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# **Comparison of GERG-2008 and Simpler EoS Models in Calculation of Phase Equilibrium and Physical Properties of Natural Gas Related Systems**

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## **Abstract**

Accurate description of thermodynamic properties of natural gas systems is of great significance in the oil and gas industry. For this application, non-cubic equations of state (EoSs) are advantageous due to their better density and compressibility description. Among the non-cubic models, GERG-2008 is a new wide-range EoS for natural gases and other mixtures of 21 natural gas components. It is considered as a standard reference equation suitable for natural gas applications where highly accurate thermodynamic properties are required. Soave's modification of Benedict-Webb-Rubin (Soave-BWR) EoS is another model that despite its empirical nature, provides accurate density description even around the critical point. It is much simpler than GERG-2008 and easier to handle and generalize to reservoir oil fluids. This study presents a comprehensive comparison between GERG-2008 and other cubic (SRK and PR) and non-cubic EoSs (Soave-BWR and PC-SAFT) with a focus on Soave-BWR in description of pure components density and compressibility in a wide temperature and pressure range, calculation of binary Vapor-Liquid-Equilibria (VLE) and density, prediction of multicomponent phase envelopes and gas compressibility factor. In addition, the performance of GERG-2008 is compared with that of cubic and non-cubic models in calculation of thermal properties such as heat capacity and Joule-Thomson coefficient for pure components and multicomponent mixtures over a wide pressure and temperature range. The results are compared with available experimental data in the literature and special emphasis has been given to the reverse Joule-Thomson effects at high pressure high temperature (HPHT) conditions.

## **Keywords**

Equation of state; Thermal Physical Properties; Joule-Thomson Coefficient; GERG-2008; Soave-BWR.

# 1. Introduction

The accurate knowledge of the thermodynamic properties of natural gases and other mixtures of natural-gas components is essential for many applications involving natural gas, such as natural gas transportation, processing, storage and liquefaction. Equations of State (EoS) are commonly used to describe phase equilibrium and physical properties over a wide range of pressure, temperature and mixture composition. As classical cubic EoS models do not satisfy the demands on the accuracy of some thermodynamic properties over the entire region of interest, it becomes more attractive to use non-cubic EoSs for description of these properties including derivative properties.

GERG-2008 is a wide-range EoS developed for 21 components of natural gases and their mixtures that meets the requirements of standard and advanced natural gas applications [1]. It is explicit in the Helmholtz free energy as a function of density  $\rho$ , temperature  $T$ , and composition  $x$  (mole fraction) and is adopted as an ISO Standard (ISO 20765-2) reference equation suitable for natural gas applications [1]. Soave-BWR [2] is a modification of Benedict-Webb-Rubin EoS [3] and has good accuracy in description of different properties such as density even around the critical region. This non-cubic EoS has three parameters  $T_c$ ,  $P_c$ , and  $\omega$  and can be applied to the oil mixtures using the existing reservoir fluid characterization methods. Soave-BWR can be potentially used for accurate modelling of natural gas and oil systems. However, there is so far no systematic comparison between GERG-2008 and Soave-BWR in the literature. Such a comparison would be useful for model selection and model improvement. Here, we present a comparison of GERG-2008 and Soave-BWR in calculation of phase equilibrium and physical properties of natural gas related systems. Three other cubic and non-cubic models of industrial importance, including SRK [4], PR [5] and PC-SAFT (Perturbed-Chain Statistical Association Fluid Theory) [6], are also included in the comparison. Soave-BWR, SRK and PR and PC-SAFT (without the association term) have simpler forms than GERG-2008.

Dauber and Span [7], [8] applied GERG-2008 to simulation of liquefied natural gas process and made comparison with cubic EoSs including SRK and PR. Recently, Perez-Sanz et al. [9] measured the speed of sound for a synthetic coal mine methane as well as second virial acoustic coefficient, adiabatic coefficient and heat capacity. They validated their measurements by comparing their results with GERG-2008 predictions, where they found good agreement between GERG-2008 and experimental measurements for speed of sound, heat capacity and adiabatic coefficient. However, a large disagreement was observed for the second virial acoustic coefficient. Yuan et al. [10] used the Aspen Plus software [11] to compare SRK, PR, the Lee-Kesler-Plocker (LKP) equation [12] and GERG-2008 in calculating gas density, saturated liquid density, specific heat capacity, enthalpy and vapor-liquid equilibrium of some gas mixtures at conditions relevant to gas liquefaction processes. They found that SRK, PR and LKP give large deviations from the experimental data for some of the properties or under certain conditions, which may lead to inaccurate results for the simulation and optimization of the liquefaction processes. In contrast, GERG-2008 shows higher accuracy in calculation of the thermodynamic properties and phase equilibrium over the temperature and pressure range tested. They recommended GERG-2008 as the basis for predicting physical parameters in natural gas liquefaction processes.

There are several studies on the comparison between non-cubic models, including PC-SAFT and Soave-BWR, and other cubic models in the recent literature. In order to provide a comprehensive understanding of the potentials and limitations of the advanced SAFT family EoS and their improvements over classical models, Villiers et al. [13], [14] studied the performance of SRK, PR, CPA, SAFT, and PC-SAFT on derivative properties for different component families. They concluded that, in general, the performance of PC-SAFT is superior in correlating most of the second-order derivative properties of investigated alkanes. Liang et al. [15] made an extensive comparison of SRK, CPA and PC-SAFT for calculation of the speed of sound in n-alkanes where they observed none of the models could describe the speed of sound with satisfactory accuracy when they are used without fitting their parameters to the experimental data. After integrating the speed of sound data into both tuning of the universal constants and the pure component

parameters estimation, Liang et al. obtained better results for PC-SAFT. Polishuk [16]–[19] has made several comparisons between cubic EoSs, Soave-BWR, PC-SAFT and SAFT+Cubic in calculation of different thermodynamic properties of pure and multicomponent systems including the derivative properties such as speed of sound and heat capacity. He pointed out some limitations of cubic EoSs, such as poorer high pressure speed of sound and density results predicted by PR as compared to PC-SAFT and SAFT+Cubic EoSs [19]. In addition, he showed the advantage of Soave-BWR in modeling the pure compound vapor pressures and phase envelope, which are the particular type of data for which the model has been developed. However, he mentioned that the Soave-BWR model fails to estimate other thermodynamic properties, such as the high-pressure densities, sound velocities and isentropic compressibilities accurately [18]. Yan et al. [20] made a comprehensive comparison between different cubic and non-cubic EoSs where they found some advantages of non-cubic models over cubics in calculation of different properties such as density of pure and multicomponent mixtures.

In the following sections, we will first briefly review the GERG-2008, Soave-BWR and PC-SAFT models. A comprehensive comparison will then be presented between the cubic and non-cubic models in description of pure components density and saturated liquid density, binary VLE, multicomponent phase envelope and compressibility factor of natural gas. In addition to covering various aspects related to the basic PVT modeling, this comparative study includes the calculation of derivative properties like compressibility and thermal properties such as heat capacity  $C_p$  and Joule-Thomson coefficients of pure and multicomponent mixtures over a wide pressure and temperature range.

A large amount of data has been included in this study, including both experimental ones collected from the open literature and synthetic ones generated by the most reliable reference EoS models. All the binary interaction parameters for GERG-2008 were regressed from experimental data [1]. In order to make a fair comparison between the selected models, we have determined the optimal values of binary interaction parameters for Soave-BWR and then used them in the subsequent calculations of binary density,

multicomponent phase envelopes and other thermal properties. The binary interaction parameters for SRK, PR, and PC-SAFT are taken from our previous study [20]. In this comparative study, we tried to avoid any particular treatments in favor of a specific model.

## 2. Equations of state

Our study mainly involves two cubic EoSs (SRK and PR) and three non-cubic models (GERG-2008, Soave-BWR, and PC-SAFT). The non-cubic EoSs are briefly described below.

### 2.1. GERG-2008 EoS

GERG-2008 is based on a multi-fluid mixture model and is valid over the temperature range of 60 K to 700 K and up to 700 bar [1]. The structure of this EoS in the dimensionless reduced form is as follows:

$$\alpha(\delta, \tau, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \sum_{i=1}^n x_i \alpha_{0i}^r(\delta, \tau) + \Delta \alpha^r(\delta, \tau, \bar{x}) \quad (1)$$

where  $\delta$  is the reduced mixture density and  $\tau$  is the inverse reduced mixture temperature according to:

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \quad (2)$$

$$\tau = \frac{T_r(\bar{x})}{T} \quad (3)$$

In these equations,  $T_r$  and  $\rho_r$  are the reducing functions, and are only dependent on the composition of the mixture. In Eq. (1),  $\alpha(\delta, \tau, \bar{x})$  is the dimensionless form of the reduced Helmholtz free energy and is defined as  $\alpha = a/(RT)$ . The dimensionless form of the Helmholtz free energy for the ideal-gas mixture is  $\alpha^0(\rho, T, \bar{x})$  and is defined as follows:

$$\alpha^0(\rho, T, \bar{x}) = \sum_{i=1}^n x_i (\alpha_{0i}^0(\rho, T) + \ln x_i) \quad (4)$$

where  $n$  is the number of components in the mixture,  $\alpha_{0i}^0$  is the dimensionless form of the Helmholtz free energy in the ideal-gas state of component  $i$ , and  $x_i$  is the mole fraction of the mixture components. The term  $x_i \ln x_i$  accounts for the entropy of mixing.

The last two terms on the right hand side of Eq. (1) represent the residual part of the reduced Helmholtz free energy of the mixture, where  $\sum_{i=1}^n x_i \alpha_{0i}^r(\delta, \tau)$  is the contribution of the pure substances in the real mixture, and  $\Delta \alpha^r(\delta, \tau, \bar{x})$  is the so-called departure function which is the summation over all binary specific and generalized departure functions  $\Delta \alpha_{ij}^r(\delta, \tau, \bar{x})$  developed for the respective binary mixtures.  $\bar{x}$  is the vector of mole fractions.

In order to apply the GERG-2008 EoS to the mixtures, the following mixing rules are used:

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^n x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \cdot \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \cdot \frac{1}{8} \left( \frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \quad (5)$$

$$T_r(\bar{x}) = \sum_{i=1}^n x_i^2 T_{c,i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \cdot \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \cdot (T_{c,i} T_{c,j})^{0.5} \quad (6)$$

In these correlations,  $\rho_{c,i}$  and  $T_{c,i}$  are critical density and critical temperature of component  $i$  and the four binary parameters  $\beta_{v,ij}$ ,  $\gamma_{v,ij}$ ,  $\beta_{T,ij}$ , and  $\gamma_{T,ij}$  are fitted to the binary mixtures data. More information about GERG-2008 and its earlier version, GERG-2004, the experimental data used for their development, and the value of the binary parameters can be found in the original articles [1], [21]–[24]. The developed mixing rules have the so-called Michelsen–Kistenmacher syndrome [25]. This means the mixture parameters, including the composition-dependent parameters of multi-fluid mixtures, calculated from mixing rules might not be invariant when a component is split into a number of identical subcomponents. The developers of GERG 2008 were aware of this limitation but decided to use these empirical mixing rules as they give better accuracy in description of the available data for the thermal and caloric properties of multicomponent mixtures.



## 2.2. Soave-BWR EoS

The Benedict-Webb-Rubin (BWR) equation of state [3] is a virial type equations of state that was developed based on n-alkanes up to n-C<sub>4</sub> and takes the following functional form:

$$z = \frac{P}{RT\rho} = 1 + B\rho + C\rho^2 + D\rho^5 + E\rho^2(1 + F\rho^2)\exp(-F\rho^2) \quad (7)$$

In this equation  $\rho$  is the density, and  $B$ ,  $C$ ,  $D$ ,  $E$  and  $F$  are the five model parameters. In the original BWR EoS, these parameters are experimentally found for each component. In 1995, Soave [26] modified the BWR equation by reducing the power of density in the fourth term of Eq. (7) to 4 and later on in 1999, he proposed his final modification of BWR EoS by dropping the  $C\rho^2$  term from the equation. The Soave-BWR EoS that is used in our study has the following functional form:

$$z = \frac{P}{RT\rho} = 1 + B\rho + D\rho^4 + E\rho^2(1 + F\rho^2)\exp(-F\rho^2) \quad (8)$$

There are four parameters in Soave-BWR,  $B$ ,  $D$ ,  $E$  and  $F$  where  $B$ ,  $D$  and  $E$  are a function of temperature and acentric factor while  $F$  is treated as temperature independent. The values of these parameters at the critical point are linked to a new set of notations defined by

$$b = B(T_c)\rho_c \quad (9)$$

$$d = D(T_c)\rho_c^4 \quad (10)$$

$$e = E(T_c)\rho_c^2 \quad (11)$$

$$f = F\rho_c^2 \quad (12)$$

The above four values  $b$ ,  $d$ ,  $e$  and  $f$  can be determined from the three critical constraints  $P_c = Z_c\rho_cRT_c$  and  $(\partial P/\partial\rho)_{T_c} = (\partial^2 P/\partial\rho^2)_{T_c} = 0$ , plus an empirical constraint  $f = 0.77$ .

In order to use this model for the mixtures, Soave developed the mixing rules for  $T_c$ ,  $P_c$  and  $\omega$  based on the mixing rules used for the classical cubic EoS models like SRK and PR. The mixing rules for  $T_c$ ,  $P_c$  and  $\omega$  are as follows:

$$T_{cm} = S_1 / (\sqrt{S_2} + \sqrt{S_3})^2 \quad (13)$$

$$P_{cm} = T_{cm} / S_3 \quad (14)$$

$$m_m = \sqrt{S_2 / S_3} \quad (15)$$

$$S_1 = \sum_i \sum_j x_i x_j (1 - k_{ij}) \frac{T_{ci} T_{cj}}{\sqrt{P_{ci} P_{cj}}} (1 + m_i)(1 + m_j) \quad (16)$$

$$S_2 = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{\frac{T_{ci} T_{cj}}{P_{ci} P_{cj}}} m_i m_j \quad (17)$$

$$S_3 = \sum_i x_i \frac{T_{ci}}{P_{ci}} \quad (18)$$

$m$  in Eqs. (15-17) is a function of  $\omega$  and a simple proportionality relationship is used for it:

$$m = \mu \omega \quad (19)$$

with an empirical value 1.2 given to  $\mu$ . A linear mixing rule is used for  $Z_c$  and it has been considered independent of  $\omega$ :

$$Z_{cm} = \frac{\sum_i (x_i Z_{c_i} T_{c_i} / P_{c_i})}{\sum_i (x_i T_{c_i} / P_{c_i})} \quad (20)$$

In this study, all the critical properties as well as acentric factor for both EoSs have been taken from DIPPR database [27].

### 2.3. PC-SAFT EoS

To model asymmetric and highly non-ideal systems Gross and Sadowski [6] proposed the PC-SAFT EoS which can be expressed in terms of the reduced Helmholtz energy  $\tilde{a}$ :

$$\tilde{a} \equiv \frac{A}{NkT} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \quad (21)$$

where  $\tilde{a}^{id}$  is the ideal gas contribution,  $\tilde{a}^{hc}$  is the contribution of the hard-sphere chain reference system,  $\tilde{a}^{disp}$  is the dispersion contribution arising from the square well attractive potential and  $\tilde{a}^{assoc}$  is the association contribution based on Wertheim's theory [28]. For systems consisting only of non-associating components, the  $\tilde{a}^{assoc}$  term in Eq. (21) would be equal to zero. Although the remaining three terms have rather complicated

forms compared with SRK or PR, there are only three model parameters for a non-associating component, the chain length  $m$ , the segment diameter  $\sigma$  and the segment energy  $\epsilon$ .

von Solms et al. [29] simplified the original PC-SAFT EoS by assuming that all the segments in the mixture have the same mean diameter  $d$ , which gives a mixture volume fraction identical to that of the actual mixture. The computation times for the simplified version is lower for non-associating systems and significantly lower for associating systems. Therefore, the simplified version of PC-SAFT is used in our calculations.

### **3. Density and compressibility of pure components**

This section is mainly dedicated to the comparison between GERG-2008, Soave-BWR, PC-SAFT, and SRK and PR with and without volume translation for calculation of phase density and compressibility of pure components over a wide temperature and pressure range (150-500 K and 0-2000 bar), and for calculation of saturated liquid density of these pure components. The tested temperature and pressure range can cover most of the conditions in the upstream and downstream processes. In addition, a sample calculation of methane and n-decane binary mixture density at different compositions, as well as gas compressibility factor ( $Z$ ) of a multicomponent natural gas mixture at different temperatures using different EoSs are presented.

High accuracy reference EoS models [30] are used to generate “synthetic” density data which have then been used in generating the compressibility data. As it was mentioned in the introduction section, GERG-2008 has been developed for 21 components of natural gases and their mixtures. We exclude  $H_2$ ,  $O_2$ ,  $CO$ ,  $H_2O$ ,  $He$  and  $Ar$  from the 21 components to form the “main components” group (Table 1). The split is based on two reasons. First, the “main components” are more commonly encountered in the upstream of oil and gas production especially in the modeling of reservoir fluids. Second, the other components are not included in the development of Soave-BWR and the comparison including all the components can be biased against Soave-BWR.

Table 1 summarizes the list of components and the applicable ranges of the reference EoS models used in this study. Since the applicable ranges of some reference EoS models cannot cover the whole range of 150-500 K and 0-2000 bar, we consider two types of absolute average deviations (AAD) in the comparison here as in our previous work [20]. AAD% is calculated in the whole temperature and pressure range of interest, i.e., neglecting the applicable ranges of the reference EoS models, and AAD0% is calculated only with the data points within the applicable ranges of the reference models. For saturated liquid density, comparison is made in the reduced temperature ( $T_r$ ) range from 0.35 to 1.0. Based on Table 1, for the components where the lowest applicable reduced temperature ( $T_{r,min}$ ) is higher than  $T_r=0.35$ ,  $T_{r,min}$  is used as the lower boundary for the reduced temperature.

Table 2 summarizes the deviations in pure components phase density within 150-500 K and 0-2000 bar using GERG-2008 and Soave-BWR. Both AAD% and AAD0% as well as maximum absolute deviations (%) are presented in this table. On average, GERG-2008 gives lower AAD% and AAD0% in phase density calculation of pure components than Soave-BWR. When GERG-2008 is used within the applicable ranges of reference EoSs, the average AAD0% is 0.07% for the 21 components and 0.03% for the so called “main components”. The average AAD0% for Soave-BWR is 2.35% for the 21 components and 1.03% for the main components. Soave-BWR shows large deviations for H<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>O, He and Ar since it is developed based mainly on n-alkanes and these components are not included in its development.

The deviations in saturated liquid density are presented in Table 3. Both models give accurate prediction of saturated liquid density for the main components while GERG-2008 is slightly better than Soave-BWR in terms of both average and maximum deviation. Again, since Soave-BWR is not developed for H<sub>2</sub>, H<sub>2</sub>O and He, large deviations can be seen for saturated liquid density of these components.

