Backone Family of Equations of State: 2. Nonpolar and Polar Fluid Mixtures

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In the BACKONE equations the Helmholtz energy F is written as the sum $F = F_H + F_A + F_D + F_Q$, *where* F_H *is the hard-body contribution,* F_A *the attractive dispersion force contribution,* F_D *the dipolar, and* F_Q *the quadrupolar contribution. In Part 1 of this article (Müller et al., 1996a) the construction of BACKONE and its application to pure fluids were presented. In the extension to mixtures, for each term of F a specific mixing rule is used. This concept requires only one adjustable state-independent binary mixture parameter. To demonstrate the feasibility of this approach, predictions of phase equilibria, including a liquid–liquid equilibrium and other thermodynamic properties, are given for 20 binary fluid mixtures from the groups: nonpolar + nonpolar; nonpolar + dipolar; nonpolar + quadrupolar; and polar + polar.*

Introduction

The development of physically based equations of state (EOS) is of great importance for chemical and energy engineering. Such equations should allow the predictions of various thermodynamic properties in the whole fluid region. For the determination of the substance-specific parameters only a few experimental data should be required. In a preceding paper (Müller et al., 1996a), hereafter called Part 1, the BACKONE family of physically based equations of state was introduced and applied to pure substances. The subject of the present article is the extension of BACKONE to mixtures.

In the BACKONE and other physically based equations of state it is assumed that the characteristic parts of the intermolecular interaction contribute additive terms to the Helmholtz energy F. For polar substances this yields

$$F = F_H + F_A + F_{\mathrm{pol}}, \tag{1}$$

where F_H represents the contribution of the molecular hard cores, F_A denotes the contribution due to attractive dispersion forces, and F_{pol} describes the sum of the polar contributions. Examples for such equations are the BACK equation (Chen and Kreglewski, 1977; Kreglewski, 1984), the extension of the BACK EOS to polar fluids (Lee and Chao, 1988a,b), the NIK equation (Nguyen et al., 1993), the MOBACK, DIBACK, and QUABACK equations (Saager and Fischer, 1994), and most recently the BACKONE family of equations of state. The latter uses the hard convex body equation of Boublik (1975) for F_H, and for F_{pol} the dipolar contribution F_D and the quadrupolar contribution F_Q, as derived by Saager and Fischer (1992) from molecular simulations.

The difference between MOBACK, DIBACK, and QUABACK, on the one hand, and the BACKONE equations, on the other hand, is in the F_A term, which contains the same three substance-specific parameters in BACKONE as are used in F_H. These are a characteristic density ρ_0, a characteristic temperature T_0, and an anisotropy parameter α. For dipolar substances a reduced dipole moment μ^* is used in the construction of F_D. Analogously, the reduced quadrupole moment Q^* is used in the construction of F_Q for quadrupolar substances. Thus, for the description of nonpolar substances by BACKONE, only three parameters are required. A fourth parameter is necessary for pure dipolar or pure quadrupolar substances. Eventually, five substance-specific parameters are required to describe substances that exhibit both dipolar and quadrupolar moments (Müller et al., 1996a; Calero et al., 1998).

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In an extension of pure-fluid equations of state to mixtures, the problem of mixing rules arises. Let us consider a mixture of components i and denote the BACKONE parameters by ρ_{0i}, T_{0i}, α_i, μ_i^*, Q_i^*. Mixing rules are the prescriptions on how to arrive at these parameters for a mixture with mol fractions x_i. With the particular form of Eq. 1 for the Helmholtz energy, basically two different concepts of mixing rules have to be distinguished. In the first concept, the same mixture parameters ρ_{ox}, T_{ox}, α_x, μ_x^*, and Q_x^* are used in all contributions to F. We call these global mixing rules. In the second concept, which we call the specific mixing rules, different sets of mixture parameters are used in the different contributions to F. The latter approach is the more appealing one for two reasons. First, the hard convex body theory for F_H offers theoretically based mixing rules (Boublik, 1975) that are difficult to apply to F_A. Second, a comparative study on Lennard-Jones mixtures (Heene, 1994) using simulation-based vapor–liquid equilibria (Vrabec et al., 1995) has shown that the specific mixing rules are superior over the global mixing rules. Ultimately, this result is a logical consequence of a higher degree of freedom in the specific mixing rules. It is worth mentioning that Sowers and Sandler (1993) have also suggested the use of specific mixing rules.

In the next section we will repeat the four terms F_H, F_A, F_D, and F_Q of BACKONE and describe the specific mixing rules used here. These mixing rules require only one adjustable state-independent mixture parameter for each binary mixture. In the subsequent sections predictions of phase equilibria and other thermodynamic properties will be given for 20 binary fluid mixtures.

Helmholtz Energy Terms and Specific Mixing Rules

Hard-body term

In the BACKONE equations for pure fluids the hard-body contribution F_H to the Helmholtz energy is taken as the hard convex body equation of Boublik (1975),

$$\frac{F_H}{RT} = (\alpha^2 - 1)\ln(1-\xi) + \frac{(\alpha^2 + 3\alpha)\xi - 3\alpha\xi}{(1-\xi)^2}, \quad (2)$$

where ξ represents the packing fraction and α the anisotropy parameter. As described in Part 1, α is a substance-specific parameter and assumed to be state independent. On the other hand, the volume of the hard cores of the molecules is assumed to be state dependent and consequently the same applies for the packing fraction ξ. The equation for ξ used in BACKONE was suggested in an earlier article (Saager et al., 1992),

$$\xi = \xi_0 \frac{\rho}{\rho_0}\left[a + (1-a)\left(\frac{T}{T_0}\right)^{\gamma}\right]^{-1}, \quad (3)$$

where $a = 0.698$, $\gamma = 0.3674$, and $\xi_0 = 0.1617$. The quantities ρ_0 and T_0 are a characteristic density and a characteristic temperature, respectively, and both are substance-specific parameters.

In the extension of the equations to mixtures, the hard convex body theory (Boublik, 1975) will be applied again. For that purpose, we have to introduce some geometric quantities. Consider a hard body i and let V_i be the volume, S_i the surface, R_i the $(1/4\pi)$-multiple of the mean curvature integral, and $Q_i = R_i^2$. For the description of a mixture with components i and mol fractions x_i, the one-fluid quantities are introduced by

$$Z_x = \sum_i x_i Z_i, \quad (4)$$

where Z stands for any of the geometric quantities, V, S, R, and Q, defined earlier.

With the help of the dimensionless quantities

$$k_1 = \frac{R_x S_x}{V_x} \quad (5)$$

and

$$k_2 = \frac{Q_x S_x^2}{9V_x^2}, \quad (6)$$

the Helmholtz energy of the hard convex body equation of state is written as

$$\frac{F_H}{RT} = (k_2 - 1)\ln(1-\xi_x) + \frac{[k_1 + k_2 - k_1\xi_x]\xi_x}{(1-\xi_x)^2}, \quad (7)$$

where ξ_x is the packing fraction of the mixture.

The question that arises now is how to obtain the quantities k_1, k_2, and ξ_x from the parameters ρ_{0i}, T_{0i}, and α_i. The procedure is obvious for the packing fraction ξ_x, which is given by

$$\xi_x = \sum_i x_i \xi_i. \quad (8)$$

The packing fraction ξ_i of each component i in the mixture is calculated by Eq. 3 with the pure-substance parameters ρ_{0i} and T_{0i}. The parameters k_1 and k_2 have to be calculated from Eqs. 4–6 using the geometric quantities V_i, S_i, and R_i of the pure components i, which requires geometric models for the molecules. In order to keep the situation simple, we assume that a molecule of nonspherical shape can be approximated in the first order by a linear molecule. This assumption is also consistent with the derivation of F_A in Part I. For a given mixture the corresponding hard-body system will consist of mixtures of hard dumbbells or hard spheres. In the case of hard dumbbells, the geometric quantities R, S, and V are related to the hard-sphere diameter d and the elongation $L_H = L/d$ by

$$V = \frac{\pi}{6}d^3\left(1 + \frac{3}{2}L_H - \frac{1}{2}L_H^3\right), \quad (9)$$

$$S = \pi d^2(1 + L_H), \quad (10)$$

and

$$R = \frac{1}{2}d\left(1 + \frac{1}{2}L_H\right). \quad (11)$$

Eventually the quantities of interest in Eqs. 9–11 are the hard-sphere diameter d, which is assumed to depend on temperature, and the temperature-independent elongation $L_H = L/d$. These quantities have to be determined for each component separately from the pure fluid parameters of the equation of state, namely ρ_0, T_0, and α. For hard dumbbells, the relation between L_H and α is known to be (Saager et al., 1992)

$$\alpha = \frac{(1+L_H)(2+L_H)}{\left(2+3L_H - L_H^3\right)} = \frac{2+L_H}{\left(2+L_H - L_H^2\right)}. \tag{12}$$

This equation can be easily inverted, which yields

$$L_H = \frac{\alpha - 1}{2\alpha} + \frac{\sqrt{9\alpha^2 - 10\alpha + 1}}{2\alpha}. \tag{13}$$

The hard-sphere diameter is determined via the packing fraction ξ. On the one hand, ξ can be calculated for a system of hard dumbbells by means of Eq. 9 as

$$\xi = \frac{\pi}{6}\rho d^3\left(1 + \frac{3}{2}L_H - \frac{1}{2}L_H^3\right). \tag{14}$$

On the other hand, ξ is also given by Eq. 3, and by combining both equations we get

$$d^3 = \frac{6\xi_0}{\pi\rho_0}\left[1 + \frac{3}{2}L_H - \frac{1}{2}L_H^3\right]^{-1} \cdot \left[a + (1-a)\left(\frac{T}{T_0}\right)^{\gamma}\right]^{-1}. \tag{15}$$

Summarizing, we have to calculate L_H and d for each pure component from Eqs. 13 and 15. From these V, S, and R are calculated via Eqs. 9–11 and $Q = R^2$. Subsequently, the one-fluid parameters are determined by Eq. 4. Finally, the parameters k_1 and k_2 are obtained from Eqs. 5 and 6, which are temperature dependent because of Eq. 15.

