

Calculation of phase equilibria for multi-component mixtures using highly accurate Helmholtz energy equations of state



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ABSTRACT

To test the thermodynamic stability and to determine the equilibrium phase compositions in case the original phase is found unstable is one of the greatest challenges associated with calculating thermodynamic properties of multi-component mixtures. The minimization of the tangent plane distance function is a widely used method to check for stability, while different approaches can be chosen to minimize the Gibbs energy in order to find the phase equilibrium. While these two problems have been applied to several different thermodynamic models, very little work has been published on such algorithms using multi-parameter Helmholtz energy equations of state. In this work, combined stability and flash calculation algorithms at given pressure and temperature (p, T), pressure and enthalpy (p, h), and pressure and entropy (p, s) are presented. The algorithms by Michelsen et al. (1982, 1982, 1987) are used as basis and are adapted to multi-parameter Helmholtz energy models. In addition, a robust and sophisticated density solver is proposed which is necessary for the calculation of properties from the Helmholtz energy model at given state variables other than temperature and density. All partial derivatives necessary to solve the isothermal, isenthalpic and isentropic flash problems using numerical methods based on the Jacobian matrix are derived analytically and given in the supplementary material to this article. Results for some multi-component systems using the GERG-2008 model (Kunz and Wagner, 2012) are shown and discussed.

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1. Introduction

The analysis of the stability of a mixture at given conditions and phase equilibrium calculations were in the focus of research over the past decades and still continue to be important problems in thermodynamics. To ensure thermodynamic stability, the total state functions $G(T, p, \bar{n})$, $A(T, V, \bar{n})$, $U(S, V, \bar{n})$, and $H(S, p, \bar{n})$ have to be at the global minimum. Hence algorithms are needed to minimize the state functions for any given mixture. Depending on the application, different demands may be formulated for such algorithms. In general a compromise for the contradictory goals of developing a fast and efficient but likewise reliable and stable algorithm has to be found. Various algorithms have been proposed to solve this kind of problem, all of them having advantages and shortcomings. The published algorithms may be split into two sub-categories: stochastic and deterministic algorithms. Deterministic algorithms (see e.g. [1–4]) utilize a separate

stability analysis and continue solving the phase equilibrium problem. Stochastic algorithms (e.g. [5–8]) minimize the state function by applying a global optimization method.

In addition to the different types of algorithms the type of the equation of state has to be considered when choosing a solution method. Some of the algorithms proposed have been designed to simplify calculations using a specific type of equation (cubic equations of state (EOS), g^E models, etc.). However, only few methods have been designed and tested for multiparameter fundamental EOS explicit in the Helmholtz energy [9]. Kunz et al. [4] described the basic principles of treating phase equilibria for mixtures using Helmholtz EOS and the method of Michelsen [2,3] in combination with analytical derivatives needed to solve the phase equilibrium conditions. This method was taken as a basis in this work; corresponding algorithms were reformulated in conjunction with the development of a new thermodynamic property program library, and extended for isentropic and isenthalpic flash calculations using analytical derivatives. Furthermore, methods are presented to predict the stability of mixtures modeled with Helmholtz EOS based on given temperature and pressure, pressure and enthalpy, and pressure and entropy.

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2. Helmholtz equations of state

Many models for thermodynamic properties of mixtures may be found in the literature. Most of these models are based on equations of state for the fluid phase(s) of pure substances. Cubic equations of state (e.g. [10–12]) with various modifications (e.g. the CPA [13] or PSRK [14] models) are most commonly used to describe phase equilibria. For this kind of equations, different approaches to model mixtures exist. Either rather simple linear or quadratic mixing rules may be applied to the parameters of the EOS or more complex mixing rules like (modified) Huron-Vidal mixing rules [15] may be chosen.

However, the models mentioned above have some weaknesses with regard to the accuracy of calculated thermodynamic properties [16], particularly at dense homogeneous states. For pure substances these problems may be overcome by using fundamental equations of state explicit in the reduced Helmholtz energy [17–19]. These equations typically comprise an ideal gas part and an empirically determined residual part:

$$\frac{a(T, \rho)}{RT} = \alpha(\tau, \delta) = \alpha^o(\tau, \delta) + \alpha^r(\tau, \delta) \quad (1)$$

where δ is the reduced density and τ is the inverse reduced temperature. It is

$$\delta = \frac{\rho}{\rho_c} \quad \text{and} \quad \tau = \frac{T_c}{T} \quad (2)$$

In recent times these models have been extended to mixtures. Based on the work of Tillner-Roth [20], Lemmon and Tillner-Roth [21], and Lemmon and Jacobson [22], Kunz and Wagner [16] developed the GERG-2008 equation of state for natural gases and other mixtures. The basic idea of this model is to combine highly accurate equations of state in the Helmholtz energy using an extended corresponding states principle. The equation for the mixture reads:

$$\alpha(\tau, \delta, \bar{x}) = \alpha^o(T, \rho, \bar{x}) + \alpha^r(\tau, \delta, \bar{x}) \quad (3)$$

where δ is the reduced density and τ is the inverse reduced temperature according to

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \quad \text{and} \quad \tau = \frac{T_r(\bar{x})}{T} \quad (4)$$

with the reducing functions T_r and ρ_r as functions of the composition. The mixing rules read:

$$\frac{1}{\rho_r(\bar{x})} = \sum_{k=1}^N x_k^2 \frac{1}{\rho_{c,k}} + \sum_{k=1}^{N-1} \sum_{m=k+1}^N c_{\rho,km} f_{\rho,km}(x_k, x_m), \quad \text{with} \quad f_{\rho,km}(x_k, x_m) = x_k x_m \frac{x_k + x_m}{\beta_{\rho,km}^2 x_k + x_m} \quad \text{and} \quad c_{\rho,km} = 2\beta_{\rho,km} \gamma_{\rho,km} \frac{1}{8} \left(\frac{1}{\rho_{c,k}^{1/3}} + \frac{1}{\rho_{c,m}^{1/3}} \right)^3$$

$$T_r(\bar{x}) = \sum_{k=1}^N x_k^2 T_{c,k} + \sum_{k=1}^{N-1} \sum_{m=k+1}^N c_{T,km} f_{T,km}(x_k, x_m), \quad \text{with} \quad f_{T,km}(x_k, x_m) = x_k x_m \frac{x_k + x_m}{\beta_{T,km}^2 x_k + x_m} \quad \text{and} \quad c_{T,km} = 2\beta_{T,km} \gamma_{T,km} (T_{c,k} \cdot T_{c,m})^{0.5} \quad (5)$$

The ideal part of the Helmholtz energy for a mixture consisting of N components is given as:

$$\alpha^o(T, \rho, \bar{x}) = \sum_{i=1}^N x_i (\alpha_{o,i}^o(T, \rho) + \ln x_i) \quad (6)$$

where $\alpha_{o,i}^o$ are the pure fluid contributions. The residual part of Eq. (3) is given as

$$\alpha^r(\tau, \delta, \bar{x}) = \sum_{i=1}^N (x_i \alpha_{o,i}^r(\tau, \delta)) + \Delta \alpha^r(\tau, \delta, \bar{x}) \quad (7)$$

where $\alpha_{o,i}^r$ are the residual contributions of the pure fluids and $\Delta \alpha^r(\tau, \delta, \bar{x})$ is an empirical multi-parameter function which can

be used to model mixture properties with higher accuracy or to model complex mixture behavior (for detailed information, see [16] or Appendix A in the supplementary material to this article). Kunz and Wagner [16] demonstrated that this type of model can be used for the very accurate and consistent description of mixture properties. However, the considerable gain in accuracy when using these models comes at the prize of high numerical complexity. It is known that the evaluation of such models is demanding. In the following, a stable algorithm for phase equilibrium calculations based on previously published approaches has been adapted to mixture models based on empirical multiparameter equations of state. New methods for the calculation of the isothermal (p, T), isenthalpic (p, h), and isentropic (p, s) flash are presented.

