

Phase stability testing and phase equilibrium calculation at specified internal energy, volume, and moles



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ABSTRACT

We have developed a fast and robust algorithm for the general multi-phase equilibrium calculation at constant internal energy, volume, and moles (specification UVN). The algorithm is based on the direct maximization of the total entropy of the system subject to the internal energy-, volume-, and mole-balance constraints. The algorithm uses the Newton-Raphson method with line-search and modified Cholesky decomposition of the Hessian matrix to produce a sequence of states with increasing values of the total entropy of the system. Unlike the previously published formulations, our method uses results of the UVN-phase stability testing for initialization of the UVN-flash calculation. As the number of phases is not known a-priori, the proposed strategy is based on repeated UVN-stability testing and UVN phase-split calculation until a stable phase split is found. The performance of the algorithm is demonstrated on many examples of different complexity.

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1. Introduction

Investigation of phase stability and multi-phase equilibrium calculation for multicomponent mixtures are basic problems in chemical engineering with numerous applications in the industry. The most frequently encountered formulation of these problems uses pressure P , temperature T , and mole numbers N_1, \dots, N_n (or mole fractions z_1, \dots, z_n) as specification variables – this is the case of the so called PTN-stability and PTN-flash equilibrium calculation. These problems have been treated extensively by many authors building mainly on the classical works of Michelsen [1–3], see e.g. Refs. [4,5]. In this work, we are interested in developing methods for phase stability testing and phase equilibrium calculation in a different variables specification – namely internal energy U , volume V , and mole numbers N_1, \dots, N_n . This is the problem of the UVN-stability and UVN-phase equilibrium computation.

Compared to PTN-stability and PTN-flash, other variables specifications are less common. Notable problems are the specification in terms of temperature T , volume V , and mole numbers N_1, \dots, N_n (TVN-based formulation) and the UVN-formulation. The TVN-formulation can be used e.g. for

simulations of equilibria in a closed vessel of known volume at constant temperature (see e.g. Refs. [6–8]), or in compositional simulation [9] where the flash calculation is performed locally on each finite element of the discretized domain at each time step under the assumptions of constant temperature and local thermodynamic equilibrium. On the other hand, the UVN-formulation is useful in non-isothermal problems as, for example, in the dynamic simulation of separation vessels [10,11] or dynamic filling of a process vessel [12]. In these problems, temperature changes during the simulation must be computed using the energy balance and the assumption of the local thermodynamic equilibrium. As evolution of the internal energy is provided by solving the energy balance equations, it is natural to solve the phase equilibrium using the UVN-formulation.

There are only few papers concerning the UVN-flash. First, Michelsen has proposed a general framework for other variables specifications in Ref. [13], including the UVN- and TVN-formulations. His approach uses PTN-flash in the inner loop while pressure and temperature are iterated in an outer loop with the goal of fulfilling the pertinent variable(s) specification(s). This approach has the advantage that existing implementations of the PTN-flash can be reused, but the price to pay is the increased CPU cost because of the nested iterations. Moreover, numerical issues can appear, as for example, during the course of the TVN-flash

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iterations, pressure can be negative and the conventional PTN-based codes may not be well suited to treat the negative pressure.

The second paper devoted to the UVN-flash equilibrium calculation is the paper [12]. Here, a sophisticated heuristics is developed to estimate the pressure and temperature corresponding to the given internal energy, volume, and moles. Initial K -values are estimated using the Wilson correlation and the estimated values of pressure and temperature. Then, an iterative method is proposed using a combination of the Newton-Raphson method for the update of the pressure and temperature, and the successive substitution iteration (SSI) for the update of the equilibrium K -values of all components. According to [12], convergence towards the trivial solution has been observed frequently. The solution method proposed in Ref. [12] is not directly applicable to a system consisting from a single component. Therefore, the authors propose a special procedure for single-component systems.

The third paper devoted specifically to the UVN-formulation is the paper [14]. The basic approach used in this paper is the direct entropy maximization, which we also use in our work. However, to get good initial phase split for the direct entropy maximization in Ref. [14], one has to use estimates of the pressure P and temperature T , which are to be specified by the user together with the input data or estimated by some heuristics. In case of numerical difficulties, the algorithm has to use nested loops in which PTN-flash is used in the inner loop and the pressure and temperature estimates are adjusted in the outer loop so that V and U are close to the specified values. When sufficiently good estimates of P and T have been found, the procedure is switched back to the direct entropy maximization. The resulting phase split is tested using the PTN-stability and the procedure is terminated when the stable phase split has been found. The detailed explanation of this procedure can be found in Ref. [14]. The procedure flow-chart in Ref. [14] is pretty complex and, as reported in Ref. [14], also prone to numerical difficulties – in some cases some parts of the algorithm have to be performed in complex arithmetics.

In this paper we propose a different algorithm for UVN-phase stability and UVN-flash equilibrium calculation. Similarly to [14], our method is based on the direct entropy maximization. Unlike in Ref. [14], we use the direct formulation of the UVN-phase stability testing for constructing an initial guess for the UVN-flash calculation. As we will show in this paper, this combination is both robust and efficient, and can be performed without numerical difficulties mentioned in the previous works. Especially, the algorithm proceeds in a straightforward way, is applicable to both single-component and multi-component systems, and there is no need for the complex arithmetics.

The paper is structured as follows. In Section 2, we derive the criterion for testing phase stability when the internal energy, volume, and mole numbers are specified. In Section 3, we describe the procedure for calculation of temperature corresponding to the specified internal energy, volume, and moles. In Section 4, we derive a numerical algorithm for the UVN-based phase stability testing. In Section 5, we describe the algorithm for the UVN-flash equilibrium calculation. In Section 6, we explain how this algorithm is combined with the UVN-phase stability test in order to treat systems that can separate into any number of phases. In Section 7, we test the algorithm on different example cases. Finally, in Section 8, we summarize the main properties of our algorithm. In the Appendix, details of the equations of state are given.

2. Single-phase stability testing at given internal energy, volume, and moles

Consider a mixture of n components with mole numbers N_1^*, \dots, N_n^* occupying volume V^* and having internal energy U^* . The

goal is to decide if this system remains in a single phase or splits into two (or more) phases. The entropy of the hypothetical single-phase system reads as

$$S^I = S(U^*, V^*, N_1^*, \dots, N_n^*). \quad (1)$$

From this system we are trying to separate a small amount of a new trial phase with internal energy U' , volume V' and mole numbers N'_1, \dots, N'_n . The total entropy of the two-phase system reads as

$$S^{II} = S(U^* - U', V^* - V', N_1^* - N'_1, \dots, N_n^* - N'_n) + S(U', V', N'_1, \dots, N'_n). \quad (2)$$

Using the Taylor expansion around the point $[U^*, V^*, N_1^*, \dots, N_n^*]$, we obtain

$$\begin{aligned} S(U^* - U', V^* - V', N_1^* - N'_1, \dots, N_n^* - N'_n) &= S(U^*, V^*, N_1^*, \dots, N_n^*) - U' \frac{\partial S}{\partial U}(U^*, V^*, N_1^*, \dots, N_n^*) \\ &\quad - V' \frac{\partial S}{\partial V}(U^*, V^*, N_1^*, \dots, N_n^*) - \sum_{i=1}^n N'_i \frac{\partial S}{\partial N_i}(U^*, V^*, N_1^*, \dots, N_n^*) \\ &\quad + R_1(U', V', N'_1, \dots, N'_n), \end{aligned} \quad (3)$$

where R_1 denotes the remainder term in the Taylor expansion. We assume that the trial phase volume can be arbitrarily small, and the internal energy density $u' = U'/V'$ and molar densities $c'_i = N'_i/V'$ can be chosen arbitrarily, but are held constant. Similarly, we denote by $u^* = U^*/V^*$ and $c_i^* = N_i^*/V^*$ the internal energy density and the molar concentrations of the components in the initial phase, respectively. Under these assumptions,

$$\lim_{V' \rightarrow 0^+} \frac{R_1(V'u', V', c'_1 V', \dots, c'_n V')}{V'} = 0. \quad (4)$$

As

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{P}{T}, \quad \frac{\partial S}{\partial N_i} = -\frac{\mu_i}{T}, \quad (5)$$

S^{II} can be rewritten as follows

$$\begin{aligned} S^{II} &= S^I - \frac{U'}{T^*} - V' \frac{P^*}{T^*} + \sum_{i=1}^n N'_i \frac{\mu_i^*}{T^*} + R_1(U', V', N'_1, \dots, N'_n) \\ &\quad + S(U', V', N'_1, \dots, N'_n). \end{aligned} \quad (6)$$

Entropy is a homogeneous function of degree one in internal energy, volume, and mole numbers. The Euler formula for homogeneous functions yields the following expression for the entropy of the trial phase

$$S(U', V', N'_1, \dots, N'_n) = \frac{U'}{T'} + \frac{P'}{T'} V' - \sum_{i=1}^n N'_i \frac{\mu'_i}{T'}. \quad (7)$$

In the equations above, we denoted by $T^* = T(U^*, V^*, N_1^*, \dots, N_n^*)$, $P^* = P(U^*, V^*, N_1^*, \dots, N_n^*)$, and $\mu_i^* = \mu_i(U^*, V^*, N_1^*, \dots, N_n^*)$ the values of temperature, pressure and chemical potentials of all components in the initial phase. Analogously, we denote by $T' = T(U', V', N'_1, \dots, N'_n)$, $P' = P(U', V', N'_1, \dots, N'_n)$, and $\mu'_i = \mu_i(U', V', N'_1, \dots, N'_n)$ the values of temperature, pressure and chemical potentials of all components in the trial phase.

Finally, we can introduce function D of variables c'_1, \dots, c'_n and u'

by

$$D = \lim_{V' \rightarrow 0^+} \frac{S^H - S^I}{V'} \\ = u' \left(\frac{1}{T'} - \frac{1}{T^*} \right) + \left(\frac{P'}{T'} - \frac{P^*}{T^*} \right) - \sum_{i=1}^n \left(\frac{\mu'_i}{T'} - \frac{\mu_i^*}{T^*} \right) c'_i \quad (8)$$

In this equation, the values of temperature, pressure, and chemical potential in the trial phase are evaluated as $X' = X(u', 1, c'_1, \dots, c'_n)$, where X stands for either T , P , or μ_i as pressure, temperature, and chemical potentials are intensive variables.

The function D can be used for testing the phase stability of a given state described by the internal energy, volume, and mole numbers. If $D(c'_1, \dots, c'_n, u') \leq 0$ for all admissible $[c'_1, \dots, c'_n, u']$, then the initial phase is stable, because no two-phase split will have higher entropy than the initial single-phase state. On the other hand, if there exists an admissible state $[c'_1, \dots, c'_n, u']$ for which $D(c'_1, \dots, c'_n, u') > 0$, then the initial state is unstable and the phase splitting will occur. In the unstable case, it follows from the definition of function D that a small positive volume V' exists for which $S^H - S^I$ is positive. The volume V' can be found by the bisectioning. Once V' has been found, denoting

$$U^{(1)} = u'V', \quad V^{(1)} = V', \quad N_i^{(1)} = c'_iV', \quad (9)$$

and

$$U^{(2)} = U^* - u'V', \quad V^{(2)} = V^* - V', \quad N_i^{(2)} = N_i^* - c'_iV', \quad (10)$$

we have constructed a two phase split of $[U^*, V^*, N_1^*, \dots, N_n^*]$ into phases described by states $[U^{(1)}, V^{(1)}, N_1^{(1)}, \dots, N_n^{(1)}]$ and $[U^{(2)}, V^{(2)}, N_1^{(2)}, \dots, N_n^{(2)}]$ with higher total entropy than the entropy of the initial phase. The phase stability testing not only decides on the phase stability but in the unstable case provides tools for constructing of an initial two-phase split with higher entropy than the entropy of the initial case. This will be advantageous for the initialization of the UVN phase equilibrium calculation.