Fig. 1 compares GERG-2008 and Soave-BWR in their AAD% and AAD0% in phase density and AAD% in saturated liquid density for both the 21 pure components and the main components. Fig. 2 illustrates the AAD% in density and saturated liquid density of the main components for all the EoSs studied here. The detailed calculation results for density and saturated liquid density using PC-SAFT, SRK and PR with and without volume translation can be found in our previous study [20]. GERG-2008 gives the lowest deviation for both density and saturated liquid density, while SRK and PR without volume translation give the largest deviation. Using Peneloux volume translation [31], [32] improves the predictions of cubics and both models give slightly lower deviation than PC-SAFT and Soave-BWR in the calculated density. For saturated liquid density, the cubic models (SRK and PR) are still poorer than the non-cubic ones (PC-SAFT, Soave-BWR and GERG-2008) even after using volume translation. It can be seen that Soave-BWR gives lower deviation than PC-SAFT in both density and saturated liquid density of the pure components and has the closest predictions to that of GERG-2008 in saturated liquid density calculations.

In order to compare the performance of Soave-BWR and GERG-2008 for the liquid density data up to extremely high pressures, we used the experimental data from Doolittle [33] for heavy n-alkanes n-C<sub>7</sub> and n-C<sub>9</sub>. The pressure ranges from 0 to 5000 bar and the temperature ranges from 303 to 573 K. Table 4 presents the AAD% in the calculated high pressure liquid densities using Soave-BWR and GERG-2008. GERG-2008 seems to have better prediction of density over the whole pressure range especially at higher pressures, while Soave-BWR gives higher deviations at higher pressures, but its average deviation is less than 2%. Fig. 3 shows the density predictions using both models for n-C<sub>9</sub> at different temperatures and up to 5000 bar. As illustrated, both models give very similar predictions of density at pressures lower than 300 bar and have accurate description of density at all temperatures and up to 300 bar. Soave-BWR starts over predicting the density at higher pressures and the deviation increases as the temperature increases.

Isothermal compressibility is a measure of the relative volume change of a fluid with pressure at constant temperature and is defined with the following equation:

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (21)$$

In order to evaluate how different EoSs perform in calculation of this derivative property, the AAD0% and maximum deviations in the calculated compressibility of the 15 main components are presented in Table 5. As can be seen, GERG-2008 gives significantly lower deviation than other EoSs both in terms of average AAD0% and maximum deviation. SRK and PR give the largest deviation in the calculated compressibility. Even using volume translation does not improve their performances significantly. In fact, using volume translation makes the predictions even worse for some of the heavier n-alkanes especially for SRK. PC-SAFT and Soave-BWR have better performance than the cubics, while Soave-BWR gives lower deviation than PC-SAFT in compressibility calculation.

In Fig. 4, we further show the contour maps of the deviations in density and compressibility of methane within 150-500 K and 0-2000 bar using GERG-2008. Fig. 5 also presents the contour maps of the deviations in compressibility of methane using SRK and PR (with/without volume translation), PC-SAFT and Soave-BWR. The results show that using volume translation slightly worsens the compressibility predictions of PR for methane.

Regueira et al. [34] compared the performance of SRK, PR, PC-SAFT and Soave-BWR in density calculation of different binary mixtures of methane and n-decane within 278.15-463.15 K and 1-1400 bar. They observed that the non-cubic models give better prediction of density than cubic ones. Although Soave-BWR is better than PC-SAFT in density and saturated liquid density of pure components (Fig. 2), Regueira et al. [34] showed that Soave-BWR gives poorer results in density calculation of methane and n-decane binary mixture.

Fig. 6 illustrates the AAD% in the calculated density as a function of the methane mole fraction ( $x_1$ ) in the binary mixture of methane and n-decane using PC-SAFT, Soave-BWR and GERG-2008. The regressed binary interaction parameters  $k_{ij}$ 's used for Soave-BWR and PC-SAFT were -0.0321 and 0.0172, respectively. For Soave-BWR, the density

results become less accurate as methane mole fraction increases in the binary mixture, while for GERG-2008 the deviation increases only up to  $x_1=0.7085$ . On average, GERG-2008 with AAD% around 0.7% seems to give better prediction of density compared to Soave-BWR with AAD% around 3.2%. PC-SAFT gives slightly higher deviation than GERG-2008 (around 0.8%), which shows it is largely comparable to GERG-2008. In fact, PC-SAFT has better prediction of density for  $x_1=0.6017$  and  $x_1=0.7085$  compared to GERG-2008. Fig. 7 shows how the density predictions differ for Soave-BWR and GERG-2008 for two mixtures of methane and n-decane at different temperatures. Soave-BWR under predicts the density especially at higher temperatures.

Table 6 summarizes the deviation in calculation of the  $Z$  factor of a gas mixture from Mollerup and Angelo [35] at three different temperatures using different EoSs. As the prediction results using GERG-2008 was very accurate and close to the experimental measurements, the comparison in Table 6 was made with the predictions from GERG-2008. The  $k_{ij}$ 's for SRK, PR, and PC-SAFT were taken from our previous study [20] and the  $k_{ij}$ 's for Soave-BWR are presented in the Binary VLE section (Tables 7 and 8). SRK and PR give the largest deviation even after using volume translation, with PR being slightly poorer than SRK. The non-cubic models have better accuracy in prediction of  $Z$  factor than cubics, while Soave-BWR is better than PC-SAFT. The deviation for almost all the models seems to decrease as the temperature increases. Fig. 8 shows how Soave-BWR is compared to the GERG-2008. Both models give almost accurate prediction of the experimental data, especially at pressures lower than 600 bar.

## 4. Binary VLE

In this section, we have made a comparison between Soave-BWR and GERG-2008 in calculation of bubble point pressure and vapor phase composition of 81 different binary mixtures. In addition, a comparison is made with other EoSs in calculation of the mentioned properties for the binary pairs of  $N_2$ ,  $CO_2$ ,  $H_2S$ , and  $C_1$ . The detailed calculation results for the latter case can be found in our previous study [20] for SRK, PR, and PC-SAFT. The binary VLE data is taken from the DECHEMA Chemical Data Series

VI [36], the Polish Academy of Science-TRC Floppy Book Series [37], and Mansfield and Outcalt [38].

The binary interaction parameters  $k_{ij}$ 's are usually considered equal to zero between symmetric hydrocarbons, while they are usually non-zero for the asymmetric hydrocarbons, and binary pairs of hydrocarbons and non-hydrocarbons such as N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S. It is very common in petroleum engineering calculations to set the binary interaction parameters between two hydrocarbon components to zero except that one of them is methane.

It was mentioned in section 2.1 that the four binary parameters  $\beta_{v,ij}$ ,  $\gamma_{v,ij}$ ,  $\beta_{T,ij}$ , and  $\gamma_{T,ij}$  in GERG-2008 EoS have already been fitted to the available binary data and their values can be found in [1]. To have a fair comparison between GERG-2008 and Soave-BWR, we regressed the  $k_{ij}$  values for Soave-BWR to minimize the deviation in bubble point pressures, as suggested in DECHEMA [36]. It should also be noted that  $k_{ij}$ 's were treated as temperature independent in the regression.

We regressed the  $k_{ij}$ 's firstly for all the binary pairs, however as it is preferred to use 0  $k_{ij}$  values between heavier hydrocarbon mixtures, in another scenario we only used regressed  $k_{ij}$ 's for binary mixtures of C<sub>1</sub>, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S.

Table 7 summarizes the AAD% in bubble point pressure and vapor phase composition using GERG-2008 and Soave-BWR with both 0  $k_{ij}$  and regressed  $k_{ij}$  values for binary pairs of C<sub>1</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and N<sub>2</sub>. The temperature range for the experimental data is also presented in this table. Soave-BWR with 0  $k_{ij}$ 's has larger deviation in bubble point pressure and vapor phase composition compared to GERG-2008. The average deviation in DP/P (%) for Soave-BWR with 0  $k_{ij}$  is around 9.4% while it is around 6.4% for GERG-2008. After regressing the  $k_{ij}$  values for the binary mixtures, the deviations in DP/P (%) and DY1(mol%) for Soave-BWR reduced to around 3.9% and 1.1%, respectively.

Yan et al. [20] made a comparison between SRK, PR, PC-SAFT and Soave-BWR in calculation of bubble point pressure and vapor phase composition for the binary pairs of



N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>1</sub>. We made a comparison between their results for SRK, PR, and PC-SAFT and our calculations using Soave-BWR and GERG-2008 (Fig. 9). As expected, SRK, PR, PC-SAFT and Soave-BWR with 0  $k_{ij}$ 's give poorer results than GERG-2008 (with optimal  $k_{ij}$ 's). However, using regressed  $k_{ij}$ 's significantly improves the results of SRK, PC, PC-SAFT and Soave-BWR both in bubble point pressure and vapor phase composition. Soave-BWR and PR seems to give the lowest deviation in bubble point pressure while PC-SAFT gives slightly lower deviation in vapor phase composition.

Table 8 presents the AAD% in bubble point pressure and vapor phase composition of other binary mixtures. The average deviation in DP/P (%) for Soave-BWR with regressed  $k_{ij}$ 's is around 2.4%. However, as it was mentioned earlier, we prefer to use 0  $k_{ij}$  for the heavy hydrocarbon pairs. Soave-BWR with 0  $k_{ij}$ 's still gives lower deviation in both bubble point pressure (3.3%) and vapor phase composition (1.3%) compared to GERG-2008, which has around 4.5% average deviation in DP/P (%) and 1.5% in DY1(mol%). Fig. 10 summarizes the performance of GERG-2008 and Soave-BWR with 0  $k_{ij}$  and regressed  $k_{ij}$  for all the 81 binary mixtures. As shown, Soave-BWR with regressed  $k_{ij}$ 's for all the binary pairs gives the lowest deviation while Soave-BWR with regressed  $k_{ij}$ 's only for the binary pairs of C<sub>1</sub>, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S gives slightly higher deviation. In general, the comparison shows that Soave-BWR with regressed  $k_{ij}$ 's has better performance than GERG-2008 in calculation of bubble point pressure and vapor phase composition. In all our calculations for binary and multicomponent mixtures, we have used Soave-BWR with regressed  $k_{ij}$ 's for binary pairs containing C<sub>1</sub>, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S.

GERG-2008 seems to give very large deviations in bubble point pressures for mixtures of N<sub>2</sub> and heavy n-alkanes, and some other hydrocarbon binary pairs such as n-butane and n-nonane. Fig. 11 shows the deviation in bubble point pressure calculation for different mixtures of n-C<sub>4</sub> and n-C<sub>9</sub> in the temperature range of 270 K to 370 K using GERG-2008 and Soave-BWR. The experimental data is taken from Mansfield and Outcalt [38]. Although GERG-2008 has been developed for n-C<sub>4</sub> and n-C<sub>9</sub> within this temperature range, it gives very large deviations up to around 130% at high mole fraction of n-C<sub>9</sub>. Soave-BWR with 0  $k_{ij}$  gives deviations no higher than around 10%. Fig. 12 illustrates that

GERG-2008 over predicts the bubble point pressures mainly at higher temperatures and high mole fraction of n-C<sub>9</sub>, while Soave-BWR gives very accurate results for bubble point pressure at lower temperature and the whole composition range of n-C<sub>9</sub>, and slightly over predicts this property at higher temperatures.

## 5. Phase envelopes

GERG-2008 and Soave-BWR are used to predict the phase envelopes of 30 synthetic gas mixtures from eleven different sources. The basic information of these gases can be found in Table 12 in our previous work [20]. Prediction calculations are made with the optimal  $k_{ij}$ 's for Soave-BWR given in Section 4. Some selected results are presented in Figures 13 to 16. From the calculation results, including those not shown in Figures 13 to 16, it was found that the two models generally give satisfactory and similar prediction results for most of the systems studied. Fig. 13 shows an example of this similarity where both models give accurate prediction of the phase envelope. It is possible to find individual cases where Soave-BWR performs better (Fig. 14) or GERG-2008 performs better (Fig. 15). In general, Soave-BWR seems to give smaller phase envelopes than GERG-2008 and slightly better prediction of phase envelope for the majority of the systems tested.

Besides, there were some highly asymmetric ternary systems such as Gases 26 and 27, measured by Urlic et al. [39] which were the most challenging ones among the multicomponent gas mixtures tested. Fig. 16 shows that neither of the two EoSs gives satisfactory prediction of the phase envelope over the whole temperature and pressure range. Soave-BWR seems to give slightly better prediction for Gas 26 which has lower molecular weight due to higher mole fraction of methane.

Regueira et al. [34] compared the performance of SRK, PR, PC-SAFT and Soave-BWR in phase envelope calculation for three different mixtures of methane and n-decane binary system. They observed that the cubic EoSs give better predictions of the experimental data compared to the non-cubic models especially at lower composition of methane. At

higher methane compositions, none of the models were able to predict the whole phase envelope correctly.

Fig. 17 shows the phase envelope calculation results using GERG-2008 and Soave-BWR for three different compositions of methane in the binary mixture of methane and n-decane. GERG-2008 seems to under predict the phase envelope at  $x_1=0.4031$  and over predict it at  $x_1=0.8497$ . Soave-BWR seems to give slightly better prediction of the phase envelope at lower composition of methane and smaller phase envelopes at higher compositions. As can be observed, it is not an easy task for complicated models like GERG-2008 to accurately model phase equilibrium for a highly asymmetric system as simple as methane and n-decane over a wide temperature, pressure and composition range.

## 6. Heat capacity and Joule-Thomson coefficients

As one of the second order derivative properties of Gibbs energy, heat capacity is difficult to describe accurately and modeling of this property is a challenging test for equations of state [40], [41]. Isobaric heat capacity can be expressed by the following equation:

$$C_p = C_p^{id} + C_p^r \quad (21)$$

where  $C_p^{id}$  is the ideal gas heat capacity and refers to the heat capacity of the free molecules at zero density, and  $C_p^r$  is the residual heat capacity and takes into account the intermolecular interactions.  $C_p^{id}$ , dependent only on temperature, is calculated from the correlations in DIPPR database [27], while  $C_p^r$  is calculated using EoSs. The following equations show how  $C_p^r$  is calculated [42]:

$$F = \frac{A^r(T, V, \mathbf{n})}{RT} \quad (22)$$

$$\frac{C_p^r(T, V, \mathbf{n})}{R} = -T^2 \left( \frac{\partial^2 F}{\partial T^2} \right)_{V, \mathbf{n}} - 2T \left( \frac{\partial F}{\partial T} \right)_{V, \mathbf{n}} \quad (23)$$

$$\frac{C_p^r}{R} = \frac{C_v^r(T, V, \mathbf{n})}{R} - \left(\frac{T}{R}\right) \frac{\left(\frac{\partial P}{\partial T}\right)_{V, \mathbf{n}}^2}{\left(\frac{\partial P}{\partial V}\right)_{T, \mathbf{n}}} - n \quad (24)$$

In these equations,  $V$  is the total volume,  $\mathbf{n}$  is the mole numbers vector,  $n$  is the total mole number,  $A^r$  is the residual Helmholtz energy,  $F$  is the reduced residual Helmholtz function,  $R$  is the universal gas constant, and  $C_v^r$  is the residual heat capacity at constant volume.

The Joule-Thomson coefficient ( $\mu_{JT}$ ) is the rate of change in temperature with pressure at constant enthalpy. This derivative property is important in reservoir engineering since it is often needed in describing the temperature change due to a large pressure drop. At low to moderate temperature and pressure, the  $\mu_{JT}$  is usually positive, meaning a decrease in pressure results in a decrease in temperature. However, at high pressure and high temperature (HPHT) conditions,  $\mu_{JT}$  is typically negative and the fluid warms up instead of cooling down after expansion. Joule-Thomson coefficient can be expressed by the following equation:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H, \mathbf{n}} = -\frac{1}{C_p} \left[ V + T \frac{\left(\frac{\partial P}{\partial T}\right)_{V, \mathbf{n}}}{\left(\frac{\partial P}{\partial V}\right)_{T, \mathbf{n}}} \right] = -\frac{1}{C_p} \left[ V - T \left(\frac{\partial V}{\partial T}\right)_{P, \mathbf{n}} \right] \quad (25)$$

The NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP, Version 9.1) uses high accuracy reference EoS models [30] to calculate different properties of pure components. This database uses GERG-2008 EoS for estimation of the properties for binary and multicomponent mixture. Fig. 18 and 19 show the heat capacity and Joule-Thomson coefficient calculations for methane using the reference EoS models in REFPROP. As can be seen, the REFPROP results are very close to the experimental data at different temperatures taken from [43]. As a result, to evaluate the performance of different cubic and non-cubic EoSs in calculation of thermal properties such as heat capacity and Joule-Thomson coefficient of pure components in a wide temperature and pressure range, we used synthetic data from REFPROP for the 15

main components (Table 1) in the temperature range of 250-500 K and pressure range of 5-1500 bar.

Fig. 20 shows the AAD% in the calculated heat capacity using SRK, PR, PC-SAFT, Soave-BWR and GERG-2008. On average, the non-cubic models give lower deviation than the cubic ones, and GERG-2008 gives the lowest deviation. Soave-BWR gives the closest deviation to that of GERG-2008 among other EoSs. A similar trend is observed in Fig. 21 where Mean Absolute Deviations (MAD) in the Joule-Thomson coefficient of the main components are reported. The reason for using MAD instead of AAD% was that the Joule-Thomson coefficient changes sign at high pressures. This means it would become zero at some pressures, which yields very large deviations if AAD% is used instead of MAD. The Mean Absolute Deviation for the Joule-Thomson coefficient was calculated using the following equation:

$$MAD = \frac{1}{n} \sum_{i=1}^n |\mu_{JT,i}^{Calc.} - \mu_{JT,i}^{Exp.}| \quad (26)$$

Table 9 presents the mole fraction of some sample binary and multicomponent mixtures. As it was mentioned earlier, REFPROP uses GERG-2008 for estimation of the properties of binary and multicomponent mixtures. We have used GERG-2008 to produce synthetic heat capacity and Joule-Thomson coefficient data in the temperature range of 250-500 K and pressure range of 5-1500 bar to see how accurate SRK, PR, PC-SAFT and Soave-BWR predict these thermal properties for multicomponent mixtures compared to GERG-2008. Figs. 22 and 23 show AAD% in heat capacity and MAD in Joule-Thomson coefficient of binary and multicomponent mixtures within 250-500 K and 5-1500 bar. PC-SAFT gives the lowest deviation in heat capacity while Soave-BWR is superior in Joule-Thomson coefficient calculations.

As Soave-BWR was superior to SRK, PR, and PC-SAFT in Joule-Thomson coefficient calculation of pure and multicomponent mixture and also heat capacity of pure components, we selected this EoS for the following calculations.

Figures 24-29 present the heat capacity and Joule-Thomson coefficient calculation results using GERG-2008 and Soave-BWR for methane, binary mixture of methane + ethane, and a multicomponent natural gas mixture. The experimental data for all these three systems is taken from Ernst et al.'s work [43]. In these figures the model predictions are presented up to very high pressures (1500 bar or 150 MPa) to see how the two models differ at HPHT conditions.

Fig. 24 shows heat capacity calculations for pure methane. Both Soave-BWR and GERG-2008 give accurate prediction of heat capacity at lower temperatures and pressures, while GERG-2008 has slightly better performance at lower temperatures and higher pressures. At higher temperatures both models seem to under predict the heat capacity for methane, while Soave-BWR gives closer predictions to the experimental data. The same behavior is observed for the methane and ethane binary system and natural gas mixture (Figs. 25, 26).

