

THERMODYNAMIC PROPERTY CALCULATION IN VAPOR-LIQUID EQUILIBRIUM FOR MULTICOMPONENT MIXTURES USING HIGHLY ACCURATE HELMHOLTZ FREE ENERGY EQUATION OF STATE

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Abstract

Thermodynamic properties of multicomponent mixtures in phase equilibrium were studied. The tangent plane criterion was used for stability analysis, and the Gibbs energy minimization was employed for phase equilibrium calculation when the successive substitution didn't converge. Thermodynamic properties of a 12-component natural gas mixture in vapor-liquid equilibrium were calculated with highly accurate Helmholtz free energy equation of state GERG-2008, simplified GERG-2008 and common cubic Peng — Robinson (PR) equation of state. Results show that in vapor-liquid equilibrium, GERG-2008 has high accuracy and works better than simplified GERG-2008 and PR-equation of state. Simplified GERG-2008 and PR-equation of state both work unsatisfactorily in vapor-liquid equilibrium calculation, especially near the saturation zone. The deviation function in GERG-2008 can significantly affect the accuracy of GERG-2008 when calculating thermodynamic properties of mixtures in vapor-liquid equilibrium

Keywords

Vapor-liquid equilibrium, stability analysis, tangent plane criterion, Helmholtz free energy equation of state, PR-equation of state

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Introduction. Accurate description of thermodynamic properties of natural gas mixtures in vapor-liquid equilibrium is of great significance for many applications involving natural gas, such as natural gas transportation, storage and liquefaction. Equations of state are commonly used to describe phase equilibrium over a wide range of pressure, temperature and mixture composition. Based on equations of state, Michelsen and Mollerup [1] proposed a combined stability analysis and phase equilibrium method to solve the vapor-liquid equilibrium problem for multicomponent mixtures.

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 when the mixture is in the state of thermodynamic stability. Based on this principle, the Gibbs' tangent plane criterion was proposed by

Baker et al. [2] to test thermodynamic stability. However, he didn't give a computational approach. Michelsen [3] proposed a number of numerical methods for stability analysis based on Gibbs' tangent plane criterion. Besides, the use of stability analysis to generate initial estimates for phase equilibrium calculation was also suggested by Michelsen [4]. In phase equilibrium calculation, successive substitution is a simple and major approach to solve the system of phase equilibrium equations. In order to improve convergence efficiency of successive substitution, Orbach and Crowe [5] proposed the dominant eigenvalue method (DEM), and Crowe and Nishio [6] proposed the general dominant eigenvalue method (GDEM), which is more effective than DEM. Successive substitution is convergent in most practical cases; however, in the vicinity of critical point, its convergence rate is very low. In order to solve this problem, Michelsen [4] and Michelsen and Mollerup [1] proposed Gibbs energy minimization by the second order method. This method is also based on the principle that the total Gibbs energy of a mixture at given temperature, pressure and overall composition is at the global minimum. In this method, cubic equations of state are mostly used models, but multi-parameter equations of state explicit in Helmholtz free energy are rarely used as models.

In this work, GERG-2008, which is a highly accurate Helmholtz free energy equation of state, was used to test phase stability of a 12-component natural gas mixture and calculate its thermodynamic properties in vapor-liquid equilibrium. In GERG-2008, a deviation function is used to model mixture behavior with higher accuracy. The influence of this deviation function on accuracy of GERG-2008 was investigated in phase equilibrium calculation. Besides, Peng — Robinson equation of state (PR-EOS) was compared with GERG-2008 in calculating thermodynamic properties of this multicomponent natural gas mixture in vapor-liquid equilibrium.

Equation of state for mixtures. This work involves one highly accurate Helmholtz free energy equation of state GERG-2008 and one cubic PR-EOS. The PR-equation of state for mixtures is described in [7], and the binary interaction coefficient is obtained from [8]. The GERG-2008 equation of state is briefly described below.

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 [9]:

$$\alpha(\delta, \tau, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}), \quad (1)$$

where \bar{x} is the molar composition in a mixture, δ is the reduced mixture density and τ is the inverse reduced mixture temperature.

The reduced mixture variables δ and τ are defined as:

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \text{ and } \tau = \frac{T_r(\bar{x})}{T}, \quad (2)$$

where ρ_r and T_r are the composition-dependent functions for the mixture density and temperature, respectively.

The following mixing rules are used:

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^N x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3; \quad (3)$$

$$T_r(\bar{x}) = \sum_{i=1}^N x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} T_{c,j})^{0.5}. \quad (4)$$

The binary parameters $\beta_{v,ij}$ and $\gamma_{v,ij}$ in equation (3), $\beta_{T,ij}$ and $\gamma_{T,ij}$ in equation (4), and the critical parameters $\rho_{c,i}$ and $T_{c,i}$ of pure components are given by Kunz and Wagner [9].