In some few cases it may happen that the pure-component parameter α that results from a fit procedure is slightly smaller than 1. As will be seen later, this happens for the noble gases. In these cases, the square root in Eq. 13 results in a complex number. In order to obtain reasonable values for k_1 and k_2, the following ad hoc procedure can be used. Let us assume that α is slightly smaller than 1 for component k: (1) L_{Hk} is constrained to be zero; (2) d_k is evaluated from Eq. 15, and therefrom V_k, S_k, while R_k and Q_k are defined by Eqs. 9–11; (3) with these values, quantities k_1^{id} and k_2^{id} are calculated from Eqs. 5 and 6; (4) in order to avoid for $x_k \to 1$, an inconsistency with the description of the pure component k, a rescaling is performed according to

$$k_1 = \left[1 + x_k(\alpha_k - 1)\right]k_1^{id} \quad \text{and} \quad k_2 = \left[1 + x_k\left(\alpha_k^2 - 1\right)\right]k_2^{id}. \tag{16}$$

We remind the reader that the hard-body contribution to the Helmholtz energy F_H for a mixture is given by Eq. 7. The quantities k_1, k_2, and the packing fraction ξ are obtained by using only the pure-component parameters ρ_{0i}, T_{0i}, α_i in combination with the density, temperature, and composition of the mixture. We emphasize that for F_H no adjustable mixture parameter is required.

Attractive dispersion-force term

The attractive dispersion-force term F_A in BACKONE was constructed in Part I under the assumption that F_A depends on the same three parameters ρ_0, T_0, and α as F_H. The mathematical expression in the form $F_A = F_A(\rho/\rho_0, T/T_0, \alpha)$ was found by fitting simultaneously to the experimental data of methane, oxygen, and ethane after subtracting appropriate hard-body terms. The search for the mathematical expression was performed with the optimizing procedure of Setzmann and Wagner (1989). The resulting equation is

$$F_A(\rho/\rho_0, T/T_0, \alpha) = RT\sum_{i=1}^{19} c_i\left(\frac{\rho}{\rho_0}\right)^{m_i}\left(\frac{T}{T_0}\right)^{n_i/2}\alpha^{j_i} + RT\sum_{i=20}^{28} c_i\left(\frac{\rho}{\rho_0}\right)^{m_i}\left(\frac{T}{T_0}\right)^{n_i/2}\alpha^{j_i}\exp\left[-\left(\frac{\rho}{\rho_0}\right)^{l_i}\right]. \tag{17}$$

The coefficients c_i and all the exponents m_i, n_i, j_i, o_i, and l_i are given in Part 1 (note that the present equation is right, while in Eq. 9 in Part 1 the term $\exp[-(\rho/\rho_0)^o]$ should be replaced by 1 for $i = 1 \div 19$). The problem is now to find for given pure-component parameters ρ_{0i}, T_{0i}, α_i, and the mol fraction, x_i, the one-fluid parameters ρ_{0x}, T_{0x}, and α_x to be used in F_A for the mixture.

One approach for the derivation of mixing rules for F_A can be found within the framework of perturbation theory (Fischer and Lago, 1983), but currently such a derivation does not exist. Hence, we follow a more pragmatic way. For α_x we will use an ad hoc assumption and the mixing rules for ρ_{0x} and T_{0x} rely on the comparative study by Heene (1994) based on molecular simulation results that will be outlined shortly.

First, it is convenient to shift from a characteristic density ρ_0 to a characteristic molecular length by

$$\sigma^3 = \frac{\xi_0}{N_m\,\rho_0}, \tag{18}$$

where N_m is Avogadro's constant and $\xi_0 = 0.1617$ is an appropriate packing fraction. Similarly, instead of a characteristic temperature T_0, we can use a characteristic intermolecular energy ϵ given by

$$\epsilon = k_B T_0, \tag{19}$$

where k_B is Boltzmann's constant. In the past, several mixing rules have been suggested for σ and ϵ. Prominent examples are

$$S1: \qquad \sigma_x^3 = \sum_{i,j} x_i x_j \sigma_{ij}^3 \tag{20}$$

$$S2: \qquad \sigma_x^3 = \sum_{i} x_i \sigma_{ii}^3 \tag{21}$$

$$E1: \qquad \epsilon_x \sigma_x^3 = \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \tag{22}$$

$$E2: \qquad \epsilon_x = \sum_i x_i x_j \epsilon_{ij}. \tag{23}$$

Here, σ_{ii} and ϵ_{ii} are the parameters of the pure components i, and the unlike mixed parameters for $i \neq j$ are defined by

$$\epsilon_{ij} = (1 - k_{ij})\sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{24}$$

and

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2}. \tag{25}$$

The quantities k_{ij} are the adjustable binary mixture parameters to be discussed below.

In the work of Heene (1994), the four combinations $E1/S1$, $E1/S2$, $E2/S1$, and $E2/S2$ were tested as mixing rules for F_A. For binary Lennard-Jones model mixtures with several size and energy ratios, molecular simulations were performed and p,ρ,T data or vapor−liquid equilibria calculated therefrom. The latter were obtained from the NpT + test particle (TP) method (Vrabec et al., 1995). Furthermore, the Mecke et al. (1996) equation of state for the pure Lennard-Jones fluid was used together with the four different sets of mixing rules $E1/S1$, $E1/S2$, $E2/S1$, and $E2/S2$. The k_{ij}-parameter was fitted to the NpT + TP phase equilibria at one temperature. It turned out that the mixing rule set $E1/S2$ is by far the best for F_A.

The use of the adjustable binary mixture parameters k_{ij} requires a short discussion. In the case of the Lennard-Jones mixture, one could argue that no adjustable parameter should be necessary at all, as all molecular interactions are well defined. The situation, however, becomes different for real mixtures where the interaction energy ϵ_{ij} between unlike molecules is in general not known. Hence, for real mixtures we have to introduce one adjustable interaction parameter for ϵ_{ij} in any case. Actually, the mixture parameters k_{ij} used here include the uncertainty of the combining rule for ϵ_{ij} as well as all deficiencies of the mixing rules.

After establishing the mixing rules for ρ_{0x} and T_{0x}, there still remains the need for an appropriate value of α_x for the mixture. Here again, a more detailed analysis via perturbation theory or simulations would be desirable. In view of the lack of such an analysis, here we make the ad hoc assumption

$$\sqrt{\alpha_x} = \sum_n x_i \sqrt{\alpha_i}. \tag{26}$$

Hence, the complete set of specific mixing rules for the attractive dispersion force term F_A is given by the combination $E1/S2$ for ρ_{ox} and T_{0x}, represented by Eqs. 21 and 22 and by α_x from Eq. 26. We point out that in BACKONE only one adjustable state independent parameter k_{ij} (Eq. 24) is needed for each binary. For multicomponent mixtures, no additional parameters are required.

Polar terms

Saager and Fischer (1992) used extensive computer simulations to construct the dipolar term F_D and the quadrupolar term F_Q in BACKONE. They simulated two-center−Lennard-Jones molecules of elongation $L = 0.505$ with embedded axial-point dipoles or quadrupoles, of various strength (Saager et al., 1991). In subsequent work (Müller et al., 1993; Kriebel et al., 1996, 1997), it was shown that the molecular elongation has little influence on the dipolar free energy. Therefore, it was suggested in Part I that F_D be assumed to be independent of the anisotropy parameter α. The quadrupolar free-energy contribution F_Q also has been assumed to be independent of elongation, although from molecular simulation results this assumption is less satisfactory (Bohn et al., 1988). Hence, F_D and F_Q depend only on the substance-specific parameters ρ_0 and T_0, and on a reduced dipole moment μ^*, or a reduced quadrupole moment Q^*, respectively. The particular form of F_D and F_Q are those given by Saager and Fischer (1992):

$$\frac{F_D}{RT} = \sum_{i=1}^{28} c_i \left(\frac{\rho}{\rho_0}\right)^{m_i/2} \left(\frac{T}{1.13T_0}\right)^{n_i/2} (\mu^{*2})^{k_i/2} \exp\left[-o_i\left(\frac{\rho}{\rho_0}\right)^2\right] \tag{27}$$

and

$$\frac{F_Q}{RT} = \sum_{i=1}^{17} c_i \left(\frac{\rho}{\rho_0}\right)^{m_i/2} \left(\frac{T}{1.13T_0}\right)^{n_i/2} (Q^{*2})^{k_i/2} \exp\left[-o_i\left(\frac{\rho}{\rho_0}\right)^2\right]. \tag{28}$$

The coefficients c_i and all the exponents m_i, n_i, k_i, and o_i are given in Part 1.

In the case of mixtures, mixing rules for ρ_{0x}, T_{0x}, μ_x^{*2}, and Q_x^{*2} are required. For ρ_{0x} and T_{0x} it is convenient to use the same mixing rules as in F_A. Hence, the remaining quantities are μ_x^* and Q_x^{*2}. Recently, Weingerl and Fischer (2000) made a derivation of a mixing rule for Q_x^{*2} using perturbation theory and one-fluid theory. The same derivation can also be used for the dipole mixing rule. Using the relations $\mu^2 = \mu^{*2}\epsilon\sigma^3$ and $Q^2 = Q^{*2}\epsilon\sigma^5$, the resulting mixing rules are

$$\sigma_x^3 \epsilon_x^2 \mu_x^{*4} = \sum_{i,j} x_i x_j \sigma_{ij}^3 \epsilon_{ij}^2 \frac{\mu_i^2 \mu_j^2}{\epsilon_{ij}^2 \sigma_{ij}^6} \tag{29}$$

and

$$\sigma_x^3 \epsilon_x^2 Q_x^{*4} = \sum_{i,j} x_i x_j \sigma_{ij}^3 \epsilon_{ij}^2 \frac{Q_i^2 Q_j^2}{\epsilon_{ij}^2 \sigma_{ij}^{10}}. \tag{30}$$

The quantities σ_{ij} and ϵ_{ij} are the same as in the attractive contribution F_A, and are given by Eqs. 24 and 25. The mixing rules for the one-fluid μ_x^{*2} suggested previously by Lee and Chao (1988b) as well as by Müller et al. (1996b) can be considered as a simplification of Eq. 29. In order to test Eqs. 29 and 30, molecular simulation studies have been performed for dipolar (Müller et al., 1996b) and quadrupolar (Weingerl and Fischer, 2000) model mixtures that showed good-to-excellent performance of the mixing rules.