The difference between two models is not significant for the Joule-Thomson coefficient calculations (Figs. 27-29). GERG-2008 gives slightly better results than Soave-BWR, but in general both models give accurate predictions of Joule-Thomson coefficient over the whole pressure and temperature range. Although the experimental data is not available at high pressures, both models seem to predict a negative Joule-Thomson coefficient at 1500 bar and all temperatures. In fact, the value of Joule-Thomson coefficient seems to reach more or less a constant value at high pressures for the pure, binary and multicomponent systems. As the Joule-Thomson coefficient is negative at high pressures, the temperature of the fluid increases with the pressure drop. The temperature increase due to the pressure drop is known as the reverse Joule-Thomson effect. Although the temperature increase is not very significant (around 0.5 K/Mpa), it should be considered in the material selection for the tubing and surface facilities because the temperature increase can damage the surface production facilities and affect well integrity and safety.

## 7. Conclusions

We compared GERG-2008 with other cubic (SRK and PR) and non-cubic EoSs (Soave-BWR and PC-SAFT) in calculation of phase equilibrium and physical properties of natural gas related systems in this study. The comparison was especially focused on Soave-BWR which is a multi-parameter non-cubic EoS as GERG-2008 but has a much simpler form.

GERG-2008 is superior to other cubic and non-cubic EoSs studied in this work, in calculation of density, saturated liquid density, and compressibility of pure components over a wide pressure and temperature range. It was found that Soave-BWR is largely comparable to GERG-2008, although not as good in density description of pure and binary mixtures. GERG-2008 has a clear advantage over SRK, PR, PC-SAFT and Soave-BWR in liquid compressibility calculation for the pure components, while Soave-BWR with regressed binary interaction parameters seems to have better performance than GERG-2008 in bubble point pressure and vapor phase composition of binary mixtures. GERG-2008 gives very large deviations for bubble point pressure calculation of some heavy and asymmetric binary systems such as n-butane + n-nonane system. This suggests that this EoS and its binary interaction parameters could still be improved for some of the binary pairs.

Soave-BWR and GERG-2008 are very similar in phase equilibrium calculation and both have challenges in describing highly asymmetric systems, even binary pairs as simple as methane and n-decane. Both models give satisfactory predictions for gas compressibility factor of multicomponent mixtures.

GERG-2008 shows some advantages over other EoSs in calculation of heat capacity and Joule-Thomson coefficient of pure components over a wide temperature and pressure range. Soave-BWR gives the closest prediction of the thermal properties to that of GERG-2008 among other EoSs tested in this study.

The comparison shows the potential of Soave-BWR as a light-weight alternative to GERG-2008 especially in PVT modeling and Joule-Thomson coefficient calculations. There is apparently room for improvement of Soave-BWR in order to improve its accuracy to the level comparable to that of GERG-2008 in description of some physical properties and to give better phase equilibrium calculation. Soave-BWR was developed

mainly based on hydrocarbons. Other components common in industrial applications should definitely be included in its further development. It is relatively easy to apply Soave-BWR to systems containing ill-defined heptanes plus fractions with the existing characterization methods. Such a characterization procedure should be developed for GERG-2008 in the future.

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## Figure captions

Fig. 1. AAD% in the calculated saturated liquid density, and AAD% and AAD0% in the calculated density of pure components within 150-500 K and 0-2000 bar using GERG-2008 and Soave-BWR.

Fig. 2. AAD% in the calculated density and saturated liquid density of the “main components” using different EoSs.

Fig. 3. Density vs. pressure for n-C<sub>9</sub> using GERG-2008 (blue lines) and Soave-BWR (red lines) at different temperatures: 303.15 K (solid lines), 323.15 K (dotted lines), 373.15 K (dashed line), 473.15 K (dash-dot lines), 523.15 K (long-dashed lines), and 573.15 K (long-dashed double dots lines). The experimental data is taken from [33].

Fig. 4. Contour map of deviation in the calculated density (a) and compressibility (b) for methane using GERG-2008. The relative deviations (%) are labeled on the contour lines. The blue dashed lines show negative deviations and solid black lines show positive deviations. The green and the red circles indicate the conditions for the minimum and the maximum deviations, respectively.

Fig. 5. Contour map of deviation in the compressibility of methane using SRK (a), PR (b), SRK with volume translation (c), PR with volume translation (d), PC-SAFT (e), and Soave-BWR (f).

Fig. 6. AAD% in the calculated densities of the binary system methane (1) + n-decane (2) using GERG-2008, PC-SAFT and Soave-BWR with regressed  $k_{ij}$  within 278.15-463.15 K and 1-1400 bar. The experimental data is taken from [34].

Fig. 7. Density vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for two mixtures of C<sub>1</sub> and C<sub>10</sub> at different temperatures. 22.27 mol% C<sub>1</sub> and 323.2 K (◇, solid lines), 22.27 mol% C<sub>1</sub> and 463.2 K (△, dashed lines),

70.85 mol% C<sub>1</sub> and 323.2 K (□, dash-dot lines), and 70.85 mol% C<sub>1</sub> and 463.2 K (○, long-dashed lines). The experimental data is taken from [34].

Fig. 8. Experimental and simulated results using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for Z-factor of the gas mixture A from [35] at different temperatures: 290 K (solid lines), 315 K (dashed lines), and 340 K (long-dashed lines).

Fig. 9. AAD% in bubble point pressure and vapor phase composition for the binary pairs of N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>1</sub> using different EoSs with 0  $k_{ij}$  and regressed  $k_{ij}$ .

Fig. 10. AAD% in bubble point pressure and vapor phase composition of 81 binary mixtures using GERG-2008 and Soave-BWR with 0  $k_{ij}$  and regressed  $k_{ij}$ .

Fig. 11. Deviations in bubble point pressure calculation as a function of temperature using GERG-2008 (blue markers) and Soave-BWR with 0  $k_{ij}$  (red markers) for different binary mixtures of n-butane (1) + n-nonane (2). 74.9 mol% n-C<sub>4</sub> (■), 50.2 mol% n-C<sub>4</sub> (▲), 26.2 mol% n-C<sub>4</sub> (◆), and 21.4 mol% n-C<sub>4</sub> (●). The experimental data is taken from [38].

Fig. 12. Bubble point pressures at different temperatures using GERG-2008 (blue lines) and Soave-BWR with 0  $k_{ij}$  (red lines) for binary mixtures of n-C<sub>4</sub> and n-C<sub>9</sub>. 74.9 mol% n-C<sub>4</sub> (□, solid lines), 50.2 mol% n-C<sub>4</sub> (△, dashed lines), 26.2 mol% n-C<sub>4</sub> (◇, dash-dot lines), and 21.4 mol% n-C<sub>4</sub> (○, dotted lines). The experimental data is taken from [38].

Fig. 13. Phase envelope for Gas 18 from [20].

Fig. 14. Phase envelopes for (a) Gas 1, and (b) Gas 3 from [20].

Fig. 15. Phase envelopes for (a) Gas 5, and (b) Gas 21 from [20].

Fig. 16. Phase envelopes for (a) Gas 26, and (b) Gas 27 from [20]

Fig. 17. Phase envelope for different binary mixtures of methane (1) + n-decane (2) using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines): 40.31 mol%  $C_1$  (solid lines), 60.21 mol%  $C_1$  (dashed lines), and 84.97 mol%  $C_1$  (dotted lines). The experimental data is taken from [34].

Fig. 18. Heat capacity prediction for methane at different temperatures using REFPROP. The experimental data is taken from [43].

Fig. 19. Joule-Thomson coefficient prediction for methane at different temperatures using REFPROP. The experimental data is taken from [43].

Fig. 20. AAD% in the heat capacity of the “main components” within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results.

Fig. 21. MAD in the Joule-Thomson coefficient of “main components” within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results.

Fig. 22. AAD% in the heat capacity of binary and multicomponent mixtures within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results (REFPROP uses GERG-2008 for mixtures).

Fig. 23. MAD in the Joule-Thomson coefficient of binary and multicomponent mixtures within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results (REFPROP uses GERG-2008 for mixtures).

Fig. 24. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR (red lines) for  $C_1$  at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines). The experimental data is taken from [43].

Fig. 25. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for C<sub>1</sub>-C<sub>2</sub> mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

Fig. 26. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for the natural gas mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

Fig. 27. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR (red lines) for C<sub>1</sub> at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines). The experimental data is taken from [43].

Fig. 28. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for C<sub>1</sub>-C<sub>2</sub> mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

Fig. 29. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for the natural gas mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).



## Tables

Table 1. Applicable ranges for the reference EoS models for various components

Component	$T_{\min}$ (K)	$T_{\max}$ (K)	$P_{\max}$ (bar)	$\rho_{\max}$ (mol/L)	$T_{r, \min}$
Main Components					
N <sub>2</sub>	63.15	2000	22000	53.15	0.50
CO <sub>2</sub>	216.59	2000	8000	37.24	0.71
H <sub>2</sub> S	187.70	760	170000	29.12	0.50
CH <sub>4</sub>	90.69	625	10000	40.07	0.48
C <sub>2</sub> H <sub>6</sub>	90.37	675	9000	22.42	0.30
C <sub>3</sub> H <sub>8</sub>	85.53	650	10000	20.60	0.23
nC <sub>4</sub> H <sub>10</sub>	134.90	575	2000	13.86	0.32
iC <sub>4</sub> H <sub>10</sub>	113.73	575	350	12.90	0.28
nC <sub>5</sub> H <sub>12</sub>	143.47	600	1000	11.20	0.31
iC <sub>5</sub> H <sub>12</sub>	112.65	500	10000	13.30	0.24
nC <sub>6</sub> H <sub>14</sub>	177.83	600	1000	8.85	0.35
nC <sub>7</sub> H <sub>16</sub>	182.55	600	1000	7.75	0.34
nC <sub>8</sub> H <sub>18</sub>	216.37	600	1000	6.69	0.38
nC <sub>9</sub> H <sub>20</sub>	219.70	600	8000	6.06	0.37
nC <sub>10</sub> H <sub>22</sub>	243.50	675	8000	5.41	0.39
Other Components					
H <sub>2</sub>	13.96	1000	2000000	102.00	0.42
O <sub>2</sub>	54.36	2000	82000	43.35	0.35
CO	68.16	500	100000	33.84	0.51
H <sub>2</sub> O	273.16	2000	1000000	73.96	0.42
He	2.18	2000	1000000	141.22	0.42
Ar	83.81	2000	1000000	50.65	0.56

Table 2. AAD% and maximum absolute deviation in the calculated density within 150-500 K and 0-2000 bar, and AAD0% and maximum absolute deviation within applicable range of reference EoS

Component	Soave-BWR		GERG-2008		Soave-BWR		GERG-2008	
	AAD%	Max Dev.	AAD%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.
N <sub>2</sub>	0.57	2.63	0.024	0.159	0.57	2.63	0.024	0.159
CO <sub>2</sub>	0.74	3.81	0.161	1.368	0.78	3.81	0.057	0.596
H <sub>2</sub> S	0.38	3.45	0.006	0.006	0.37	3.45	0.006	0.006
CH <sub>4</sub>	0.88	4.08	0.025	0.123	0.88	4.08	0.025	0.123
C <sub>2</sub> H <sub>6</sub>	0.64	4.15	0.111	0.296	0.64	4.15	0.111	0.296
C <sub>3</sub> H <sub>8</sub>	1.44	4.57	0.057	0.927	1.44	4.57	0.057	0.927
nC <sub>4</sub> H <sub>10</sub>	1.81	3.46	0.070	0.891	1.81	3.46	0.070	0.891
iC <sub>4</sub> H <sub>10</sub>	2.17	4.48	0.166	0.627	0.84	4.48	0.078	0.627
nC <sub>5</sub> H <sub>12</sub>	1.70	4.73	0.006	0.007	1.01	4.73	0.006	0.007
iC <sub>5</sub> H <sub>12</sub>	2.78	4.72	0.006	0.006	2.78	4.72	0.006	0.006
nC <sub>6</sub> H <sub>14</sub>	1.35	3.39	0.006	0.006	0.87	2.18	0.006	0.006
nC <sub>7</sub> H <sub>16</sub>	1.29	3.51	0.006	0.006	0.74	2.25	0.006	0.006
nC <sub>8</sub> H <sub>18</sub>	1.04	3.22	0.006	0.006	0.56	1.55	0.006	0.006
nC <sub>9</sub> H <sub>20</sub>	0.85	3.38	0.006	0.006	1.13	3.38	0.006	0.006
nC <sub>10</sub> H <sub>22</sub>	0.78	3.44	0.006	0.006	1.09	3.44	0.006	0.006
H <sub>2</sub>	12.19	16.84	0.096	0.464	12.19	16.84	0.096	0.464
O <sub>2</sub>	0.29	4.81	0.276	0.724	0.28	4.81	0.175	0.714
CO	0.88	3.71	0.006	0.006	0.91	3.71	0.006	0.006
H <sub>2</sub> O <sup>a</sup>	16.52	21.38	0.252	2.000	17.48	21.38	0.126	1.050
He	-	-	0.415	4.129	-	-	0.415	4.129
Ar	0.72	3.71	0.245	0.654	0.72	3.71	0.245	0.654
Average	2.45	5.37	0.09	0.59	2.35	5.17	0.07	0.51
Average - Main Components	1.23	3.80	0.04	0.30	1.03	3.53	0.03	0.24

<sup>a</sup> For water the calculations are made within 230-500 K.

Table 3. AAD% and maximum absolute deviations in the calculated saturated liquid density

Component	Soave-BWR		GERG-2008	
	AAD%	Max Dev.	AAD%	Max Dev.
N <sub>2</sub>	1.18	1.31	0.06	0.561
CO <sub>2</sub>	1.47	3.20	0.04	0.075
H <sub>2</sub> S	1.19	3.93	0.07	0.006
CH <sub>4</sub>	0.85	3.07	0.05	0.195
C <sub>2</sub> H <sub>6</sub>	0.44	1.61	0.10	0.165
C <sub>3</sub> H <sub>8</sub>	0.21	0.74	0.17	0.282
nC <sub>4</sub> H <sub>10</sub>	0.55	1.12	0.21	0.765
iC <sub>4</sub> H <sub>10</sub>	0.57	1.54	0.29	0.527
nC <sub>5</sub> H <sub>12</sub>	0.34	1.04	0.11	0.006
iC <sub>5</sub> H <sub>12</sub>	1.17	1.50	0.09	0.006
nC <sub>6</sub> H <sub>14</sub>	0.32	4.72	0.22	0.007
nC <sub>7</sub> H <sub>16</sub>	0.55	6.83	0.17	0.006
nC <sub>8</sub> H <sub>18</sub>	0.63	8.39	0.15	0.007
nC <sub>9</sub> H <sub>20</sub>	0.54	3.94	0.11	0.006
nC <sub>10</sub> H <sub>22</sub>	0.72	6.77	0.13	0.006
H <sub>2</sub>	31.47	39.20	0.61	2.258
O <sub>2</sub>	0.43	2.79	0.18	0.173
CO	1.49	2.17	0.17	0.006
H <sub>2</sub> O	16.11	18.07	0.12	0.298
He	58.69	78.77	0.45	1.240
Ar	0.13	2.27	0.18	0.152
Average	5.67	9.19	0.18	0.32
Average - Main Components	0.72	3.31	0.13	0.17

Table 4. AAD% in the calculated high pressure liquid densities for n-C<sub>7</sub> and n-C<sub>9</sub>

EoS	nC <sub>7</sub>	nC <sub>9</sub>	Average
Soave-BWR	2.13	1.57	1.85
GERG-2008	0.55	0.34	0.45

Table 5. AAD0% and maximum absolute deviations in the calculated compressibility of the “main components”

Component	SRK		PR		SRK-VT		PR-VT		PC-SAFT		Soave-BWR		GERG-2008	
	AAD0%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.	AAD0%	Max Dev.
N <sub>2</sub>	6.01	33.74	7.84	33.31	5.84	35.59	6.90	42.01	3.09	14.31	2.77	8.57	0.220	1.027
CO <sub>2</sub>	12.87	79.18	13.80	67.73	9.90	69.36	11.67	61.87	4.71	61.73	2.49	20.56	1.065	7.291
H <sub>2</sub> S	12.26	55.32	12.51	46.31	10.28	50.80	11.14	36.41	4.26	29.95	3.43	30.66	0.006	0.019
CH <sub>4</sub>	8.69	77.34	10.20	70.33	8.53	75.22	10.26	56.61	3.41	24.51	3.28	19.13	0.175	1.301
C <sub>2</sub> H <sub>6</sub>	15.94	84.54	17.06	75.03	16.27	79.22	18.86	63.48	5.81	27.86	5.65	17.79	0.846	2.324
C <sub>3</sub> H <sub>8</sub>	20.81	89.26	22.08	78.06	22.12	81.47	24.60	68.66	11.05	35.16	10.41	20.97	0.914	4.743
nC <sub>4</sub> H <sub>10</sub>	25.03	95.42	26.64	83.10	27.43	85.49	29.16	75.58	15.40	49.92	12.95	21.07	0.547	5.667
iC <sub>4</sub> H <sub>10</sub>	28.16	90.82	24.20	76.96	22.56	81.41	20.69	68.52	17.35	49.96	9.09	18.85	1.538	6.311
nC <sub>5</sub> H <sub>12</sub>	21.41	99.05	22.45	85.16	21.76	86.33	23.17	79.98	21.52	59.73	11.92	22.6	0.006	0.008
iC <sub>5</sub> H <sub>12</sub>	28.27	97.79	29.99	85.42	31.27	86.53	32.25	78.98	21.22	60.33	16.05	25.52	0.006	0.009
nC <sub>6</sub> H <sub>14</sub>	20.00	106.60	20.84	93.29	21.41	91.94	21.39	90.42	15.97	44.10	10.71	18.5	0.006	0.007
nC <sub>7</sub> H <sub>16</sub>	21.19	101.69	21.93	83.76	23.33	83.69	21.96	83.62	21.21	51.40	13.29	21.11	0.006	0.006
nC <sub>8</sub> H <sub>18</sub>	20.67	97.09	21.38	79.31	23.87	77.52	20.70	82.29	18.66	41.01	12.29	20.53	0.006	0.006
nC <sub>9</sub> H <sub>20</sub>	31.52	110.34	32.86	87.79	37.59	86.14	30.90	94.41	20.27	48.87	16.92	25.82	0.006	0.006
nC <sub>10</sub> H <sub>22</sub>	31.19	93.78	32.42	70.51	37.91	68.28	29.37	80.49	21.46	43.22	17.18	27.5	0.006	0.006
Average	20.27	87.47	21.08	74.40	21.34	75.93	20.87	70.89	13.69	42.80	9.89	21.28	0.36	1.92

Table 6. AAD% in the calculated gas Z factor of gas mixture A from [35] using different EoSs. The results are compared with GERG-2008 predictions.