3. Combined stability analysis and isothermal flash calculation

Given the overall composition \bar{x}_{spec} and the temperature T_{spec} and pressure p_{spec} of a mixture, algorithms for property calculation need to test whether the given phase is stable or whether it splits in two (or more) phases. If the mixture is found to be unstable, flash calculations are performed subsequently.

3.1. Stability analysis

The phase stability calculation algorithm used in this work is based on the formulation by Michelsen [2,3] and [23] and is also described in the GERG-2004 monograph by Kunz et al., Sect. 7.5 [4]. It uses the tangent plane condition of the Gibbs energy of mixing as stability criterion, which was first introduced by Baker et al. [24]. The tangent plane distance function TPD

$$TPD(\bar{w}) = \sum_{i=1}^N w_i [\mu_i(\bar{w}) - \mu_i(\bar{x}_{\text{spec}})] \geq 0, \quad (8)$$

has to be non-negative for any trial phase with the composition \bar{w} to ensure that the initial phase with the composition \bar{x}_{spec} is stable. The expression above can be transformed to a more convenient reduced form, which uses the fugacity coefficients φ_i rather than the chemical potentials μ_i

$$tpd(\bar{w}) = \frac{TPD(\bar{w})}{RT_{\text{spec}}} = \sum_{i=1}^N w_i [\ln w_i + \ln \varphi_i(\bar{w}) - \ln x_{i,\text{spec}} - \ln \varphi_i(\bar{x}_{\text{spec}})]. \quad (9)$$

The relation between the fugacity and the reduced Helmholtz energy is given in Appendix A in the supplementary material (Eq. A.12). The stability check for a thermodynamic system at given T_{spec} and p_{spec} is performed in three steps.

3.1.1. Step 1: Generation of trial phase compositions

Starting with the assumption that two coexisting phases are present, initial estimates of trial phase compositions are generated using the generalized Wilson correlation [25] to calculate K -values for all N components

$$\ln K_i = \ln \frac{P_{c,i}}{P_{spec}} + 5.373(1 + \omega_i) \left(1 - \frac{T_{c,i}}{T_{spec}} \right), \quad i = 1, \dots, N. \quad (10)$$

From the K -values the phase compositions can be calculated using the relation

$$\ln K_i = \ln \frac{x_i''}{x_i'} = \ln \frac{\varphi_i'}{\varphi_i''}, \quad i = 1, \dots, N \quad (11)$$

and the Rachford–Rice equation g :

$$g = \sum_{i=1}^N (x_i'' - x_i') = 0. \quad (12)$$

In order to solve Eq. (12), the following relations between the phase compositions x'' and x' , the feed composition $x_{i,spec}$, the vapor fraction $\beta = n''/n$, where n'' is the molar amount of substance in the gas phase and $n = n' + n''$ is the overall molar amount of substance, and the K -values K_i are used

$$x_i'' = \frac{K_i x_{i,spec}}{1 - \beta(1 - K_i)} \quad \text{and} \quad x_i' = \frac{x_{i,spec}}{1 - \beta(1 - K_i)}, \quad i = 1, \dots, N. \quad (13)$$

When combining Eqs. (12) and (13), the Rachford–Rice equation is expressed as a function of the vapor fraction β and reads:

$$g(\beta) = \sum_{i=1}^N x_{i,spec} \left(\frac{K_i - 1}{1 - \beta(1 - K_i)} \right) = 0 \quad (14)$$

If the rewritten Rachford–Rice equation (Eq. (14)) is evaluated with the Wilson K -values, the resulting vapor fraction does not necessarily fulfill the condition $0 \leq \beta \leq 1$. Therefore, the following checks are performed:

- The Rachford–Rice equation is solved with the assumption that the mixture is at its bubble point ($\beta = 0$). Eq. (14) becomes

$$g(0) = \sum_{i=1}^N x_{i,spec} (K_i - 1)$$

or $\tilde{g}(0) = \sum_{i=1}^N x_{i,spec} K_i$, with $\tilde{g}(0) = g(0) + 1$. (15)

If $g(0) \leq 0$, respectively $\tilde{g}(0) \leq 1$ holds, the mixture is assumed to be at its bubble point or at a lower temperature, and the phase compositions are calculated according to

$$x_i'' = \frac{x_{i,spec} K_i}{\tilde{g}(0)} \quad \text{and} \quad x_i' = x_{i,spec}, \quad i = 1, \dots, N. \quad (16)$$

- The Rachford–Rice equation is solved with the assumption that the mixture is at its dew point ($\beta = 1$). Eq. (14) becomes

$$g(1) = \sum_{i=1}^N x_{i,spec} \left(1 - \frac{1}{K_i} \right), \quad \text{respectively} \quad \tilde{g}(1) = \sum_{i=1}^N \frac{x_{i,spec}}{K_i},$$

with $\tilde{g}(1) = -g(1) + 1$. (17)

If $g(1) \geq 0$ or $\tilde{g}(1) \leq 1$ holds, the mixture is assumed to be at its dew point or at a higher temperature, and the phase compositions are calculated according to

$$x_i'' = x_{i,spec} \quad \text{and} \quad x_i' = \frac{x_{i,spec}}{K_i \tilde{g}(1)}, \quad i = 1, \dots, N. \quad (18)$$

- If neither of the first two tests leads to initial phase compositions, the mixture is assumed to be in the two-phase region, and Eq. (14) has to be solved iteratively for the vapor fraction β . Once β is found, the test phase compositions can be calculated from Eq. (13).

3.1.2. Step 2: Successive substitution method

Based on the initial estimates of the phase compositions, three steps of successive substitution are performed in order to increase the accuracy of the estimates. The successive substitution has been introduced for the solution of phase equilibria conditions by Prausnitz and Chueh [26]. It includes the following three steps:

- Using the previous estimates for the phase compositions, the fugacity coefficients φ_i'' and φ_i' are calculated from the equation of state.
- New K -values are calculated using the fugacity coefficients and the relation given in Eq. (11).
- From the K -values new phase compositions x_i'' and x_i' and a new vapor fraction β are calculated by solving the Rachford–Rice equation as given in Eq. (14).