Table 1. Pure Substance-Specific Parameters

Substance	ρ_0 [mol/L]	T_0 [K]	α	μ^{*2}	Q^{*2}
Methane	10.139	190.564	1.0	—	—
Ethane	6.800	305.33	1.2126	—	—
Propane	5.032	370.800	1.3215	—	—
Argon	13.487	150.16	0.9876	—	—
Xenon	8.556	289.896	0.9887	—	—
R32	8.706	332.276	1.4287	5.0900	—
R41	9.391	281.133	1.139	6.362	—
CO_2	10.549	291.28	1.3919	—	2.181
Nitrogen	11.133	125.74	1.0471	—	0.489
Ethene	7.577	281.78	1.1716	—	0.522
R125	4.593	312.748	1.4154	1.0179	3.133
R134a	4.957	332.065	1.4287	4.6339	2.588
R143a	5.216	324.541	1.4128	4.0755	1.284

Results and Discussion

Adjustment of the binary mixture parameters k_{ij}

We consider 20 binary mixtures composed of 13 pure components. The substance-specific parameter of the pure components are determined by fit-to-vapor pressures and saturated liquid densities. Details of the procedure are given elsewhere (Calero et al., 1998; Müller et al., 1996b). For the convenience of the reader the pure-substance parameters of the fluids investigated here are compiled in Table 1.

The presentation of the mixture results is organized such that we split up the mixtures into the groups (a) nonpolar + nonpolar, (b) nonpolar + dipolar, (c) nonpolar + quadrupolar, and (d) polar + polar. For each group we consider one or two mixtures as key mixtures and present their results in greater detail.

In order to describe the mixture, the mixture parameter k_{ij} in Eq. 24 has to be determined. The procedure followed for all mixtures is to adjust k_{ij} to the author-selected VLE measurements we had available for each binary. Due to the fit to several data from different authors, we could balance the probable inaccuracies of the measurements. Nevertheless some data had to be excluded for the fit because the measurements turned out to be inconsistent. The resulting values for k_{ij} for all 20 systems are given in Table 2. We remind the reader that k_{ij} is a constant for each binary system and independent from temperature and composition. The values were used without modification for all comparisons of the respective binary.

Mixtures of nonpolar substances

Methane + Ethane. The methane + ethane system is one of the few mixtures for which a variety of accurate experimental data is available. Therefore, this system is frequently used for testing equations of state, and previous work is summarized in the article of Nguyen and Kohler (1995). In Figure 1 we show the VLE-isotherms of BACKONE in comparison with measurements for a temperature range from 144.26 K to 283.15 K. For all temperatures we observe good-to-excellent agreement. Taking into account all six authors whose VLE data are compared (Table 3), the resulting average deviation in pressure is 3.415% and the deviation in vapor composition is 0.891% for the temperature range from 90.7 K to 283.15 K.

Table 2. Mixture Parameters k_{ij} of the 20 Binaries Investigated

Type of Interaction	Subst. 1	Subst. 2	k_{ij}
Nonpolar + nonpolar	**Methane**	**Ethane**	−0.0284
	Methane	Propane	−0.0601
	Ethane	Propane	0.0018
	Argon	Methane	0.0165
	Xenon	Ethane	−0.0232
Nonpolar + dipolar	**Xe**	**R41**	0.0398
	R32	**Propane**	0.1118
Nonpolar + quadrupolar	**CO_2**	**Ethane**	0.0915
	CO_2	Propane	0.0967
	Methane	CO_2	−0.0070
	Xenon	Ethene	0.0032
	Nitrogen	Methane	0.0299
	Nitrogen	**Ethane**	−0.0110
Polar + polar	**R41**	**CO_2**	−0.1287
	R32	R134a	−0.0278
	R32	R143a	0.0092
	R32	R125	−0.0527
	R125	R134a	−0.0194
	R125	R143a	−0.0321
	R143a	R134a	−0.0082

Now regarding homogenous p,ρ,T-data, Figure 2 shows the calculated densities compared with the experimental results of Haynes et al. (1985) at almost equimolar composition. We

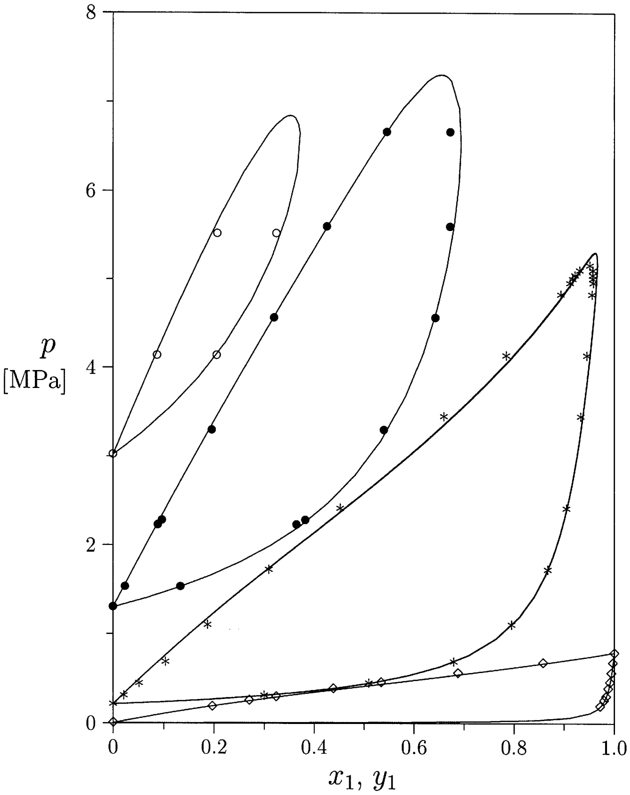

Figure 1. Vapor–liquid equilibrium isotherms for methane(1) + ethane(2) from BACKONE (—) in comparison with experimental data.

○ $T = 283.15$ K (Price, 1957), ● $T = 250.00$ K (Davalos et al., 1976), $*$ $T = 199.93$ K (Wichterle and Kobayashi, 1972b), and ◇ $T = 144.26$ K (Wichterle and Kobayashi, 1972b).

Table 3. Absolute Average Deviations of Vapor Pressures and Vapor Compositions of VLE Data from BACKONE in Comparison with Measurements for Nonpolar Mixtures

Author	Data Points	T-range K	Δp_{AAD} %	Δy_{AAD} %
System: $CH_4 + C_2H_6$				
Wichterle and Kobayashi (1972b)	138	130.4–199.9	2.821	1.025
Wichterle and Kobayashi (1972c)	22	158.2–213.7	4.501	1.341
Price (1957)	23	144.3–283.2	2.327	0.657
Miller et al. (1977)	24	160.0–180.0	4.602	0.485
Davalos et al. (1976)	8	250.0	1.044	1.126
Gomes de Azevedo and Calado (1989)	17	90.7–104.0	7.745	0.004
Sum	232	90.7–283.2	3.415	0.891
System: $CH_4 + C_3H_8$				
Wichterle and Kobayashi (1972a)	102	130.4–213.7	4.784	0.138
Reamer et al. (1950)	125	277.6–360.9	2.935	1.985
Sum	227	130.4–360.9	3.766	1.155
System: $C_2H_6 + C_3H_8$				
Maschke and Thodos (1962)	84	255.4–366.5	1.146	0.837
System: $Ar + CH_4$				
Christiansen and Fredenslund (1974)	5	123.4–164.0	1.798	0.598
Christiansen et al. (1973)	37	150.7–178.0	0.687	0.864
Calado and Staveley (1972)	10	115.8	3.163	0.656
Shatskaya and Zhirnova (1976)	31	112.6–133.0	4.673	1.711
Sum	83	112.6–178.0	2.541	1.139
System: $Xe + C_2H_6$				
Nuñes da Ponte et al. (1985)	182	210.0–304.4	0.656	0.619

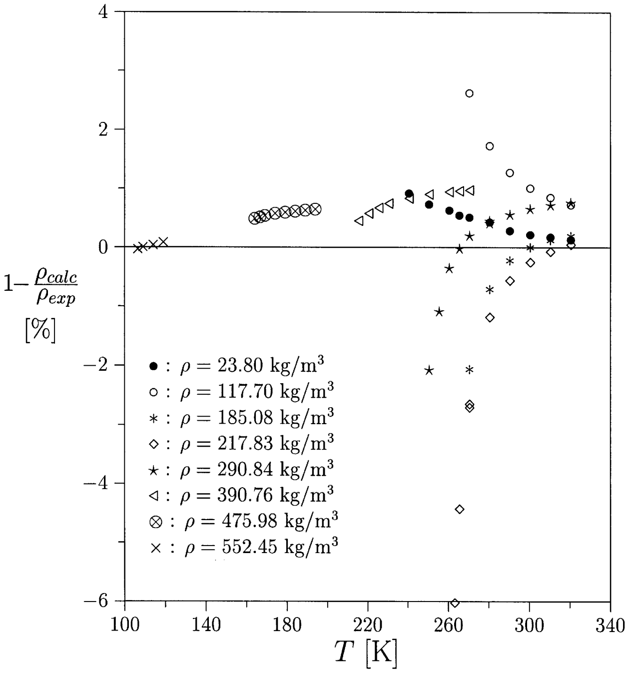

Figure 2. Comparision of homogenous isochoric p, ρ, T measurements (Haynes et al., 1985) with BACKONE results for methane + ethane ($x_{CH_4} = 0.50217$).