The ideal-gas part α^0 is given by

$$\alpha^0(\rho, T, \bar{x}) = \sum_{i=1}^N x_i [\alpha_{oi}^0(\rho, T) + \ln x_i], \quad (5)$$

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

The residual part α^r is

$$\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \alpha_{oi}^r(\delta, \tau) + \Delta \alpha^r(\delta, \tau, \bar{x}), \quad (6)$$

where α_{oi}^r is the residual part of the reduced Helmholtz free energy of the pure component i and $\Delta \alpha^r$ 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 equation (6) doesn't include the deviation function $\Delta \alpha^r$.

For PR-EOS, the method in [10] can be used to calculate thermodynamic properties of a mixture, for example fugacity coefficients and their derivatives, which are needed in the stability analysis and phase equilibrium calculation. Since GERG–2008 is a Helmholtz free energy equation of state, all thermodynamic properties of a mixture can be obtained by combining various derivatives of equation (1), which is described in detail in [9, 11].

Stability analysis. The stability analysis is based on the tangent plane criterion, which is first introduced by Baker et al. [2]. It can be used to test whether the original phase of a mixture is stable if overall composition $\bar{z}(z_1, z_2, \dots, z_n)$, temperature T , and pressure p of the mixture are given. If the original phase of the mixture is tested to be unstable, the tangent plane criterion also provides the composition of a new phase which can be split to decrease the Gibbs free energy of the mixture. A computational approach based on minimizing the tangent plane distance was suggested by Michelsen [3].

For a n -component mixture of composition $\bar{z}(z_1, z_2, \dots, z_n)$ 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 $\bar{w}(w_1, w_2, \dots, w_n)$ [3].

The reduced tangent plane distance is:

$$\begin{aligned} \text{tpd}(\bar{w}) &= \sum_i w_i (\ln w_i + \ln \varphi_i(\bar{w}) - \ln z_i - \ln \varphi_i(\bar{z})) = \\ &= \sum_i w_i (\ln w_i + \ln \varphi_i(\bar{w}) - d_i), \end{aligned} \quad (7)$$

where φ_i is the fugacity coefficient of component i and $d_i = \ln z_i + \ln \varphi_i(\bar{z})$.

By using the Gibbs — Duhem relation [12], straightforward differentiation of $\text{tpd}(\bar{w})$ with respect to the $(n-1)$ independent mole fractions yields the stationarity condition:

$$\ln w_i + \ln \varphi_i(\bar{w}) - d_i = k, \quad i = 1, 2, \dots, n, \quad (8)$$

where k is independent of the component index i .

Introducing new variables $W_i = \exp(-k) w_i$, a different but equivalent criterion can be formulated as [3]

$$\text{tm}(\bar{W}) = 1 + \sum_i W_i (\ln W_i + \ln \varphi_i(\bar{W}) - d_i - 1) \geq 0, \quad (9)$$

where no constraints on the W_i except $W_i > 0$ are required.

The stationary points of $\text{tm}(\bar{W})$ satisfy

$$\left(\frac{\partial \text{tm}(\bar{W})}{\partial W_i} \right)_{T, p, W_j, j \neq i} = \ln W_i + \ln \varphi_i(\bar{W}) - d_i = 0, \quad (10)$$

where when deriving the of equation (10), the Gibbs — Duhem relation [12] is also used.

Finally the modified tangent plane function $\text{tm}(\bar{W})$ can be written as

$$\begin{aligned}\text{tm}(\bar{W}) &= 1 + W_s \sum_i w_i (\ln W_s + \ln w_i + \ln \varphi_i(\bar{w}) - d_i - 1) = \\ &= (1 - W_s + W_s \ln W_s) + W_s \text{tpd}(\bar{w}),\end{aligned}\quad (11)$$

where $W_s = \sum_i W_i > 0$.

Since the term $(1 - W_s + W_s \ln W_s)$ in the equation (11) is always non-negative, $\text{tpd}(\bar{w})$ will be negative at all points where $\text{tm}(\bar{W})$ is negative; thus a negative $\text{tm}(\bar{W})$ implies that the system is unstable.

In order to verify stability, we need to determine the global minimum of the tangent plane distance, i.e., locate all local minima of $\text{tm}(\bar{W})$. However, this is a very time-consuming task in the general case. Michelsen [1] presented a practical computational approach in which the search for local minima is performed with a number of selected initial estimates in the hope that these searches will uncover at least all negative minima.

The Dominant Eigenvalue Method [5] can be used to solve equation (10). In the vicinity of the critical point, a second order minimization of $\text{tm}(\bar{W})$ [1] is used instead of the successive substitution method.

Phase equilibrium calculation. For the common vapor-liquid equilibrium of a multicomponent mixture, the following phase equilibrium conditions must be satisfied:

– equality of temperature

$$T^l = T^v = T; \quad (12)$$

– equality of pressure

$$p^l = p^v = p; \quad (13)$$

– equality of chemical potentials

$$\mu_i^l = \mu_i^v \quad (i = 1, 2, \dots, n), \quad (14)$$

where l denotes the liquid phase and v denotes the vapor phase.

