust algorithm for compositional modeling: Part II - two-phase flash computations, *SPE J.* (2003), <https://doi.org/10.2118/87335-PA>.
- [12] D. Paterson, M.L. Michelsen, E.H. Stenby, W. Yan, RAND-based formulations for isothermal multiphase flash, *SPE J.* (2018), <https://doi.org/10.2118/182706-pa>.
- [13] H. Hoteit, A. Firoozabadi, Simple phase stability-testing algorithm in the reduction method, *AIChE J.* (2006), <https://doi.org/10.1002/aic.10908>.
- [14] D. Paterson, M.L. Michelsen, E.H. Stenby, W. Yan, New formulations for isothermal multiphase flash, in: *Soc. Pet. Eng. - SPE Reserv. Simul. Conf.*, 2017, <https://doi.org/10.2118/182706-MS>.
- [15] M. Castier, Helmholtz function-based global phase stability test and its link to the isothermal-isochoric flash problem, *Fluid Phase Equil.* (2014), <https://doi.org/10.1016/j.fluid.2014.07.008>.
- [16] D.V. Nichita, New unconstrained minimization methods for robust flash calculations at temperature, volume and moles specifications, *Fluid Phase Equil.* (2018), <https://doi.org/10.1016/j.fluid.2018.03.012>.
- [17] J. Mikyška, A. Firoozabadi, Investigation of mixture stability at given volume, temperature, and number of moles, *Fluid Phase Equil.* (2012), <https://doi.org/10.1016/j.fluid.2012.01.026>.
- [18] D.V. Nichita, Fast and robust phase stability testing at isothermal-isochoric conditions, *Fluid Phase Equil.* (2017), <https://doi.org/10.1016/j.fluid.2017.05.022>.
- [19] M. Cismondi, P.M. Ndiaye, F.W. Tavares, A new simple and efficient flash algorithm for T-v specifications, *Fluid Phase Equil.* (2018), <https://doi.org/10.1016/j.fluid.2018.02.019>.
- [20] T. Jindrová, J. Mikyška, Fast and robust algorithm for calculation of two-phase equilibria at given volume, temperature, and moles, *Fluid Phase Equil.* (2013), <https://doi.org/10.1016/j.fluid.2013.05.036>.
- [21] T. Jindrová, J. Mikyška, General algorithm for multiphase equilibria calculation at given volume, temperature, and moles, *Fluid Phase Equil.* (2015), <https://doi.org/10.1016/j.fluid.2015.02.013>.
- [22] J. Kou, S. Sun, A stable algorithm for calculating phase equilibria with capillarity at specified moles, volume and temperature using a dynamic model, *Fluid Phase Equil.* (2018), <https://doi.org/10.1016/j.fluid.2017.09.018>.
- [23] T. Smejkal, J. Mikyška, VTN-phase stability testing using the Branch and Bound strategy and the convex-concave splitting of the Helmholtz free energy density, *Fluid Phase Equil.* (2020), <https://doi.org/10.1016/j.fluid.2019.112323>.
- [24] M.L. Michelsen, State function based flash specifications, *Fluid Phase Equil.* (1999), [https://doi.org/10.1016/s0378-3812\(99\)00092-8](https://doi.org/10.1016/s0378-3812(99)00092-8).
- [25] M. Castier, Solution of the isochoric-isoenergetic flash problem by direct entropy maximization, *Fluid Phase Equil.* (2009), <https://doi.org/10.1016/j.fluid.2008.10.005>.
- [26] A.R.J. Arendsen, G.F. Versteeg, Dynamic thermodynamics with internal energy, volume, and amount of moles as states: application to liquefied gas tank, *Ind. Eng. Chem. Res.* (2009), <https://doi.org/10.1021/ie801273a>.
- [27] D. Paterson, M.L. Michelsen, W. Yan, E.H. Stenby, Extension of modified RAND to multiphase flash specifications based on state functions other than (T,P), *Fluid Phase Equil.* (2018), <https://doi.org/10.1016/j.fluid.2017.10.019>.
- [28] T. Smejkal, J. Mikyška, Phase stability testing and phase equilibrium calculation at specified internal energy, volume, and moles, *Fluid Phase Equil.* (2017), <https://doi.org/10.1016/j.fluid.2016.09.025>.
- [29] A. Firoozabadi, *Thermodynamics and Applications in Hydrocarbon Energy Production*, McGraw-Hill Education, 2015.
- [30] T. Smejkal, J. Mikyška, Unified presentation and comparison of various formulations of the phase stability and phase equilibrium calculation problems, *Fluid Phase Equil.* (2018), <https://doi.org/10.1016/j.fluid.2018.03.013>.
- [31] S.I. Sandler, *Chemical, Biochemical, and Engineering Thermodynamics*, 2006.
- [32] John M. Prausnitz, Rudiger N. Lichtenthaler, Edmundo Gomes de Azevedo, *Molecular Thermodynamics of Fluid-phase Equilibria*, 1998.
- [33] H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, second ed., 1985.
- [34] M.L. Michelsen, J. Mollerup, *Thermodynamic Models: Fundamentals & Computational Aspects*, Tie-Line Publication, 2007.
- [35] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.* (1976), <https://doi.org/10.1021/i160057a011>.
- [36] G.M. Kontogeorgis, G.K. Folas, *Thermodynamic Models for Industrial Applications: from Classical and Advanced Mixing Rules to Association Theories*, 2009, <https://doi.org/10.1002/9780470747537>.