EoS	290 K	315 K	340 K	Average
SRK	2.05	1.99	1.93	1.99
PR	5.28	4.83	4.46	4.86
SRK-VT	1.75	1.58	1.44	1.59
PR-VT	1.90	1.72	1.54	1.72
PC-SAFT	0.87	0.78	0.84	0.83
Soave-BWR	0.40	0.26	0.19	0.28

Table 7. Deviation in bubble point pressure and vapor phase composition by GERG-2008 and Soave-BWR with 0 and regressed  $k_{ij}$  values for binary pairs of N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S and C<sub>1</sub> (experimental data from [36], [37])

System		Temp. Range		Soave-BWR (0 $k_{ij}$ )		Soave-BWR (Regressed $k_{ij}$ )			GERG-2008	
COMP1	COMP2	$T_{min}$ (K)	$T_{max}$ (K)	$DP/P$ (%)	$DYI$ (mol%)	$k_{ij}$	$DP/P$ (%)	$DYI$ (mol%)	$DP/P$ (%)	$DYI$ (mol%)
C <sub>1</sub>	C <sub>2</sub>	91	283	1.63	0.38	0.0003	1.60	0.38	1.73	0.45
	C <sub>3</sub>	90	363	3.54	0.68	0.0021	3.11	0.67	2.77	0.84
	iC <sub>4</sub>	110	378	3.20	1.04	-0.0079	2.62	1.01	2.40	0.99
	C <sub>4</sub>	115	411	4.04	0.81	-0.0046	4.37	0.84	5.00	0.96
	iC <sub>5</sub>	344	444	9.75	3.08	-0.0142	8.72	3.16	9.65	3.85
	C <sub>5</sub>	176	455	3.96	1.42	-0.0076	3.04	1.25	3.53	1.48
	C <sub>6</sub>	183	444	5.46	0.74	-0.0046	5.08	0.66	5.79	0.77
	C <sub>7</sub>	143	511	12.24	0.71	-0.0153	9.42	0.61	11.85	1.26
	C <sub>8</sub>	223	423	10.51	0.19	-0.0164	5.20	0.23	9.09	0.32
	C <sub>9</sub>	223	423	14.68	0.28	-0.0181	6.67	0.24	9.89	0.28
CO <sub>2</sub>	C <sub>10</sub>	244	583	17.72	1.10	-0.0321	6.97	0.74	9.10	1.17
	H <sub>2</sub> S	225	367	12.70	4.37	0.0735	1.40	0.89	1.31	1.05
	C <sub>1</sub>	153	301	11.64	3.60	0.0803	2.01	0.87	2.42	1.08
	C <sub>2</sub>	207	301	16.62	6.27	0.0935	2.53	2.23	2.83	2.34
	C <sub>3</sub>	233	361	14.58	3.76	0.0891	3.35	0.60	3.35	0.98
	iC <sub>4</sub>	273	398	10.59	2.20	0.0656	2.23	0.90	2.50	1.22
	C <sub>4</sub>	228	418	13.14	2.46	0.0737	2.93	1.33	2.98	1.20
	iC <sub>5</sub>	278	453	13.19	2.02	0.0550	1.58	0.63	3.41	0.77
	C <sub>5</sub>	253	463	11.35	2.12	0.0567	3.00	0.63	5.40	1.01
	C <sub>6</sub>	238	393	14.53	0.72	0.0538	3.18	0.50	6.09	1.00
H <sub>2</sub> S	C <sub>7</sub>	238	502	7.90	0.68	0.0300	6.69	0.73	6.08	1.23
	C <sub>8</sub>	216	441	11.63	0.40	0.0388	5.53	0.17	10.20	0.38
	C <sub>9</sub>	343	343	8.77	0.08	0.0205	2.43	0.03	4.19	0.45
	C <sub>10</sub>	236	584	7.83	0.48	0.0178	5.11	0.49	9.78	1.25
	C <sub>1</sub>	193	367	16.26	5.46	0.0712	3.84	1.80	4.24	2.08
	C <sub>2</sub>	200	360	12.26	5.90	0.0608	1.44	1.60	0.83	1.41
	C <sub>3</sub>	217	366	9.31	3.89	0.0491	2.04	1.73	1.75	1.65
	iC <sub>4</sub>	344	398	3.69	1.58	0.0294	2.18	1.20	1.87	0.93
	C <sub>4</sub>	366	418	4.09	1.48	0.0364	1.90	1.02	1.96	0.85
	iC <sub>5</sub>	323	413	4.43	2.10	0.0182	3.50	1.66	2.63	1.09
H <sub>2</sub> S	C <sub>5</sub>	278	444	4.45	1.29	0.0152	1.58	1.43	3.12	1.44
	C <sub>6</sub>	323	423	2.79	0.43	0.0016	2.73	0.44	1.85	0.69
	C <sub>7</sub>	311	478	3.64	0.88	0.0000	3.64	0.88	4.24	1.18
	C <sub>10</sub>	278	444	15.08	0.20	-0.0335	4.23	0.14	6.96	0.13

Continued

System		Temp. Range		Soave-BWR (0 $k_{ij}$ )		Soave-BWR (Regressed $k_{ij}$ )			GERG-2008	
COMP1	COMP2	$T_{min}$ (K)	$T_{max}$ (K)	$DP/P$ (%)	$DYI$ (mol%)	$k_{ij}$	$DP/P$ (%)	$DYI$ (mol%)	$DP/P$ (%)	$DYI$ (mol%)
N <sub>2</sub>	CO <sub>2</sub>	220	301	4.99	1.54	0.0167	1.95	1.78	1.49	0.45
	H <sub>2</sub> S	200	344	19.05	6.42	0.1197	6.17	2.10	6.65	1.25
	C <sub>1</sub>	78	184	7.56	2.09	0.0250	1.73	1.21	1.79	1.19
	C <sub>2</sub>	111	290	8.58	1.46	0.0334	2.78	0.91	2.00	0.51
	C <sub>3</sub>	92	353	14.05	1.70	0.0445	8.34	0.89	5.64	0.85
	iC <sub>4</sub>	255	394	11.09	1.96	0.0361	3.59	1.49	4.11	1.37
	C <sub>4</sub>	250	411	10.02	2.71	0.0339	4.06	3.29	4.12	2.64
	iC <sub>5</sub>	278	377	5.56	1.33	0.0148	3.16	1.08	6.37	1.72
	C <sub>5</sub>	277	378	7.14	1.01	0.0145	4.30	0.98	6.48	1.11
	C <sub>6</sub>	311	444	10.71	1.49	0.0300	5.19	1.76	12.29	1.36
C <sub>7</sub>	305	497	7.30	1.88	0.0087	5.97	1.94	23.80	2.67	
C <sub>8</sub>	322	344	7.77	-	0.0143	4.74	-	49.35	-	
C <sub>9</sub>	322	344	4.48	-	0.0048	3.81	-	8.96	-	
C <sub>10</sub>	311	411	15.12	0.09	-0.0413	4.72	0.08	12.80	0.17	
Average				9.39	1.88		3.88	1.07	6.39	1.15

Table 8. Deviation in bubble point pressure and vapor phase composition by GERG-2008 and Soave-BWR with 0 and regressed  $k_{ij}$  values (experimental data from [36]–[38])

System		Temp. Range		Soave-BWR (0 $k_{ij}$ )		Soave-BWR (Regressed $k_{ij}$ )			GERG-2008		
COMP1	COMP2	$T_{min}$ (K)	$T_{max}$ (K)	$DP/P$ (%)	$DYI$ (mol%)	$k_{ij}$	$DP/P$ (%)	$DYI$ (mol%)	$DP/P$ (%)	$DYI$ (mol%)	
C <sub>2</sub>	C <sub>3</sub>	128	368	2.43	0.84	-0.0035	2.34	0.90	2.36	0.97	
	iC <sub>4</sub>	311	394	2.75	0.93	-0.0138	1.16	1.01	1.53	1.17	
	C <sub>4</sub>	229	403	1.89	0.70	-0.0043	2.32	0.69	1.64	0.64	
	C <sub>5</sub>	278	444	1.79	1.17	-0.0036	1.44	1.13	1.71	1.60	
	C <sub>6</sub>	298	450	8.52	1.40	-0.0149	7.93	1.25	9.85	1.65	
	C <sub>7</sub>	230	505	3.74	0.38	-0.0132	1.95	0.36	4.28	1.10	
	C <sub>8</sub>	185	373	3.99	2.27	-0.0071	2.60	2.26	3.31	2.28	
	C <sub>10</sub>	185	511	8.33	0.59	-0.0207	4.06	0.52	3.02	0.79	
	C <sub>3</sub>	iC <sub>4</sub>	267	394	1.41	0.34	-0.0032	1.26	0.33	1.20	0.32
		C <sub>4</sub>	260	413	1.61	0.56	-0.0006	1.59	0.56	1.49	0.57
C <sub>5</sub>		337	444	3.06	0.60	0.0137	1.05	0.80	1.03	0.84	
C <sub>6</sub>		273	483	1.39	-	-0.0045	1.19	-	3.10	-	
C <sub>7</sub>		332	513	1.14	-	-0.0044	0.95	-	1.09	-	
C <sub>8</sub>		340	546	2.19	1.67	-0.0080	1.44	1.51	2.75	3.25	
C <sub>9</sub>		377	377	8.16	0.04	-0.0245	0.70	0.11	0.29	0.08	
C <sub>10</sub>		210	511	4.73	0.72	-0.0081	3.71	0.61	2.48	0.54	
iC <sub>4</sub>		C <sub>4</sub>	273	344	12.17	1.14	-0.0035	12.28	1.02	11.97	1.02
C <sub>4</sub>		C <sub>5</sub>	298	458	0.75	6.94	0.0049	0.72	6.11	0.75	6.87
	C <sub>6</sub>	253	497	2.41	-	-0.0079	2.65	-	2.73	-	
	C <sub>7</sub>	337	526	0.89	0.28	0.0003	0.90	0.28	1.26	0.51	
	C <sub>8</sub>	270	375	4.31	-	-0.0005	4.30	-	7.73	-	
	C <sub>9</sub>	270	370	4.26	-	-0.0051	3.07	-	53.60	-	
	C <sub>10</sub>	311	511	1.52	-	-0.0012	1.35	-	1.56	-	
	iC <sub>5</sub>	C <sub>5</sub>	328	385	2.01	9.39	0.0116	1.20	9.20	1.96	9.38
	C <sub>6</sub>	301	335	0.67	0.33	0.0016	0.36	0.45	1.84	0.83	
C <sub>5</sub>	C <sub>6</sub>	298	309	3.30	1.01	0.0056	2.88	0.93	3.02	0.99	
	C <sub>7</sub>	404	513	1.14	0.64	0.0050	0.84	0.52	1.04	0.73	
	C <sub>8</sub>	304	314	3.85	0.43	0.0000	3.85	0.43	4.06	0.46	
	C <sub>10</sub>	318	334	1.33	0.24	0.0012	1.25	0.24	1.20	0.24	
C <sub>6</sub>	C <sub>7</sub>	287	369	1.33	0.75	-0.0016	1.31	0.83	1.88	0.61	
	C <sub>8</sub>	287	388	7.89	0.72	-0.0202	4.61	1.87	11.40	1.51	
C <sub>7</sub>	C <sub>8</sub>	313	394	1.33	0.86	0.0021	1.25	0.65	1.32	0.59	
C <sub>8</sub>	C <sub>10</sub>	349	392	1.10	0.36	-0.0030	0.70	0.56	0.62	0.75	
Average				3.25	1.31		2.40	1.30	4.52	1.49	



Table 9. Mole fraction of different binary and multicomponent mixtures used for heat capacity and Joule-Thomson coefficient calculations

Component	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
N <sub>2</sub>	-	-	-	-	-	0.10	-
CO <sub>2</sub>	-	-	0.50	-	-	0.02	-
CH <sub>4</sub>	0.50	0.50	0.50	0.81	0.60	0.80	0.70
C <sub>2</sub> H <sub>6</sub>	0.50	-	-	-	-	0.05	0.13
C <sub>3</sub> H <sub>8</sub>	-	-	-	-	-	0.03	0.11
nC <sub>4</sub> H <sub>10</sub>	-	-	-	0.14	0.31	-	0.06
nC <sub>10</sub> H <sub>22</sub>	-	0.50	-	0.05	0.09	-	-

## Figures

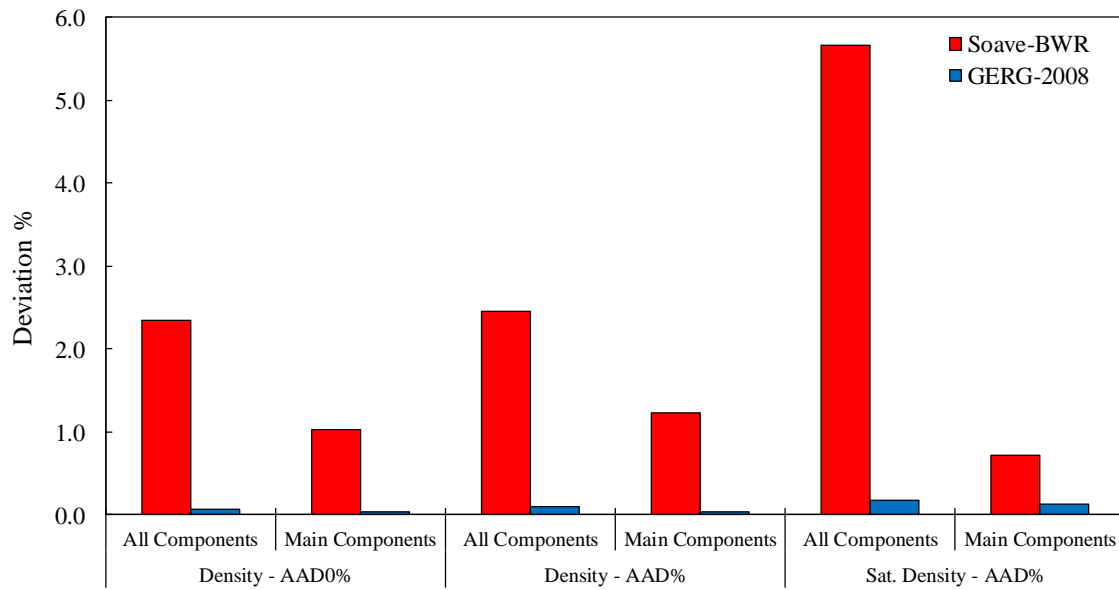


Fig. 1. AAD% in the calculated saturated liquid density, and AAD% and AAD0% in the calculated density of pure components within 150-500 K and 0-2000 bar using GERG-2008 and Soave-BWR.

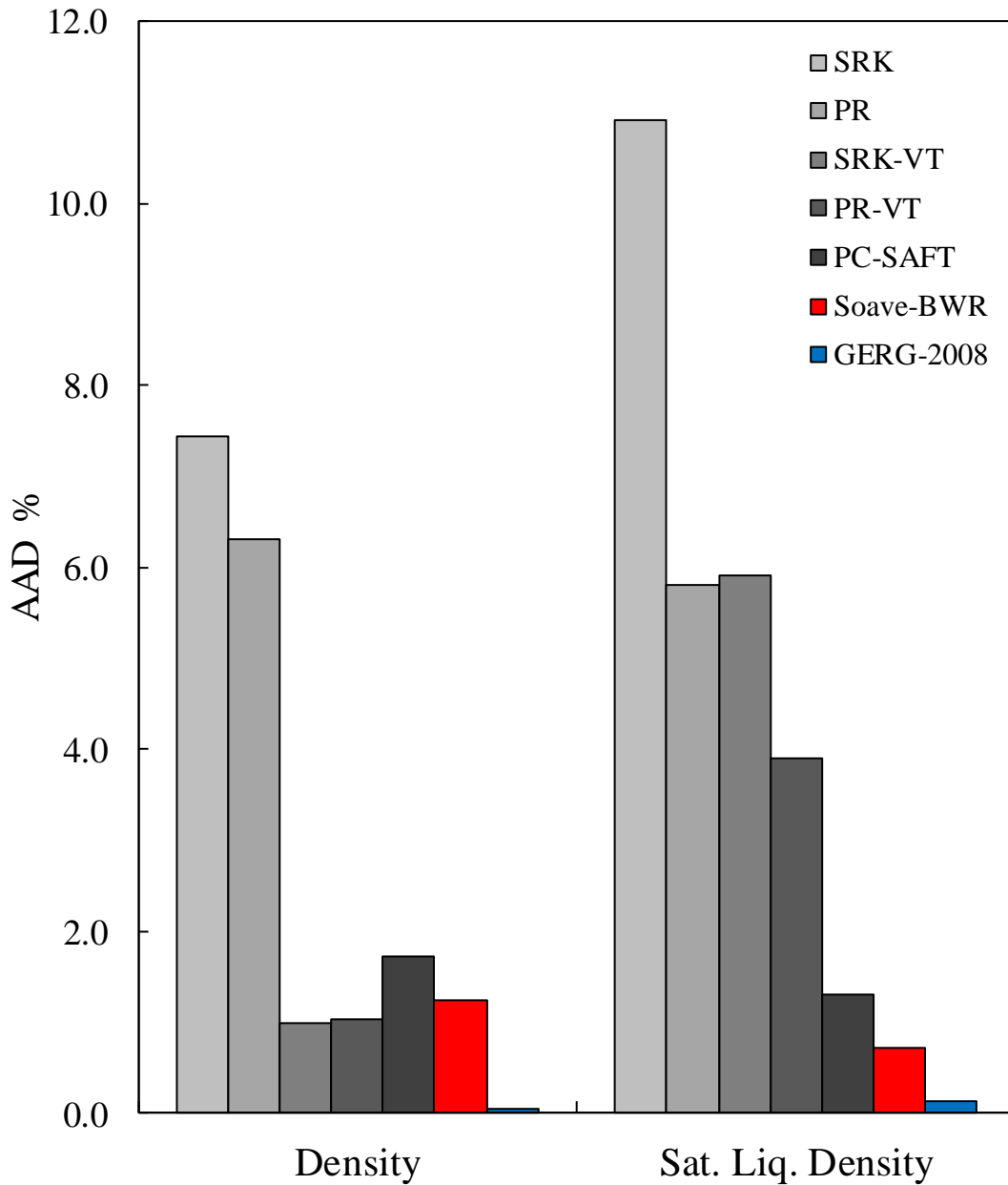


Fig. 2. AAD% in the calculated density and saturated liquid density of the “main components” using different EoSs.

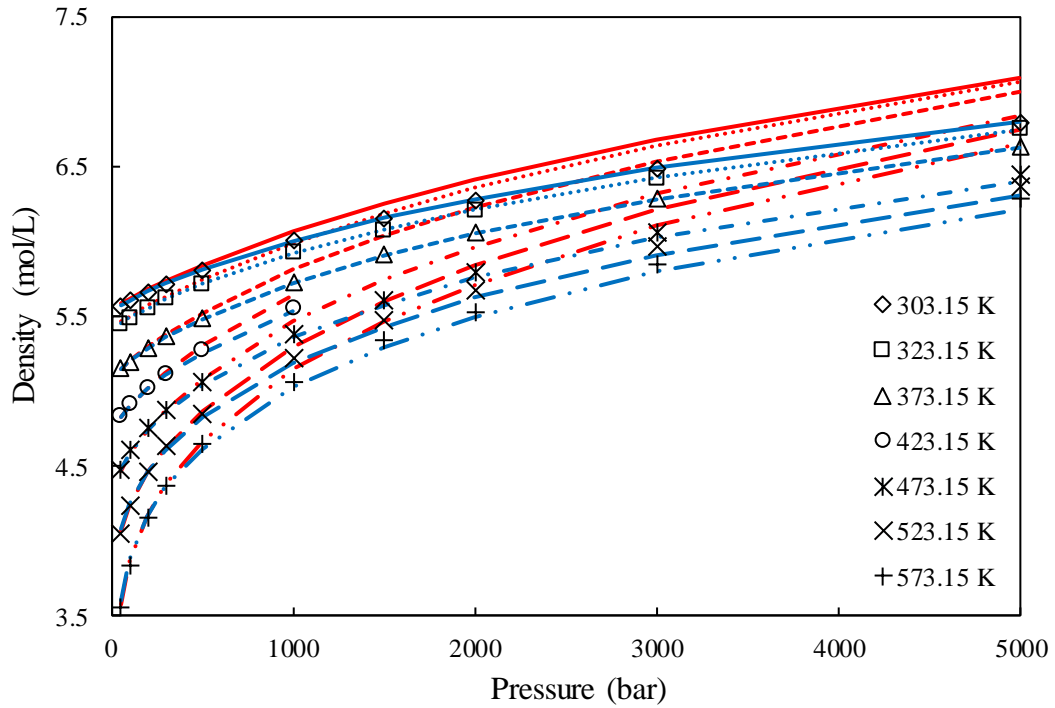
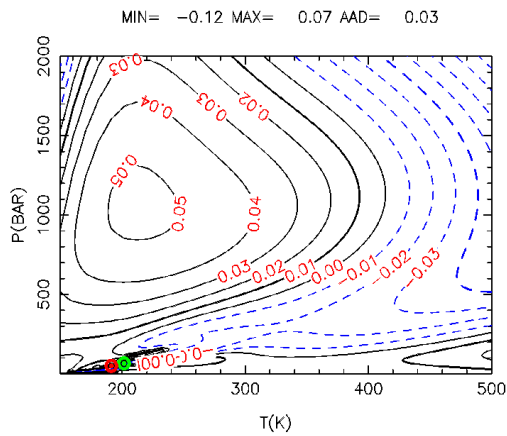


Fig. 3. Density vs. pressure for n-C<sub>9</sub> using GERG-2008 (blue lines) and Soave-BWR (red lines) at different temperatures: 303.15 K (solid lines), 323.15 K (dotted lines), 373.15 K (dashed line), 473.15 K (dash-dot lines), 523.15 K (long-dashed lines), and 573.15 K (long-dashed double dots lines). The experimental data is taken from [33].