The General Dominant Eigenvalue Method (GDEM) [6] can be used to solve the system of equations (12), (13) and (14). If the efficiency of the GDEM decreases, it is recommended to use the Gibbs energy minimization by the second order method [1, 11]. At specified T , p and \bar{z} , the vapor-liquid equilibrium calculation can be formulated as

$$\min G(T, p, \bar{v}, \bar{z} - \bar{v}), \quad (15)$$

where G is the Gibbs energy and \bar{v} is vapor amounts (per mole of mixture).

For the convenience of calculation, $G/(RT)$ is used as the objective function in the unconstrained minimization. Newton's method for solving the minimization problem calculates correction vector from:

$$H\Delta\bar{v} + \bar{g} = \bar{0}. \quad (16)$$

The gradient vector of $G/(RT)$ is obtained as:

$$\frac{\partial}{\partial v_i} \left(\frac{G}{RT} \right) = g_i = \ln f_i^v - \ln f_i^l, \quad (17)$$

where f_i^v and f_i^l are the fugacities of component i in the vapor and liquid phases respectively.

The elements H_{ij} of the Hessian matrix H are calculated according to

$$H_{ij} = \frac{\partial g_i}{\partial v_j} = \frac{\partial \ln f_i^v}{\partial v_j} + \frac{\partial \ln f_i^l}{\partial l_j}, \quad (18)$$

where l_j is liquid amount (per mole of mixture).

If the current estimate is sufficiently close to the solution, the Hessian matrix is positive definite and second order convergence is obtained. However, if the Hessian matrix is not positive definite, the iterations may fail, which is frequently the case in early iterations. In order to guarantee convergence, a trust region method [13] was suggested by Michelsen and Mollerup [1].

Results. In order to study thermodynamic properties of the multicomponent mixture in vapor-liquid equilibrium, we select a 12-component natural gas named as N75 from the literature [11]. The molar fractions of components in the natural gas N75 are as follows: methane 85.9284 %, nitrogen 0.9617 %, carbon dioxide 1.5021 %, ethane 8.4563 %, propane 2.3022 %, *n*-butane 0.4604 %, isobutane 0.2381 %, *n*-pentane 0.0630 %, isopentane 0.0588 %, *n*-hexane 0.0228 %, *n*-heptane 0.0057 %, *n*-octane 0.0005 %.

Thermodynamic properties of the natural gas N75 in vapor-liquid equilibrium were calculated with the help of PR-EOS, GERG-2008 without DF and GERG-2008. The tangent plane criterion is first used to find out whether the mixture is in vapor-liquid equilibrium. If the mixture is in vapor-liquid equilibrium, the estimates obtained from the tangent plane criterion are used for solving the system of phase equilibrium equations. The successive substitution is first used to solve the system of phase equilibrium equations. If the successive substitution can't converge, the Gibbs energy minimization by the second order method is used. In stability analysis and vapor-liquid equilibrium calculations the input variables are T , p and overall (or phase) composition \bar{x} , while in GERG-2008 the input variables are ρ , T and composition \bar{x} , so a density

solver is required. The density solver [14, 15], which is modified from [16], can provide reliable density solutions although it is relatively time-consuming.

Figs. 1–5 show thermodynamic property predictions of the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG–2008 without DF and GERG–2008. Their relative deviations from NIST (National Institute of Standards and Technology) database were also calculated. Table shows comparison of thermodynamic property predictions in vapor-liquid equilibrium with the help of PR-EOS, GERG–2008 without DF and GERG–2008 for the natural gas N75.

**Comparison of thermodynamic property predictions in vapor-liquid equilibrium
with the help of PR-EOS, GERG–2008 without DF and GERG–2008
within 5–60 bar for the natural gas N75**

Thermodynamic property	PR-EOS		GERG–2008 without DF		GERG–2008	
	Av. (%) [*]	Max. (%) ^{**}	Av. (%)	Max. (%)	Av. (%)	Max. (%)
Density (ρ)	2.34	14.33	0.77	19.90	0.02	0.28
Isobaric enthalpy difference (Δh)	4.25	92.84	1.42	22.66	0.03	0.37
Vapor fraction	3.99	144.63	1.64	31.05	0.03	0.51
Molar fraction of methane in liquid phase	3.56	11.47	7.96	30.35	0.06	0.26
Molar fraction of methane in vapor phase	0.14	0.45	0.12	0.69	0.00	0.01
Molar fraction of <i>n</i> -octane in liquid phase	19.17	213.88	6.89	24.78	0.28	2.47
Molar fraction of <i>n</i> -octane in vapor phase	35.98	272.10	10.05	34.20	0.40	2.31

* Average relative deviation, $(100\% / N) \sum_{i=1}^N |(x_i - x_i^{\text{NIST}}) / x_i^{\text{NIST}}|$;

** Maximum relative deviation, $\max\{100\% |(x_i - x_i^{\text{NIST}}) / x_i^{\text{NIST}}|\}$.

Fig. 1 shows that GERG–2008 has high accuracy in predicting molar density of the natural gas N75 in vapor-liquid equilibrium. Table shows that the average