3. Evaluation of the UVN-dependent functions

In the above derivations, pressure P , temperature T , and chemical potentials of all components μ_i were considered as functions of the internal energy U , volume V , and mole numbers N_1, \dots, N_n . Commonly used equations of state are, however, usually formulated as functions of temperature T , volume V , and mole numbers N_1, \dots, N_n . It is therefore necessary to establish connection between these two sets of variables, especially to specify how to find the value of temperature T corresponding to the specified values of U , V , and N_1, \dots, N_n .

We assume that the system is described by a pressure-explicit equation of state of the form

$$P = P^{(EOS)}(T, V, N_1, \dots, N_n). \quad (11)$$

This equation has to be complemented with a compatible thermal equation of state of the form

$$U = U^{(EOS)}(T, V, N_1, \dots, N_n), \quad (12)$$

prescribing relation between internal energy and temperature and by the entropy equation of state

$$S = S^{(EOS)}(T, V, N_1, \dots, N_n), \quad (13)$$

which allows to evaluate entropy as a function of T, V, N_1, \dots, N_n .

Specific forms of the functions $P^{(EOS)}$, $U^{(EOS)}$, and $S^{(EOS)}$ are given in the Appendix.

Assuming that the dependency of U on T in (12) is strictly increasing, (12) provides an implicit definition of function $T = T(U, V, N_1, \dots, N_n)$ by

$$U = U^{(EOS)}(T(U, V, N_1, \dots, N_n), V, N_1, \dots, N_n). \quad (14)$$

For any admissible set of values $[U, V, N_1, \dots, N_n]$, equation (14) can be solved numerically for T either by the bisection technique or by the Newton method. Once the value of $T(U, V, N_1, \dots, N_n)$ has been calculated, pressure P is established by the equation of state

$$P(U, V, N_1, \dots, N_n) = P^{(EOS)}(T(U, V, N_1, \dots, N_n), V, N_1, \dots, N_n), \quad (15)$$

entropy reads as

$$S(U, V, N_1, \dots, N_n) = S^{(EOS)}(T(U, V, N_1, \dots, N_n), V, N_1, \dots, N_n), \quad (16)$$

and the chemical potential can be evaluated using

$$\mu_i(U, V, N_1, \dots, N_n) = \frac{\partial U^{(EOS)}}{\partial N_i}(T(U, V, N_1, \dots, N_n), V, N_1, \dots, N_n) \\ - T(U, V, N_1, \dots, N_n) \frac{\partial S^{(EOS)}}{\partial N_i}(T(U, V, N_1, \dots, N_n), V, N_1, \dots, N_n). \quad (17)$$

4. Numerical algorithm for the single phase stability testing at given internal energy, volume, and moles

To find out if there exists a state $[c'_1, \dots, c'_n, u']$ for which $D(c'_1, \dots, c'_n, u') > 0$, we will seek for local maxima of D . Components of the gradient of function D can be derived by differentiation of D with respect to c'_k and u' and using the Gibbs-Duhem relation, which results into

$$\frac{\partial D}{\partial c'_k} = \frac{\mu_k^*}{T^*} - \frac{\mu'_k}{T'}, \quad \frac{\partial D}{\partial u'} = \frac{1}{T'} - \frac{1}{T^*}. \quad (18)$$

If we define a vector $F \in \mathbb{R}^{n+1}$ by

$$F = \left(\frac{\partial D}{\partial c'_1}, \dots, \frac{\partial D}{\partial c'_n}, \frac{\partial D}{\partial u'} \right)^T, \quad (19)$$

(T denotes the transposed matrix), then we are going to solve a system of $(n + 1)$ non-linear algebraic equations

$$F(c'_1, \dots, c'_n, u') = 0. \quad (20)$$

We now consider two ways to solve the system.

4.1. A direct solution using the Newton-Raphson method

The system (20) can be solved iteratively using the modified Newton-Raphson method. If we denote

$$x = (c'_1, \dots, c'_n, u')^T, \quad (21)$$

then the modified Newton-Raphson iterations can be performed as

$$x^{(k+1)} = x^{(k)} + \lambda^{(k)} \Delta x^{(k)}, \quad (22)$$

where $\lambda^{(k)} \in (0, 1]$ is a damping parameter and $\Delta x^{(k)}$ is an increment, which is determined as a solution of the system

$$\mathbb{J}(x^{(k)}) \Delta x^{(k)} = -F(x^{(k)}). \quad (23)$$

Here \mathbb{J} is the Jacobian matrix of function F (or the Hessian of function D), which can be written in a block-matrix form as

$$\mathbb{J} = \begin{pmatrix} \mathbb{B} & \mathbb{C} \\ \mathbb{C}^T & \mathbb{D} \end{pmatrix}, \quad (24)$$

where the matrix blocks are of the following forms

$$\mathbb{B} \in \mathbb{R}^{n,n}, \mathbb{B}_{ij} = \frac{\partial^2 D}{\partial c_i' \partial c_j'}, \quad (25)$$

$$\mathbb{C} \in \mathbb{R}^n, \mathbb{C}_i = \frac{\partial^2 D}{\partial c_i' \partial u'}, \quad (26)$$

$$\mathbb{D} \in \mathbb{R}, \mathbb{D} = \frac{\partial^2 D}{\partial (u')^2}. \quad (27)$$

The derivatives can be evaluated using (18) as

$$\frac{\partial^2 D}{\partial c_i' \partial c_j'} = -\frac{\frac{\partial \mu_i'}{\partial N_j} T' - \mu_i' \frac{\partial T'}{\partial N_j}}{(T')^2}, \quad (28)$$

$$\frac{\partial^2 D}{\partial c_i' \partial u'} = -\frac{\frac{\partial \mu_i'}{\partial V} T' - \mu_i' \frac{\partial T'}{\partial V}}{(T')^2}, \quad (29)$$

$$\frac{\partial^2 D}{\partial (u')^2} = -\frac{1}{(T')^2} \frac{\partial T'}{\partial U}. \quad (30)$$

Once the increment direction $\Delta x^{(k)}$ has been established, the damping factor has to be determined. First we try to set $\lambda^{(k)} = 1$. If $x^{(k+1)}$ is out of the admissible domain, we halve $\lambda^{(k)}$ until the new approximation belongs to the admissible domain. Using this modification of the Newton-Raphson method (the so-called line-search technique) allows to attain global convergence in the Newton-Raphson method.

When testing stability at given pressure, temperature, and moles (PTN-flash), one usually uses Wilson's correlation [15] for construction of initial approximations. Similarly, available algorithms for testing phase stability at constant volume, temperature, and moles (TVN-flash) [16] obtains initial approximations using saturation pressures of the individual components of the mixture. Neither of these two approaches is possible in the UVN-formulation because in this case temperature is not known a-priori. Therefore, we propose the following method for initialization of the UVN-phase stability algorithm. The admissible molar concentrations c_i' must obey

$$\sum_{i=1}^n c_i' b_i < 1, \quad (31)$$

$$c_i' \geq 0, i = 1, \dots, n, \quad (32)$$

where $b_i > 0$ is the co-volume parameter from the Peng-Robinson equation of state. The set of admissible concentrations forms an

n -simplex. The first initial approximation for $[c_1', \dots, c_n']$ will be the barycenter of the simplex. Another $n + 1$ initial approximations for $[c_1', \dots, c_n']$ will be at the midpoints between the barycenter and any of the $n + 1$ vertices of the admissible domain. This way we obtain $n + 2$ initial approximations for $[c_1', \dots, c_n']$. These initial molar concentrations are supplemented by several initial approximations of the internal energy density u' so that the resulting state $[c_1', \dots, c_n', u']$ corresponds to a certain temperature T . The lowest temperature is $T = 100 \text{ K}$ and then we increase the temperature by 50 K up to $T = 400 \text{ K}$. This way we construct $7(n + 2)$ initial approximations for UVN-stability testing which can be used in the modified Newton-Raphson method. Numerical experiments presented in later sections indicate that using this choice of initial approximations, we obtain the global maximum of function D .

4.2. Solution of a reduced system

The last equation in (20) reads as

$$\frac{1}{T'} - \frac{1}{T^*} = 0. \quad (33)$$

This equation implies that $T' = T^*$, i.e. the trial phase should have the same temperature as the initial phase. Substituting this equality into the first n equations in (20), we obtain a reduced set of equations

$$\frac{1}{T^*} (\mu_k^* - \mu_k') = 0, \quad k = 1, \dots, n. \quad (34)$$

Multiplying these equations by T^* we get the following set of n non-linear algebraic equations

$$\mu_k^* - \mu_k' = 0, \quad i = 1, \dots, n, \quad (35)$$

for unknown trial phase concentrations c_1', \dots, c_n' . These are the same equations as those in the TVN-stability testing. It is thus tempting to use the TVN-stability testing algorithm described in Ref. [16], but our numerical experiments show that this procedure does not provide good results in some cases. Similarly, in Ref. [14] Castier proposed to use PTN-stability testing for testing the stability of a given state. However, this procedure can also fail, as e.g. for a two-phase system, the pressure evaluated from the equation of state for the single-phase system can be negative. For most PTN-stability testing algorithms, the specification of a negative pressure leads to the failure of the computation. For negative pressure one can tell that the system is unstable without stability testing, but without stability testing, we do not get any reasonable initial guess for the flash calculation (c.f. also the discussion in Ref. [17]). All these issues are avoided by resorting to the UVN-based stability testing.

The viable alternative is to apply the algorithm described in the previous subsection to the reduced system of equations. The modification of the algorithm is straightforward – the matrix \mathbb{J} will contain the block \mathbb{B} only and the vector F will contain just the first n components. Initial approximations of the solutions $x^{(0)} = [c_1', \dots, c_n']^T$ will be covering the admissible domain of concentrations only. We use the same choice of the initial molar concentrations as in the previous subsection. This results into $n + 2$ different initial approximations of the solution. Compared to the previous section, the number of initial guesses to be tested is seven times reduced. This reduction of the number of initial guesses is important especially in case of multicomponent mixtures with many components in the stable case (in the unstable case, the search for unstable state is terminated when the first unstable state is found, but if the mixture is stable, we have to test stability using

each of the initial guesses).