For equimolar mixture the critical data are $T_c = 261$ K, $\rho_c = 203$ kg/m³, $p_c = 6.825$ MPa (Nguyen and Kohler, 1995).

find good prediction of the densities in the gas region, as well as in the liquid region. The largest deviations can be found close to the critical point, which is for equimolar composition $T_c = 261$ K, $\rho_c = 203$ kg/m³, $p_c = 6.825$ MPa (Nguyen and Kohler, 1995).

For the calculation of caloric properties the residual contributions of BACKONE have to be supplemented by ideal-gas contributions. For methane and ethane the ideal contributions are taken from Younglove and Ely (1987). In Table 4 isochoric heat capacities from BACKONE are compared with the experimental data of Mayrath and Magee (1989) on three liquid isochors at different compositions. As with the VLE and p, ρ, T data, we observe good-to-excellent predictions of caloric data from BACKONE.

Remember that methane and ethane have been used in the construction of F_A, and the pure-component properties are represented with good accuracy by BACKONE. Hence, comparison of the calculated data with the experimental data for this mixture is a crucial test for the mixing rules for F_H and F_A. The results indicate that the mixing rules perform quite well except in the critical region.

Other Nonpolar Mixtures. Within the group of nonpolar mixtures we also investigate the methane + propane and ethane + propane mixtures, as well as the argon + methane and xenon + ethane mixtures. In Table 3 we list the absolute average deviations of vapor pressures and vapor compositions of the VLE data of all authors for the nonpolar systems.

We observe the smallest deviations for the ethane + propane and xenon + ethane systems. Measurements from only one reference have been available for these mixtures. The deviations for methane + propane and argon + methane are of the same order as for methane + ethane. As mentioned before, the parameter k_{ij} for each binary mixture has been fitted to selected experimental data and subsequently used for comparison with all experimental data. Thus, the deviations of the calculated from the experimental data are partly due to the equations, but also partly due to the inconsistencies in the experimental data from different references.

Mixtures of nonpolar with dipolar substances

Xenon + R41. In the xenon + R41 mixture, the nonpolar nobel gas xenon and the refrigerant R41 (CH_3F), which shows a strong dipole moment (see Table 1), are combined. In general, mixtures of nonpolar with strongly dipolar components show strong nonidealities, and the challenge is whether BACKONE is able to describe such mixtures properly. A fundamental problem for such investigations is that only a few experimental data for nonpolar + dipolar mixtures are available.

For R41 + xenon we only had the data of Fonseca and Lobo (1989), who measured vapor–liquid equilibria at three isotherms. As can be seen in Figure 3 we find surprisingly good predictions for this strong nonideal system. Taking into account all 28 VLE data of Fonseca and Lobo (1989), the absolute average deviation of the vapor pressure is 1.432% and of the vapor composition is 0.514%.

R32 + Propane. Another mixture of a nonpolar fluid with a strongly dipolar fluid we investigated is propane with R32 (CH_2F_2). The measurements of Holcomb et al. (1997) indi-

Table 4. Isochoric Heat Capacities of Methane + Ethane from BACKONE in Comparison with Experimental Results of Mayrath and Magee (1989)

x_{CH_4}	T K	ρ mol/L	$\frac{C_{v,\mathrm{exp}}}{R}$	$\frac{C_{v,\mathrm{EOS}}}{R}$	$\frac{\Delta C_v}{C_{v,\mathrm{exp}}}$ %
0.34528	101.44	23.31	5.155	5.227	−1.392
	109.53	23.25	5.166	5.313	−2.844
	114.26	23.22	5.183	5.332	−2.875
0.50217	106.89	24.00	4.855	4.950	−1.956
	112.59	23.96	4.834	4.978	−2.988
	120.99	23.90	4.817	4.989	−3.565
0.68526	106.61	25.31	4.659	4.683	−0.506
	109.79	25.29	4.651	4.686	−0.749
	113.01	25.27	4.647	4.686	−0.850

cated that this system shows liquid–liquid equilibria at low temperatures and a very strong positive pressure azeotrope. As can be seen in Figure 4 these properties can be reproduced by BACKONE, but the uncertainties are relatively high. Averaging over all given 75 VLE data, the absolute average deviation of the vapor pressure is 3.371% and the absolute average deviation of the vapor composition is 1.499%.

One reason for the higher deviations is the great sensitivity of the bubble-point pressure to small uncertainties in the composition. Another reason is due to the difficulties of the VLE measurements (Holcomb et al., 1997). The vapor–liquid equilibrium apparatus of Holcomb et al. (1997) was not designed to measure liquid–liquid equilibria, and the presence of two liquid phases is only indicated by an unstable liquid composition.

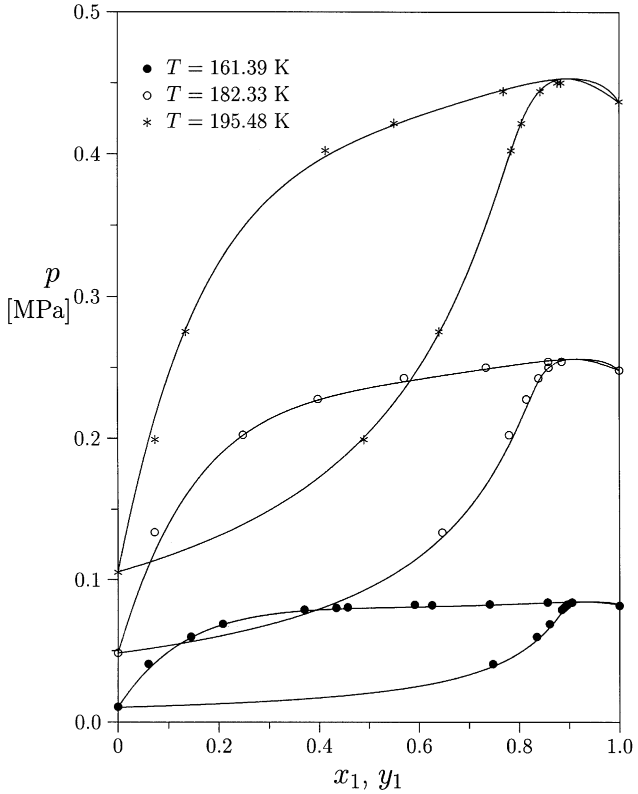

Figure 3. Vapor–liquid equilibrium isotherms for xenon (1) + R41(2) from BACKONE (—) in comparison with experimental data from Fonseca and Lobo (1989).

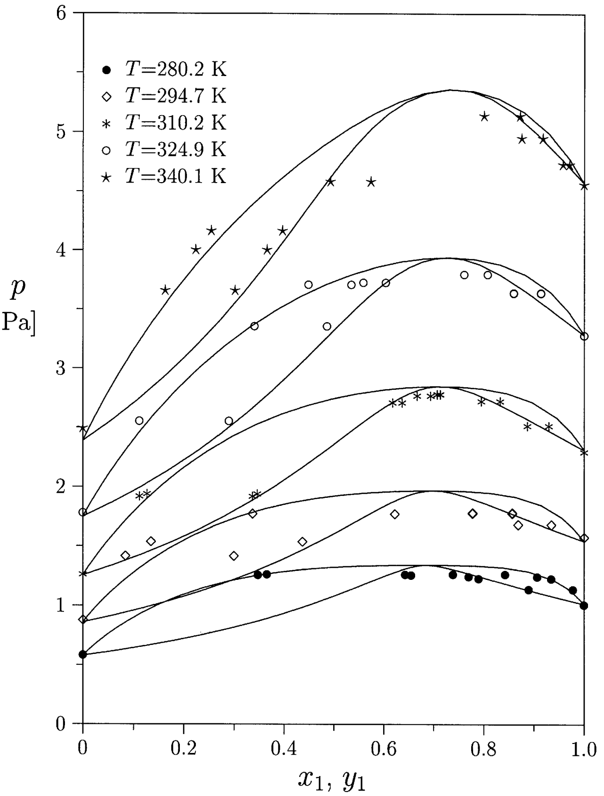

Figure 4. Vapor–liquid equilibrium isotherms for R32 (1) + propane(2) from BACKONE (—) in comparison with experimental data from Holcomb et al. (1997).

Figure 5 shows a comparison of the measured near-saturation liquid (p,ρ,T data) of Holcomb et al. (1997) with the predicted values of BACKONE. For small fractions of R32 we find that the calculations agree satisfactorily with the measurements, while at R32-rich compositions, the agreement is only within ±8% for the lowest and highest temperature measured. The thick lines at $x_1 = 0$ and $x_1 = 1$ in Figure 5 depict the deviations of our calculations from the measurements for the bubble-point densities of pure propane (Younglove and Ely, 1987) and pure R32 (Tillner-Roth and Yokozeki, 1997), respectively, for the temperature range of 270 to 345 K. As can be seen, the propane-rich mixtures can be reproduced with similar accuracy as pure propane, whereas the R32-rich mixtures have significantly larger deviations. For mixtures containing about 90% R32, the deviations scatter between ±7%, which is also an indication of the inconsistencies in the measurements.

