Calculation of thermodynamic properties of mixtures in two-phase equilibrium

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Abstract. Thermodynamic properties of mixtures in vapor-liquid equilibrium (VLE) were studied. Thermodynamic properties of the methane-ethane mixtures in VLE were calculated with highly accurate Helmholtz free energy equation of state GERG-2008, simplified GERG-2008 and common cubic PR equation of state (EOS). Results show that GERG-2008 has high accuracy in VLE calculations. However, simplified GERG-2008 and PR-EOS both work unsatisfactorily in VLE calculations.

1. Introduction
Calculation of the thermodynamic properties of mixtures in phase equilibrium is an important element in the modeling of chemical processes such as distillation and extraction. In this article, the stability analysis of a mixture at given temperature, pressure and overall composition was carried out before the phase equilibrium calculations, because the generated initial estimates by the stability analysis can be used for phase equilibrium calculations [1].

The stability analysis is based on the principle that the total Gibbs energy of a mixture at given temperature, pressure and overall composition has to be at the global minimum. Based on this principle, Baker et al. [2] proposed the Gibbs’ tangent plane criterion to test thermodynamic stability, and Michelsen [3] proposed a computational approach based on this tangent plane criterion.

Successive substitution is a commonly used approach in phase equilibrium calculations, but sometimes it doesn’t converge quickly. Therefore, Orbach and Crowe [4] proposed the dominant eigenvalue method, and Crowe and Nishio [5] proposed the general dominant eigenvalue method, in order to improve the convergence efficiency of successive substitution.

In the vicinity of critical point, the convergence rate of successive substitution is very low. Because of this, Michelsen and Mollerup [6] proposed Gibbs energy minimization by the second order method. In this method, the mostly used models are cubic equations of state, but multi-parameter Helmholtz free energy equations of state are rarely used as models. In this work, PR-EOS and GERG-2008, which is a highly accurate Helmholtz energy-based equation of state, were used to calculate thermodynamic properties of the methane-ethane mixtures in VLE. Besides, the influence of the deviation function (see Eq.(3)), which is used to model mixture behavior with higher accuracy, on accuracy of GERG-2008 was also investigated in phase equilibrium calculations.

2. Equation of state for mixtures
The GERG-2008 equation of state is the dimensionless form of the Helmholtz free energy which
includes an ideal gas part and an empirically residual part [7]:

$$\alpha(\delta, r, x) = \alpha^0(\rho, T, x) + \alpha'(\delta, r, x),$$  \hspace{1cm} (1)

where $\alpha$ is the molar composition in a mixture, $\delta$ is the reduced mixture density and $r$ is the inverse reduced mixture temperature.

The ideal-gas part $\alpha^0$ is given by

$$\alpha^0(\rho, T, x) = \sum_{i=1}^{N} x_i [\alpha^0_{oi}(\rho, T) + \ln x_i],$$ \hspace{1cm} (2)

where $\alpha^0_{oi}$ is the reduced Helmholtz free energy in the ideal-gas state of the pure component $i$.

The residual part $\alpha'$ is

$$\alpha'(\delta, r, x) = \sum_{i=1}^{N} x_i \alpha'_{oi}(\delta, \tau) + \Delta \alpha'(\delta, r, x),$$ \hspace{1cm} (3)

where $\alpha'_{oi}$ is the residual part of the reduced Helmholtz free energy of the pure component $i$ and $\Delta \alpha'$ is a deviation function used to model complex mixture behavior.

The simplified GERG-2008, i.e. GERG-2008 without the deviation function (DF), means that Eq. (3) doesn’t include the deviation function $\Delta \alpha'$.

The PR-EOS for mixtures is described in [8], and the binary interaction coefficient is obtained from [9].

3. Phase equilibrium calculation

For a given $n$-component mixture of composition $x(z_1, z_2, ..., z_n)$ at specified temperature $T$ and pressure $p$, the necessary and sufficient condition for stability of this mixture is that the reduced tangent plane distance is non-negative for any trial phase composition $w(z_1, z_2, ..., z_n)$ [3]:

$$\text{tpd}(w) = \sum w_i \left[ \ln w_i + \ln \phi_i(w_i) - \ln w_i + \ln \phi_i(\overline{w}) \right] = \sum w_i \left[ \ln w_i + \ln \phi_i(\overline{w}) - d_i \right],$$ \hspace{1cm} (4)

where $\phi_i$ is the fugacity coefficient of component $i$ and $d_i = \ln z_i + \ln \phi_i(x)$.

The generated initial estimates by the tangent plane criterion can be used for phase equilibrium calculations. The successive substitution is a commonly used method in vapour-liquid equilibrium calculations. However, if the efficiency of the successive substitution decreases, it is recommended to use the Gibbs energy minimization by the second order method [6, 10]. At specified $T$, $p$ and $x$, the VLE calculations can be formulated as

$$\min G(T, p, \overline{v}, x - \overline{v}),$$ \hspace{1cm} (5)

where $G$ is the Gibbs energy and $\overline{v}$ is vapor amounts (per unit feed).

The algorithm for calculating the VLE is described in [11]. In the stability analysis and phase equilibrium calculations, fugacity coefficients and their derivatives are needed. For PR-EOS, the method in [12] is used to calculate these properties. For GERG-2008, all thermodynamic properties of a mixture can be obtained by combining various derivatives of Eq. (1), which is described in detail in [7, 10].

Thermodynamic properties of the methane-ethane mixture at methane mole fraction of 15% in VLE were calculated with the help of PR-EOS, GERG-2008 without DF and GERG-2008. Figure 1 shows that GERG-2008 has high accuracy in predicting molar density of the methane-ethane mixture in VLE. The average relative deviation of molar density predicted by GERG-2008 is much smaller than the average relative deviation of molar density predicted by GERG-2008 without DF and PR-
EOS. Besides, GERG-2008 without DF works better than PR-EOS in prediction of molar density in VLE.

![Graphs](image)

**Figure 1.** Density versus temperature and its average relative deviation from reference data for the methane-ethane mixture at methane mole fraction of 15% in VLE with the help of PR-EOS, GERG-2008 without DF and GERG-2008 at different pressures: (a) 10 bar, (b) 30 bar and (c) 50 bar.

Figure 2 shows that PR-EOS works worse than GERG-2008 and GERG-2008 without DF in predicting enthalpy difference of the methane-ethane mixture in VLE. The average relative deviation of predicted enthalpy difference by GERG-2008 is smaller than the average relative deviation of enthalpy difference predicted by GERG-2008 without DF and PR-EOS.
Figure 2. Enthalpy difference versus temperature and its average relative deviation from reference data for the methane-ethane mixture at methane mole fraction of 15\% in VLE with the help of PR-EOS, GERG-2008 without DF and GERG-2008 at different pressures: (a) 10 bar, (b) 30 bar and (c) 50 bar.

4. Conclusions
In VLE calculations, GERG-2008 is superior to PR-EOS and GERG-2008 without DF. GERG-2008 without DF and PR-EOS both work unsatisfactorily in VLE calculations, but in general GERG-2008 without DF works better than PR-EOS. The deviation function in GERG-2008 (see Eq. (3)) can significantly affect the accuracy of GERG-2008 in VLE calculations.

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