(a) Density



(b) Compressibility

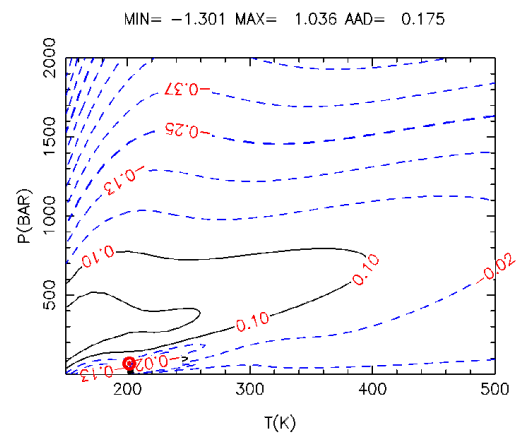
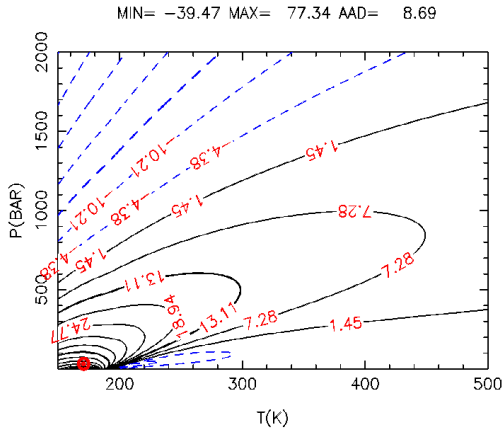
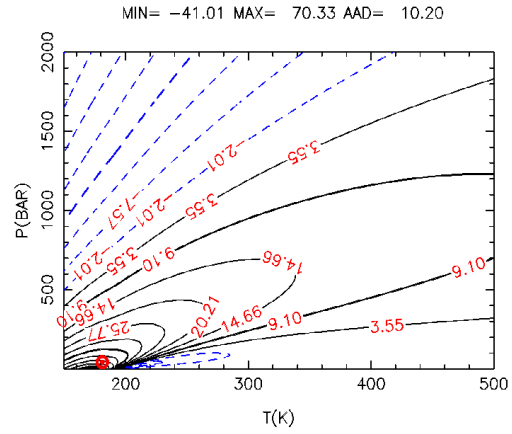


Fig. 4. Contour map of deviation in the calculated density (a) and compressibility (b) for methane using GERG-2008. The relative deviations (%) are labeled on the contour lines. The blue dashed lines show negative deviations and solid black lines show positive deviations. The green and the red circles indicate the conditions for the minimum and the maximum deviations, respectively.

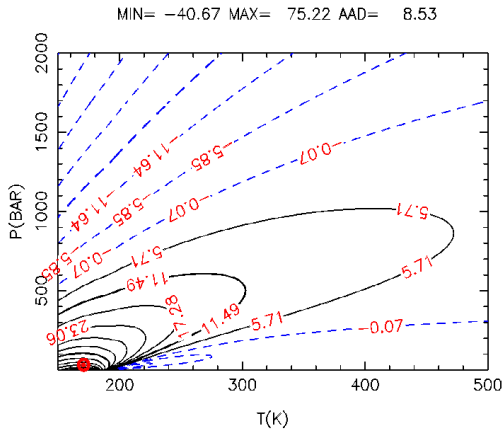
(a) SRK



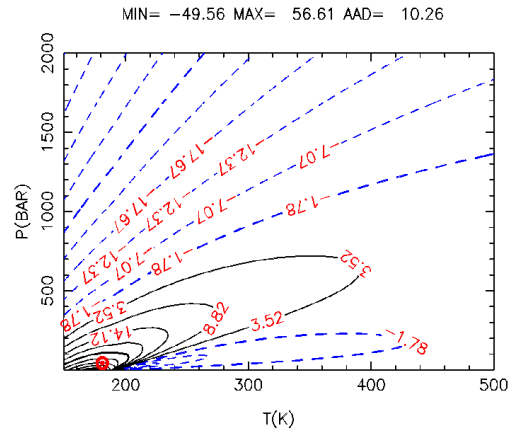
(b) PR



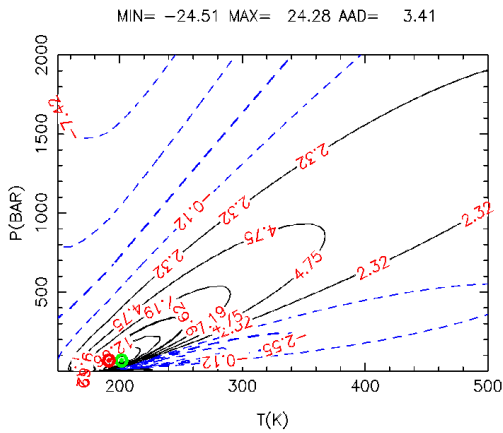
(c) SRK-VT



(d) PR-VT



(e) PC-SAFT



(f) Soave-BWR

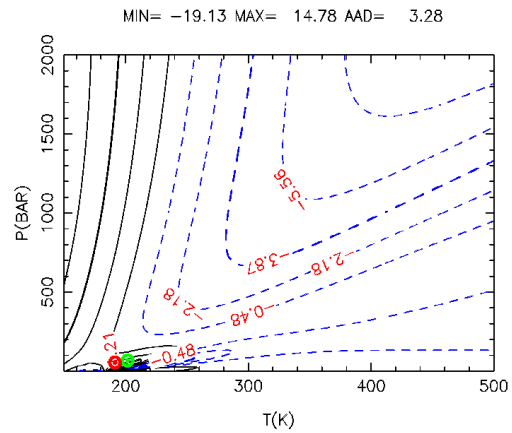


Fig. 5. Contour map of deviation in the compressibility of methane using SRK (a), PR (b), SRK with volume translation (c), PR with volume translation (d), PC-SAFT (e), and Soave-BWR (f).

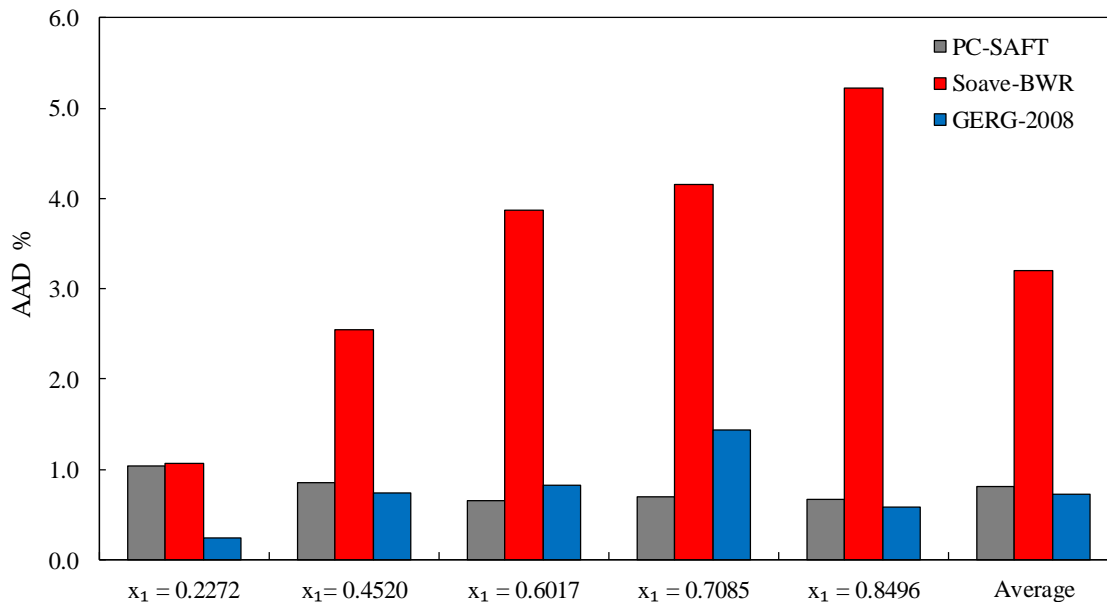


Fig. 6. AAD% in the calculated densities of the binary system methane (1) + n-decane (2) using GERG-2008, PC-SAFT and Soave-BWR with regressed  $k_{ij}$  within 278.15-463.15 K and 1-1400 bar. The experimental data is taken from [34].

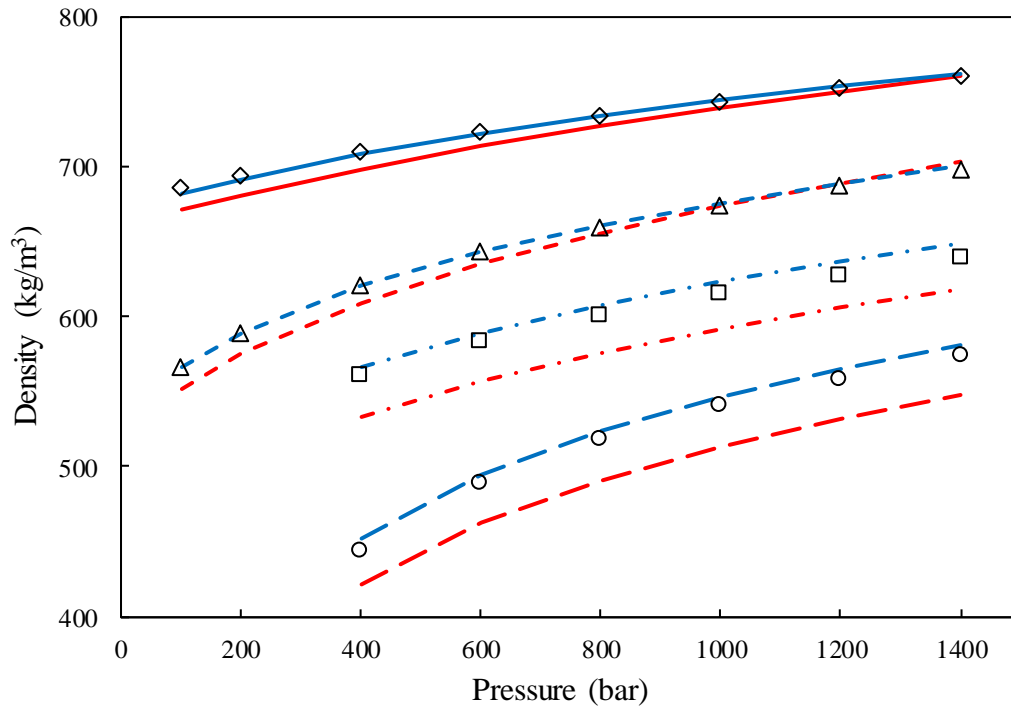


Fig. 7. Density vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for two mixtures of  $C_1$  and  $C_{10}$  at different temperatures. 22.27 mol%  $C_1$  and 323.2 K ( $\diamond$ , solid lines), 22.27 mol%  $C_1$  and 463.2 K ( $\triangle$ , dashed lines), 70.85 mol%  $C_1$  and 323.2 K ( $\square$ , dash-dot lines), and 70.85 mol%  $C_1$  and 463.2 K ( $\circ$ , long-dashed lines). The experimental data is taken from [34].



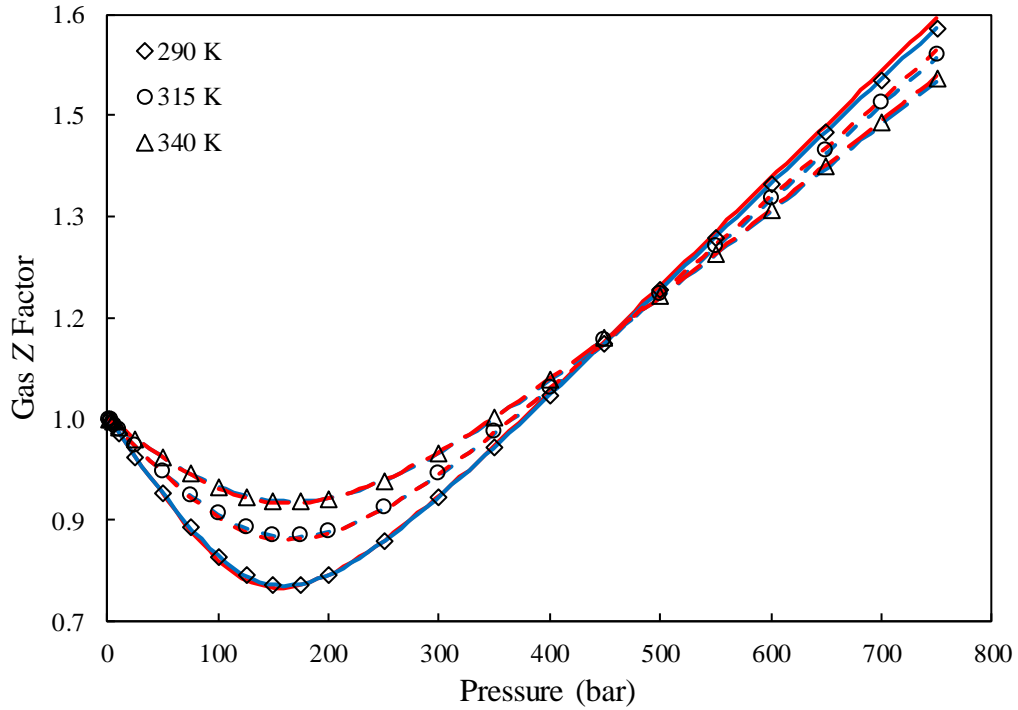


Fig. 8. Experimental and simulated results using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for Z-factor of the gas mixture A from [35] at different temperatures: 290 K (solid lines), 315 K (dashed lines), and 340 K (long-dashed lines).

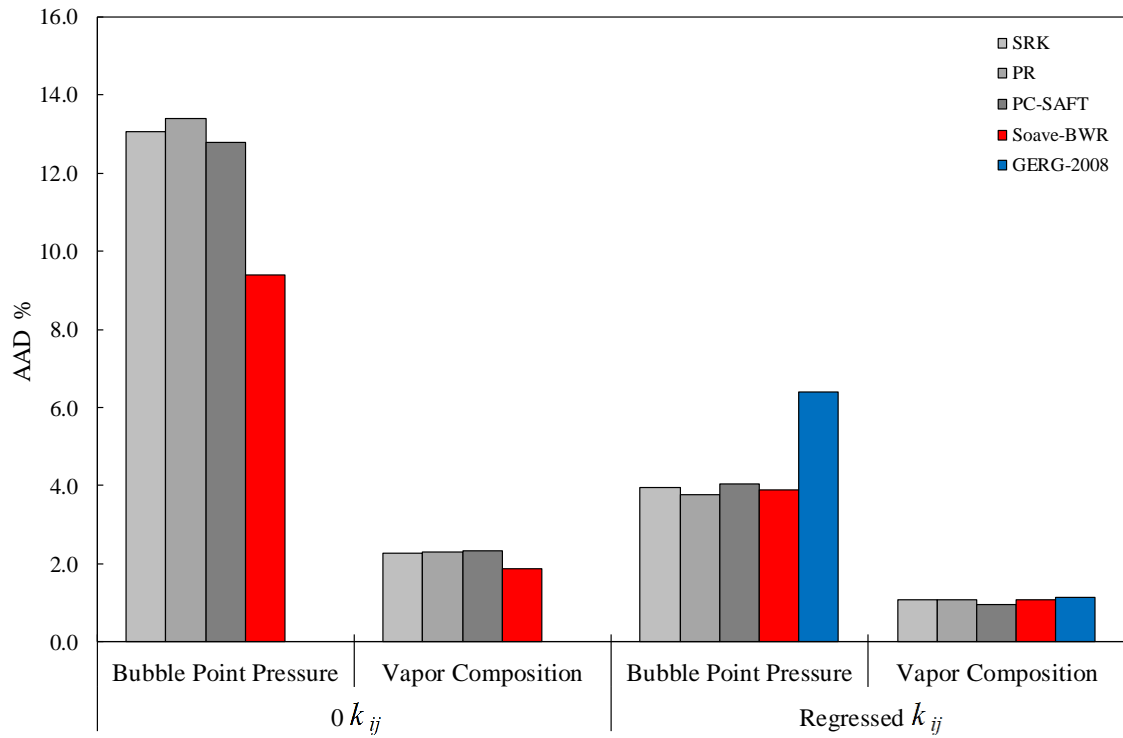


Fig. 9. AAD% in bubble point pressure and vapor phase composition for the binary pairs of  $N_2$ ,  $CO_2$ ,  $H_2S$ , and  $C_1$  using different EoSs with  $0 k_{ij}$  and regressed  $k_{ij}$ .

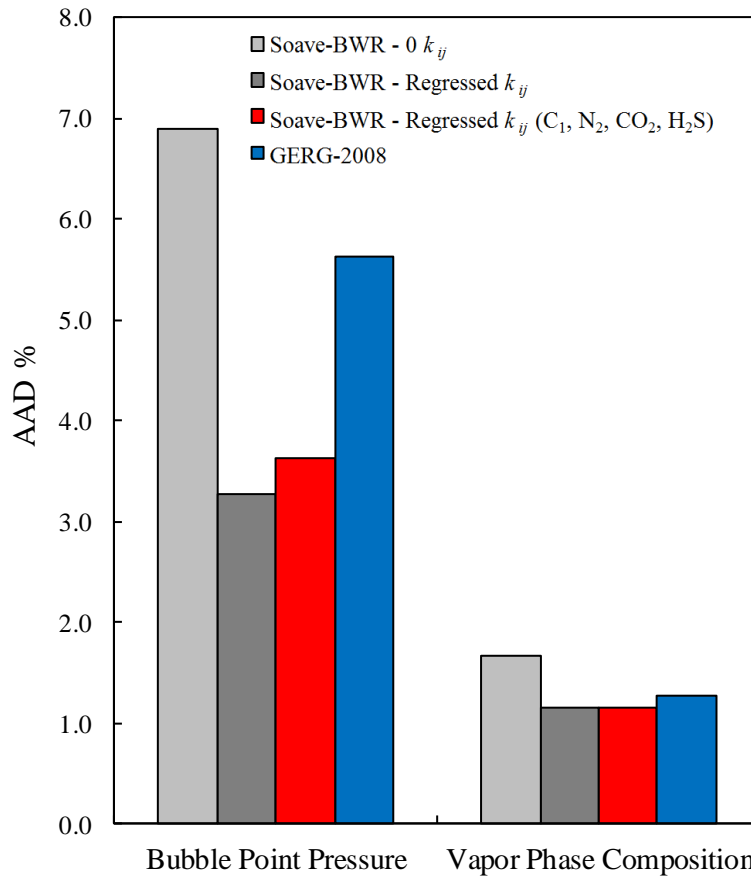


Fig. 10. AAD% in bubble point pressure and vapor phase composition of 81 binary mixtures using GERG-2008 and Soave-BWR with 0  $k_{ij}$  and regressed  $k_{ij}$ .