3.1.3. Step 3: Tangent plane analysis

If the vapor fraction exceeds the bounds $0 \leq \beta \leq 1$ after the successive substitution steps, the algorithm suggests a stable phase and continues with the tangent plane stability analysis. For $0 \leq \beta \leq 1$, the system is assumed to be unstable and to split into two phases. In this case the difference between the Gibbs energy of the split phases and the feed phase

$$\frac{\Delta G}{nRT} = (1 - \beta) \sum_{i=1}^N x_i' [\ln x_i' + \ln \varphi_i'] + \beta \sum_{i=1}^N x_i'' [\ln x_i'' + \ln \varphi_i''] - \sum_{i=1}^N x_{i,spec} (\ln x_{i,spec} + \ln \varphi_i), \quad (19)$$

will be negative, with $\ln \varphi_i' = \ln \varphi_i(T_{spec}, p_{spec}, \bar{x}')$ and $\ln \varphi_i'' = \ln \varphi_i(T_{spec}, p_{spec}, \bar{x}'')$. Written in terms of tangent plane distances tpd , Eq. (19) reads:

$$\frac{\Delta G}{nRT} = (1 - \beta) tpd' + \beta tpd'', \quad (20)$$

where

$$tpd' = tpd(\bar{x}') = \sum_{i=1}^N x_i' (\ln x_i' + \ln \varphi_i' - \ln x_{i,spec} - \ln \varphi_i) \quad (21)$$

and

$$tpd'' = tpd(\bar{x}'') = \sum_{i=1}^N x_i'' (\ln x_i'' + \ln \varphi_i'' - \ln x_{i,spec} - \ln \varphi_i) \quad (22)$$

are the reduced tangent plane distance functions for the feed composition, using the liquid and vapor compositions as trial phases. If the change of the Gibbs energy according to Eq. (19) is negative, the instability of the feed phase is confirmed and the algorithm continues with the isothermal flash calculation. Even if the change of the Gibbs energy with the two trial phases is positive, but one of the tangent plane distance functions tpd'' or tpd' is negative, the feed is proven to be unstable [4].

In case both tangent plane distance functions tpd' and tpd'' of the initial trial phases and the change in the Gibbs energy $\Delta G/nRT$ are positive, the algorithm continues with a more detailed stability analysis. In principle, the whole composition range needs to be checked for negative tangent plane distances. Since such a multi-dimensional search is impractical for multi-component mixtures another more practical approach was suggested by Michelsen and Mollerup [23]. From the initial Wilson K -values and the feed composition, heavy and light trial phase compositions, $\bar{x}_{\text{trial,H}}$ and $\bar{x}_{\text{trial,L}}$, are calculated from

$$x_{i,\text{trial,H}} = \frac{x_{i,\text{spec}}}{K_i} \quad \text{and} \quad x_{i,\text{trial,L}} = x_{i,\text{spec}} K_i, \quad i = 1, \dots, N. \quad (23)$$

Using each of these initial trial phase compositions as starting point, a successive substitution search for the composition where the tangent plane distance function has a minimum is performed by repeating the following steps a given number of times:

- Calculate the tangent plane distance of the current trial phase $tpd(\bar{x}_{\text{trial},n})$. In the first run ($n = 1$), save the tangent plane distance value as $tpd_{\text{min}} = tpd(\bar{x}_{\text{trial},1})$.
- Compare the values of the tangent plane distances of the current trial phase $tpd(\bar{x}_{\text{trial},n})$ and the minimum trial phase tpd_{min} . If the current value is lower, save it together with the corresponding trial phase composition: $tpd_{\text{min}} = tpd(\bar{x}_{\text{trial},n})$, $\bar{x}_{\text{min}} = \bar{x}_{\text{trial},n}$.
- Calculate the fugacity coefficients $\varphi_{i,\text{trial},n} = \varphi_i(T, p, \bar{x}_{\text{trial},n})$.
- Calculate a new trial phase composition from

$$x_{i,\text{trial},n+1} = x_{i,\text{spec}} \frac{\varphi_i}{\varphi_{i,\text{trial},n}}, \quad i = 1, \dots, N. \quad (24)$$

Here, the index n denotes the n th step in the iteration process. The iteration process has several break criteria:

- The maximum number of iteration steps is reached.
- The value of tpd_{min} becomes negative and thus the feed composition is found unstable. In this case, three more iterations are performed in order to create more accurate initial values for the following flash calculation.
- The change of the trial phase compositions $\bar{x}_{\text{trial},n}$ and $\bar{x}_{\text{trial},n+1}$ becomes very small. This indicates that a stationary point of the tangent plane distance function is found (which does not necessarily have to indicate instability of the feed composition).
- The trial composition $\bar{x}_{\text{trial},n}$ merges with the feed composition \bar{x} . This indicates that in the vicinity of the initial trial phase composition the tangent plane distance function has no local minima and no negative values. In this case the system is most likely stable at the original composition.

Two values for tpd_{min} are returned from the search for stationary points of the tangent plane distance function using both the heavy and the light trial phase compositions as starting points. If one or both of these values are negative, the feed composition is unstable and the algorithm continues with a flash calculation. If both values are positive, the feed composition is assumed to be stable.

3.2. The isothermal two-phase flash

The calculation of an isothermal flash (phase equilibrium calculation at given T_{spec} and p_{spec} and overall composition) is a common procedure in thermodynamics. It relates directly to the thermal, mechanical, and chemical phase stability conditions at equilibrium,

$$\text{Equality of temperatures in both phases} \quad T' = T'' = T_{\text{sat}} \quad (25)$$

$$\text{Equality of pressures in both phases} \quad p' = p'' = p_{\text{sat}} \quad (26)$$

Equality of chemical potential in both phases

$$\mu'_i = \mu''_i = \mu_i, \quad i = 1, \dots, N, \quad (27)$$

where $'$ denotes the saturated liquid phase and $''$ the saturated vapor (or more volatile liquid in case of a liquid–liquid equilibrium). The third equilibrium condition is commonly replaced by the equivalent expression in terms of the fugacities

$$f'_i = f''_i = f_i, \quad i = 1, \dots, N. \quad (28)$$

For a mixture with N components at two-phase equilibrium, $2(N-1)$ unknowns have to be determined, namely the compositions of the first $N-1$ components in each phase of the mixture. The composition of the N th component can be determined by the relation

$$\sum_{i=1}^N x_i = 1 \quad \text{or} \quad x_N = 1 - \sum_{i=1}^{N-1} x_i, \quad (29)$$

which has to be fulfilled for each phase. This concept is well established, see e.g. [1] for the solution of phase equilibria problems. From the chemical equilibrium condition given in Eq. (28), the first N equations can be directly derived

$$F_k = \ln f_i(T_{\text{spec}}, p_{\text{spec}}, \bar{x}') - \ln f_i(T_{\text{spec}}, p_{\text{spec}}, \bar{x}'') = 0, \quad k = i = 1, \dots, N. \quad (30)$$