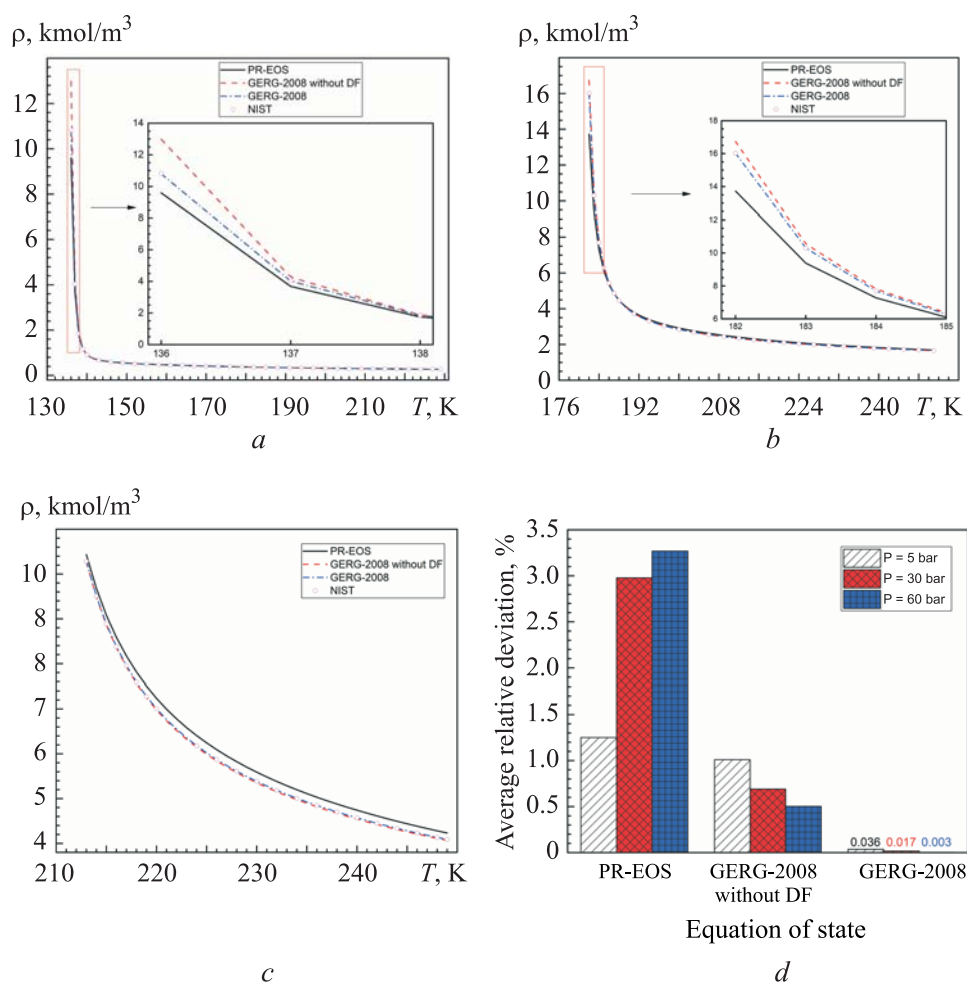


Fig. 1. Density versus temperature and its average relative deviation (*d*) from reference data for the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG–2008 without DF and GERG–2008 at different pressures:

a) 5 bar; *b*) 30 bar; *c*) 60 bar

relative deviation of molar density predicted by GERG–2008 is 0.02 %. In prediction of molar density in vapor-liquid equilibrium GERG–2008 without DF works better than PR-EOS in general, but much worse than GERG–2008. However, near the saturation zone where density varies sharply, GERG–2008 without DF and PR-EOS both work unsatisfactorily in predicting molar density. Table shows that the maximum relative deviations of predicted molar density by PR-EOS and GERG–2008 without DF are 14.33 and 19.90 % respectively.

Fig. 2 shows that PR-EOS works worse than GERG–2008 and GERG–2008 without DF in predicting isobaric enthalpy difference of the natural gas N75

