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

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A B S T R A C T

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.

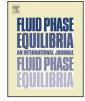© 2014 Elsevier B.V. All rights reserved.

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:

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

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

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

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:

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

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

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

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

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

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

$$\tag{5}$$

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

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

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

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

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 $\bar{x}_{\text{spec}}$ 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

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

has to be non-negative for any trial phase with the composition $\bar{w}$ to ensure that the initial phase with the composition $\bar{x}_{\text{spec}}$ 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

$$tpd(\bar{w}) = \frac{TPD(\bar{w})}{RT_{\text{spec}}}$$

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

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.