Note that the logarithm of the fugacities is used to increase the numerical stability for very small and very large values of f_i . The missing $N-2$ equations can be derived from the material balance. For each component i , the material balance $n_i = n'_i + n''_i$ has to be fulfilled, which is directly linked to the definition of the molar vapor fraction. Since the vapor fraction has to have the same value, independent of the component i that is used for its calculation, this relation can be used to form the missing $N-2$ equations according to

$$F_k = \frac{x_{i,\text{spec}} - x'_i}{x''_i - x'_i} - \frac{x_{N-1,\text{spec}} - x'_{N-1}}{x''_{N-1} - x'_{N-1}} = 0, \quad i = 1, \dots, N-2, \quad k = i + N. \quad (31)$$

The resulting set of $2(N-1)$ nonlinear equations $\bar{F}(\bar{X})$ with the same number of unknowns \bar{X} can only be solved numerically by iterative methods, like the Gauß-Newton, Levenberg–Marquardt [27,28] or Powells Dogleg method [29], which shall not be discussed here. However, for the most common numerical methods the Jacobian matrix $\mathbf{J}_{\bar{F}}(\bar{X})$ is needed, which holds the partial derivatives of the system of equations with respect to all unknowns according to

$$\mathbf{J}_{\bar{F}}(\bar{X}) = \begin{pmatrix} \frac{\partial F_1}{\partial x'_1} & \cdots & \frac{\partial F_1}{\partial x'_{N-1}} & \frac{\partial F_1}{\partial x''_1} & \cdots & \frac{\partial F_1}{\partial x''_{N-1}} \\ \vdots & & \vdots & \vdots & & \vdots \\ \frac{\partial F_{2N-2}}{\partial x'_1} & \cdots & \frac{\partial F_{2N-2}}{\partial x'_{N-1}} & \frac{\partial F_{2N-2}}{\partial x''_1} & \cdots & \frac{\partial F_{2N-2}}{\partial x''_{N-1}} \end{pmatrix}. \quad (32)$$

Depending on the thermodynamic mixture model the derivatives of the fugacity $\ln f_i$ with respect to the mole fraction x_j , which are incorporated in the Jacobian, may become quite complex. Kunz et al. [4] avoided these derivatives by approximating the expression

$$\left(\frac{\partial \ln \varphi_i}{\partial x_j} \right)_{T,p,x_k \neq j} \quad (33)$$

with

$$n \left(\frac{\partial \ln \varphi_i}{\partial n_j} \right)_{T,p,n_k \neq j} \quad (34)$$

In this work the analytical derivative given in Eq. (33) was used. Note that the partial derivative with respect to the mole fraction of component j can only be physically reasonable, if the mole fractions are independent variables, which is ensured by the transformation given in Eq. (29). A detailed derivation of all derivatives needed for the isothermal flash problem is given in Appendix A in the supplementary material. The derivatives of the last $N - 2$ equations with respect to the first $N - 2$ mole fractions of the liquid and vapor phase are

$$\frac{\partial F_k}{\partial x'_i} = \frac{x_{i,\text{spec}} - x''_i}{(x''_i - x'_i)^2}, \quad i = 1, \dots, N - 2 \quad \text{and} \quad k = i + N \quad (35)$$

and

$$\frac{\partial F_k}{\partial x''_i} = -\frac{x_{i,\text{spec}} - x'_i}{(x''_i - x'_i)^2}, \quad i = 1, \dots, N - 2 \quad \text{and} \quad k = i + N, \quad (36)$$

respectively. The derivatives of the last $N - 2$ equations with respect to the mole fraction of component $N - 1$ in the liquid and vapor phase are

$$\frac{\partial F_k}{\partial x'_{N-1}} = -\frac{x_{N-1,\text{spec}} - x''_{N-1}}{(x''_{N-1} - x'_{N-1})^2}, \quad k = N + 1, \dots, 2N - 2 \quad (37)$$

and

$$\frac{\partial F_k}{\partial x''_{N-1}} = \frac{x_{N-1,\text{spec}} - x'_{N-1}}{(x''_{N-1} - x'_{N-1})^2}, \quad k = N + 1, \dots, 2N - 2, \quad (38)$$

respectively. All other partial derivatives $\partial F_k / \partial x_j$ are zero.

3.3. Calculation of dew and bubble points

For sake of completeness the system of equations for saturation point calculations and the derivatives needed to solve it with gradient methods like the Newton–Raphson method are also supplied. The calculation of saturation points is an important task in mixture thermodynamics, to e.g. construct the phase envelope of a mixture (see e.g. [30] or [31]) and thus determine the boundary of phase stability for a mixture. The calculation of saturation points at given T_{spec} or p_{spec} only requires the determination of N unknowns for a mixture with N components, namely $N - 1$ mole fractions of the incipient phase and the pressure or temperature, respectively. The system of equations necessary to solve for the unknowns can be set up from the equality of the fugacities of each component in both phases as given in Eq. (30). The Jacobian then includes the derivatives of the equations F_k with respect to the first $N - 1$ mole fractions of the incipient phase plus the derivatives with respect to pressure or temperature. For the calculation of a dew point (with the saturated liquid phase \bar{x}' being the incipient phase) the Jacobian reads

$$\mathbf{J}_{\bar{F}}(\bar{X}) = \begin{pmatrix} \frac{\partial F_1}{\partial x'_1} & \dots & \frac{\partial F_1}{\partial x'_{N-1}} & \frac{\partial F_1}{\partial T} \text{ or } \frac{\partial F_1}{\partial p} \\ \vdots & & \vdots & \vdots \\ \frac{\partial F_N}{\partial x'_1} & \dots & \frac{\partial F_N}{\partial x'_{N-1}} & \frac{\partial F_N}{\partial T} \text{ or } \frac{\partial F_N}{\partial p} \end{pmatrix}. \quad (39)$$

The derivatives of $\ln f_i$ with respect to T and p at constant \bar{x} , which are needed to set up the Jacobian for Helmholtz-type mixture models, are supplied elsewhere [4] and can be taken from Appendix A in the supplementary material. For the calculation of a bubble

point the saturated vapor is the incipient phase. Thus, \bar{x}' must be replaced by \bar{x}'' in Eq. (39).

4. p,h and p,s flash

The calculation of fluid properties of mixtures with the feed composition \bar{x}_{spec} , the enthalpy h_{spec} or the entropy s_{spec} , and the pressure p_{spec} as independent variables is of special importance in process calculations. In these cases none of the natural input variables T and ρ of the equation of state is known and thus a two-dimensional iteration is needed. Still, the system needs to be analyzed for phase stability. Finally, if the system is found to be unstable, a flash calculation has to be performed to find the compositions of the coexisting stable phases. As far as the authors know, these flash calculations have not been described in detail for Helmholtz EOS in literature. Unpublished algorithms to perform p,s and p,h flash calculations are available in the commercially available software REFPROP 9.1 [32] and in the GERG-2004XT08 software [33].