4.3. Modified Cholesky decomposition

When using modified Newton-Raphson method, iterates may not converge towards a local maximum, but also to a local minimum or towards a saddle point. This problem can be avoided using a modification of the Hessian. The aim of the modification is to guarantee that the value of function D will increase in each iteration. It is well known that if the Hessian is negative definite, then the increment shows the ascent direction of function D . For sufficiently low values of the damping parameter $\lambda^{(k)}$, we have $D(x^{(k+1)}) > D^{(k)}$. If the Hessian is not negative definite, then the value of D in the next iteration can be either higher or lower than in the previous iteration. In this case we have to modify the Hessian matrix so that it becomes negative definite. Negative definiteness of the modified Hessian is ensured using the modified Cholesky decomposition of the Hessian matrix \mathbb{J} . The standard Cholesky decomposition of a symmetric positive definite matrix $-\mathbb{J}$ factorizes the matrix to the product of a lower triangular matrix \mathbb{L} and its transpose, i.e.

$$\mathbb{J} = -\mathbb{L}\mathbb{L}^T. \quad (36)$$

If $-\mathbb{J}$ is not positive definite, its Cholesky decomposition may not exist or can be unstable. The modified Cholesky decomposition is performed in the same way as the standard Cholesky decomposition, however, when a negative or too small element appears at the diagonal of the factorized matrix, the corresponding diagonal element of $-\mathbb{J}$ is increased, so as to become sufficiently large. This way we obtain a Cholesky factorization of a modified matrix $\mathbb{J} - \mathbb{E}$, where \mathbb{E} is a diagonal matrix with non-negative elements. When constructing the modified Cholesky decomposition of matrix $-\mathbb{J}$, we have to satisfy four requirements:

1. If $-\mathbb{J}$ is sufficiently positive definite, then $\mathbb{E} = 0$.
2. If $-\mathbb{J}$ is not positive definite, then the norm $\|\mathbb{E}\|$ should be as low as possible.
3. Matrix $\mathbb{J} - \mathbb{E}$ should be well-conditioned.
4. The construction should be cheap.

The first two requirements guarantee fast convergence of the Newton method. The third point guarantees good solvability and stability of the solution of the resulting system of linear algebraic equations. In our previous works [6–8], we have used the modified Cholesky decomposition from Ref. [18]. However, it is shown in Ref. [19] that the algorithm from Ref. [18] is not optimal because the requirement 1 is not fulfilled sufficiently well. In this work, we use the algorithm introduced in Ref. [20]. This new algorithm distinguishes better whether the matrix is positive definite or not and provides better results compared to the algorithm from Ref. [18]. For the details of the algorithm, the reader is referred to the original paper [20].

4.4. Summary of the numerical algorithm for UVN-stability testing

We summarize essential steps of the algorithm for the single-phase stability testing at given internal energy, volume, and moles. We will describe the version of the algorithm derived in Section 4.1.

1. Let the values $U^*, V^*, N_1^*, \dots, N_n^*$ be given. Construct $7(n+2)$ initial approximations of the solutions as described in Section 4.1. Set $m = 1$.

2. Set iteration count $k = 0$. Let $x^{(0)}$ be the m -th initial approximation of the solution in the form

$$x^{(0)} = [c'_1, \dots, c'_n, u']^T.$$

3. Assemble matrix $\mathbb{J}(x^{(k)})$ and vector $F(x^{(k)})$ using equations (24) and (19).
4. Evaluate the increment of the solution $\Delta x^{(k)} \in \mathbb{R}^{n+1}$ by solving the system of linear algebraic equations

$$\mathbb{J}(x^{(k)})\Delta x^{(k)} = -F(x^{(k)}).$$

If $\mathbb{J}(x^{(k)})$ is not negative definite, use the modified Cholesky decomposition to get the modified Hessian and obtain the increment $\Delta x^{(k)}$ by solving the modified system

$$\widehat{\mathbb{J}}(x^{(k)})\Delta x^{(k)} = -F(x^{(k)}),$$

where $\widehat{\mathbb{J}} = \mathbb{J} - \mathbb{E}$.

5. Determine $\lambda^{(k)} > 0$ so that

$$D(x^{(k)} + \lambda^{(k)}\Delta x) > D(x^{(k)}). \quad (37)$$

Set $\lambda^{(k)} = 1$ and test condition (37). If the condition does not hold, iterate $\lambda^{(k)} = \frac{\lambda^{(k)}}{2}$, until (37) is fulfilled.

6. Update the solution using (22)

$$x^{(k+1)} = x^{(k)} + \lambda^{(k)}\Delta x^{(k)}.$$

7. Test the convergence. The iterations can be stopped, if

$$\|\Delta x^{(k)}\| = \left(\sum_{i=1}^n \frac{\Delta x_i^{(k)2}}{c^2} + \frac{\Delta x_{n+1}^{(k)2}}{u^2} \right)^{\frac{1}{2}} < \varepsilon, \quad (38)$$

where ε is the required tolerance, e.g. $\varepsilon = 10^{-6}$. If the condition is satisfied, go to step 8, if not, set $k = k + 1$ and go to step 3.

8. If $D(x^{(k)}) > 0$, terminate the algorithm and declare the state as unstable. In the opposite case see if $m < 7(n+2)$. If yes, set $m = m + 1$ and go to step 2, in the opposite case terminate algorithm and declare the state as stable.

5. Solution of the UVN-phase equilibrium problem by direct entropy maximization

In this section we describe an algorithm for calculation of the equilibrium state of a multicomponent mixture at specified internal energy U^* , volume V^* and mole numbers N_1^*, \dots, N_n^* , with an a-priori known number $p \geq 2$ phases. This algorithm and the algorithm for testing the phase stability will be combined in Section 6 leading to a general strategy for establishing the equilibrium state in a system in which the number of phases p is a-priori unknown.

Let us consider a mixture that is split among $p \geq 2$ phases. The total entropy of this p -phase split reads as

$$S^{(p)} = \sum_{k=1}^p S(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}), \quad (39)$$

where $U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}$ are the internal energy, volume, and mole numbers of individual components in phase k . The

superscript (p) denotes the fact that this entropy is a function of variables of all p phases. Entropy is a subject to the following constraints

$$U^* = \sum_{k=1}^p U^{(k)}, \tag{40}$$

$$V^* = \sum_{k=1}^p V^{(k)}, \tag{41}$$

$$N_i^* = \sum_{k=1}^p N_i^{(k)}, \quad i = 1, \dots, n. \tag{42}$$

The equilibrium state is the state which maximizes entropy (39) and obeys the constraints (40)–(42), i.e. we are solving a constrained maximization problem for $p(n + 2)$ unknowns with $n + 2$ constraints. After elimination of the constraints, the problem can be transformed into an unconstrained maximization problem in a lower dimension. Eliminating the variables of the p -th phase using the constraints, we obtain

$$S_{red}^{(p)} = \sum_{k=1}^{p-1} S(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) + S\left(U^* - \sum_{k=1}^{p-1} U^{(k)}, V^* - \sum_{k=1}^{p-1} V^{(k)}, N_1^* - \sum_{k=1}^{p-1} N_1^{(k)}, \dots, N_n^* - \sum_{k=1}^{p-1} N_n^{(k)}\right).$$

Denoting

$$x^* = \left(U^* - \sum_{k=1}^{p-1} U^{(k)}, V^* - \sum_{k=1}^{p-1} V^{(k)}, N_1^* - \sum_{k=1}^{p-1} N_1^{(k)}, \dots, N_n^* - \sum_{k=1}^{p-1} N_n^{(k)} \right), \tag{43}$$

we can write

$$S_{red}^{(p)} = \sum_{k=1}^{p-1} S(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) + S(x^*). \tag{44}$$

To determine the equilibrium state, one must solve the unconstrained maximization problem for $(p-1)(n + 2)$ unknown variables $U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}$ for $k \in \{1, 2, \dots, p-1\}$.

5.1. Numerical procedure

The maximum of function (44) can be found using the modified Newton-Raphson method. Denoting the vectors of unknowns for the reduced unconstrained problem as well as for the original constrained problem as

$$x = \left(N_1^{(1)}, \dots, N_n^{(1)}, V^{(1)}, U^{(1)}, \dots, N_1^{(p-1)}, \dots, N_n^{(p-1)}, V^{(p-1)}, U^{(p-1)} \right)^T, \tag{45}$$

$$X = \left(N_1^{(1)}, \dots, N_n^{(1)}, V^{(1)}, U^{(1)}, \dots, N_1^{(p)}, \dots, N_n^{(p)}, V^{(p)}, U^{(p)} \right)^T, \tag{46}$$

the modified Newton-Raphson method updates any given approximation as

$$X^{(j+1)} = X^{(j)} + \lambda^{(j)} \Delta X^{(j)}. \tag{47}$$

In the above equation $\lambda^{(j)} \in (0, 1]$ is a damping parameter and

$\Delta X^{(j)} = Z \Delta x^{(j)}$ is the solution increment, which is obtained by solving the following system of linear algebraic equations

$$\mathbb{H}(x^{(j)}) \Delta x^{(j)} = -g(x^{(j)}). \tag{48}$$

Matrix $Z \in \mathbb{R}^{p(n+2), (p-1)(n+2)}$ is of the following block form

$$Z = \begin{pmatrix} \mathbb{I}_{n+2} & \mathbb{O} & \mathbb{O} & \dots & \mathbb{O} \\ \mathbb{O} & \mathbb{I}_{n+2} & \mathbb{O} & \dots & \mathbb{O} \\ \mathbb{O} & \mathbb{O} & \mathbb{I}_{n+2} & \dots & \mathbb{O} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \mathbb{O} & \mathbb{O} & \dots & \mathbb{O} & \mathbb{I}_{n+2} \\ -\mathbb{I}_{n+2} & -\mathbb{I}_{n+2} & \dots & -\mathbb{I}_{n+2} & -\mathbb{I}_{n+2} \end{pmatrix}, \tag{49}$$

where \mathbb{I}_{n+2} is the square identity matrix of size $n + 2$ and \mathbb{O} is the square zero matrix of size $n + 2$. In equation (48), $\mathbb{H}(x^{(j)}) \in \mathbb{R}^{(p-1)(n+2), (p-1)(n+2)}$ is the Hessian, i.e. the matrix of the second derivatives of function $S_{red}^{(p)}$ and $g(x^{(j)}) \in \mathbb{R}^{(p-1)(n+2)}$, is the gradient of function $S_{red}^{(p)}$.