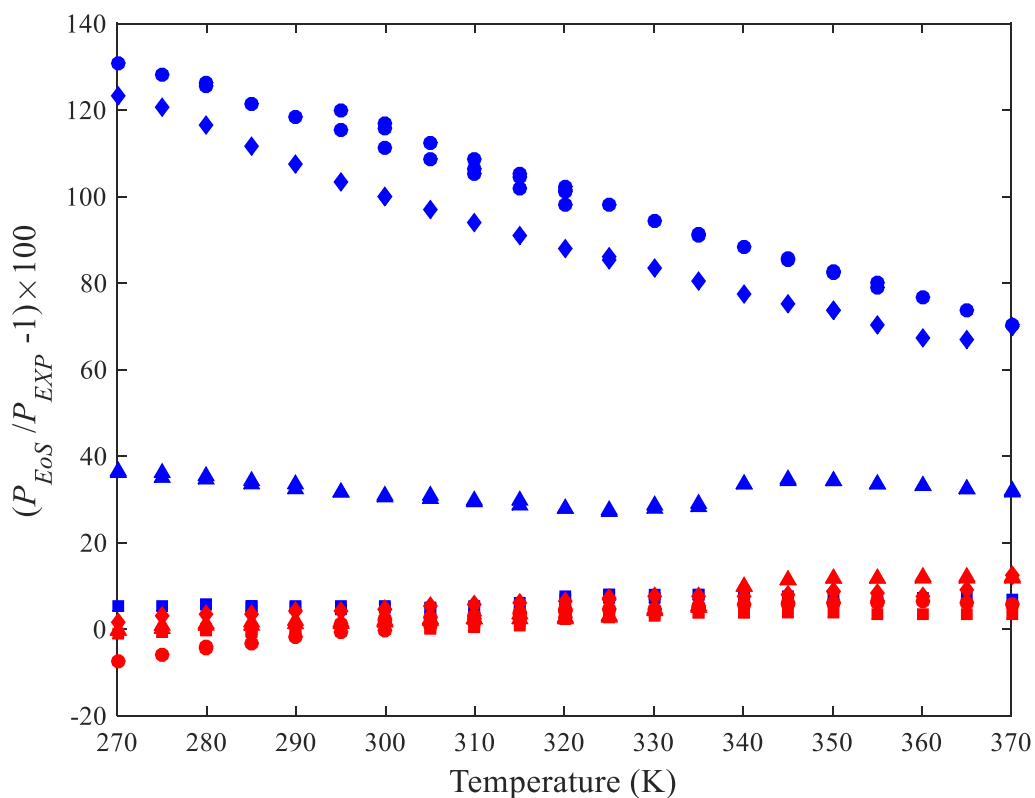


Fig. 11. Deviations in bubble point pressure calculation as a function of temperature using GERG-2008 (blue markers) and Soave-BWR with 0  $k_{ij}$  (red markers) for different binary mixtures of n-butane (1) + n-nonane (2). 74.9 mol% n-C<sub>4</sub> (■), 50.2 mol% n-C<sub>4</sub> (▲), 26.2 mol% n-C<sub>4</sub> (◆), and 21.4 mol% n-C<sub>4</sub> (●). The experimental data is taken from [38].

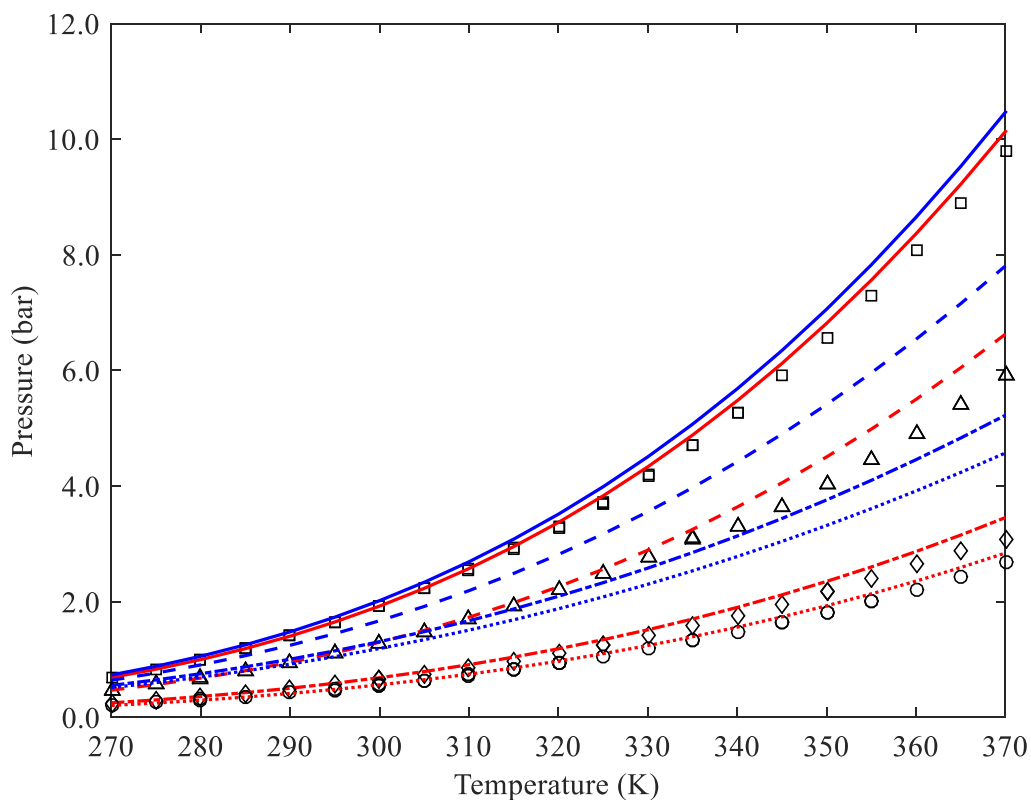


Fig. 12. Bubble point pressures at different temperatures using GERG-2008 (blue lines) and Soave-BWR with 0  $k_{ij}$  (red lines) for binary mixtures of n-C<sub>4</sub> and n-C<sub>9</sub>. 74.9 mol% n-C<sub>4</sub> (□, solid lines), 50.2 mol% n-C<sub>4</sub> (△, dashed lines), 26.2 mol% n-C<sub>4</sub> (◇, dash-dot lines), and 21.4 mol% n-C<sub>4</sub> (○, dotted lines). The experimental data is taken from [38].

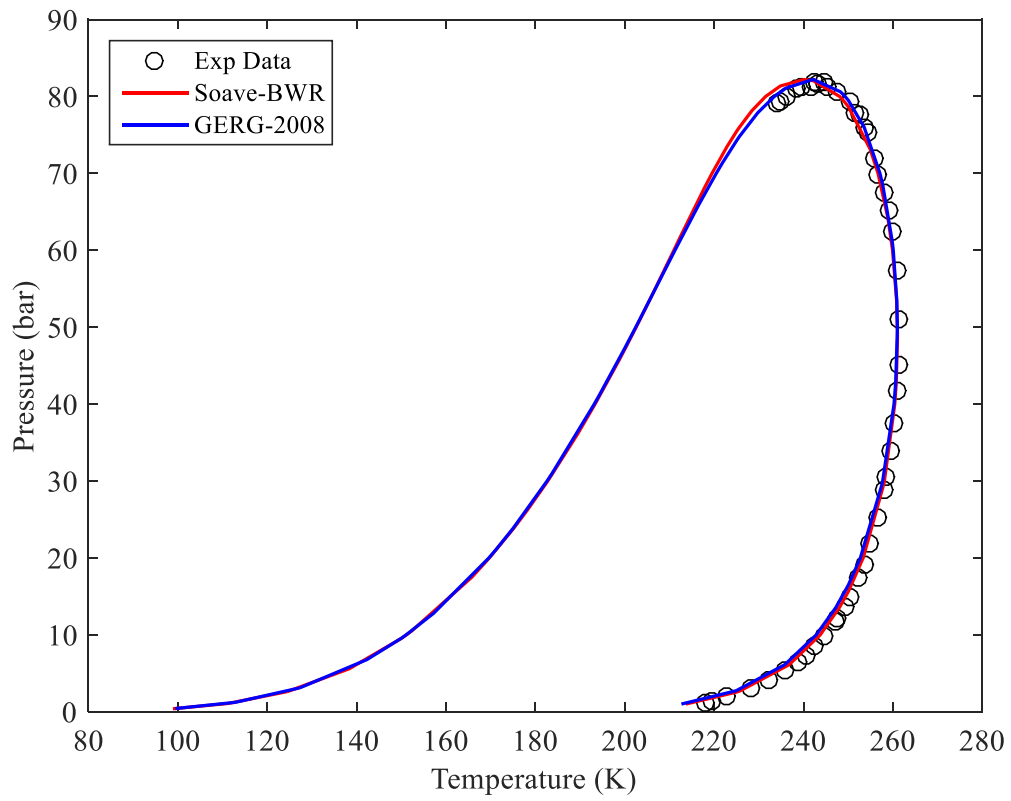
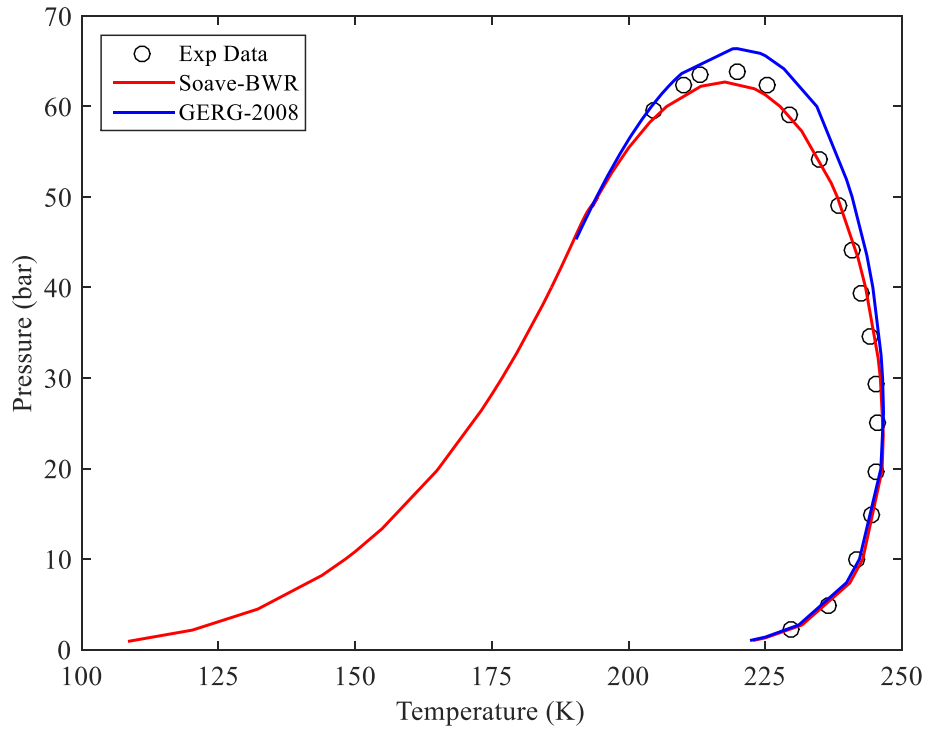


Fig. 13. Phase envelope for Gas 18 from [20].

(a)



(b)

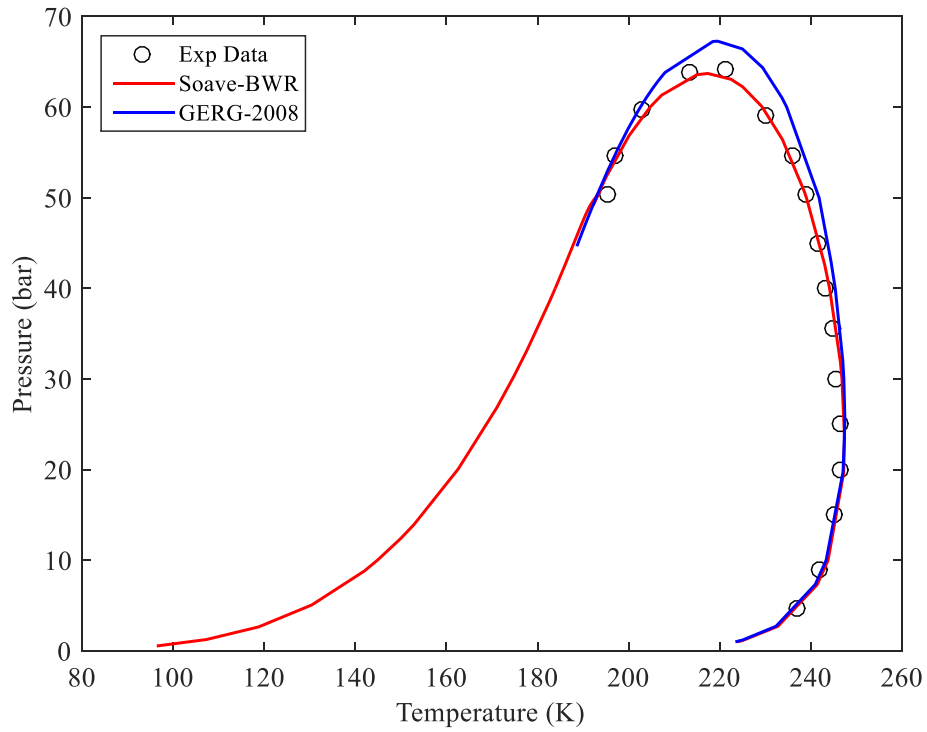
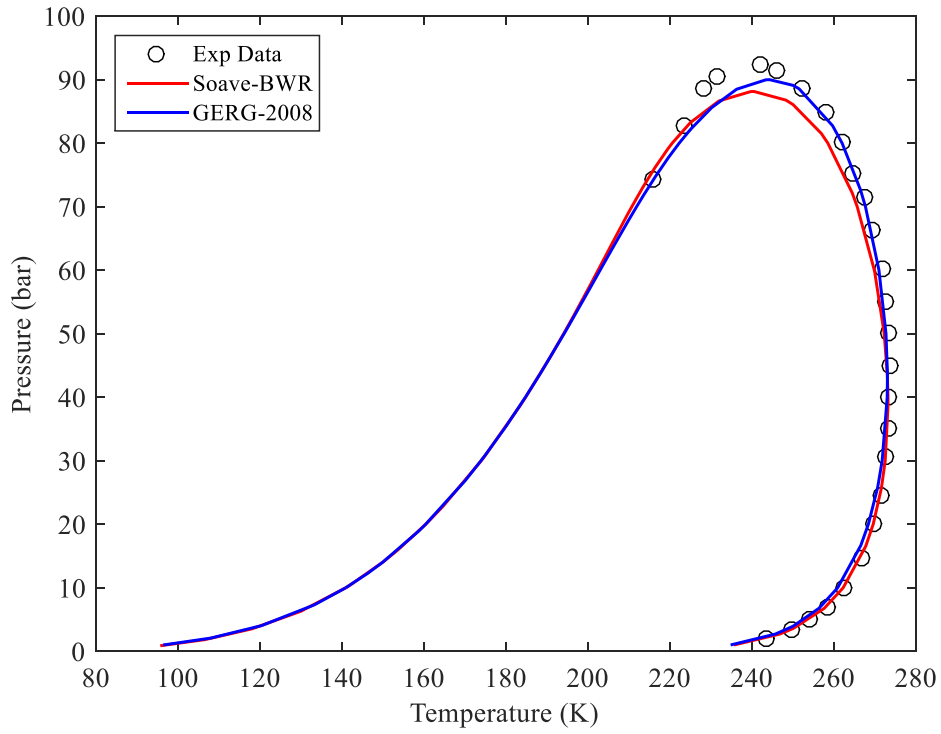


Fig. 14. Phase envelopes for (a) Gas 1, and (b) Gas 3 from [20].

(a)



(b)

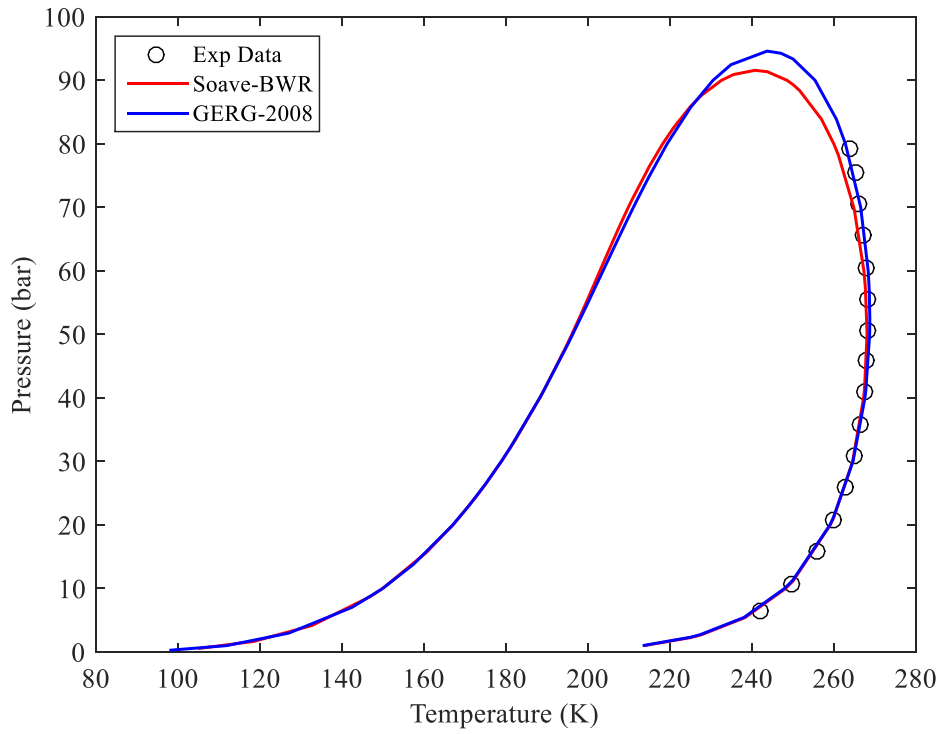
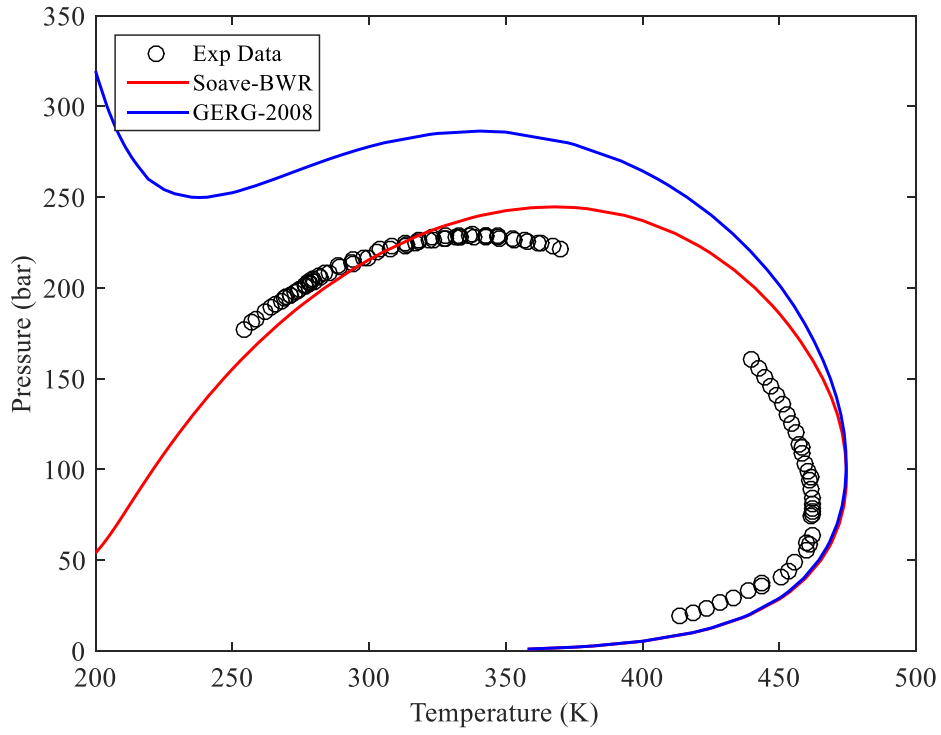


Fig. 15. Phase envelopes for (a) Gas 5, and (b) Gas 21 from [20].