Mixtures of nonpolar with quadrupolar substances

Carbon Dioxide + Ethane. The binary mixture of carbon dioxide with ethane is interesting because CO_2 is strongly

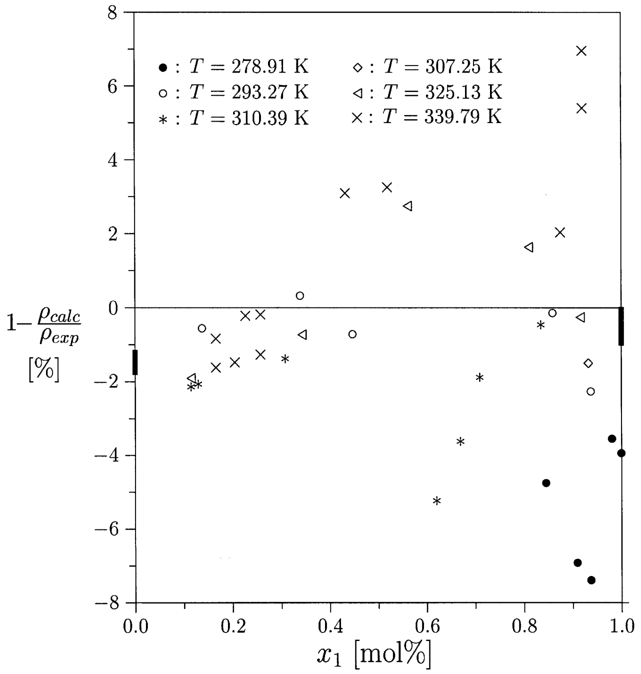

Figure 5. Comparison of homogenous near-saturation measurements (Holcomb et al., 1997) with BACKONE results for R32(1) + propane(2) at different compositions.

The thick lines at $x_1 = 0$ and $x_1 = 1$ denote the deviations of pure propane (Younglove and Ely, 1987), and pure R32 (Tillner-Roth and Yokozeki, 1997) respectively, in the temperature range of the measurements of the binary.

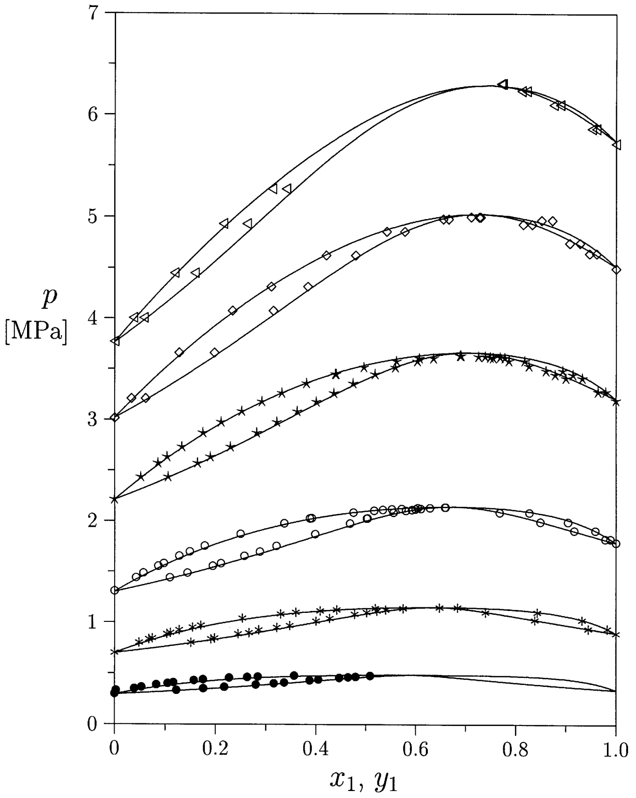

Figure 6. Vapor–liquid equilibrium isotherms for CO_2 (1) + ethane(2) from BACKONE (—) in comparison with experimental data.

● $T = 207.0$ K, ∗ $T = 230.0$ K, ○ $T = 250.0$ K, ★ $T = 270.0$ K (Brown et al., 1988), ◇ $T = 283.15$ K, ◁ $T = 293.15$ K (Fredenslund and Mollerup, 1974).

quadrupolar and ethane nonpolar. Moreover the system has a strong maximum-pressure azeotrope. A multitude of mostly accurate measurements of VLE as well as of homogenous properties are available.

In Figure 6 we present six VLE isotherms from 207.0 to 293.15 K that are comparable to the measurements from Fredenslund and Mollerup (1974) and Brown et al. (1988). Considering the data of all authors, including the highest isotherm of 298.15 K (Ohgaki and Katayama, 1977), the VLE data can be reproduced within an accuracy of ±0.921% in pressure and ±0.878% in the vapor composition (see Table 5). Higher deviations in vapor composition have been found only for the data of Hamam and Lu (1974), and these can be assumed to be due to inconsistencies in the measurements.

Similarly, good agreement between the measurements and the predictions from the BACKONE equation of state can be found for p, ρ, T data in the gaseous and in the liquid regions. A comparison of measurements with Lau (1986) at almost equimolar composition is given in Figure 7. Here again we find the largest deviations close to the critical point ($T_c = 297.4$ K, $\rho_c = 305.2$ kg/m^3, $p_c = 6.42$ MPa, according to BACKONE).

In Table 6 we also compare the measured enthalpy differences (Möller, 1991) with the results from BACKONE. For BACKONE, the ideal contributions for CO_2 are taken from Ely et al. (1987) and for ethane from Younglove and Ely (1987). The calculated data and the experimental data are in close agreement within the limits of the experimental uncertainties.

Nitrogen + Ethane. The nitrogen + ethane mixture was chosen as the second key mixture within this group because of liquid–liquid separation at low temperatures. As can be seen in Table 5, the VLE measurements of three different authors can be reproduced within an accuracy of ±3.919% in pressure and ±2.226% in vapor composition. In Figure 8 we show measurements of liquid–liquid equilibrium (Wisotzki and Schneider, 1985) at two different isobars in comparison with the calculations. Although the mixture parameter has been adjusted to VLE data, and no further adjustment has been made for LLE, the measurements can be reproduced with a good degree of accuracy.

Other Nonpolar + Quadrupolar Mixtures. In addition to the two key mixtures discussed in the previous two subsections, we also investigated the mixtures of methane and propane with CO_2, the xenon + ethene mixture, and nitrogen mixed with methane. Table 5 lists the average deviations of vapor pressures and vapor compositions of the VLE data for all the nonpolar-quadrupolar binaries.

For the CO_2 + propane mixture the VLE measurements of four authors can be reproduced with a good degree of accuracy. We also made a comparison with the VLE data of Aker

Table 5. Absolute Average Deviations of Vapor Pressures and Vapor Compositions of VLE Data from BACKONE in Comparison with Measurements for Mixtures of Nonpolar with Quadrupolar Fluids

Author	Data Points	T-range K	Δp_{AAD} %	Δy_{AAD} %
System: $CO_2 + C_2H_6$				
Davalos et al. (1976)	15	250.0	0.510	0.611
Fredenslund and Mollerup (1974)	65	223.2–293.2	0.669	0.535
Hamam and Lu (1974)	40	222.0–288.7	0.906	1.944
Nagahama et al. (1974)	15	253.0	1.270	0.701
Ohgaki and Katayama (1977)	74	283.2–298.2	0.714	0.638
Gugnoni et al. (1974) p,T,x	57	241.5–283.2	0.950	—
Brown et al. (1988)	133	207.0–270.0	1.131	0.909
Sum	399	207.0–298.2	0.921	0.878
System: $CO_2 + C_3H_8$				
Hamam and Lu (1976)	21	244.3–266.5	2.491	0.786
Nagahama et al. (1974)	24	253.0–273.2	4.197	1.250
Poettmann and Katz (1945)	43	272.6–369.0	5.856	1.359
Reamer et al. (1951)	78	277.6–344.3	1.715	2.207
Sum	166	244.3–369.0	3.245	1.669
System: $CH_4 + CO_2$				
Davalos et al. (1976)	33	230.0–270.0	9.661	4.201
Mraw et al. (1978)	52	153.2–219.3	5.023	1.896
Neumann and Walch (1968)	62	173.4–219.3	3.457	0.380
Somait and Kidnay (1978)	8	270.0	7.507	3.565
Donnelly and Katz (1954)	57	199.8–271.5	7.244	2.772
Mraw et al. (1978) p,T,y	45	153.2–219.3	3.694	—
Mraw et al. (1978) p,T,x	7	153.2–219.3	1.780	—
Hwang et al. (1976) p,T,y	60	153.2–219.3	4.738	—
Sum	324	153.2–271.5	5.340	2.110
System: $Xe + C_2H_4$				
Nuñes da Ponte et al. (1986)	175	203.0–287.2	0.628	0.406
System: $N_2 + CH_4$				
Bloomer and Parent (1953)	64	88.7–188.7	0.880	0.841
Parrish and Hiza (1974)	60	95.0–120.0	0.452	0.404
Kidnay et al. (1975)	91	112.0–180.0	0.575	0.763
McClure et al. (1976)	10	90.7	0.616	0.051
Stryjek et al. (1974a)	146	113.7–183.2	1.064	0.730
Miller et al. (1973) p,T,x	11	112.0	1.136	—
Miller et al. (1973) p,T,y	11	112.0	1.421	—
Sum	393	88.7–183.2	0.828	0.686
System: $N_2 + C_2H_6$				
Stryjek et al. (1974b)	52	138.7–194.3	4.397	1.516
Grauso et al. (1977)	33	200.0–290.0	3.721	2.662
Brown et al. (1989)	23	220.0–270.0	3.123	3.206
Sum	108	138.7–290.0	3.919	2.226

et al. (1954), but these results are not contained in Table 5, because their measurements are inconsistent with the other experimental sources. The absolute average deviation for the data of Aker et al. (1954) from BACKONE are ±11.6% for the pressure and ±1.96% for the vapor composition.

The VLE measurements for the xenon + ethene mixture as well as for nitrogen + methane, can be predicted by BACKONE with excellent accuracy (Table 5).