4.1. Stability analysis

The algorithm described in this section is based on the work by Michelsen [34]. In a first step an initial estimate for the temperature T is generated for the specified value q_{spec} by solving the objective function:

$$F_T = q(T, p_{\text{spec}}, \bar{x}_{\text{spec}}) - q_{\text{spec}} = 0 \quad (40)$$

with p_{spec} and \bar{x}_{spec} held constant over the whole temperature search range and q being either the enthalpy h or the entropy s . In order to evaluate Eq. (40) using a Helmholtz equation of state, the density needs to be calculated first as a function of temperature and pressure (see Section 5). Eq. (40) then becomes

$$F_T = q(T, \rho_{Tp}, \bar{x}_{\text{spec}}) - q_{\text{spec}} = 0, \quad \text{with} \\ \rho_{Tp} = \rho(T_{\text{spec}}, p_{\text{spec}}, \bar{x}_{\text{spec}}). \quad (41)$$

For the generation of the temperature estimate the mixture is treated as homogeneous phase. No stability checks are performed for these calculations, hence physically metastable and unstable solutions may occur. When calculating the function $q(T, p_{\text{spec}}, \bar{x}_{\text{spec}})$ at constant p_{spec} and \bar{x}_{spec} , two cases have to be considered. If the pressure is above the maximum pressure, at which two phases are present (*cricondenbar*), the function $q(T, p_{\text{spec}}, \bar{x}_{\text{spec}})$ is continuously increasing with T and differentiable and the solution of Eq. (40) already represents the correct temperature associated with the given pressure and enthalpy or entropy (see Fig. 1 at $p = 10$ MPa for an example). In case the given pressure is below the cricondenbar, the function $q(T, p_{\text{spec}}, \bar{x}_{\text{spec}})$ passes a region where the feed phase is unstable and decomposes into two or more phases. Within this region the function passes a point of inconsistency where it jumps to a higher value, which corresponds to the point where the density jumps from a liquid like density to a vapor like density (see Fig. 1 at $p = 2$ MPa). At the inconsistency the Gibbs energy of the metastable overall phase is the same for the liquid like and the vapor like density solution.

For the solution of the objective function F_T in Eq. (40) the regula falsi method is applied, which does not need any derivatives of F_T . Since this method is an interval search algorithm, a range for q has to be defined, which can be derived from the temperature range of validity of the property model. This search method is advantageous for this application, since it can handle functions that are not defined over the whole search range. In the example (Fig. 1, $p = 2$ MPa) the enthalpy is not defined for values between 5.8 kJ mol^{-1} and 14.7 kJ mol^{-1} . For specified enthalpies

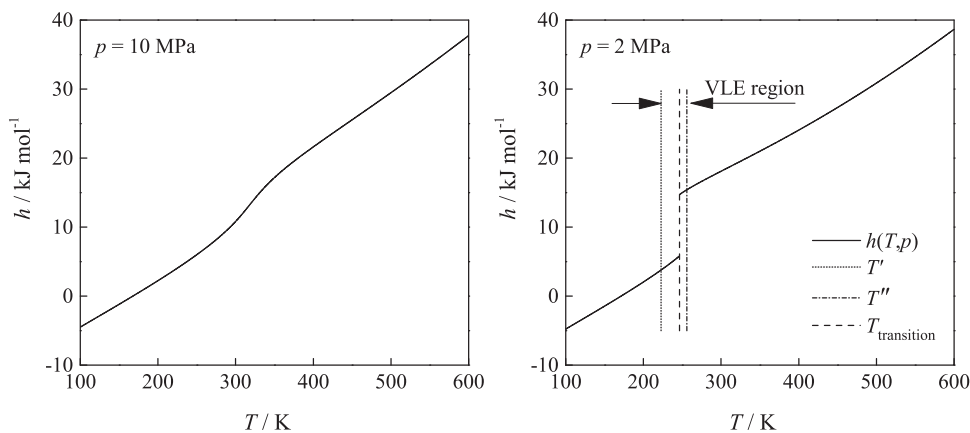


Fig. 1. The molar enthalpy as a function of temperature at constant pressure and composition (no phase stability is considered) for the system methane – ethane (20% methane) at 10 MPa and 2 MPa, calculated with the GERG-2008 [16] model.

h_{spec} within this range, the algorithm returns the transition temperature $T_{\text{transition}}$ as solution. Once the temperature is found, the system is analyzed for stability using the algorithm described in Section 3. If it is found to be unstable the algorithm continues with a flash calculation, using the results of the temperature search and the stability analysis as initial values.

4.2. Flash calculation

For the calculation of two-phase equilibria at given feed composition, enthalpy h_{spec} or entropy s_{spec} , and pressure p_{spec} the number of unknowns to be determined includes compositions of the phases and temperature T . Thus the resulting number of unknowns is $2N - 1$. In order to solve the phase equilibrium condition for this set of unknowns a set of the same number of objective functions is needed, i.e. an additional objective function has to be added to the set of equations given in Eqs. (30) and (31), namely

$$F_{2N-1} = q(T, p_{\text{spec}}, \bar{x}', \bar{x}'') - q_{\text{spec}} = 0, \quad (42)$$

where q_{spec} denotes the value of the specified property (either h or s) and $q(T, p_{\text{spec}}, \bar{x}', \bar{x}'')$ denotes the same property calculated from the equation of state at the current flash conditions according to

$$q(T, p_{\text{spec}}, \bar{x}', \bar{x}'') = \beta \cdot q(T, p_{\text{spec}}, \bar{x}'') + (1 - \beta) \cdot q(T, p_{\text{spec}}, \bar{x}'). \quad (43)$$

The system of equations can be solved again by applying iterative methods. The Jacobian matrix for this flash type reads:

$$\mathbf{J}_{\bar{F}}(\bar{X}_n) = \begin{pmatrix} \frac{\partial F_1}{\partial x'_1} & \cdots & \frac{\partial F_1}{\partial x'_{N-1}} & \frac{\partial F_1}{\partial x''_1} & \cdots & \frac{\partial F_1}{\partial x''_{N-1}} & \frac{\partial F_1}{\partial T} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ \frac{\partial F_{2N-1}}{\partial x'_1} & \cdots & \frac{\partial F_{2N-1}}{\partial x'_{N-1}} & \frac{\partial F_{2N-1}}{\partial x''_1} & \cdots & \frac{\partial F_{2N-1}}{\partial x''_{N-1}} & \frac{\partial F_{2N-1}}{\partial T} \end{pmatrix}. \quad (44)$$

The derivatives needed for the p,s and p,h flash calculations can be taken from Appendix B in the supplementary material.

5. Density solver

The independent variables of the Helmholtz EOS are density ρ , temperature T and the composition of the mixture \bar{x} (see Eqs. (3) and (4)). The given variables for flash calculations are in general T and/or p and the overall (or phase) composition \bar{x} . Thus, a solver for the density at given $T_{\text{spec}}, p_{\text{spec}}$ and \bar{x}_{spec} is required when using equations of state explicit in the Helmholtz energy. The importance of the density solver for flash calculations was already pointed out by Kunz et al. [4]. In this work a stable and reliable routine for the

calculation of density is presented. The function to be solved has the following form:

$$F_{\rho} := p_{\text{spec}} - p(T_{\text{spec}}, \rho, \bar{x}_{\text{spec}}) \\ = p_{\text{spec}} - \rho RT_{\text{spec}} \left(1 + \delta \left(\frac{\partial \alpha^r(\delta, \tau_{\text{spec}}, \bar{x}_{\text{spec}})}{\partial \delta} \right)_{\tau, \bar{x}} \right) = 0, \quad (45)$$

with the specified variables $p_{\text{spec}}, T_{\text{spec}}$, and \bar{x}_{spec} and ρ as unknown variable. For cubic equations of state this function can be solved analytically, but for multi-parameter equations of state explicit in the reduced Helmholtz energy, the objective function F_{ρ} has to be solved numerically using an iterative method (we found the regula falsi method useful).