5.1.1. Evaluation of the gradient of function $S_{red}^{(p)}$

Gradient of function $S_{red}^{(p)}$, denoted as $g(x)$, can be written as follows

$$g(x) = \begin{pmatrix} g^{(1)} \\ \vdots \\ g^{(p-1)} \end{pmatrix}, \tag{50}$$

where $g^{(k)} \in \mathbb{R}^{n+2}$ for $k = 1, \dots, p-1$ and

$$g^{(k)} = \begin{pmatrix} \frac{\partial S_{red}^{(p)}}{\partial N_1^{(k)}} \\ \vdots \\ \frac{\partial S_{red}^{(p)}}{\partial N_n^{(k)}} \\ \frac{\partial S_{red}^{(p)}}{\partial V^{(k)}} \\ \frac{\partial S_{red}^{(p)}}{\partial U^{(k)}} \end{pmatrix} = \begin{pmatrix} -\frac{\mu_1}{T}(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) + \frac{\mu_1}{T}(x^*) \\ \vdots \\ -\frac{\mu_n}{T}(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) + \frac{\mu_n}{T}(x^*) \\ \frac{P}{T}(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) - \frac{P}{T}(x^*) \\ \frac{1}{T}(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)}) - \frac{1}{T}(x^*) \end{pmatrix}. \tag{51}$$

5.1.2. Evaluation of the Hessian of function $S_{red}^{(p)}$

The matrix \mathbb{H} can be written in the following block form

$$\mathbb{H} = \begin{pmatrix} \mathbb{H}^{(1,1)} & \mathbb{H}^{(1,2)} & \mathbb{H}^{(1,3)} & \dots & \mathbb{H}^{(1,p-1)} \\ \mathbb{H}^{(2,1)} & \mathbb{H}^{(2,2)} & \mathbb{H}^{(2,3)} & \dots & \mathbb{H}^{(2,p-1)} \\ \mathbb{H}^{(3,1)} & \mathbb{H}^{(3,2)} & \mathbb{H}^{(3,3)} & \dots & \mathbb{H}^{(3,p-1)} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \mathbb{H}^{(p-1,1)} & \mathbb{H}^{(p-1,2)} & \dots & \mathbb{H}^{(p-1,p-2)} & \mathbb{H}^{(p-1,p-1)} \end{pmatrix}, \tag{52}$$

where the blocks $\mathbb{H}^{(k,l)} \in \mathbb{R}^{n+2, n+2}$ for $k, l \in \{1, \dots, p-1\}$ read as

$$\mathbb{H}^{(k,l)} = \begin{pmatrix} \mathbb{B}^{(k,l)} & \mathbb{C}^{(k,l)} & \mathbb{E}^{(k,l)} \\ \left(\mathbb{C}^{(k,l)} \right)^T & \mathbb{D}^{(k,l)} & \mathbb{F}^{(k,l)} \\ \left(\mathbb{E}^{(k,l)} \right)^T & \mathbb{F}^{(k,l)} & \mathbb{G}^{(k,l)} \end{pmatrix}. \tag{53}$$

Furthermore,

$$\mathbb{B}^{(k,l)} \in \mathbb{R}^{n,n}, \mathbb{B}_{ij}^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial N_i^{(k)} \partial N_j^{(l)}}(\mathbf{x}), \quad (54)$$

$$\mathbb{C}^{(k,l)} \in \mathbb{R}^n, \mathbb{C}_i^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial N_i^{(k)} \partial V^{(l)}}(\mathbf{x}), \quad (55)$$

$$\mathbb{E}^{(k,l)} \in \mathbb{R}^n, \mathbb{E}_i^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial N_i^{(k)} \partial U^{(l)}}(\mathbf{x}), \quad (56)$$

$$\mathbb{D}^{(k,l)} \in \mathbb{R}, \mathbb{D}^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial V^{(k)} \partial V^{(l)}}(\mathbf{x}), \quad (57)$$

$$\mathbb{F}^{(k,l)} \in \mathbb{R}, \mathbb{F}^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial U^{(k)} \partial V^{(l)}}(\mathbf{x}), \quad (58)$$

$$\mathbb{G}^{(k,l)} \in \mathbb{R}, \mathbb{G}^{(k,l)} = \frac{\partial^2 S_{red}^{(p)}}{\partial U^{(k)} \partial U^{(l)}}(\mathbf{x}). \quad (59)$$

These partial derivatives can be expressed as

$$\begin{aligned} \mathbb{B}_{ij}^{(k,l)} &= -\frac{\frac{\partial \mu_i}{\partial N_j} - \mu_i \frac{\partial T}{\partial N_j}}{T^2} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} \\ &\quad - \frac{\frac{\partial \mu_i}{\partial N_j} - \mu_i \frac{\partial T}{\partial N_j}}{T^2} (\mathbf{x}^\star), \end{aligned} \quad (60)$$

$$\begin{aligned} \mathbb{C}_i^{(k,l)} &= \frac{\frac{\partial P}{\partial N_i} T - P \frac{\partial T}{\partial N_i}}{T^2} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} \\ &\quad + \frac{\frac{\partial P}{\partial N_i} T - P \frac{\partial T}{\partial N_i}}{T^2} (\mathbf{x}^\star), \end{aligned} \quad (61)$$

$$\mathbb{E}_i^{(k,l)} = -\frac{1}{T^2} \frac{\partial T}{\partial N_i} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} - \frac{1}{T^2} \frac{\partial T}{\partial N_i} (\mathbf{x}^\star), \quad (62)$$

$$\begin{aligned} \mathbb{D}^{(k,l)} &= \frac{\frac{\partial P}{\partial V} T - P \frac{\partial T}{\partial V}}{T^2} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} \\ &\quad + \frac{\frac{\partial P}{\partial V} T - P \frac{\partial T}{\partial V}}{T^2} (\mathbf{x}^\star), \end{aligned} \quad (63)$$

$$\mathbb{F}^{(k,l)} = -\frac{1}{T^2} \frac{\partial T}{\partial V} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} - \frac{1}{T^2} \frac{\partial T}{\partial V} (\mathbf{x}^\star), \quad (64)$$

$$\mathbb{G}^{(k,l)} = -\frac{1}{T^2} \frac{\partial T}{\partial U} \left(U^{(k)}, V^{(k)}, N_1^{(k)}, \dots, N_n^{(k)} \right) \delta_{k,l} - \frac{1}{T^2} \frac{\partial T}{\partial U} (\mathbf{x}^\star). \quad (65)$$

Here, $\delta_{k,l}$ is the Kronecker symbol, which is equal to 1 for $k = l$ and 0 for $k \neq l$. Note that for $k \neq l$ the right hand sides of equations (60) to (65) do not depend on k and l . As a consequence, all non-diagonal block matrices $\mathbb{H}^{(k,l)}$ in equation (52) are the same.

5.1.3. Preconditioning of the system $\mathbb{H}\Delta\mathbf{x} = -\mathbf{g}$

To determine $\Delta\mathbf{x}$, we have to solve the system

$$\mathbb{H}\Delta\mathbf{x} = -\mathbf{g}. \quad (66)$$

This system is solved using the modified Cholesky decomposition, which was described in Section 4.3. This method guarantees that the value of $S_{red}^{(p)}$ will increase in each iteration. Therefore, the modified Newton method will converge to at least local maximum of function $S_{red}^{(p)}$. Numerical experiments indicate that it is advantageous to use a symmetric diagonal preconditioning of matrix \mathbb{H} so as to equilibrate the diagonal elements of \mathbb{H} . Instead of solving (66), we solve the equivalent system

$$\mathbb{P}\mathbb{H}\mathbb{P}^T \mathbf{y} = -\mathbb{P}\mathbf{g}, \quad (67)$$

where $\Delta\mathbf{x} = \mathbb{P}^T \mathbf{y}$ and $\mathbb{P} \in \mathbb{R}^{(p-1)(n+2), (p-1)(n+2)}$ is a diagonal matrix with nonzero diagonal elements which are chosen so that the diagonal elements of the preconditioned matrix $\mathbb{P}\mathbb{H}\mathbb{P}^T$ are equal to ± 1 . This procedure significantly improves convergence of the Newton-Raphson method. At the same time, the condition number of matrix $\mathbb{P}\mathbb{H}\mathbb{P}^T$ is much lower compared to \mathbb{H} and we are thus solving a much better conditioned problem.

5.1.4. The stopping criteria

In our previous works ([7]) we have used the stopping criterium in the modified Newton-Raphson method based on the norm of the increment in the form

$$\|\Delta\mathbf{x}\| < \varepsilon, \quad (68)$$

where the norm $\|\cdot\|$ is defined as

$$\|\mathbf{x}\| = \left(\sum_{k=1}^p \left(\sum_{i=1+(k-1)(n+2)}^{n+(k-1)(n+2)} \frac{x_i^2}{N^2} + \frac{x_{k(n+2)-1}^2}{V^2} + \frac{x_{k(n+2)}^2}{U^2} \right) \right)^{\frac{1}{2}} \quad (69)$$

This criterium is not optimal. In some examples the computation was stopped too early. Therefore, following the discussion in Ref. [18], we propose the stopping criterium based on three parameters – increase of function $S^{(p)}$, size of the increment of solution, and the size of the gradient of function $S_{red}^{(p)}$. The modified Newton-Raphson iterations are terminated when all the following conditions hold

$$S^{(p)}(X^{(j)}) - S^{(p)}(X^{(j-1)}) < \Theta_j, \quad (70)$$

$$\|X^{(j)} - X^{(j-1)}\| < \sqrt{\tau} \left(1 + \|X^{(j)}\| \right), \quad (71)$$

$$\|\mathbf{g}(X^{(j)})\|_2 < \sqrt[3]{\tau} \|\nabla S^{(p)}(X^{(j)})\|_2, \quad (72)$$

where

$$\Theta_j = \tau \left(1 + |S^{(p)}(X^{(j)})| \right).$$

Table 1

Parameters of the Peng-Robinson equation of state used in Problems 1–9.

Component	T_{crit} [K]	P_{crit} [bar]	ω [-]
C ₁	190.4	46.0	0.011
H ₂ S	373.2	89.4	0.081
C ₂	305.4	48.8	0.099
C ₃ H ₆	364.9	46.0	0.144
C ₃	369.8	42.5	0.153
iC ₄	408.2	36.5	0.183
nC ₄	425.2	38.0	0.199
nC ₅	469.7	33.7	0.251
H ₂ O	647.3	221.2	0.344

Table 2
Correlation coefficients for evaluation of c_p^{ig} in Problems 1–9. Data taken over from Ref. [22].

Component	α_0	α_1	α_2	α_3
C ₁	19.25	5.213×10^{-2}	1.197×10^{-5}	-1.132×10^{-8}
H ₂ S	31.94	1.463×10^{-3}	2.432×10^{-5}	-1.176×10^{-8}
C ₂	5.409	1.781×10^{-1}	-6.938×10^{-5}	8.713×10^{-9}
C ₃ H ₆	3.710	2.345×10^{-1}	-1.160×10^{-4}	2.205×10^{-8}
C ₃	-4.224	3.063×10^{-1}	-1.586×10^{-4}	3.215×10^{-8}
iC ₄	-1.390	3.847×10^{-1}	-1.846×10^{-4}	2.895×10^{-8}
nC ₄	9.487	3.313×10^{-1}	-1.108×10^{-4}	-2.822×10^{-9}
nC ₅	-3.626	4.873×10^{-1}	-2.580×10^{-4}	5.305×10^{-8}
H ₂ O	32.24	1.924×10^{-3}	1.055×10^{-5}	-3.596×10^{-9}

Table 3
Specifications of Problems 1–4. The reference state for internal energy U is described in the Appendix.

Property [unit]	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

Parameter τ is the prescribed tolerance. In this work we use $\tau = \sqrt{\epsilon}$, where ϵ is the machine precision. In (71) the norm $\|\cdot\|$ denotes the norm defined by equation (69), the norm $\|\cdot\|_2$ in (72) is the standard Euclidean norm.

5.1.5. Summary of the computational algorithm

Now we summarize the essential steps of the algorithm for calculating the equilibrium state of a p -phase system with specified internal energy, volume, and moles.