VLE measurements indicate liquid separation at temperatures below 205 K for the methane + carbon dioxide mixture. This liquid separation is also indicated by BACKONE, though no measurements were available for comparison with the calculations. The problem with this system is that liquid–liquid separation occurs already above the critical temperature of methane which caused serious difficulties at the adjustment of k_{ij}. Thus the value of the mixture parameter given in Table 2 is rather an estimated than a properly fitted value.

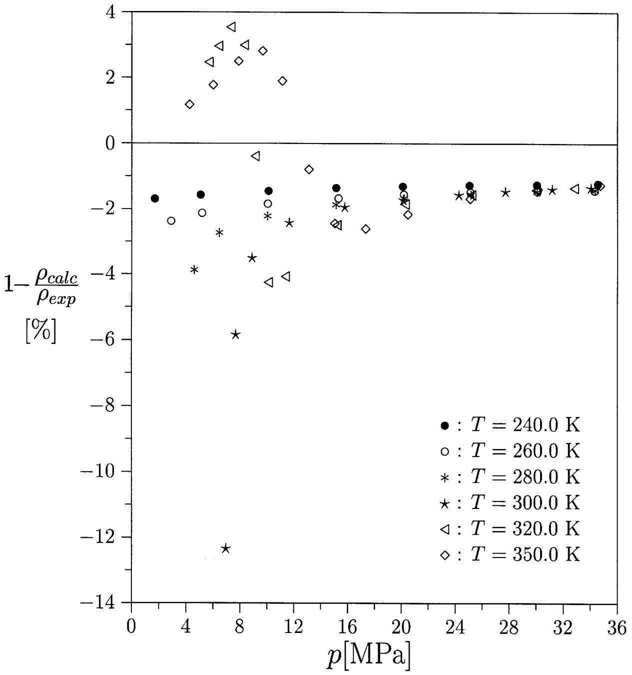

Figure 7. Comparision of homogenous isothermal p, ρ, T measurements (Lau, 1986) with BACKONE results for $CO_2(1)$ + ethane(2) at x_{CO_2} = 0.49245.

The critical data for this composition are T_c = 297.4 K, ρ_c = 305.2 kg/m^3, p_c = 6.42 MPa.

Mixtures of polar substances

R41 + Carbon Dioxide. Among the polar mixtures, R41 + carbon dioxide is of special interest, because R41 is a fluid with a strong dipole moment and no quadrupole moment, while carbon dioxide has a quadrupole moment and no dipole moment. Thus there is no dipole + dipole or quadrupole + quadrupole interaction between unlike molecules.

When we adjusted the binary mixing parameter to each of the isothermal VLE data given by Holcomb et al. (1997), we

Table 6. Isobaric Enthalpy Differences of CO_2 + Ethane (x_{CO_2} = 0.50161, T_{ref} = 284.65–284.43 K) from BACKONE in Comparison with Experimental Results of Möller (1991) ($\delta\Delta H = \Delta H_{exp} - \Delta H_{calc}$)

T [K]	p [MPa]	ΔH_{exp} [J/g]	$\delta\Delta H$ [J/g]
229.88	15.562	−120.53	−1.85
244.94	15.573	−89.11	−1.14
259.82	15.542	−57.20	−0.82
269.98	15.519	−35.65	−1.69
304.98	15.519	51.28	−0.26
315.09	15.572	78.84	0.12
330.08	15.575	122.36	0.72
350.20	15.589	181.27	−2.14
		AAD:	1.09

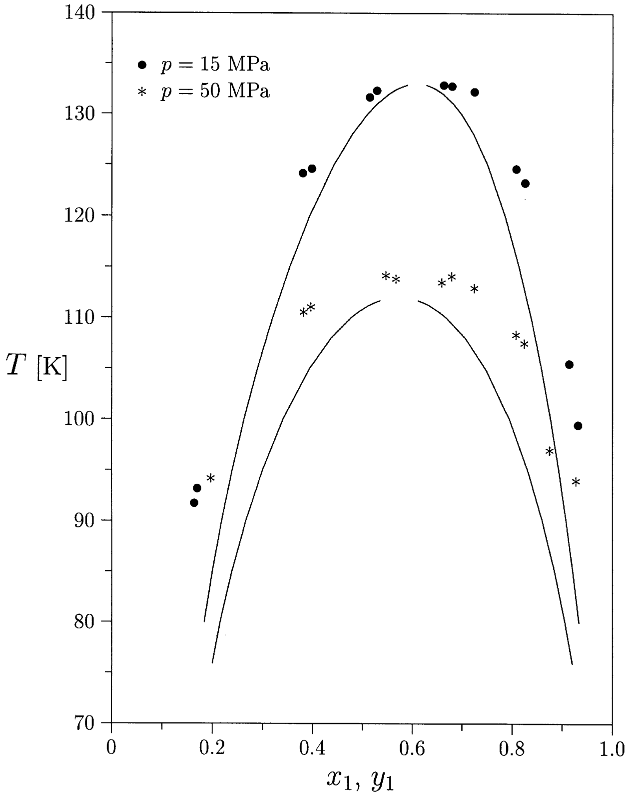

Figure 8. Liquid–liquid isobars for $N_2 + C_2H_6$ from BACKONE (—) in comparison with experimental data from Wisotzki and Schneider (1985).

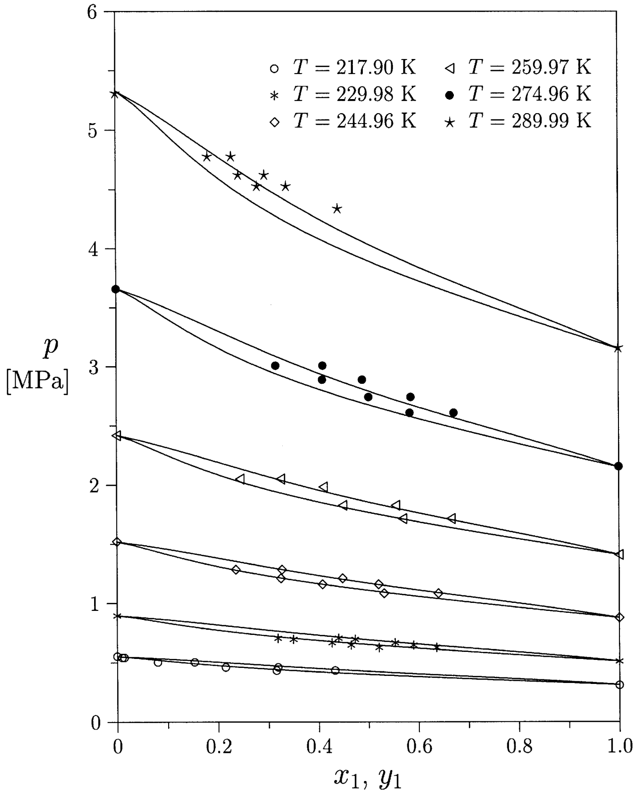

Figure 9. Vapor–liquid equilibrium isotherms for R41 (1) + CO_2(2) from BACKONE (—) in comparison with experimental data from Holcomb et al. (1997).

found a significant temperature dependency of k_{ij}. The value given in Table 2 corresponds to the optimum value for the isotherm at $T = 245$ K. As can be seen in Figure 9, the deviations of the measured data from the calculated curves increase with increasing distance from the 245 K-isotherm. We assume that this shift in temperature is a consequence of the dipole + quadrupole interactions, which the BACKONE equations of state actually cannot refer to. This deficiency of the equations is partly compensated by fitting the interaction parameter.

In Figure 10 we show comparisons of isochoric p,ρ,T data with the values predicted by BACKONE equations of state. We find good agreement with the predicted values for the liquid-phase points. Nevertheless, here again the model fails close to the critical point ($T_c = 341.0$ K, $\rho_c = 406.2$ kg/m^3, $p_c = 9.48$ MPa according to BACKONE), resulting in very large deviations.

Other Polar Mixtures. Other polar mixtures that have been investigated are the six crosswise combinations of R32, R125, R134a, and R143a. The binaries and the ternary for R125, R134a, and R143a are also presented in Weingerl and Wendland (2000). The absolute average deviation in pressure and in vapor composition for the VLE measurements are summarized for each system in Table 7. Looking over the results, we find the best agreement of the VLE measurements with the BACKONE calculations for the R32 + R143a and R143a + 134a mixtures, and the weakest agreement for the R32 + R125 mixture.

For all these mixtures the thermodynamic behavior is mainly governed by the differences in the polar moments (Table 1). With the exception of R32, which has a larger value for the characteristic density, the values for T_0, ρ_0, and α are similar. Written in the order of decreasing dipole moment and increasing quadrupole moment, respectively, we get the row R32, R134a, R143a, and R125. Thus good results for mixtures might be expected if the polar moments of the pure fluids are similar. This assumption is confirmed by the results for the R143a + R134a mixtures. Eventually, the worst agreement found for R32 + R125 follows as a result of the largest differences in their polarity. As with the R41 + CO_2 mixture we observe an increasing temperature dependency of the deviation as the differences in polarity increase.

Conclusions

In essence, the present investigations have shown that the BACKONE equations of state are able to describe phase equilibria, thermal and caloric properties of nonpolar and polar mixtures with only one adjustable independent state mixture parameter very well. However, there are some points that deserve particular attention.