(a)



(b)

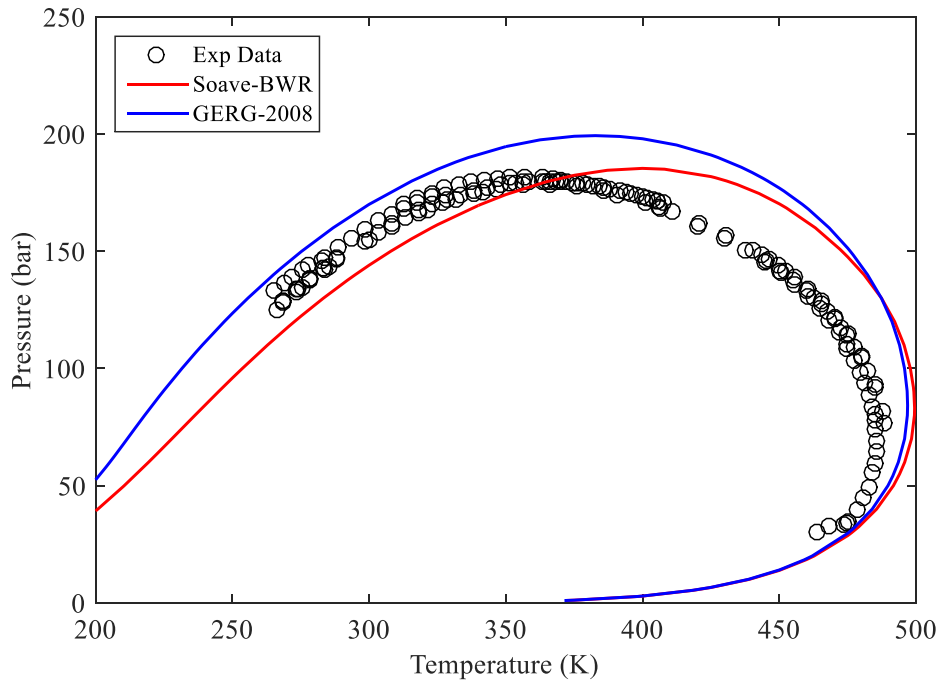


Fig. 16. Phase envelopes for (a) Gas 26, and (b) Gas 27 from [20].

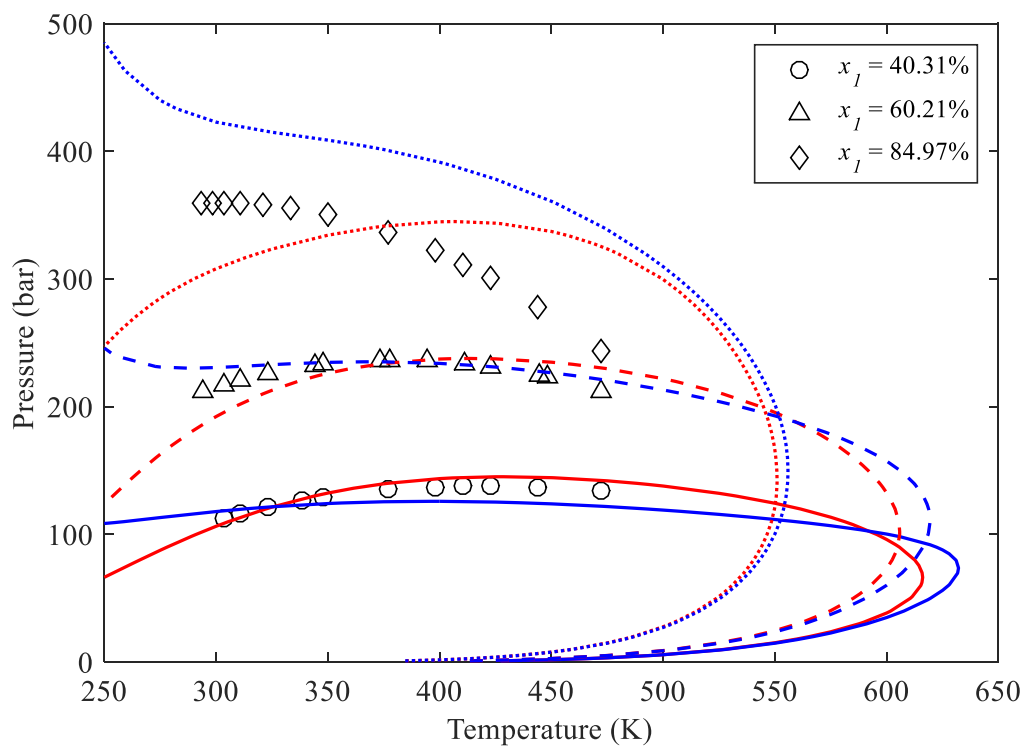


Fig. 17. Phase envelope for different binary mixtures of methane (1) + n-decane (2) using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines): 40.31 mol% C<sub>1</sub> (solid lines), 60.21 mol% C<sub>1</sub> (dashed lines), and 84.97 mol% C<sub>1</sub> (dotted lines). The experimental data is taken from [34].

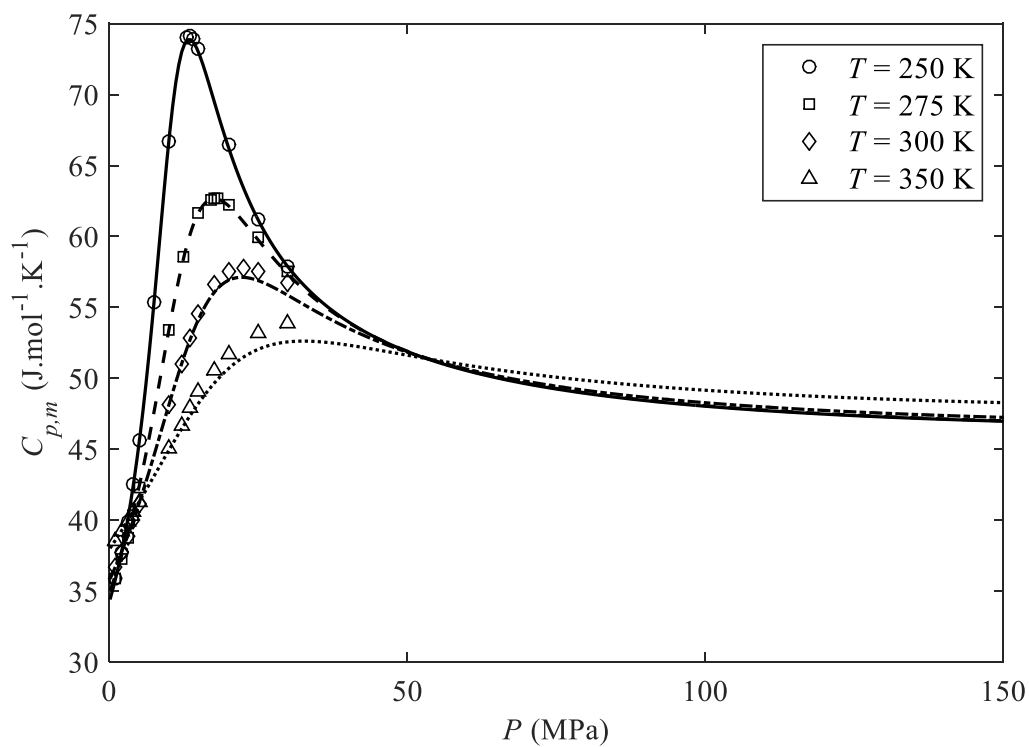


Fig. 18. Heat capacity prediction for methane at different temperatures using REFPROP. The experimental data is taken from [43].

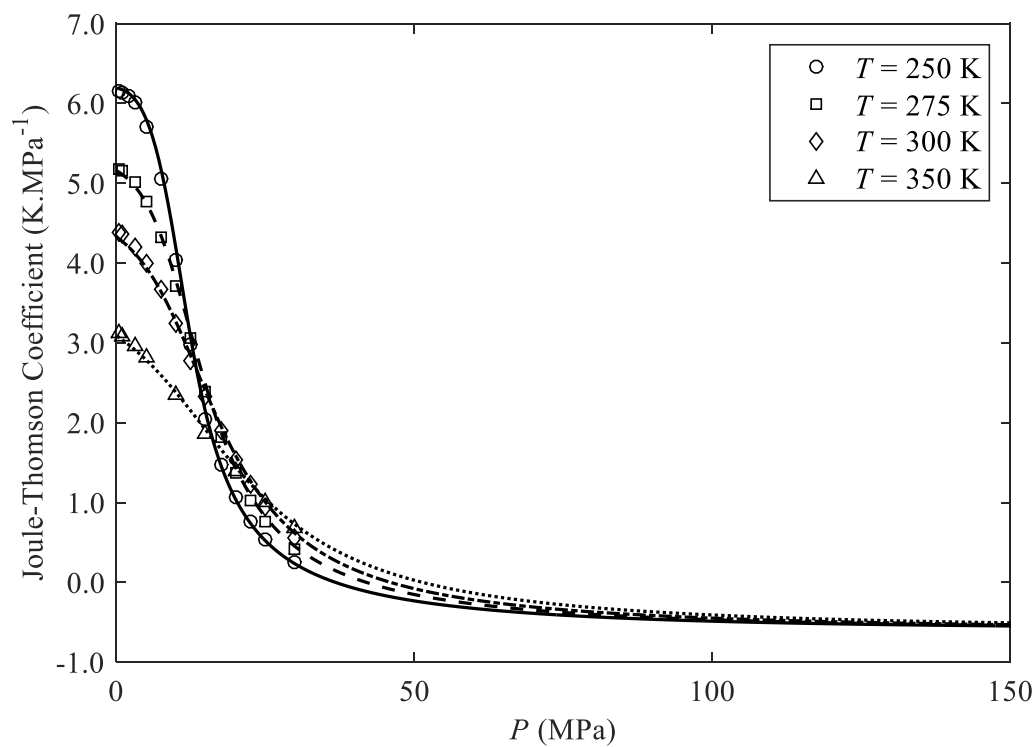


Fig. 19. Joule-Thomson coefficient prediction for methane at different temperatures using REFPROP. The experimental data is taken from [43].

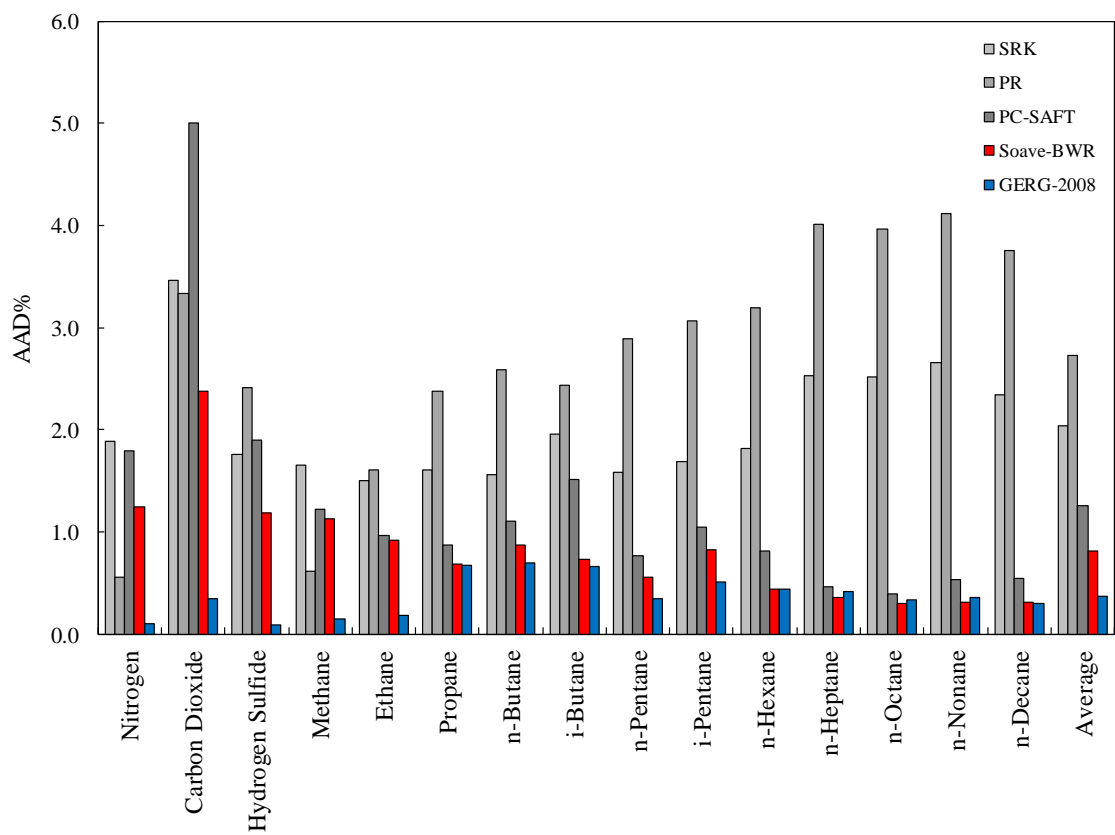


Fig. 20. AAD% in the heat capacity of the “main components” within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results.

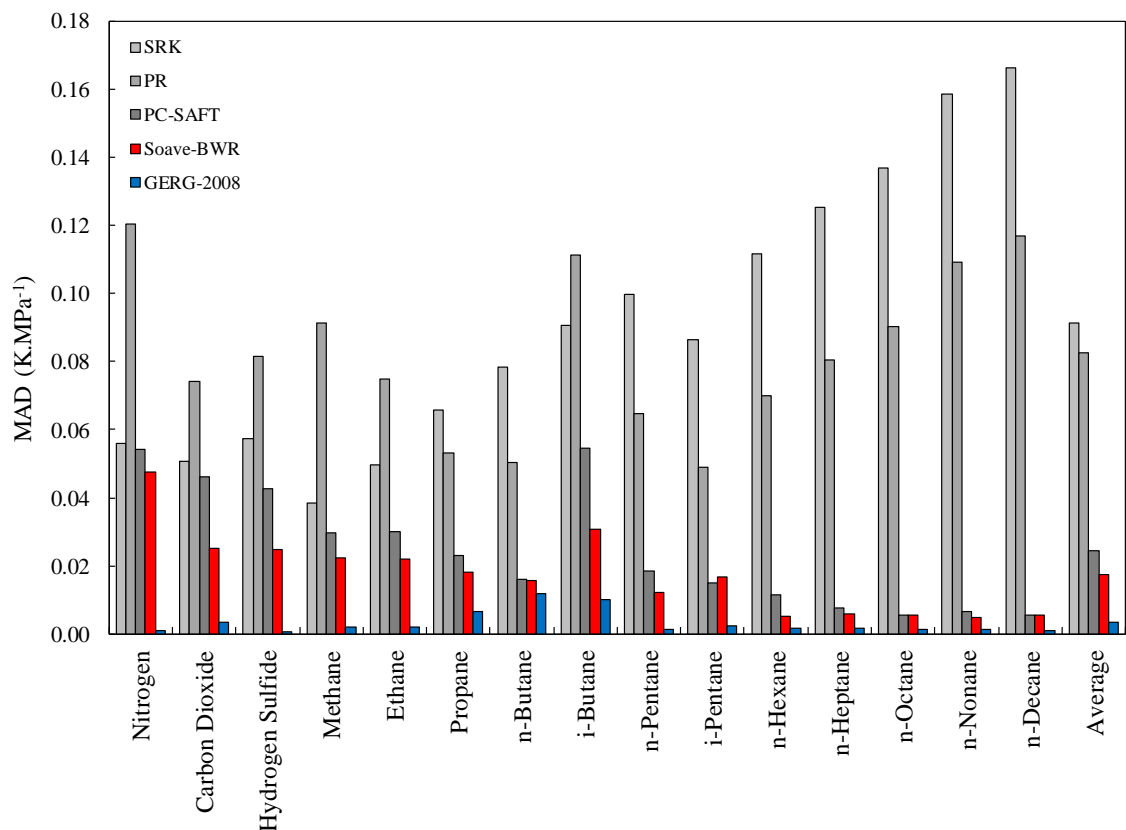


Fig. 21. MAD in the Joule-Thomson coefficient of the “main components” within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results.

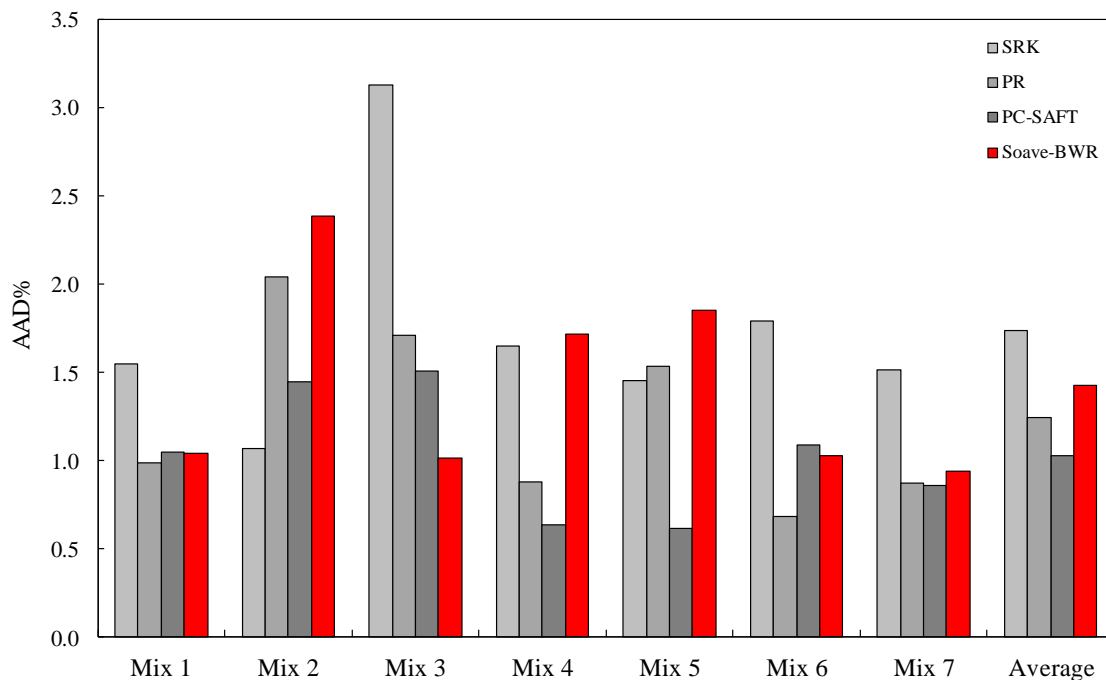


Fig. 22. AAD% in the heat capacity of binary and multicomponent mixtures within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results (REFPROP uses GERG-2008 for mixtures).