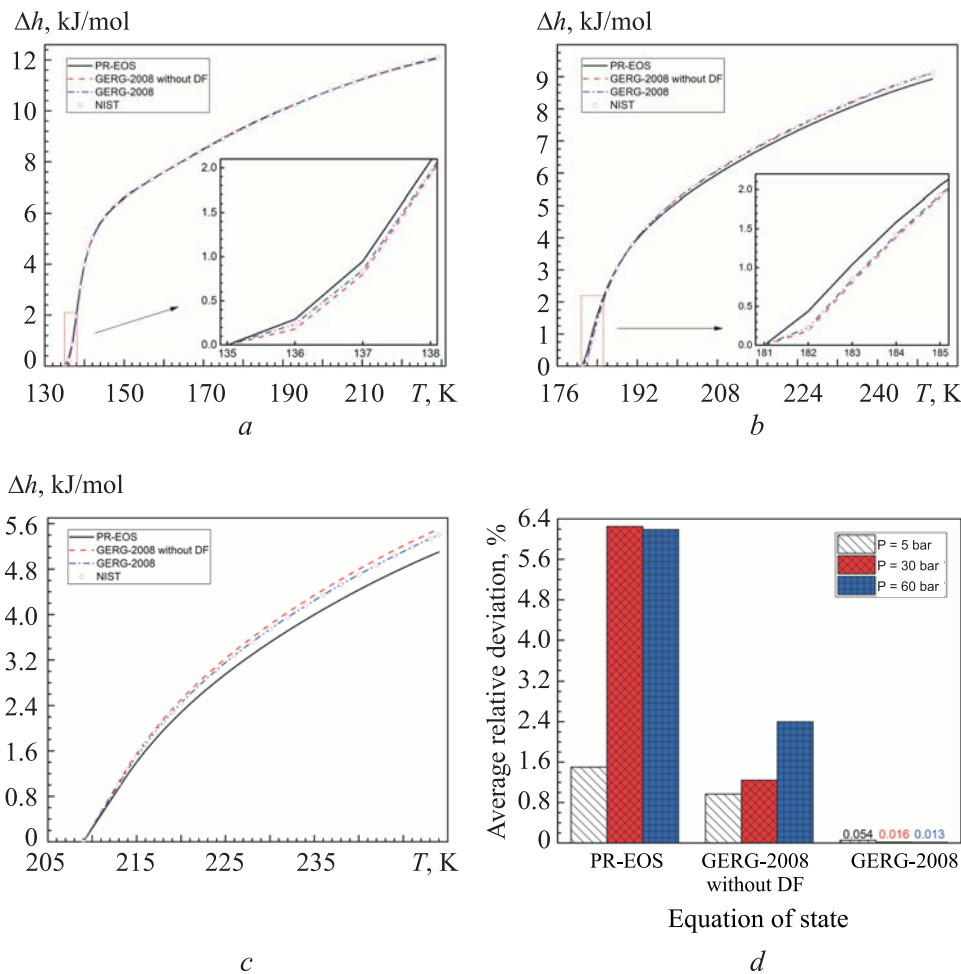


Fig. 2. Isobaric enthalpy difference versus temperature and its average relative deviation (*d*) from reference data for the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG–2008 without DF and GERG–2008 at different pressures:
a) 5 bar; *b*) 30 bar; *c*) 60 bar

in vapor-liquid equilibrium. Table shows that the average relative deviation of isobaric enthalpy difference predicted by PR-EOS is 4.25 %. GERG–2008 works much better than GERG–2008 without DF in predicting isobaric enthalpy difference in vapor-liquid equilibrium. Table shows that the average relative deviations of predicted isobaric enthalpy difference by GERG–2008 and GERG–2008 without DF are 0.03 and 1.42 % respectively.

Fig. 3 shows that GERG–2008 has high accuracy in predicting vapor fraction of the natural gas N75 in vapor-liquid equilibrium. Table shows that the average relative deviation of vapor fraction predicted by GERG–2008 is 0.03 %.