An important advantage of Helmholtz EOS over cubic EOS is the gain in accuracy for the liquid and liquid like supercritical phase. However, the higher accuracy of Helmholtz models comes at a prize. When T, p (and \bar{x}) are given, cubic EOS return up to three solutions for density, where only the outer density solutions correspond to physically correct solutions representing a gas and a liquid density. On the contrary, Helmholtz models may have multiple loops in the two phase region yielding more than three solutions for density where again only the outermost solutions correspond to physically correct densities.

This behavior results in a much more complex situation with regard to the density search at given p and T (see Fig. 2):

- At pressures close to the saturation pressure p_{sat} , the equation of state used in this example returns five densities corresponding to one pressure and one temperature. The two outermost solutions (I and V) are the two physically correct phase densities. For $p = p_{\text{sat}}$, density I and V correspond to the saturated vapor and saturated liquid density respectively; for $p > p_{\text{sat}}$ only the liquid density is stable and for $p < p_{\text{sat}}$ the vapor density corresponds to the stable phase.
- For pressures above the saturation pressure the density with the highest value (III) corresponds to the physically correct solution.
- For pressures below the saturation pressure the density with the lowest value (I) corresponds to the physically correct solution.

For pure substances the procedure used to find the physically correct solution is rather straight forward, as soon as the two outermost solutions for the density have been found [17]. When it comes to mixtures and especially to flash calculations, finding the correct (or more likely) density becomes much more challenging [4]. In case more than one density root is present at a specified

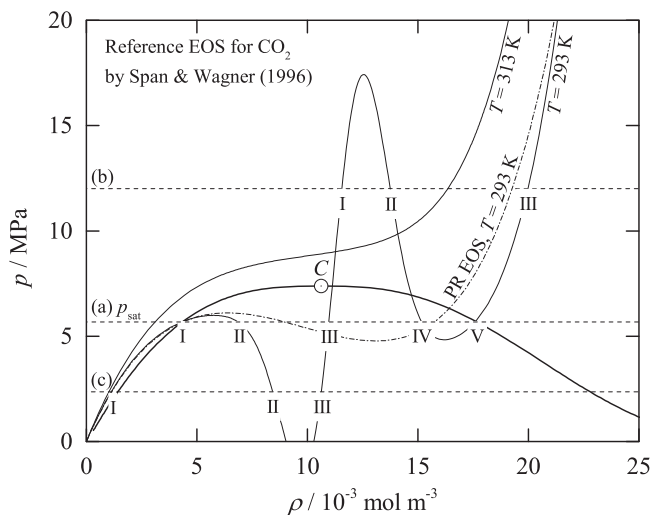


Fig. 2. The problem of multiple density roots at given T and p , using the example of the reference EOS of CO_2 by Span and Wagner [18], compared to the cubic Peng–Robinson equation (PR EOS). The meaning of the roman numbers is explained in the body of the text.

temperature, pressure and composition, the challenge for the density solver is to find and identify the physically most reasonable root. If a good initial estimate is available (e.g. from the previous iteration step in a flash or from phase envelope calculations), this estimate can be used to find a solution to Eq. (45). In case no such estimate is available, an initial estimate is generated from cubic EOS. In most cases this estimate is accurate enough to create a density interval containing the correct root. Otherwise a more elaborate search procedure is mandatory. Since the regula falsi method is an interval search method, the most crucial part is to determine an appropriate search interval that contains exactly one root. In case a vapor density is needed, this is the root to the left of the “first” maximum of the isotherm in a p – ρ diagram (at the lowest density), in case of a liquid density it is the root to the right of the “last” minimum (at the highest density, see Fig. 3).

The advanced root finding algorithm developed in the course of this work uses the following steps to determine the phase density at given temperature, pressure and composition:

1. *Initial root search:* Use an estimated density value (either passed by the calling routine or generated using the SRK equation of state) to create a density interval for an initial density search using the regula falsi method. In case a root is found, continue with step 4.
2. *Stationary point search:* In case a liquid density is required, search for the pressure minimum at the highest density, in case a vapor

density is required, search for the pressure maximum at the lowest density by using the necessary criterion

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}} = 0, \tag{46}$$

as the definition of a stationary point. In order to test the result, the sufficient criteria

$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}} > 0 \tag{47}$$

for a minimum, and

$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}} < 0 \tag{48}$$

for a maximum are applied. The start values for the maximum and minimum search are set to a density close to zero and a very large density (e.g. a multiple of ρ_r or the inverse of the covolume b of a cubic EOS), respectively.

3. *Phase density root search:* Compare the pressures p_{\max} and p_{\min} at the stationary points to the given pressure p_{spec} . For $p_{\text{spec}} < p_{\max}$ a vapor phase density can be calculated at the given temperature, and for $p_{\text{spec}} > p_{\min}$ a liquid phase density can be calculated. The density at the pressure stationary point, ρ_{\max} or ρ_{\min} (note: $\rho_{\min}(T_{\text{spec}}, p_{\min}, \bar{x}_{\text{spec}}) > \rho_{\max}(T_{\text{spec}}, p_{\max}, \bar{x}_{\text{spec}})$, see Fig. 3), respectively, is used as limit for the search interval, since the following conditions apply:

$$0 < \rho(T_{\text{spec}}, p_{\text{spec}}, \bar{x}_{\text{spec}}) < \rho_{\max} \tag{49}$$

for a vapor phase density, and

$$\rho(T_{\text{spec}}, p_{\text{spec}}, \bar{x}_{\text{spec}}) > \rho_{\min} \tag{50}$$

for a liquid phase density. While Eq. (49) can be used as search interval for a vapor phase density without further modifications, the upper limit of the search interval for liquid densities is not defined by physical limits. The limiting factor is here the physically correct extrapolation behavior of the equation of state. Therefore, a user defined maximum density has to be chosen as limit.

With the density search interval determined by this method it is guaranteed that only one physically correct density root exists within the interval. The algorithm continues with the root search using the regula falsi method.

4. *Thermodynamic tests:* A number of tests is performed to make sure that the density root shows physically correct characteristics. In case a liquid like density was searched for, the following conditions have to be fulfilled:

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}} > 0, \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}} > 0. \tag{51}$$

However, roots on the middle branch of a typical subcritical isotherm may fulfill these conditions as well, although they are physically meaningless. Only for a correct liquid density these conditions are also fulfilled for all densities larger than the root. Therefore this check is performed a number of times with increasing densities until a defined maximum density is reached.