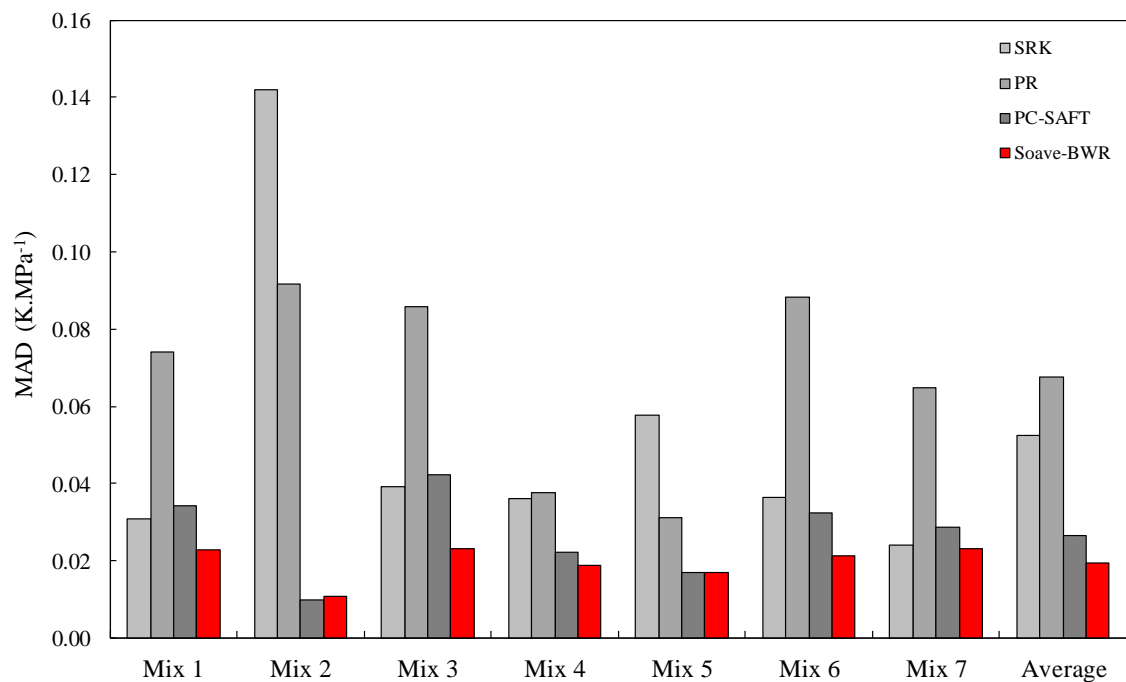


Fig. 23. MAD in the Joule-Thomson coefficient of binary and multicomponent mixtures within 250-500 K and 5-1500 bar using different EoSs. The model predictions are compared with REFPROP results (REFPROP uses GERG-2008 for mixtures).



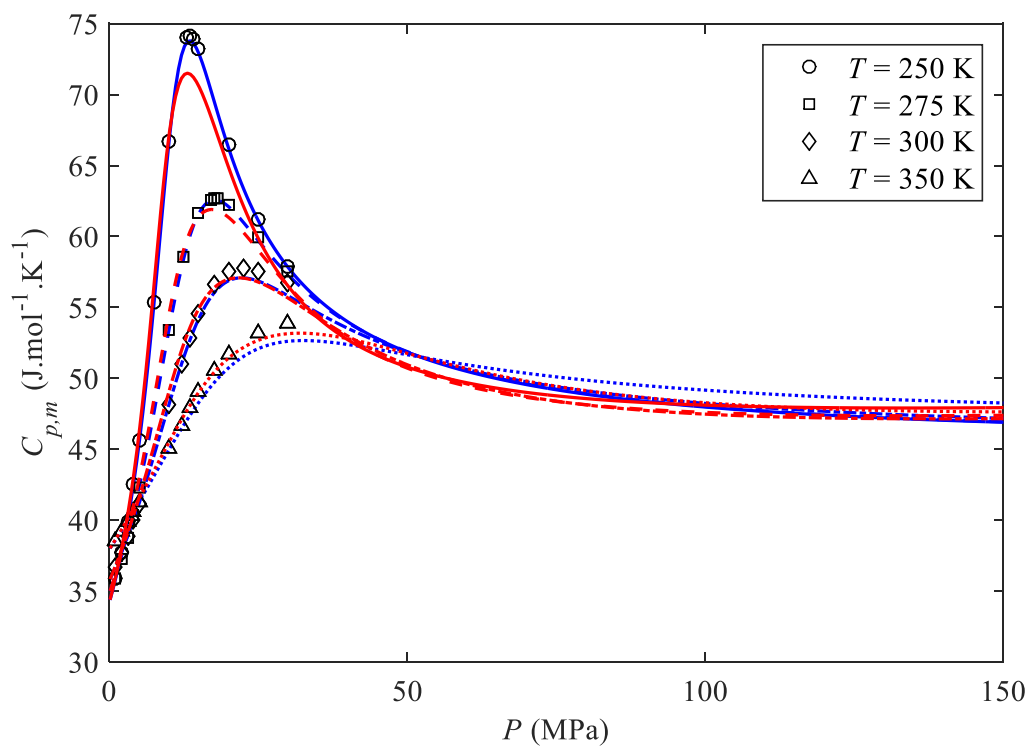


Fig. 24. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR (red lines) for  $C_1$  at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines). The experimental data is taken from [43].

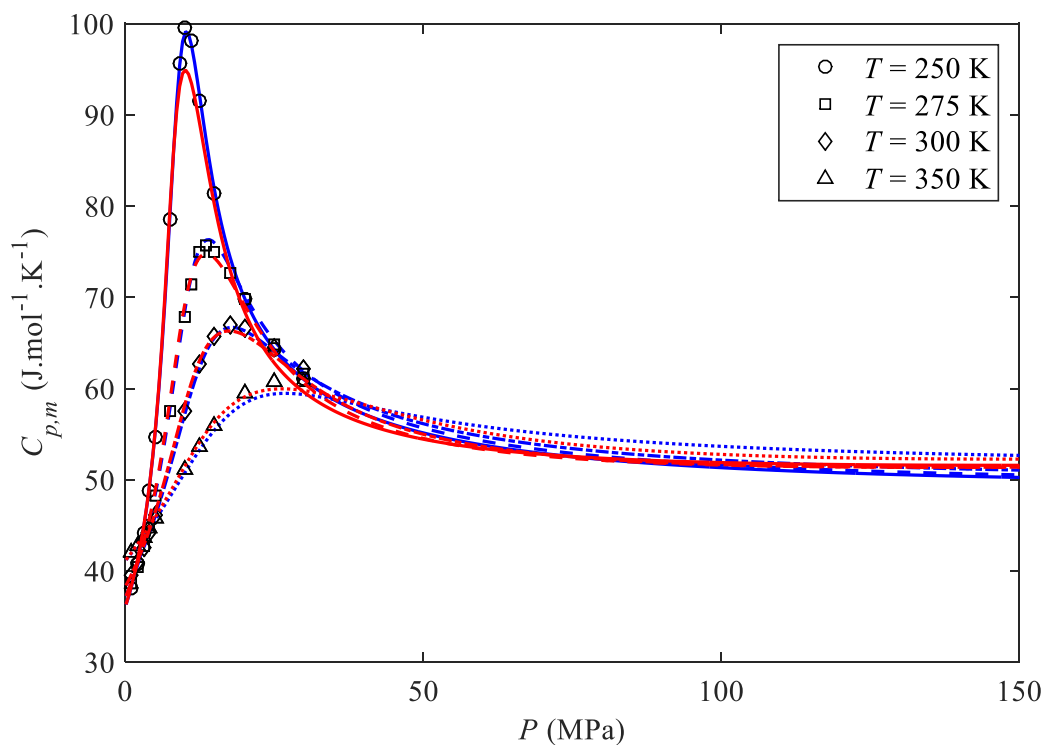


Fig. 25. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for C<sub>1</sub>-C<sub>2</sub> mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

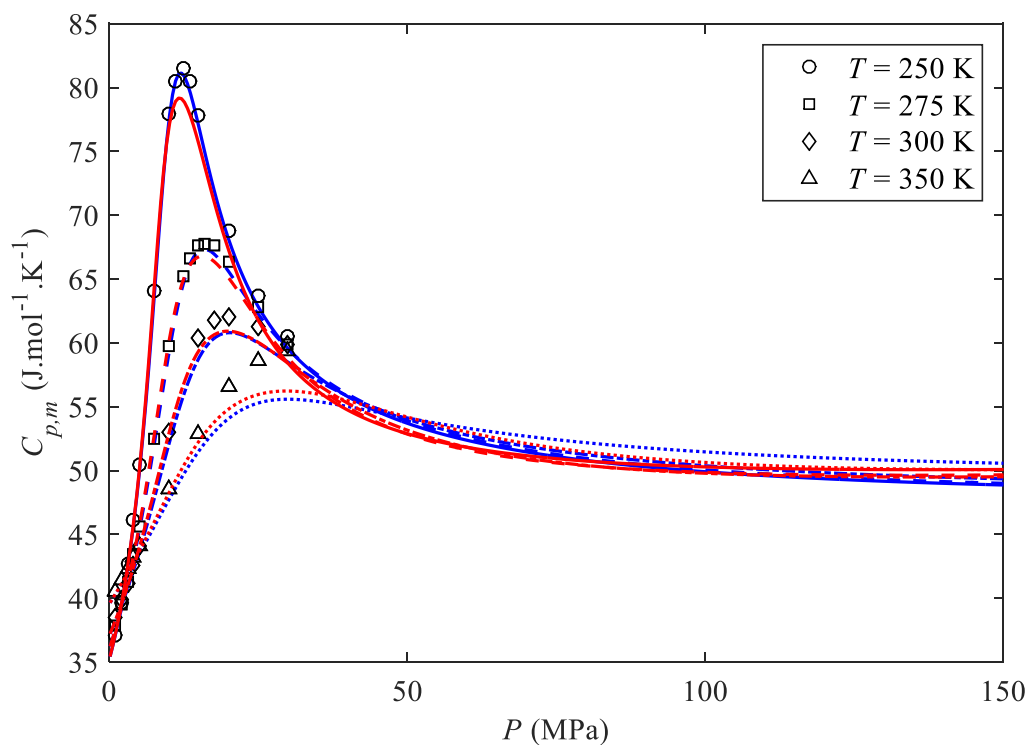


Fig. 26. Heat capacity vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for the natural gas mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

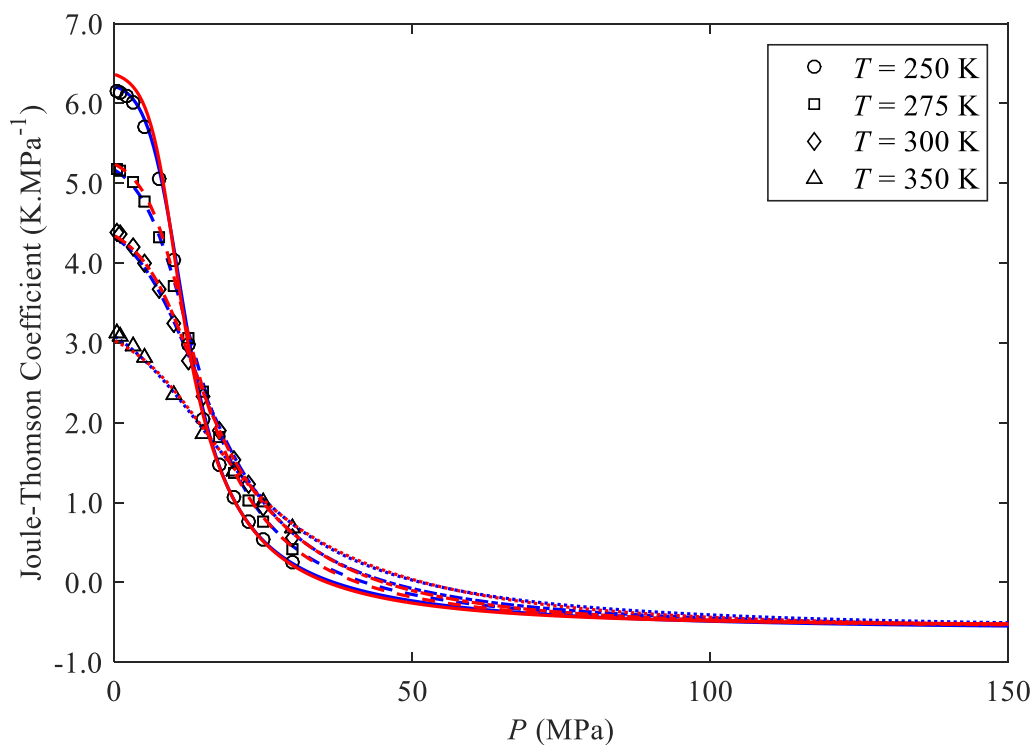


Fig. 27. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR (red lines) for  $C_1$  at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines). The experimental data is taken from [43].

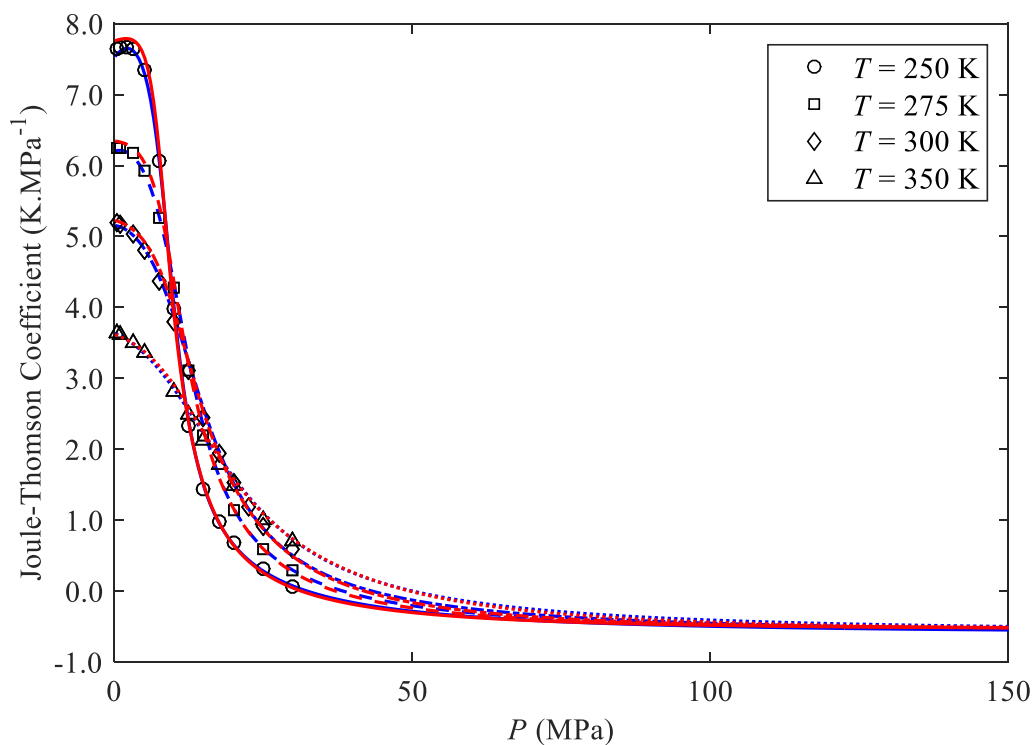


Fig. 28. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for  $C_1$ - $C_2$  mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).

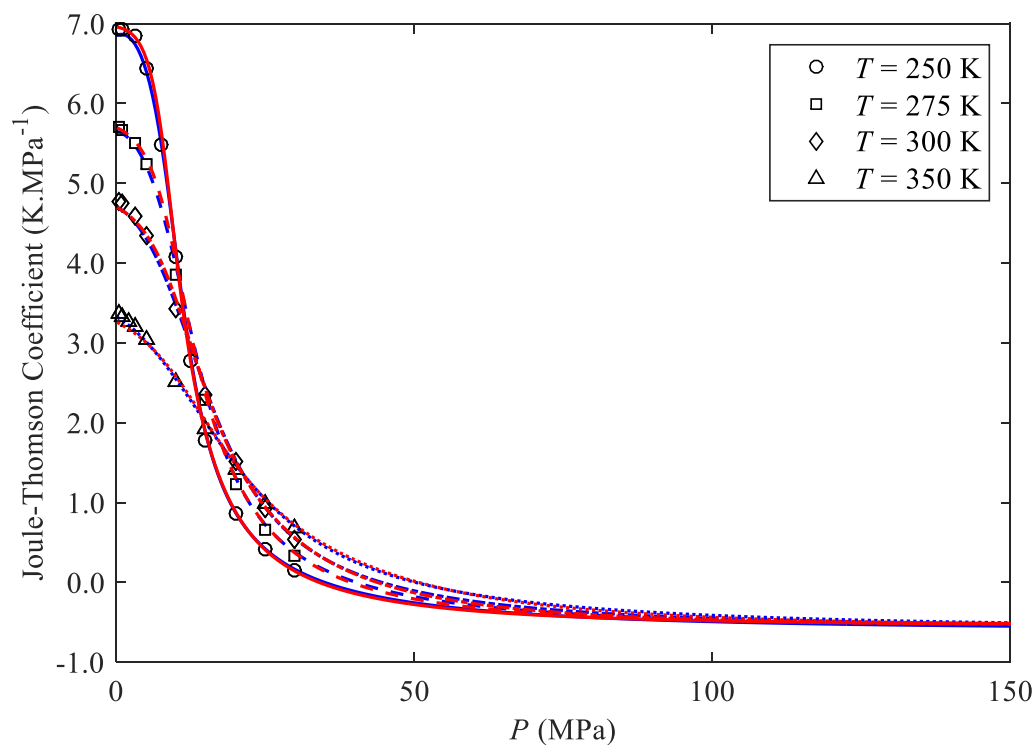


Fig. 29. Joule-Thomson coefficient vs. pressure using GERG-2008 (blue lines) and Soave-BWR with regressed  $k_{ij}$  (red lines) for the natural gas mixture from [43] at different temperatures: 250 K (solid lines), 275 K (dashed lines), 300 K (dash-dot lines), 350 K (dotted lines).