One point is the consistency of the experimental data of the mixtures. In some cases, we fitted the adjustable binary

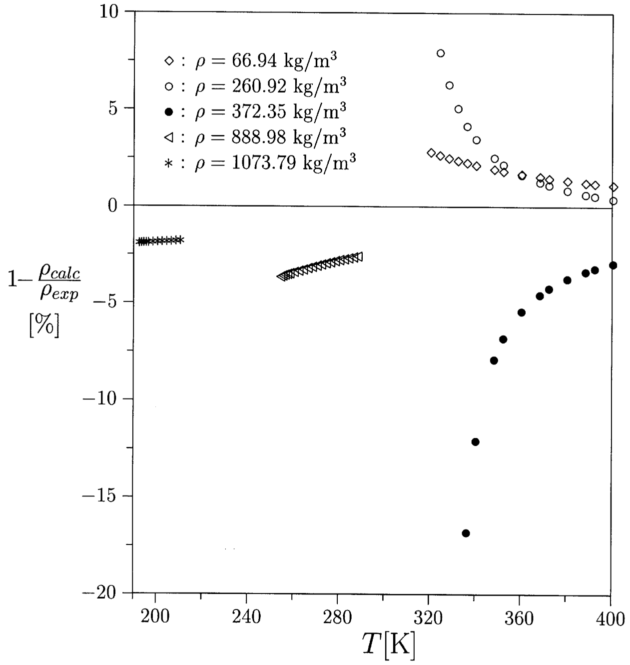

Figure 10. Comparision of homogenous isochoric p, ρ, T-measurements (Holcomb et al., 1997) with BACKONE results for R41(1) + CO$_2$(2) at $x_{R41} = 0.49982$.

The critical data for this composition are $T_c = 341.0$ K, $\rho_c = 406.2$ kg/m^3, $p_c = 9.48$ MPa.

parameter to one set of experimental data that could then be described very well. But the description of the same properties in the same region of state for the same mixture taken from another experimental source was not so perfect. This can be definitely attributed to the inconsistency of the experimental data rather than to the equation of state. Unfortunately, financial support for improving the quality of the experimental database is currently not very high.

Regarding the equation, it can be seen from Figures 2, 7 and 10 that the prediction of the densities is bad in the extended critical region. This behavior is not only for the description of mixtures with BACKONE, but is a general feature of any classic equation of state. These equations tend to produce a critical temperature that is too high. An improvement could be obtained if the classic equations were combined with scaling laws by a crossover concept, as was done by Kiselev and Friend (1999).

It also seems possible to improve the performance of BACKONE for the group "mixtures of polar substances," where the binary mixture parameter k_{ij} tends to be temperature dependent. We assume that this tendency is caused by the fact that in those mixtures the dipole–quadrupole interactions have not yet been accounted for. Therefore, it will be necessary to develop a mixing rule for the dipole–quadrupole interaction, too.

Finally, we point out that BACKONE was already applied by Weingerl and Wendland (2000) with good success for the description of the ternary mixture, R125 + R143a + R134a, using only the mixture parameters k_{ij} that were fitted to the binary data.

Table 7. Absolute Average Deviations of Vapor Pressures and Vapor Compositions of VLE Data from BACKONE in Comparison with Measurements for Mixtures of Polar Fluids

Author	Data Points	T-range K	Δp_{AAD} MPa	Δy_{AAD} %
System: R41 + CO$_2$				
Holcomb et al. (1997)	35	217.6–290.0	1.155	0.581
System: R32 + R134a				
Holcomb et al. (1997)	48	280.0–340.2	0.776	0.517
Nagel and Bier (1995)	50	202.9–368.9	2.907	1.060
Kleemiss (1997)	6	303.2–343.2	0.834	0.173
Kleemiss (1997) p,T,x	10	223.4–298.2	1.913	—
Sum	114	202.9–368.9	1.814	0.758
System: R32 + R143a				
Holcomb et al. (1997)	27	279.9–340.1	0.326	0.541
System: R32 + R125				
Holcomb et al. (1997)	30	279.8–340.2	0.987	0.358
Nagel and Bier (1995)	34	204.8–345.5	3.841	0.964
Kleemiss (1997)	5	303.2–333.2	2.120	0.600
Kleemiss (1997) p,T,x	47	223.6–344.2	2.803	—
Sum	116	204.8–345.5	2.608	0.674
System: R125 + R134a				
Holcomb et al. (1997)	28	280.0–340.2	1.031	0.820
Nagel and Bier (1995)	31	206.1–364.6	1.420	0.796
Kleemiss (1997)	6	303.2–343.2	1.303	0.982
Holcomb et al. (1997) p,T,x	12	280.4–340.4	1.190	—
Kleemiss (1997) p,T,x	18	224.5–303.0	0.789	—
Sum	95	206.1–364.6	1.149	0.823
System: R125 + R143a				
Holcomb et al. (1997)	21	280.0–326.0	0.631	0.382
Nagel and Bier (1996)	19	205.3–343.1	2.141	0.645
Kleemiss (1997)	8	302.4–338.2	0.494	0.285
Holcomb et al. (1997) p,T,x	14	280.0–325.0	1.348	—
Kleemiss (1997) p,T,x	8	223.1–293.1	2.554	—
Widiatmo et al. (1995) p,T,x	34	280.0–330.0	0.715	—
Sum	104	205.3–343.1	1.168	0.470
System: R143a + R134a				
Holcomb et al. (1997)	27	280.1–340.2	0.501	0.511
Nagel and Bier (1996)	12	205.0–360.7	0.548	0.451
Kleemiss (1997)	9	302.6–353.6	0.303	0.501
Holcomb et al. (1997) p,T,x	13	280.2–340.1	0.589	—
Kleemiss (1997) p,T,x	9	223.3–298.2	0.543	—
Sum	70	205.0–360.7	0.505	0.494

Acknowledgment

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Literature Cited

Aker, W. W., R. E. Kelley, and T. G. Lipscomb, "Carbon Dioxide–Propane System," *Ind. Eng. Chem.*, **46**(12), 2535 (1954).

Bloomer, O., and J. Parent, "Liquid–Vapor Phase Behaviour of the Methane–Nitrogen System," *Chem. Eng. Prog. Symp. Ser.*, **49**(3), 11 (1953).

Bohn, M., J. Fischer, and J. M. Haile, "Effect of Molecular Elongation on the Quadrupolar Free Energy in Diatomic Fluids," *Mol. Phys.*, **65**, 797 (1988).

Boublik, T., "Hard Convex Body Equation of State," *J. Chem. Phys.*, **63**, 4084 (1975).

Brown, T., A. J. Kidnay, and E. Sloan, "Vapour–Liquid Equilibria in the Carbon Dioxide–Ethane System," *Fluid Phase Equilib.*, **40**, 169 (1988).

Brown, T., E. Sloan, and A. Kidnay, "Vapour–Liquid Equilibria in the Nitrogen + Carbon Dioxide + Ethane System," *Fluid Phase Equilib.*, **51**, 299 (1989).

Calado, J. C. G., and L. A. K. Staveley, "Excess Gibbs Energy of Argon-Methane Liquid Mixtures at 115.77 K," *J. Chem. Phys.*, **56**, 4718 (1972).

Calero, S., M. Wendland, and J. Fischer, "Description of Alternative Refrigerants with BACKONE Equations," *Fluid Phase Equilibria*, **152**, 1 (1998).

Chen, S. S., and A. Kreglewski, "Application of the Augmented Van der Waals Theory of Fluids. I. Pure Fluids," *Ber. Bunsenges. Phys. Chem.*, **81**, 1048 (1977).

Christiansen, L. J., and A. Fredenslund, "Vapour–Liquid Equilibria of the CH_4-Ar-CO System," *Cryogenics*, **14**, 10 (1974).

Christiansen, L. J., A. Fredenslund, and J. Mollerup, "Vapour–Liquid Equilibrium of the CH_4–Ar, CH_4–CO, and Ar–CO Systems at Elevated Pressures," *Cryogenics*, **13**, 405 (1973).

Davalos, J., W. R. Anderson, R. E. Phelps, and A. J. Kidnay, "Liquid–Vapor Equilibria at 250.00 K for Systems Containing Methane, Ethane, and Carbon Dioxide," *J. Chem. Eng. Data*, **21**(1) 81, (1976).

Donnelly, H. G., and D. L. Katz, "Phase Equilibria in the Carbon Dioxide–Methane System," *Ind. Eng. Chem.*, **46**(1), 511 (1954).

Ely, J. R., J. W. Magee, and W. M. Haynes, "Thermophysical Properties for Special High CO_2 Content Mixtures," Research Report-110, Gas Processors Assoc. (1987).

Fischer, J., and S. Lago, "Thermodynamic Perturbation Theory for Molecular Liquid Mixtures," *J. Chem. Phys.*, **78**, 5750 (1983).

Fonseca, I. M. A., and L. Q. Lobo, "Thermodynamics of Liquid Mixtures of Xenon and Methylfluoride," *Fluid Phase Equilib.*, **49**, 249 (1989).

Fredenslund, A., and J. Mollerup, "Measurement and Prediction of Equilibrium Ratios for the $C_2H_6 + CO_2$ System," *J. Chem. Soc. Faraday Trans. I*, **70**, 1653 (1974).

Gomes de Azevedo, E. J. S., and J. C. G. Calado, "Thermodynamics of Liquid Methane + Ethane," *Fluid Phase Equilibria*, **49**, 21 (1989).

Grauso, L., A. Fredenslund, and J. Mollerup, "Vapour–Liquid Equilibrium Data for the Systems $C_2H_6 + N_2$, $C_2H_4 + N_2$, $C_3H_8 + N_2$, and $C_3H_6 + N_2$," *Fluid Phase Equilibria*, **1**, 13 (1977).

Gugnoni, R. J., J. W. Eldridge, V. C. Okay, and T. J. Lee, "Carbon Dioxide–Ethane Phase Equilibrium and Densities from Experimental Measurements and the B. W. R. Equation," *AIChE J.*, **20**(2), 357 (1974).

Hamam, S., and B.-Y. Lu, "Isothermal Vapor–Liquid Equilibria in Binary System Propane-Carbon Dioxide," *J. Chem. Eng. Data*, **21**(2), 200 (1976).

Hamam, S. E. M., and B. C.-Y. Lu, "Vapor–Liquid Equilibrium in the Ethane–Carbon Dioxide System," *Can. J. Chem. Eng.*, **52**(4), 283 (1974).