1. Let U, V, N_1, \dots, N_n assume the values given in the specification. Set $j = 0$ and consider an initial approximation of the phase split $X^{(0)}$

$$X^{(0)} = \left(N_1^{(1)}, \dots, N_n^{(1)}, V^{(1)}, U^{(1)}, \dots, N_1^{(p)}, \dots, N_n^{(p)}, V^{(p)}, U^{(p)} \right)^T. \tag{73}$$

2. Assemble matrix H and vector g using (52) and (50)
3. Evaluate $\Delta X^{(j)} \in \mathbb{R}^{(p-1)(n+2)}$ by solving the system $H\Delta X^{(j)} = -g$ using the modified Cholesky decomposition.
4. Evaluate $\Delta X^{(j)} \in \mathbb{R}^{p(n+2)}$ using $\Delta X^{(j)} = Z\Delta X^{(j)}$, where Z is defined by (49).

Table 4
Results of Problems 1–4. S^I denotes the entropy of the hypothetical single-phase state, while S^{II} denotes the equilibrium entropy of the stable two-phase system. The reference states for internal energy U and entropy S are described in the Appendix.

	Problem 1		Problem 2		Problem 3		Problem 4	
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
U [J]	-544956.214319	-211544.585681	-1510985.753624	-421.846376	-566.777015	-330516.922985	-245807.965175	-390660.034825
V [cm ³]	1502.361229	51366.638771	4165.673900	102.426100	1.562506	80256.537494	3512.626019	6414.083981
N_{C_1} [mol]	0.335680	9.664320	0.930730	0.019270	0.000349	15.099651	3.551418	6.448582
N_{H_2S} [mol]	35.684022	54.315978	98.941685	0.108315	0.037113	84.862887	33.609473	56.390527
T [K]	297.997716	297.997716	298.000861	298.000856	297.996887	297.996887	361.997885	361.997885
P [Pa]	2500170.787203	2500170.787153	2500317.847486	2500317.776275	2500125.243552	2500124.858262	10130505.626170	10130505.626049
μ_{C_1} [J mol ⁻¹]	3303.806129	3303.806129	3303.775622	3303.775371	3303.775698	3303.775686	8352.778379	8352.778379
μ_{H_2S} [J mol ⁻¹]	7051.238967	7051.238967	7051.480304	7051.480059	7051.175471	7051.175450	11536.674427	11536.674427
S^I [J K ⁻¹]	-4847.824318		-7391.709463		-2613.988230		-4579.402758	
S^{II} [J K ⁻¹]	-4335.499136		-7390.326639		-2613.987835		-4579.402147	
Iterations	9		3		3		5	

Table 5
Specifications of Problems 5 and 6. The reference state for internal energy U is described in the Appendix.

Property [unit]	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_{C_5} [mol]	15.9	15.9

5. Find $\lambda^{(j)} > 0$ so that

$$S^{(p)} \left(X^{(j)} + \lambda^{(j)} \Delta X \right) > S^{(p)} \left(X^{(j)} \right) \tag{74}$$

First, set $\lambda^{(j)} = 1$ and test condition (74). If the condition is not satisfied, iterate $\lambda^{(j)} = \lambda^{(j)}/2$, until the condition (74) holds.

6. Update the solution by

$$X^{(j+1)} = X^{(j)} + \lambda^{(j)} \Delta X^{(j)}. \tag{75}$$

7. Check the convergence. If the conditions (70)–(72) are satisfied, terminate the iterations and the vector $X^{(j)}$ is the solution. In the opposite case, set $j = j + 1$ and return to step 2.

6. General UVN-phase equilibrium computation with a-priori unknown number of phases

In the previous section, we have described the computation of phase equilibria for a system with specified internal energy, volume, and moles assuming an a-priori given number of phases p . The number of phases is often unknown and it is the expected result of the computation.

6.1. Phase addition and removal

In Sections 2 and 4, we have described the algorithm for testing single-phase stability at specified internal energy, volume, and moles. As the criterion depends only on the values of pressure, temperature, and chemical potentials (which in the equilibrium system are the same in all phases), the same algorithm can be used for testing stability of a general p -phase equilibrium system. In this situation it is necessary to test stability of only one (arbitrarily

Table 6
Results of Problems 5–6. S^I denotes the entropy of the hypothetical single-phase state, while S^{II} denotes the equilibrium entropy of the stable two-phase system. The reference states for internal energy U and entropy S are described in the Appendix.

	Problem 5		Problem 6	
	Phase 1	Phase 2	Phase 1	Phase 2
U [J]	−15892619.468615	−379886.931385	−150012.775415	174870.975415
V [cm ³]	78647.609580	401197.390420	16232.876572	273147.423428
N_{C_2} [mol]	6.596564	4.203436	0.735307	10.064693
$N_{C_3H_6}$ [mol]	292.574168	68.225832	27.089302	333.710698
N_{C_3} [mol]	122.083040	24.416960	11.174346	135.325654
N_{iC_4} [mol]	214.470841	18.529159	19.334487	213.665513
N_{nC_4} [mol]	219.114563	13.885437	19.881086	213.118914
N_{C_5} [mol]	15.574400	0.325600	1.508810	14.391190
T [K]	299.999735	299.999735	394.998501	394.998501
P [Pa]	700082.833469	700082.833469	4230233.608414	4230233.576530
μ_{C_2} [J mol ^{−1}]	−3805.672092	−3805.672092	−3002.464669	−3002.464675
$\mu_{C_3H_6}$ [J mol ^{−1}]	2997.221501	2997.221501	7239.889856	7239.889846
μ_{C_3} [J mol ^{−1}]	397.265640	397.265640	3882.999701	3882.999692
μ_{iC_4} [J mol ^{−1}]	−445.138790	−445.138790	3964.389004	3964.388995
μ_{nC_4} [J mol ^{−1}]	−1196.477103	−1196.477103	3693.302135	3693.302127
μ_{C_5} [J mol ^{−1}]	−10746.440440	−10746.440440	−6800.367303	−6800.367304
S^I [J K ^{−1}]		−73647.697512		−9052.552759
S^{II} [J K ^{−1}]		−54939.068244		−9052.431373
Iterations		10		5

Table 7
Specifications of Problems 7–9. The reference state for internal energy U is described in the Appendix.

Property [unit]	Problem 7	Problem 8	Problem 9
U [J]	−17008802.6	−4575454.3	−7088052.5
V [cm ³]	401916.6	2209.9	265831.3
N_{C_2} [mol]	10.8	0.0108	10.8
$N_{C_3H_6}$ [mol]	360.8	0.3608	360.8
N_{C_3} [mol]	146.5	0.1465	146.5
N_{iC_4} [mol]	233	0.233	233
N_{nC_4} [mol]	233	0.233	233
N_{C_5} [mol]	15.9	0.0159	15.9
N_{H_2O} [mol]	14	100	200

selected) phase from the equilibrium phase split. As already described at the end of Section 2, the phase stability testing provides a way to introduce a new phase in an unstable equilibrium system so that the total entropy of the new system is higher than the entropy of the equilibrium system. Phase stability testing thus provides an excellent way for initialization of the phase equilibrium calculation.

During the computation of the phase equilibrium in systems at $p \geq 3$ phases, it may happen that one of the phases disappears. This may be consequence of the fact that during computation of the phase equilibrium in a $(p-1)$ -phase system, the algorithm has converged to the local maximum only, and therefore, there exists an $(p-1)$ -phase state with higher entropy than the computed state. For this reason, the algorithm must involve a test whether some of the current phases should be removed. We use the following criterion for the phase removal. A phase k is removed when

$$\frac{V^{(k)}}{V^*} < \sqrt{\varepsilon}, \quad (76)$$

where ε is the machine precision. If this condition is satisfied for some k , we remove the phase from the system, split uniformly its internal energy, volume, and moles among the remaining phases, and continue the computation using the $(p-1)$ -phase UVN-flash.

The proposed algorithm ensures increase of the entropy in each iteration (including the steps in which the number of phases is

changing). Thanks to this property, the convergence towards the trivial solution is avoided, which is not the case of some other methods available in the literature (see e.g. Refs. [1,2,4]).

6.2. General strategy for the UVN-phase equilibrium calculation

As we do not know the number of phases a-priori, we start with $p = 1$, and we will consecutively add and remove phases until the phase stability test indicates the stable phase split.

0. Let $U^*, V^*, N_1^*, \dots, N_n^*$ be given. Set $p = 1$.
1. Test the stability of the p -phase split. If the state is stable, terminate the algorithm.
2. If the state is unstable, increase the number of phases by one. Introduce the new phase using the strategy described in Section 2.
3. Evaluate the equilibrium state in the system with p phases using the algorithm from Section 5. Use the resulting trial phase from the stability testing for constructing the initial approximation of the solution.
4. Test if for some phase $\frac{V^{(k)}}{V^*} < \sqrt{\varepsilon}$. If yes, remove the pertinent phase and decrease the number of phases by one.
5. Repeat the steps 1–4, until the stability test indicates the stable state.

7. Numerical examples

We have implemented the algorithms described above in C++. In the following section, we report results of the code that were computed using examples available in the literature, and also our own test problems.

7.1. Examples from paper [14]

In this section we test our algorithm on all examples from paper [14]. Parameters of all components used in Problems 1–9 are given in Table 1. Values of the correlation coefficients for the molar heat capacity at c_p^{ig} are presented in Table 2.

Table 8 Results of Problems 7–9. Iterations X + Y means X iterations in the 2-phase and Y iterations in the 3-phase UVN-flash calculations. S^l denotes the entropy of the hypothetical single-phase state, while S^u denotes the equilibrium entropy of the stable two- or three-phase system, respectively. The reference states for internal energy U and entropy S are described in the Appendix.

	Problem 7			Problem 8			Problem 9		
	Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3
U [J]	-13481.947036	-16692030.289355	-303290.363609	-4556984.999158	-18469.300842	-4248079.288176	-3197022.030237	99659.564416	357048.818413
V [cm ³]	6.272850	81021.288073	320889.039078	2120.250219	89.649781	2558.556768	99659.564416	5.516386	163613.178816
N_{C_1} [mol]	0.000000	7.247817	3.552183	0.000032	0.010768	0.000813	5.516386	151.683155	5.282801
N_{C_2} [mol]	0.000000	306.177159	54.622840	0.000173	0.360627	0.013817	209.103028	86.413985	60.083721
N_{C_3} [mol]	0.000000	127.045435	19.454565	0.000014	0.146486	0.002294	150.396122	82.603483	78.241932
N_{C_4} [mol]	0.000000	218.558557	14.441443	0.000000	0.233000	0.000395	11.577650	4.322345	28.819505
N_{nC_4} [mol]	0.000000	222.262356	10.737644	0.000001	0.232999	0.000684	59.314485	392.998062	4000181.828791
N_{nC_3} [mol]	0.000000	15.651320	0.248680	0.000000	0.015900	0.000005	392.998062	4000181.828791	-2911.962428
N_{H_2O} [mol]	0.295804	13.205980	0.498216	99.985323	0.014677	111.866010	7042.451019	3674.467867	7042.451019
T [K]	299.999610	299.999610	299.999610	300.024831	300.024831	300.024831	392.998062	392.998062	392.998062
P [Pa]	700079.813661	700079.562268	700079.562267	1018719.106609	1018719.108927	4000181.828793	4000181.828793	4000181.828793	4000181.828791
μ_{C_1} [J mol ⁻¹]	-3666.963414	-3666.963422	-3666.963422	-2928.755308	-2928.755272	-2911.962428	-2911.962428	-2911.962428	-2911.962428
μ_{C_2} [J mol ⁻¹]	3001.678870	3001.678922	3001.678922	3165.466979	3165.466979	7042.451019	7042.451019	7042.451019	7042.451019
μ_{C_3} [J mol ⁻¹]	383.559360	389.822378	389.822378	501.933729	501.933729	3674.467867	3674.467867	3674.467867	3674.467867
μ_{C_4} [J mol ⁻¹]	-507.024620	-507.024327	-507.024327	-584.801381	-584.801380	3526.187438	3526.187438	3526.187438	3526.187438
μ_{nC_4} [J mol ⁻¹]	-1278.467315	-1277.812907	-1277.812907	-1397.224869	-1397.224869	3147.780938	3147.780938	3147.780938	3147.780938
μ_{nC_3} [J mol ⁻¹]	-10963.269047	-10858.073503	-10858.073503	-11050.066041	-11050.066040	-7673.646488	-7673.646488	-7673.646488	-7673.646488
μ_{H_2O} [J mol ⁻¹]	-8731.106730	-8731.106738	-8731.106738	-8721.253771	-8721.253897	1691.295413	1691.295413	1691.295413	1691.295413
S^l [J K ⁻¹]	-75123.865978	-75123.865978	-75123.865978	-12337.725969	-12337.725969	-12420.400838	-12420.400838	-12420.400838	-12420.400838
S^u [J K ⁻¹]	-57057.389544	-57057.389544	-57057.389544	17	17	8 + 6	8 + 6	8 + 6	8 + 6
Iterations	15 + 13	15 + 13	15 + 13	17	17	8 + 6	8 + 6	8 + 6	8 + 6