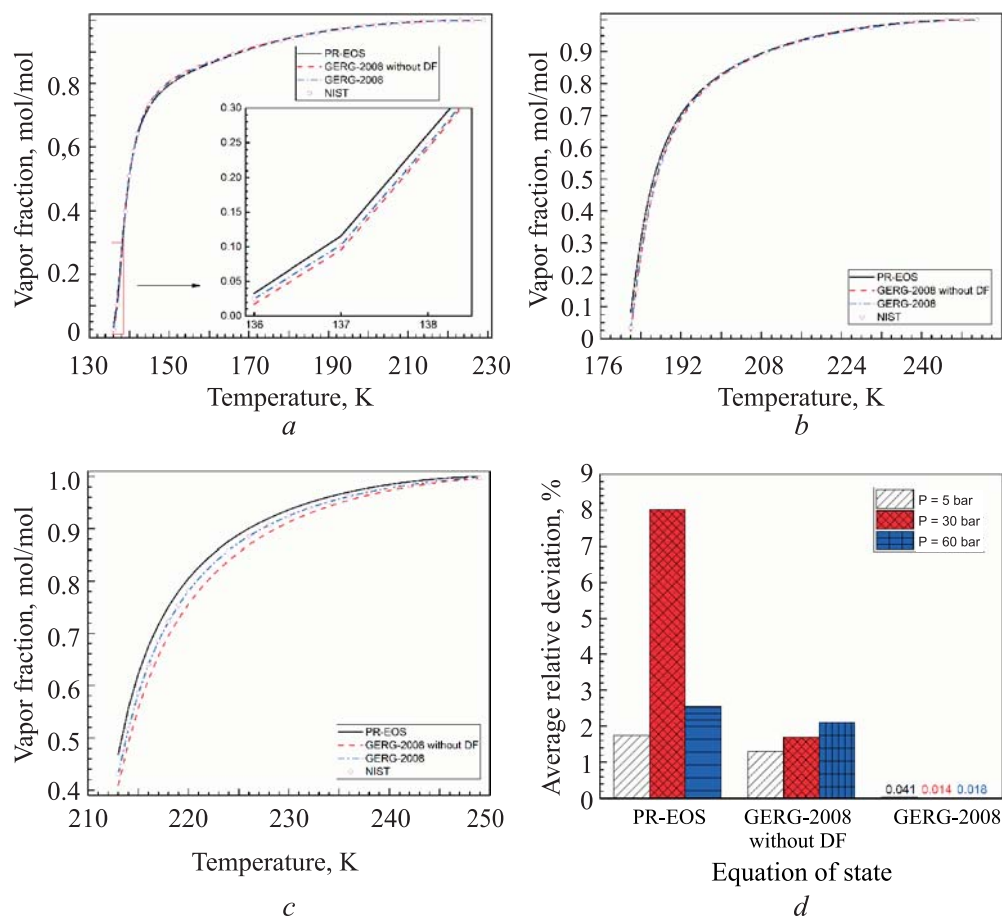


Fig. 3. Vapor fraction versus temperature and its average relative deviation (*d*) from reference data for the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG-2008 without DF and GERG-2008 at different pressures:

a) 5 bar; *b)* 30 bar; *c)* 60 bar

In prediction of vapor fraction in vapor-liquid equilibrium, GERG-2008 without DF works better than PR-EOS, but much worse than GERG-2008. Table shows that the average relative deviations of predicted vapor fraction by PR-EOS and GERG-2008 without DF are 3.99 and 1.64 % respectively. However, near the bubble point, PR-EOS and GERG-2008 without DF both work unsatisfactorily in predicting vapor fraction. Table shows that the maximum relative deviations in predicting vapor fraction are 144.63 % for PR-EOS and 31.05 % for GERG-2008 without DF.

Fig. 4 shows that PR-EOS works worse than GERG-2008 and GERG-2008 without DF in predicting molar fraction of *n*-octane in liquid phase. Table shows that the average relative deviation of molar fraction of *n*-octane in liquid

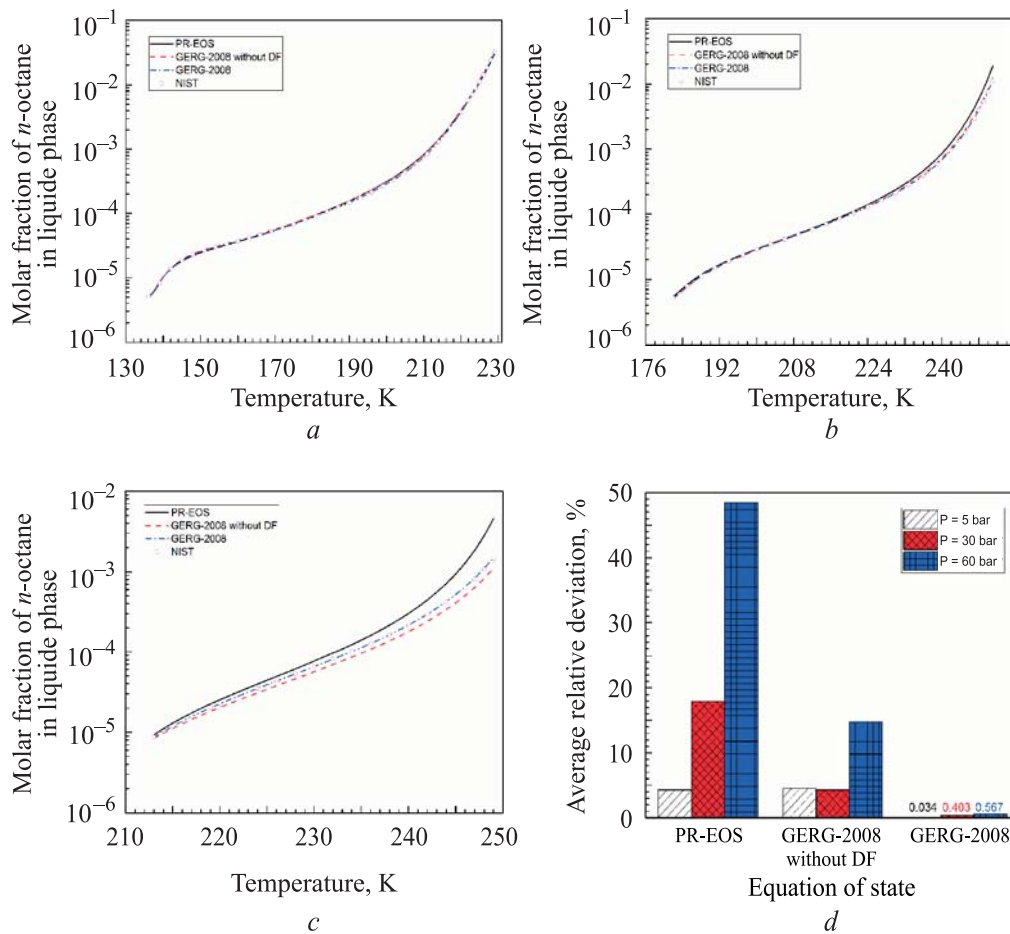


Fig. 4. Molar fraction of *n*-octane in liquid phase versus temperature and its average relative deviation (*d*) from reference data for the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG–2008 without DF and GERG–2008 at different pressures:

a) 5 bar; *b)* 30 bar; *c)* 60 bar

phase predicted by PR-EOS is 19.17 %. GERG–2008 works much better than GERG–2008 without DF in predicting molar fraction of *n*-octane in liquid phase. Table shows that the average relative deviations of predicted molar fraction of *n*-octane in liquid phase by GERG–2008 and GERG–2008 without DF are 0.28 and 6.89 % respectively.