All vapor densities must fulfill the following conditions:

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}} > 0, \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}} < 0. \tag{52}$$

Therefore, in order to check if a root is really a vapor density, the root itself and all densities on the same isotherm below this root must fulfill these conditions.

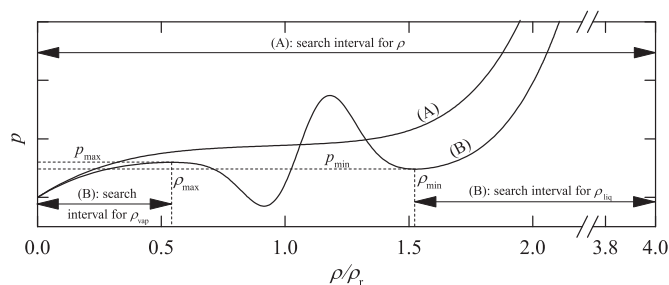


Fig. 3. Determination of search intervals for the density root finding algorithm. (A) Isotherm with only one density root and (B) isotherm with multiple density roots at given p and T .

This root search algorithm returns the physically correct density, as long as the numerical search methods converge and as long as a physically correct root exists. When the density of a certain mixture at given composition, temperature and pressure needs to be determined, e.g. as part of the stability analysis, the phase in which this mixture is stable is usually not known in advance. Consequently, the density solver has to locate all valid density roots and, in case two roots were found, determine the more likely solution. The search strategy for the correct (or more stable) density root includes the following steps:

1. *Liquid phase density search:* The advanced root finding algorithm is used to determine a density root with liquid like characteristics.

2. *Vapor phase density search:* The advanced root finding is used to determine a density root with vapor like characteristics.

For both phases, the search may fail at several points in the search algorithm: the stationary point search fails, no liquid density root exists or the regula falsi method fails, or the density root does not pass the thermodynamic stability test. In case two densities were found, the algorithm continues with step 4; if only one density was found due to a failure, the algorithm continues with step (3.a); if no density was found, it continues with step (3.b).

3. (a) *Second root search:* If only one stationary point was found (the numerical method failed finding the second point) the second stationary point is determined using the regula falsi method. Once the second stationary point is found, the second phase density is determined as described above (steps 3 and 4). If this search also fails, the stationary point found most likely corresponds to an inflection point and thus only one correct root exists and the algorithm is completed. (b) *Single root search:* In case both searches for the pressure minimum and maximum fail, the isotherm of the specified mixture is assumed to be a monotonously increasing function (i.e. supercritical for pure fluids, see Fig. 3). In this case only one density solution exists for a given set of temperature, pressure and composition and the search interval for the density search includes the whole density range up to a user defined maximum density. The actual density search is performed, e.g., using the regula falsi method.

4. *Two density values – Gibbs Energy Criterion:* In case two densities were found in the previous steps, only one density represents a thermodynamically stable phase while the other density represents a metastable state. In this case the density corresponding to the lower Gibbs energy is chosen as the more likely solution. However, since the overall Gibbs energy needs to be at a minimum for a stable system, the density solution corresponding to the lowest Gibbs energy of the phase does not necessarily need to be the stable solution for the phase equilibrium.

6. Results

The algorithm proposed in this work was implemented into computer code and compiled into the thermodynamic property calculation tool TREND 1.1 [35]. The algorithm and the computer code were developed with emphasis on reliability and stability in order to enable the calculation of thermodynamic properties of a wide range of mixtures and states, without prior knowledge of the location of the phase boundaries. Major other software tools that offer the calculation of thermodynamic properties of mixtures from Helmholtz energy mixture models are the GERG-2004XT08 software package developed together with the GERG-2004 and GERG-2008 models [33], and REFPROP [32]. The algorithm used in the GERG-2004XT08 software is partly discussed in the GERG-2004 monograph [4]. While the stability analysis and flash calculation

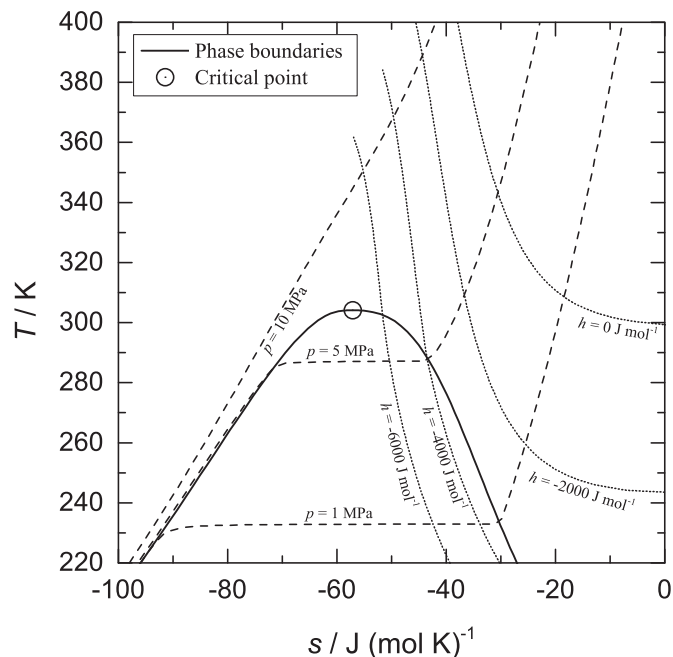


Fig. 4. T,s -diagram for the mixture $x_{\text{CO}_2} = 0.997$, $x_{\text{N}_2} = 0.001$, $x_{\text{O}_2} = 0.001$, and $x_{\text{Ar}} = 0.001$ with selected isobars and lines of constant enthalpy, calculated with the algorithm proposed in this work (TREND 1.1), using the EOS-CG mixture model [36]. The reference state of the pure substances is defined at $T = 298.15$ K and $p = 0.101325$ MPa. At these conditions, the density is calculated by the ideal gas law and the entropy and enthalpy calculated at this density are set to zero.

with temperature and pressure as input are described in detail, the respective algorithms using pressure and enthalpy or pressure and entropy as input – which were introduced in the GERG-2008 extension – have not been published. The REFPROP software uses a different algorithm, which – to our knowledge – has never been published, either. Since the comparison of different software implementations has only limited significance concerning the validation of calculation speed or robustness of a numerical algorithm, the other software tools were merely used for the verification of the calculation results from the algorithm proposed in this work.

The application of the new algorithm is demonstrated in two examples. In the first example, a T,s -diagram was constructed for a CO_2 -rich mixture with nitrogen, oxygen and argon as impurities (molar composition: $x_{\text{CO}_2} = 0.997$, $x_{\text{N}_2} = 0.001$, $x_{\text{O}_2} = 0.001$, and $x_{\text{Ar}} = 0.001$, see Fig. 4). In order to show lines of constant pressure and enthalpy in such a diagram, the calculation of properties with enthalpy and pressure and with entropy and pressure as input is necessary including stability checks, with a subsequent flash calculation for points in the two-phase region. All points on the isolines were calculated independently without prior information on the phase boundaries or initial estimates from the previous point. Fig. 4 shows isobars and lines of constant enthalpy, calculated with the TREND 1.1 software using the EOS-CG mixture model [36]. The new algorithm succeeds in the calculation of all points and returns smooth, consistent values over a wide temperature and entropy range. REFPROP 9.1 returns values identical to those calculated with TREND 1.1 (within numerical tolerance).