Table 9

Problem 7: Result of the single-phase stability testing – values presented are the concentrations and internal energy density of a trial phase that maximizes function D , the value of D at this state, and the number of iterations in the UVN-stability test. The reference state for internal energy U is described in the Appendix.

c_{C_2} [mol m ⁻³]	0.000003
$c_{C_3H_6}$ [mol m ⁻³]	0.000011
c_{C_3} [mol m ⁻³]	0.000000
c_{nC_4} [mol m ⁻³]	0.000000
c_{nC_3} [mol m ⁻³]	0.000000
c_{H_2O} [mol m ⁻³]	50790.652384
u [J m ⁻³]	-3029929171.784120
D [Pa K ⁻¹]	9790660.167058
Iterations	124

7.1.1. Mixture of C_1 and H_2S

In the first set of examples we consider a binary mixture of methane (C_1) and hydrogen sulfide (H_2S). The binary interaction parameter between C_1 and H_2S is $\delta_{C_1-H_2S} = 0.083$. Four different specifications are given in Table 3. According to [14], these specifications were chosen so that large amounts of both (vapor and liquid) phases are present in equilibrium in Problem 1, specifications of Problems 2 and 3 lead to states close to the bubble and dew points, respectively, while the solution of Problem 4 is close to the critical point. All four problems have been solved using our method. Results are given in Table 4 in which we report the phase split properties together with values of pressure, temperature, and chemical potentials of all components in each phase. These data allow to check whether the iterations have converged towards the equilibrium state. We also provide values of entropy of the hypothetical single-phase state, the total entropy of the phase split, and the numbers of iterations needed for convergence.

The match of our results and the results given in Ref. [14] is quite satisfactory. The numbers of iterations needed for convergence are either the same or lower in our method than those reported in Ref. [14], but these numbers depend on the stopping criterion. Interestingly, in Problem 4, which is deemed to be close-critical, convergence is achieved in 5 iterations only. Unlike in Ref. [14], our method does not need any estimates of the pressure and temperature. Instead, it constructs an initial guess for 2-phase flash calculation using the UVN-phase stability analysis. In Problems 1–4, stability detects the two-phase state using one initial guess only and provides an initial guess for the UVN-phase equilibrium calculation. Iterations reported in Table 4 count iterations of the modified Newton method in UVN-flash calculation using this single

Table 10

Problem 7: Initial 2-phase split for 2-phase UVN-phase equilibrium calculation constructed using the single-phase stability analysis. S^l denotes the entropy of the two-phase split, while S^u is the entropy of the hypothetical (unstable) single-phase state. The reference states for internal energy U and entropy S are described in the Appendix.

	Phase 1	Phase 2
U [J]	-594618.569807	-16414184.030193
V [cm ³]	196.248340	401720.351660
N_{C_2} [mol]	0.000000	10.800000
$N_{C_3H_6}$ [mol]	0.000000	360.800000
N_{C_3} [mol]	0.000000	146.500000
N_{nC_4} [mol]	0.000000	233.000000
N_{nC_3} [mol]	0.000000	233.000000
N_{C_5} [mol]	0.000000	15.900000
N_{H_2O} [mol]	9.967581	4.032419
S^l [J K ⁻¹]		-73383.490865
S^u [J K ⁻¹]		-75123.865978

Table 11

Problem 7: 2-phase split obtained from the 2-phase UVN-flash equilibrium calculation. The reference states for internal energy U and entropy S are described in the Appendix.

	Phase 1	Phase 2
U [J]	-819369.896249	-16189432.703751
V [cm ³]	275.324119	401641.275881
N_{C_2} [mol]	0.000000	10.8
$N_{C_3H_6}$ [mol]	0.000000	360.8
N_{C_3} [mol]	0.000000	146.5
N_{iC_4} [mol]	0.000000	233.0
N_{nC_4} [mol]	0.000000	233.0
N_{C_5} [mol]	0.000000	15.9
N_{H_2O} [mol]	14.000000	0.0000
T [K]	145.637031	145.637031
P [Pa]	-5338578.032320	-5338578.032331
μ_{C_2} [J mol ⁻¹]	-8212.719344	-8212.719344
$\mu_{C_3H_6}$ [J mol ⁻¹]	-5846.099219	-5846.099170
μ_{C_3} [J mol ⁻¹]	-7640.732298	-7640.731359
μ_{iC_4} [J mol ⁻¹]	-9531.520073	-9531.520028
μ_{nC_4} [J mol ⁻¹]	-9937.110132	-9937.109580
μ_{C_5} [J mol ⁻¹]	-15845.701333	-15845.701333
μ_{H_2O} [J mol ⁻¹]	-31867.132701	-31867.132707
Iterations	15	
S^{III} [J K ⁻¹]	-72803.265597	

Table 12

Problem 7: Result of 2-phase stability testing – values presented are the concentrations and internal energy density of a trial phase that maximizes function D , the value of D at this state, and the number of iterations in the UVN-stability test. The reference state for internal energy U is described in the Appendix.

c_{C_2} [mol m ⁻³]	44.606046
$c_{C_3H_6}$ [mol m ⁻³]	4819.073335
c_{C_3} [mol m ⁻³]	1489.109655
c_{iC_4} [mol m ⁻³]	2262.318729
c_{nC_4} [mol m ⁻³]	5356.898847
c_{C_5} [mol m ⁻³]	636.576083
c_{H_2O} [mol m ⁻³]	0.007316
u [J m ⁻³]	-513216740.034418
D [Pa K ⁻¹]	669527.524959
Iterations	23

initial guess from UVN-stability. Finally, let us point out that our algorithm is fully performed in real arithmetics. On the other hand, in Ref. [14] it is reported that in some cases it is necessary to perform some parts of the algorithm in complex arithmetics.

7.1.2. Liquefied petroleum gas (LPG) mixture

Another two examples from Ref. [14] deal with a 6-component

Table 13

Problem 7: Initial 3-phase split for 3-phase UVN-phase equilibrium calculation constructed using the UVN-stability analysis. S^{III} denotes the entropy of the 3-phase split. The reference states for internal energy U and entropy S are described in the Appendix.

	Phase 1	Phase 2	Phase 3
U [J]	-819369.896249	-3145.279332	-16186287.424419
V [cm ³]	275.324119	6.128560	401635.147322
N_{C_2} [mol]	0.000000	0.000273	10.799727
$N_{C_3H_6}$ [mol]	0.000000	0.029534	360.770466
N_{C_3} [mol]	0.000000	0.009126	146.490874
N_{iC_4} [mol]	0.000000	0.013865	232.986135
N_{nC_4} [mol]	0.000000	0.032830	232.967170
N_{C_5} [mol]	0.000000	0.003901	15.896099
N_{H_2O} [mol]	14.000000	0.000000	0.000000
S^{III} [J K ⁻¹]	-72799.163197		

Table 14

Problem 7: Numbers of iterations needed to achieve convergence in the UVN-phase stability testing and the maximum values of function D for each of 9 initial guesses in testing stability of the final 3-phase equilibrium split.

Initial guess	Iterations	D
1	18	-106.400525
2	19	-106.430255
3	19	-105.906830
4	18	-106.464686
5	18	-106.296797
6	18	-106.369733
7	18	-106.108887
8	30	-0.547776
9	21	-106.098904

Table 15

Parameters of the Peng-Robinson equation of state used in Problem 10.

Component	T_{crit} [K]	P_{crit} [bar]	ω [-]
C ₁	190.56	45.99	0.011
CO ₂	304.14	73.75	0.239

LPG mixture. As in Ref. [14], binary interaction coefficients between all components are set to zero. The specification of Problems 5 and 6 are given in Table 5. Castier [14] reports that in Problem 5, because of appearance of the negative pressure in one part of the computation, his algorithm has to be modified to use the nested loops. Using the UVN-phase stability analysis for the construction of the initial phase split, our method converges directly in 10 iterations in Problem 5 and in 5 iterations in Problem 6. These numbers are the same and lower than those reported in Ref. [14], but they depend on the formulation of the stopping criterion. The resulting

Table 16

Correlation coefficients for evaluation of c_p^{IG} in Problem 10. Data taken over from Ref. [22].

Component	α_0	α_1	α_2	α_4
C ₁	19.25	5.213×10^{-2}	1.197×10^{-5}	-1.132×10^{-8}
CO ₂	19.80	7.344×10^{-2}	-5.602×10^{-5}	-1.715×10^{-8}

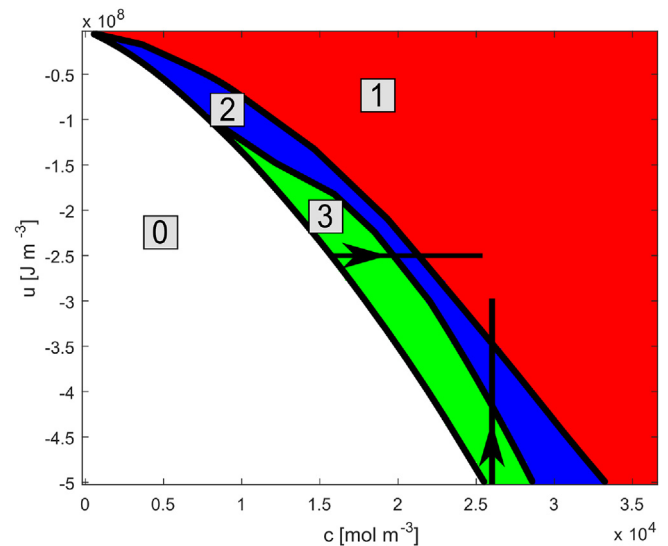


Fig. 1. Approximate boundaries between the single-phase, two-phase, and three-phase domains: mixture of CO₂ and C₁ at constant $z_{CO_2} = 0.452587$ and $z_{C_1} = 0.547413$.