Fig. 5 shows that GERG–2008 has high accuracy in predicting molar fraction of *n*-octane in vapor phase. Table shows that the average relative deviation of molar fraction of *n*-octane in vapor phase predicted by GERG–2008 is 0.40 %. In predicting molar fraction of *n*-octane in vapor phase, PR-EOS works worse than GERG–2008 without DF. Table shows that the average

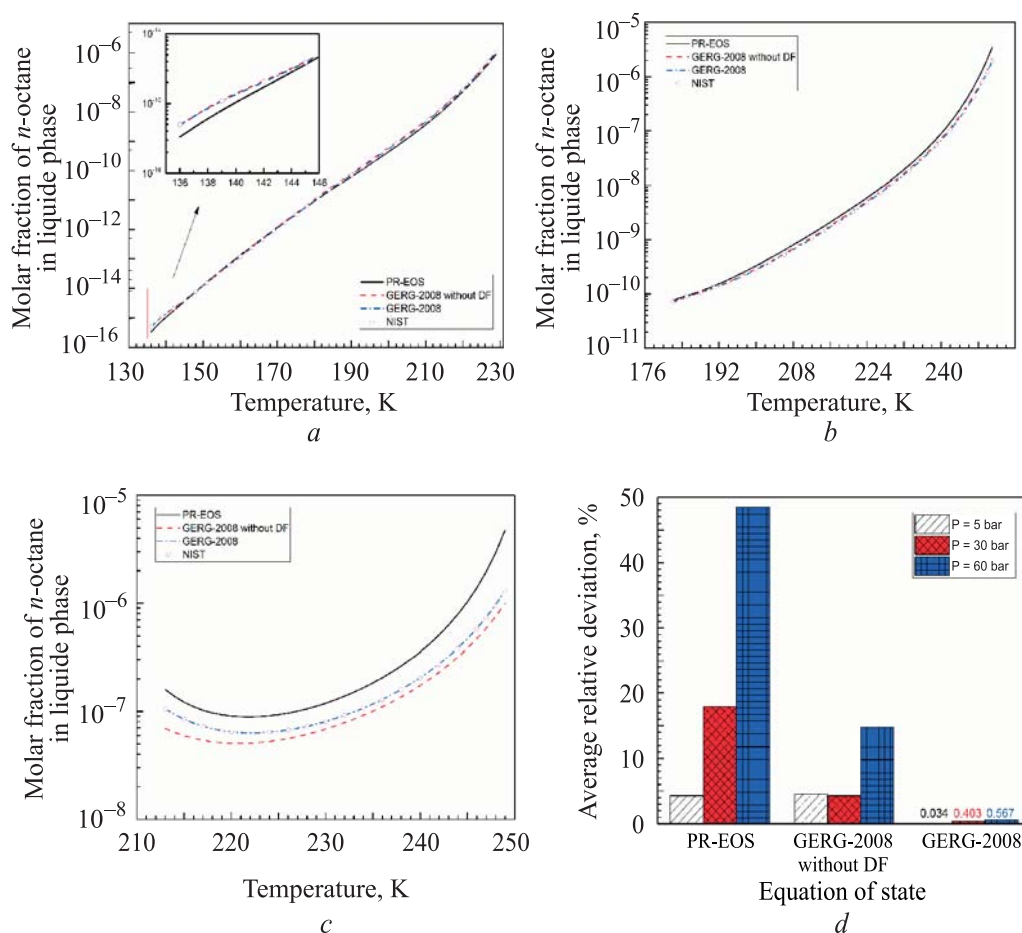


Fig. 5. Molar fraction of *n*-octane in vapor phase versus temperature and its average relative deviation (*d*) from reference data for the natural gas N75 in vapor-liquid equilibrium with the help of PR-EOS, GERG-2008 without DF and GERG-2008 at different pressures:

a) 5 bar; *b*) 30 bar; *c*) 60 bar

relative deviations of predicted molar fraction of *n*-octane in vapor phase by PR-EOS and GERG-2008 without DF are 35.98 and 10.05 % respectively.

Conclusion. We compared GERG-2008 with PR-EOS and simplified GERG-2008 (GERG-2008 without DF) in calculation of thermodynamic properties of the natural gas N75 in vapor-liquid equilibrium.

In vapor-liquid equilibrium calculation, GERG-2008 is superior to PR-EOS and GERG-2008 without DF. Both GERG-2008 without DF and PR-EOS work unsatisfactorily in vapor-liquid equilibrium calculation, especially near the saturation zone, but in general, GERG-2008 without DF works better than PR-EOS. For the component with a very small molar fraction in a mixture,

PR-EOS and GERG–2008 without DF have very large deviation in predicting molar fractions of this component in liquid and vapor phases. In addition, calculations show that the deviation function in GERG–2008 (see equation (6)) can significantly affect the accuracy of GERG–2008 when calculating thermodynamic properties of mixtures in vapor-liquid equilibrium.