In the second example (see Fig. 5), a p,T -diagram was constructed for a typical liquefied natural gas (LNG) mixture (molar composition: $x_{\text{CH}_4} = 0.918$, $x_{\text{N}_2} = 0.008$, $x_{\text{C}_2\text{H}_6} = 0.057$, $x_{\text{C}_3\text{H}_8} = 0.013$, $x_{\text{n-C}_4\text{H}_{10}} = 0.004$). Again, the new algorithm succeeds to calculate all points on a selection of lines of constant enthalpy and entropy, using pressure and enthalpy, or pressure and entropy as input variables for the iterative calculation of temperature. For this mixture both the GERG-2004XT08 software and REFPROP 9.1 were

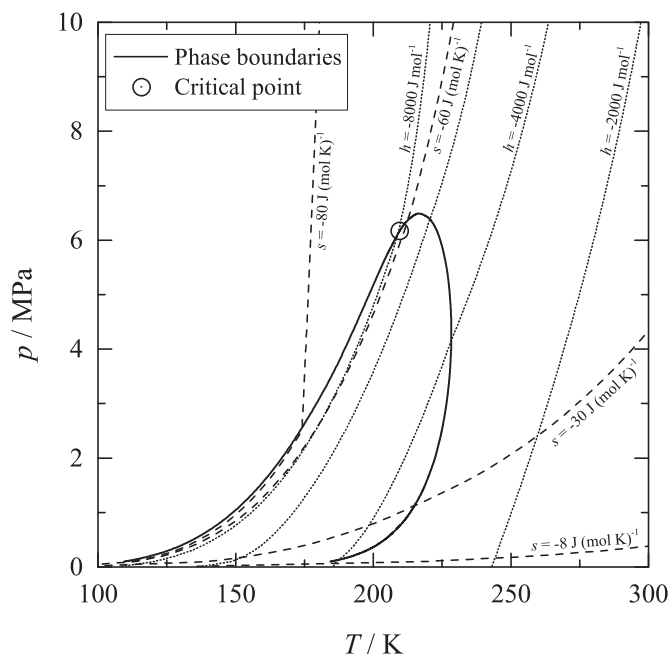


Fig. 5. p,T -diagram for the mixture $x_{\text{CH}_4} = 0.918, x_{\text{N}_2} = 0.008, x_{\text{C}_2\text{H}_6} = 0.057, x_{\text{C}_3\text{H}_8} = 0.013, x_{n\text{-C}_4\text{H}_{10}} = 0.004$ with selected lines of constant enthalpy and entropy, calculated with the new algorithm proposed in this work (TREND 1.1), using the GERG-2008 mixture model.

used as verification. Both calculation tools return identical results to TREND 1.1 (within numerical tolerance).

Beside these two examples the algorithm was tested successfully for a large number of binary and multi-component mixtures, with a focus on systems with large differences in volatilities and complex phase equilibria. Tested systems include water–gas mixtures (showing complex phase behavior including liquid–liquid equilibria), CO_2 -mixtures with inert gases, and multi-component natural gas mixtures with large differences in volatilities resulting from higher-order alkanes and e.g. hydrogen as mixture components. The presented algorithm was successfully applied in fitting a CO_2 hydrate model [37] as well.

7. Conclusions

During the last decades many different algorithms have been proposed to determine the phase stability of multi-component mixtures at various combinations of input variables. Still, no algorithm can be emphasized as the best solution for any kind of problem. Depending on the equations of state used and the kind of application, different demands can be formulated and a sound balance between stability and speed has to be found. However, the choice of a robust algorithm as well as its careful implementation is mandatory to achieve good results in practical work.

The combined stability and flash calculation algorithm proposed by Michelsen [2,3] has proven to be one of the most sophisticated and at the same time practical algorithms that returns reliable results even for complex systems. Kunz and Wagner [4,16] adapted computer code supplied by Michelsen to the requirements of Helmholtz energy mixture models by providing the analytical derivatives of the reduced Helmholtz energy necessary to solve the isothermal flash problem. However, one of the main derivatives needed to set up the Jacobian, the derivative of the fugacity with respect to composition, was replaced by scaled composition derivatives [4].

The new algorithm suggested in this work is essentially based on the same approach but includes some important new elements. The

system of equations describing the isothermal (p,T) flash problem is reformulated in a way that the $N - 1$ first mole fractions become independent variables, and derivatives of the reduced Helmholtz energy with respect to the composition are developed. Algorithms for the isenthalpic (p,h) and for the isentropic (p,s) stability and flash problem proposed by Michelsen [34] are applied to Helmholtz mixture models. All analytical derivatives necessary to solve the p,h and p,s flash with numerical methods using the Jacobian are supplied (see supplementary material, Appendix B). Finally, a robust and sophisticated density solver is presented that addresses the special requirements and problems associated with multi-parameter Helmholtz energy equations of state.

List of symbols

A	total Helmholtz energy
a	molar Helmholtz energy
c_Y	part of the reducing function
EOS	“equation of state” or “equations of state”
F	objective function, weighing factor of the mixture model
f	fugacity
f_Y	part of the reducing function
G	total Gibbs energy
g	molar Gibbs energy, Rachford–Rice equation
H	total enthalpy
h	molar enthalpy
\mathbf{J}	Jacobian matrix
K	K -value
N	number of components in the mixture
n	molar amount of substance
p	pressure
q	function
R	universal gas constant
S	total entropy
s	molar entropy
T	temperature
TPD	tangent plane distance function
tpd	reduced tangent plane distance function
U	total internal energy
V	total volume
v	molar volume
VLE	vapor–liquid equilibrium
\tilde{w}	vector of mole fractions of the emerging phase
w_i	mole fraction of the emerging phase
\tilde{x}	vector of mole fractions
x_i	element i of mole fraction vector
Y_T	reducing function
Z	compressibility factor

Greek letters

α	reduced Helmholtz energy
β	molar vapor fraction
β_Y	reducing function parameter
γ_Y	reducing function parameter
δ	reduced density
μ	chemical potential
ρ	density
τ	inverse reduced temperature
φ	fugacity coefficient
ω	acentric factor

Subscripts

c	critical parameter
min	pressure minimum of an isotherm in the metastable liquid region

max	pressure maximum of an isotherm in the metastable vapor region
<i>o</i>	pure fluid property
<i>p</i>	isobaric
<i>r</i>	reduced variable
sat	property at saturation conditions
spec	property value specified by the user
<i>i, j, k</i>	component indices
δ, τ, x	derivative with respect to the respective variable

Superscripts

<i>E</i>	excess property
<i>o</i>	ideal-gas part of a property
<i>r</i>	residual part of a property
'	property of the saturated liquid
"	property of the saturated vapor

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.fluid.2014.05.012](https://doi.org/10.1016/j.fluid.2014.05.012).

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