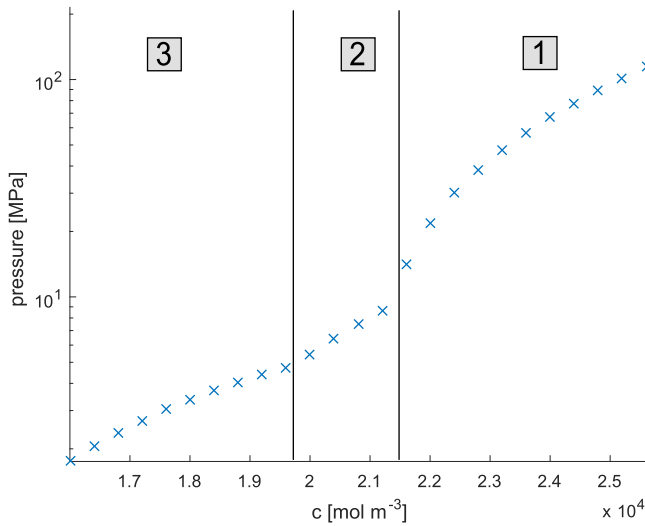


Fig. 2. Equilibrium pressure at $u = -2.5 \times 10^8 \text{ J m}^{-3}$ as a function of the overall molar concentration c : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

phase splits together with values of pressure, temperature, chemical potentials of all components in all phases, values of the entropy in both single-phase and two-phase systems, and the numbers of iterations are given in Table 6.

7.1.3. LPG gas mixture with water

The last three problems from Ref. [14] (denoted as Problems 7–9) deal with the 6 component LPG mixture from the last subsection mixed with water. In agreement with [14], all binary interaction coefficients are set equal to zero. The specifications of the problems are given in Table 7. According to [14], the specifications are chosen so that the Problem 7 leads to a 3-phase vapor-liquid-liquid equilibrium, Problem 8 is a 2-phase liquid-liquid equilibrium, and Problem 9 represents a high-pressure 3-phase equilibrium calculation. Resulting phase splits together with values of pressure, temperature, chemical potentials of all components in all phases, entropies, and numbers of iterations of the

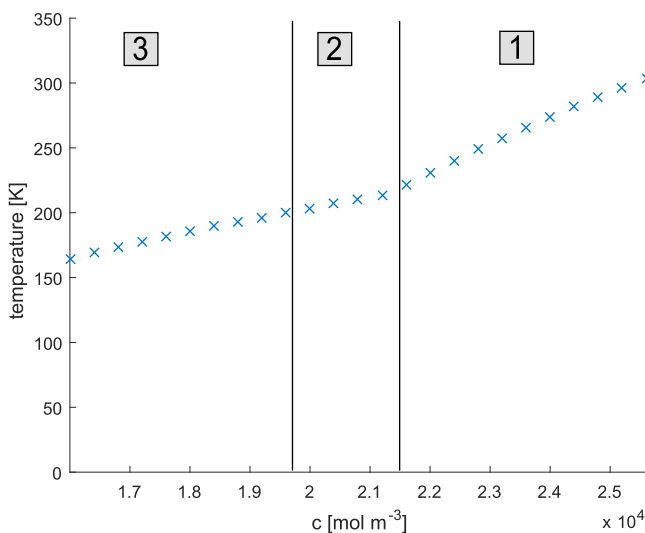


Fig. 3. Equilibrium temperature at $u = -2.5 \times 10^8 \text{ J m}^{-3}$ as a function of the overall molar concentration c : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

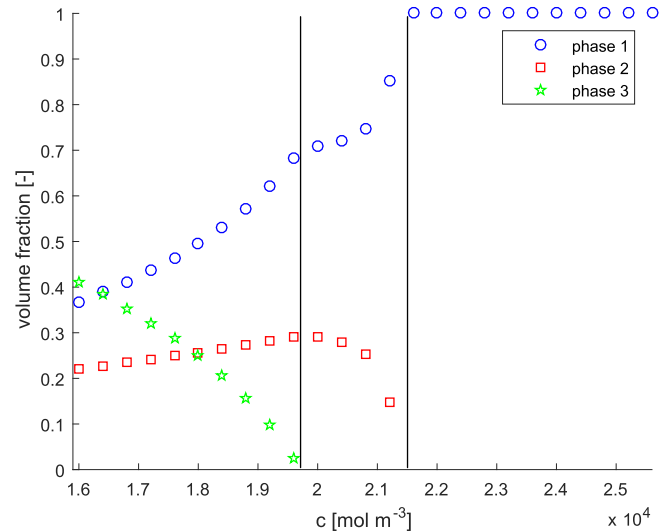


Fig. 4. Volume fractions of the equilibrium phases at $u = -2.5 \times 10^8 \text{ J m}^{-3}$ as functions of the overall molar concentration c : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

modified Newton method in the 2-phase and 3-phase UVN-flash equilibrium calculations are summarized in Table 8. The number of iterations in Problems 8 and 9 are similar (same or lower in our method) to those reported in Ref. [14]. For Problem 7, Castier [14] reports 3 iterations in 3-phase calculation together with 24 outer loop iterations for initial estimates, while we have 15 iterations in 2-phase and 13 iterations in 3-phase UVN-flash equilibrium calculation using a single initial guess provided by the UVN-stability testing algorithm. Let us point out again that unlike in Ref. [14], our approach does not require any initial estimates of the equilibrium pressure and temperature and the whole algorithm proceeds in a straightforward way using the real arithmetics only.

7.1.4. Detailed computation of Problem 7

To demonstrate main features of the UVN-stability analysis and its application in the UVN-phase equilibrium calculation, we present a detailed description of computation for Problem 7 from the

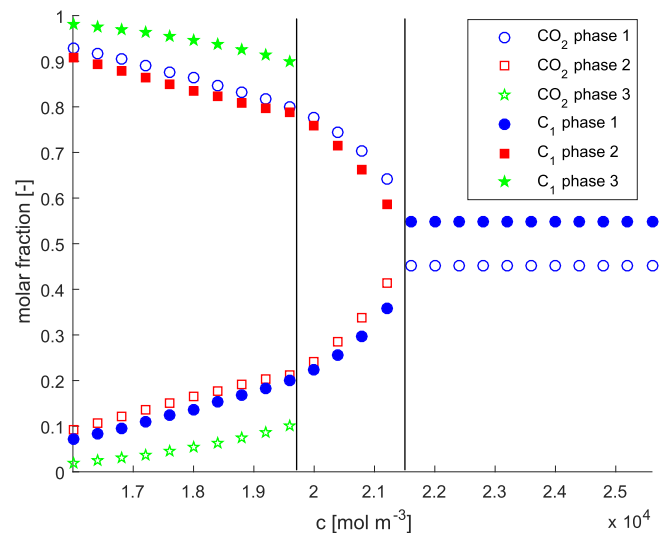


Fig. 5. Molar fractions of all components in all phases at $u = -2.5 \times 10^8 \text{ J m}^{-3}$ as functions of the overall molar concentration c : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

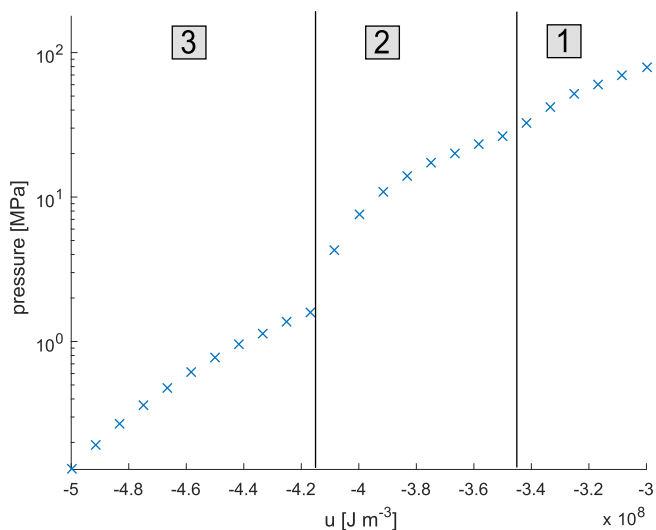


Fig. 6. Equilibrium pressure at $c = 26000 \text{ mol m}^{-3}$ as a function of the internal energy density u : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

previous paragraph. The procedure starts by testing the single-phase stability of the proposed UVN-specification. The stability test indicates the unstable single-phase using only one initial guess (the first guess indicated the phase as unstable, so the other initial guesses are not tested) and needed 124 iterations to converge. The result of stability testing is summarized in Table 9. This result is used for the construction of a two-phase split with higher entropy than that of the single-phase state using the procedure described at the end of Section 2. The initial phase split for two-phase equilibrium calculation is presented in Table 10. Then, the two-phase UVN-flash is performed. In 15 iterations the algorithm converges towards the 2-phase split presented in Table 11. This split is tested for stability (the second phase is tested). The stability test indicates the unstable 2-phase split using the first available initial guess (therefore, other initial guesses are not tested) and needed 23 iterations to converge. The result of two-phase stability testing is summarized in Table 12. This result is used for the construction of an initial three-phase split with higher entropy than that of the two-phase state. The initial phase split for three-phase equilibrium

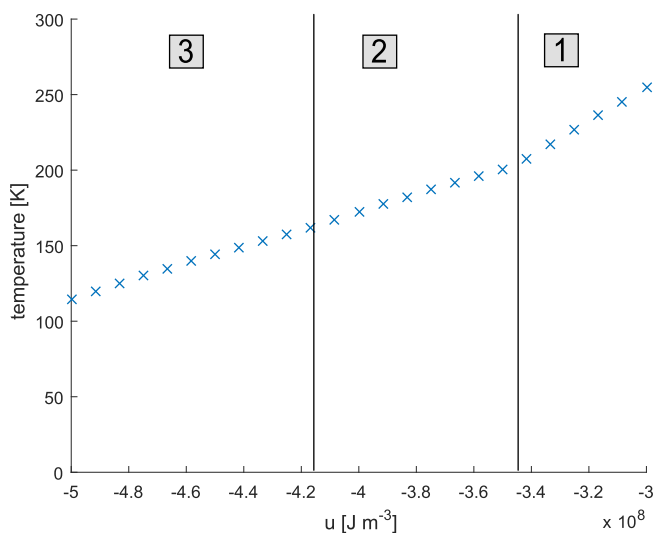


Fig. 7. Equilibrium temperature at $c = 26000 \text{ mol m}^{-3}$ as a function of the internal energy density u : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

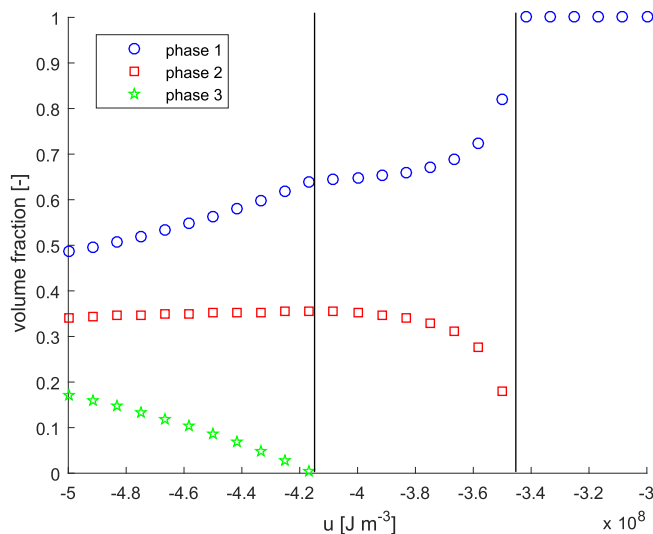


Fig. 8. Volume fraction of equilibrium phases at $c = 26000 \text{ mol m}^{-3}$ as a function of the internal energy density u : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

calculation is presented in Table 13. Then, the three-phase UVN-flash is performed. In 13 iterations the algorithm converges towards the final result presented previously in Table 8. To confirm stability of this 3-phase split, the UVN-phase stability test is performed. We use the reduced number of 9 initial guesses as described in Section 4.2. Numbers of iterations needed to achieve convergence in the UVN-stability testing and the maximum values of function D for each initial guess are summarized in Table 14. As all maximum values of D are negative, the 3-phase split is deemed to be stable and the computation is terminated.