The tangent plane criterion can be successfully used to find whether the original phase of a mixture is stable or not. If the original phase is unstable, the estimates, which are produced by the tangent plane criterion, can be considered as relatively accurate estimates to solve the system of vapor-liquid equilibrium equations.

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REFERENCES

- [1] Michelsen M.L., Mollerup J.M. Thermodynamic models. Fundamentals & computational aspects. Denmark, Holte, Tie-Line Publications, 2004.
- [2] Baker L.E., Pierce A.C., Luks K.D. Gibbs energy analysis of phase equilibria. *SPE J.*, 1982, vol. 22, no. 5, pp. 731–742. DOI: <https://doi.org/10.2118/9806-PA>
- [3] Michelsen M.L. The isothermal flash problem. Part I. Stability. *Fluid Phase Equilib.*, 1982, vol. 9, no. 1, pp. 1–19. DOI: [https://doi.org/10.1016/0378-3812\(82\)85001-2](https://doi.org/10.1016/0378-3812(82)85001-2)
- [4] Michelsen M.L. The isothermal flash problem. Part I. Phase-split calculation. *Fluid Phase Equilib.*, 1982, vol. 9, no. 1, pp. 21–40. DOI: [https://doi.org/10.1016/0378-3812\(82\)85002-4](https://doi.org/10.1016/0378-3812(82)85002-4)
- [5] Orbach O., Crowe C.M. Convergence promotion in the simulation of chemical processes with recycle — the Dominant Eigenvalue Method. *Can. J. Chem. Eng.*, 1971, vol. 49, no. 4, pp. 509–513. DOI: <https://doi.org/10.1002/cjce.5450490414>
- [6] Crowe C.M., Nishio M. Convergence promotion in the simulation of chemical processes — the General Dominant Eigenvalue Method. *AIChE J.*, 1975, vol. 21, no. 3, pp. 528–533. DOI: <https://doi.org/10.1002/aic.690210314>
- [7] Peng D.Y., Robinson D.B. A new two-constant equation of state. *Ind. Eng. Chem. Fundamen.*, 1976, vol. 15, no. 1, pp. 59–64. DOI: <https://doi.org/10.1021/i160057a011>
- [8] Nishiumi H., Arai T., Takeuchi K. Generalization of the binary interaction parameter of the Peng — Robinson equation of state by component family. *Fluid Phase Equilib.*, 1988, vol. 42, pp. 43–62. DOI: [https://doi.org/10.1016/0378-3812\(88\)80049-9](https://doi.org/10.1016/0378-3812(88)80049-9)
- [9] Kunz O., Wagner W. The GERG–2008 wide-range equation of state for natural gases and other mixtures: an Expansion of GERG–2004. *J. Chem. Eng. Data*, 2012, vol. 57, no. 11, pp. 3032–3091. DOI: <https://doi.org/10.1021/jc300655b>
- [10] Mollerup J.M., Michelsen M.L. Calculation of thermodynamic equilibrium properties. *Fluid Phase Equilib.*, 1992, vol. 74, pp. 1–15. DOI: [https://doi.org/10.1016/0378-3812\(92\)85049-E](https://doi.org/10.1016/0378-3812(92)85049-E)

- [11] Kunz O., Klimeck R., Wagner W., et al. The GERG–2004 wide-range equation of state for natural gases and other mixtures. Düsseldorf, VDI, 2007.
- [12] Tester J.W., Modell M. Thermodynamics and its applications. Cambridge, Pearson, 1997.
- [13] Dennis J.E., Schnabel R.B. Numerical methods for unconstrained optimization and nonlinear equations. Philadelphia, SIAM, 1996.
- [14] Luo T., Chirkov A.Yu. Phase equilibrium modelling for multi-component mixtures using highly accurate Helmholtz energy equation of state. *IJESMS*, 2020, vol. 11, no. 4, pp. 138–146. DOI: <https://doi.org/10.1504/IJESMS.2020.111265>
- [15] Luo T., Chirkov A.Yu. Phase envelope construction for mixtures using a highly accurate Helmholtz energy equation of state. *Vestnik TyumGU. Fiziko-matematicheskoe modelirovanie. Neft', gaz, energetika* [Tyumen State University Herald. Physical and Mathematical Modeling. Oil, Gas, Energy], 2020, vol. 6, no. 4, pp. 8–27 (in Russ.). DOI: <https://doi.org/10.21684/2411-7978-2020-6-4-8-27>
- [16] Gernert J., Jäger A., Span R. Calculation of phase equilibria for multi-component mixtures using highly accurate Helmholtz energy equations of state. *Fluid Phase Equilib.*, 2014, vol. 375, pp. 209–218. DOI: <https://doi.org/10.1016/j.fluid.2014.05.012>

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