7.2. Mixture of CO_2 and C_1 at various conditions

To demonstrate robustness of our method, we consider a binary mixture of carbon dioxide (CO_2) and methane (C_1) with overall mole fractions $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$. Parameters of the Peng-Robinson equation of state for these components are presented in Table 15. Correlation coefficients for the evaluation of c_p^{ig} are presented in Table 16. The binary interaction coefficient between CO_2 and C_1 is $\delta_{\text{CO}_2-\text{C}_1} = 0.15$. In Fig. 1 we present the

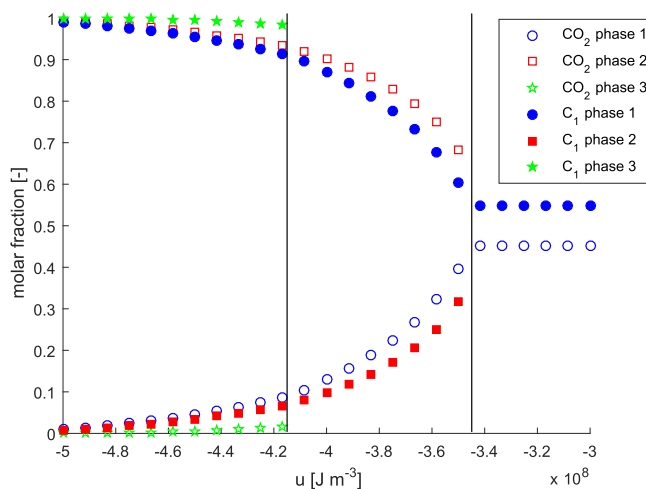


Fig. 9. Molar fractions of all components in all phases at $c = 26000 \text{ mol m}^{-3}$ as a function of the internal energy density u : mixture of CO_2 and C_1 at constant $z_{\text{CO}_2} = 0.452587$ and $z_{\text{C}_1} = 0.547413$.

Table 17

Suggested two-phase split with higher entropy than that of single-phase state for pure CO₂ at $U = -87211375.744478$ J, $V = 1$ m³, and $N_{\text{CO}_2} = 10^4$ mol. The reference states for internal energy U and entropy S are described in the Appendix.

	Phase 1	Phase 2
U [J]	-31246919.908809	-55964455.835669
V [cm ³]	125000.0	875000.0
N_{CO_2} [mol]	2433.647310	7566.352690
S^{II} [J K ⁻¹]	-584220.924005	

number of equilibrium phases and boundaries between the single-phase, two-phase and three-phase subdomains in the u - c domain (i.e. as a function of the internal energy density $u = U/V$ and overall molar concentration of the mixture c assuming that the overall composition of the mixture remains the same). Note that for sufficiently low values of the internal energy U , there may be no temperature corresponding to the given values U , V , and N_1, \dots, N_n . The set of physically reasonable values of U is thus bounded from below. In Fig. 1, the unphysical domain is denoted as 0-phase domain.

Next, we investigate two cases, which are indicated in Fig. 1. First, we study compression of the mixture in a closed vessel while keeping the constant value of the internal energy density $u = -2.5 \times 10^8$ J m⁻³. In Figs. 2–5, we plot the equilibrium pressure of the mixture, equilibrium temperature of the mixture, volume fractions of the phases, and molar fractions of all components in all phases, respectively, as functions of the overall molar density of the mixture. Second, we study heating of the mixture in a closed vessel of constant volume. The total molar density of the mixture is kept constant with $c = 26000$ mol m⁻³. In Figs. 6–9, we plot the equilibrium pressure of the mixture, equilibrium temperature of the mixture, volume fractions of the phases, and molar fractions of all components in all phases, respectively, as functions of the internal energy density u .

7.3. A single-component fluid

In the last example we investigate phase equilibrium of pure CO₂. We consider volume $V = 1$ m³ containing $N_{\text{CO}_2} = 10^4$ mol of CO₂ with internal energy $U = -87211375.744478$ J. Parameters of the Peng-Robinson equation of state and correlation coefficients for the evaluation of c_p^{lg} for CO₂ are presented in Tables 15 and 16. The single-phase stability test indicates that CO₂ is unstable using the first initial guess and the test needed 71 iterations to converge with the final value of $D = 4608.218797$ Pa K⁻¹ attained for $c' = 19469.178481$ mol m⁻³, and $u' = -249975359.270471$ J m⁻³. Then, an initial phase split with higher entropy than that of the single-phase state is constructed, see Table 17. This two-phase split is then used as an initial guess in two-phase flash equilibrium calculation, which converges in 8 iterations to the final two-phase

Table 18

Equilibrium phase split for pure CO₂ at $U = -87211375.744478$ J, $V = 1$ m³, and $N_{\text{CO}_2} = 10^4$ mol. The reference states for internal energy U and entropy S are described in the Appendix.

	Phase 1	Phase 2
U [J]	-70337586.354061	-16873789.390417
V [cm ³]	518716.380364	481283.619636
N_{CO_2} [mol]	7181.961116	2818.038884
T [K]	299.040785	299.040785
P [Pa]	6570486.596964	6570486.595448
μ_{CO_2} [J mol ⁻¹]	9384.232798	9384.232798
S^{I} [J K ⁻¹]	-584388.217059	
S^{II} [J K ⁻¹]	-583476.321606	
Iterations	8	

equilibrium state that is presented in Table 18. Note that the computation of the UVN-phase equilibrium for the single-component fluid proceeds without problems in the same way as for the multi-component mixture. This is not the case of the UVN-flash presented in Ref. [12], where the single-component case required special treatment.

8. Discussion and conclusions

In this work, we have proposed algorithms for the phase stability testing and phase equilibrium calculation for multicomponent mixtures with prescribed internal energy, volume, and molar numbers of individual components which can split to an arbitrary number of phases. As the number of phases is not necessarily known a-priori, the proposed strategy is based on the repeated UVN-phase stability testing and UVN-phase-split calculation until a stable state is found. The proposed algorithm has been tested on a number of examples that were available in the literature, and also on our own problems. In all cases, the algorithm proceeded without difficulties and has found a sequence of states with increasing value of the total entropy converging towards an equilibrium state consisting up to three phases. Thanks to this property, convergence towards the trivial solution does not occur. Using the initial guess in the UVN-flash from the UVN-stability analysis allows to avoid the need for estimates of the pressure and temperature of the system which were required in the previous works [12,14]. Compared to the previous works, the computational algorithm is much simplified, treats both single-component and multi-component mixtures in the same way, and can be performed in real arithmetics only. The numerical difficulties mentioned in Ref. [14], which required some parts of the algorithm to be performed in the complex arithmetics, are thus avoided.

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Appendix

We use the Peng-Robinson equation of state [21] in the following form

$$p^{(EOS)}(T, V, N_1, \dots, N_n) = \frac{NRT}{V - Nb} - \frac{a(T)N^2}{V^2 + 2bNV - N^2b^2}. \quad (77)$$

The parameters a, b of the Peng-Robinson equation of state are defined as

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}, \quad (78)$$

$$a_{ij} = (1 - \delta_{i-j}) \sqrt{a_i a_j}, \quad (79)$$

$$a_i(T) = 0.45724 \frac{R^2 T_{i,crit}^2}{P_{i,crit}} \left[1 + m_i \left(1 - \sqrt{T_{i,r}} \right) \right]^2, \quad (80)$$

$$b = \sum_{i=1}^n x_i b_i, \quad (81)$$

$$b_i = 0.0778 \frac{RT_{i,crit}}{P_{i,crit}}, \quad (82)$$

$$m_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 & \omega_i < 0.5, \\ 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3 & \omega_i \geq 0.5. \end{cases} \quad (83)$$

In the above equations $x_i = N_i/N$ denotes the molar fraction of component i , $N = \sum_{i=1}^n N_i$ is the total number of moles, R is the universal gas constant, δ_{i-j} is the binary interaction coefficient between components i and j , $T_{i,crit}$, and $P_{i,crit}$ are the critical temperature and critical pressure of component i , respectively, $T_{i,r}$ is the reduced temperature defined as $T_{i,r} = \frac{T}{T_{i,crit}}$, and ω_i is the acentric factor of component i .

Expressions for $U = U^{(EOS)}(T, V, N_1, \dots, N_n)$ and $S = S^{(EOS)}(T, V, N_1, \dots, N_n)$ are derived following the procedures described in Refs. [22,23]. The derived expression involves correlation coefficients α_{ik} to estimate the molar heat capacity at constant pressure of component i considered as the ideal gas as

$$c_{p,i}^{ig}(T) = \sum_{k=0}^3 \alpha_{ik} T^k. \quad (84)$$

The superscript ig indicates that the component is considered to be in the ideal gas state. For the Peng-Robinson equation of state we obtain

$$U^{(EOS)}(T, V, N_1, \dots, N_n) = N \frac{T \partial_T(a) - a}{2\sqrt{2}b} \ln \left| \frac{V + (1 + \sqrt{2})bN}{V + (1 - \sqrt{2})bN} \right| - NR(T - T_0) + \sum_{i=1}^n N_i \sum_{k=0}^3 \alpha_{ik} \frac{T^{k+1} - T_0^{k+1}}{k+1} + Nu_0, \quad (85)$$

and

$$S^{(EOS)}(T, V, N_1, \dots, N_n) = NR \ln \left| \frac{V - bN}{V} \right| + N \frac{\partial_T(a)}{2\sqrt{2}b} \ln \left| \frac{V + (1 + \sqrt{2})bN}{V + (1 - \sqrt{2})bN} \right| + R \sum_{i=1}^n N_i \ln \frac{VP_0}{N_i RT} + \sum_{i=1}^n N_i \int_{T_0}^T \frac{c_{p,i}^{ig}(\xi)}{\xi} d\xi, \quad (86)$$

where ∂_T denotes the partial derivative with respect to T , $T_0 = 298.15$ K, $P_0 = 1$ bar, and $u_0 = u(T_0, P_0) = h(T_0, P_0) - RT_0 = -2478.95687512$ J mol⁻¹. This reference state for the internal energy was chosen so that the molar enthalpy of the ideal gas $h(T, P)$ obeys $h(T_0, P_0) = 0$. The molar entropy of pure component i as an ideal gas at temperature T_0 and pressure P_0 is equal to zero.

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