Haynes, W. M., R. D. McCarty, B. E. Eaton, and J. C. Holste, "Isochoric (p, v_m, x, T) Measurements on (Methane + Ethane) from 100 to 320 K at Pressures to 35 MPa," *J. Chem. Thermodyn.*, **17**, 209 (1985).

Heene, D. L., "Test von Mischungsregeln für den Beitrag der attraktiven Dispersionswechselwirkung zur Freien Energie im Rahmen einer verallgemeinerten van der Waals Zustandsgleichung," Diploma Thesis, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany (1994).

Holcomb, C. D., J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, *Selected Thermodynamic Properties for Mixtures of R-32* (*Difluoromethane*), *R-125* (*Pentafluoroethane*), *R-134a* (*1,1,1,2-Tetrafluoroethane*), *R-143a* (*1,1,1,-Trifluoroethane*), *R-41* (*Fluoromethane*), *R-290* (*Propane*), *and R-744* (*Carbon Dioxide*), NIST Technical Note 1397, National Institute of Standards and Technology, Boulder, CO (1997).

Hwang, S.-C., H. M. Lin, P. S. Chappelear, and R. Kobayashi, "Dew Point Study in the Vapor–Liquid Region of the Methane–Carbon Dioxide System," *J. Chem. Eng. Data*, **21**(4), 493 (1976).

Kidnay, A. F., R. C. Miller, W. R. Parrish, and M. J. Hiza, "Liquid–Vapor Phase Equilibria in the N_2-CH_4 System from 130 to 180 K," *Cryogenics*, **15**(9), 531 (1975).

Kiselev, S. B., and D. G. Friend, "Cubic Crossover Equation of State for Mixtures," *Fluid Phase Equilibria*, **162**, 51 (1999).

Kleemiss, M., "Thermodynamische Eigenschaften zweier ternärer Kältemittelgemische," *Fortschritts-Berichte VDI*, ***Reihe*** **19**, Nr. 98, VDI-Verlag, Düsseldorf (1997).

Kreglewski, A., *Equilibrium Properties of Fluids and Fluid Mixtures*, Texas A&M Univ. Press, College Station (1984).

Kriebel, C., M. Mecke, J. Winkelmann, J. Vrabec, and J. Fischer, "An Equation of State for Dipolar Two-Center Lennard-Jones Molecules and Its Application to Refrigerants," *Fluid Phase Equilib.*, **142**, 15 (1997).

Kriebel, C., A. Müller, J. Winkelmann, and J. Fischer, "A Hybrid Equation of State for Stockmayer Pure Fluids and Mixtures," *Fluid Phase Equilib.*, **119**, 67 (1996).

Lau, W.-W. R., *A Continuously Weighed Pycnometer Providing Densities for Carbon Dioxide + Ethane Mixtures Between 240 and 350 K at Pressures up to* 35 *MPa*, PhD Thesis, Texas A&M Univ., College Station (1986).

Lee, M. J., and K. C. Chao, "Augmented BACK Equation of State for Polar Fluids," *AIChE J.*, **34**, 825 (1988a).

Lee, M. J., and K. C. Chao, "Augmented BACK Equation of State II: Polar Fluid Mixtures," *AIChE J.*, **34**, 1773 (1988b).

Maschke, D. E., and G. Thodos, "Vapor–Liquid Equilibria for the Ethane–Propane System," *J. Chem. Eng. Data*, **7**(2), 232 (1962).

Mayrath, J. E., and J. W. Magee, "Measurements of Molar Heat Capacity at Constant Volume: $C_{V,m}\{xCH_4 + (1-x)C_2H_6, T = 100$ to 320 K, $p \leq 35$ MPa$\}$," *J. Chem. Thermodyn.*, **21**, 499 (1989).

McClure, D. W., K. L. Lewis, R. C. Miller, and L. A. K. Staveley, "Excess Enthalpies and Gibbs Free Energies for Nitrogen + Methane at Temperatures Below the Critical Point of Nitrogen," *J. Chem. Thermodyn.*, **8**, 785 (1976).

Mecke, M., A. Müller, J. Winkelmann, J. Vrabec, J. Fischer, R. Span, and W. Wagner, "An Accurate Van der Waals-Type Equation of State for the Lennard-Jones Fluid," *Int. J. Thermophys.*, **17**, 391 (1996).

Miller, R. C., A. J. Kidnay, and M. J. Hiza, "Liquid–Vapor Equilibria at 112.00 K for Systems Containing Nitrogen, Argon, and Methane (Gibbs Free Energy)," *AIChE J.*, **19**(1), 145 (1973).

Miller, R. C., A. J. Kidnay, and M. J. Hiza, "Liquid + Vapor Equilibria in Methane + Ethene and in Methane + Ethane from 150.00 to 190.00 K," *J. Chem. Thermodyn.*, **9**, 167 (1977).

Möller, D., "Thermodynamik fluider Mischungen: Kalorimetrie und Computersimulationen," *Fortschritts-Berichte VDI*, ***Reihe*** **3**, Nr. 260, VDI-Verlag, Düsseldorf (1991).

Mraw, S. C., S.-C. Hwang, and R. Kobayashi, "Vapor–Liquid Equilibrium of the CH_4–CO_2 System," *J. Chem. Eng. Data*, **23**(2), 135 (1978).

Müller, A., J. Winkelmann, and J. Fischer, "Effect of Elongation on the Dipolar Free Energy," *J. Chem. Phys.*, **99**, 3946 (1993).

Müller, A., J. Winkelmann, and J. Fischer, "BACKONE Family of Equations of State: 1. Nonpolar and Polar Pure Fluids," *AIChE J.*, **42**, 1116 (1996a).

Müller, A., J. Winkelmann, and J. Fischer, "Simulation Studies on Mixtures of Dipolar and Non Polar Linear Molecules: II. A Mixing Rule for the Dipolar Contributions to the Helmholtz Energy," *Fluid Phase Equilib.*, **120**, 107 (1996b).

Nagahama, K., H. Konishi, D. Hoshino, and M. Hirata, "Binary Vapor–Liquid Equilibrium of Carbon Dioxide–Light Hydrocarbons at Lower Temperatures," *J. Chem. Eng. Jpn.*, **7**, 323 (1974).

Nagel, M., and K. Bier, "Vapour–Liquid Equilibrium of Ternary Mixtures of the Refrigerants R32, R125, and R134a," *Int. J. Refrig.*, **18**, 534 (1995).

Nagel, M., and K. Bier, "Vapour–Liquid Equilibrium of Ternary Mixtures of the Refrigerants R125, R143a, and R134a," *Int. J. Refrig.*, **19**, 264 (1996).

Neumann, A., and W. Walch, "Dampf und Flüssigkeits-Gliechgewicht CO_2/CH_4 im Bereich tiefer Temperaturen und kleiner CO_2-Molenbrüche," *Chem. Ing. Technik.*, **40**(5), 241 (1968).

Nguyen, V. N., G. A. Iglesias-Silva, and F. Kohler, "An Equation of State for Nonpolar Substances Based on the Generalized van der Waals Model," *Fluid Phase Equilib.*, **91**, 215 (1993).

Nguyen, V. N., and F. Kohler, "Excess Properties and Phase Equilibria from a Generalized van der Waals Equation of State for the Example of the Mixture Methane + Ethane," *Fluid Phase Equilib.*, **105**, 153 (1995).

Nuñes da Ponte, M. N., D. Chokappa, J. C. G. Calado, J. Clancy, and W. B. Streett, "Vapour–Liquid Equilibria in the Xenon + Ethane System," *J. Chem. Phys.*, **89**(13), 2746 (1985).

Nuñes da Ponte, M., D. Chokappa, J. C. G. Calado, J. Zollweg, and W. B. Streett, "Vapour–Liquid Equilibria in the Xenon + Ethene System," *J. Chem. Phys.*, **90**(6), 1147 (1986).

Ohgaki, K., and T. Katayama, "Isothermal Vapor–Liquid Equilibrium Data for the Ethane–Carbon Dioxide System at High Pressures," *Fluid Phase Equilibria*, **1**, 27 (1977).

Parrish, W., and M. Hiza, "Liquid–Vapor Equilibrium in the Nitrogen–Methane System Between 95 and 120 K," *Adv. Cryog. Eng.*, **19**, 300 (1974).

Poettmann, F., and D. Katz, "Phase Behavior of Binary Carbon Dioxide–Paraffin System," *Ind. Eng. Chem.*, **37**(9), 847 (1945).

Price, A. R., "Low Temperature Vapor–Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane–Ethane–Propane System," PhD Thesis, Chemical Engineering Dept., Rice Univ., Houston, TX (1957).

Reamer, H. H., B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems," *Ind. Eng. Chem.*, **42**(3), 543 (1950).

Reamer, H., B. Sage, and W. Lacey, "Phase Equilibria in Hydrocarbon Systems," *Ind. Eng. Chem.*, **43**(11), 2515 (1951).

Saager, B., and J. Fischer, "Construction and Application of Physically Based Equations of State: II. The Dipolar and Quadrupolar Contributions to the Helmholtz Energy," *Fluid Phase Equilib.*, **72**, 67 (1992).

Saager, B., and J. Fischer, "Construction and Application of Physically Based Equations of State. III. Correlative and Predicative Application to the Refrigerants R22 and R125a," *Fluid Phase Equilib.*, **93**, 101 (1994).

Saager, B., J. Fischer, and M. Neumann, "Reaction Field Simulations of Monatomic and Diatomic Dipolar Fluids," *Mol. Simulations*, **6**, 27 (1991).

Saager, B., R. Hennenberg, and J. Fischer, "Construction and Application of Physically Based Equations of State. I. Modification of the BACK Equation," *Fluid Phase Equilib.*, **72**, 41 (1992).

Setzmannn, U., and W. Wagner, "A New Method for Optimizing the Structure of Thermodynamic Correlation Equations," *Int. J. Thermophys.*, **10**, 1103 (1989).

Shatskaya, L. V., and N. A. Zhirnova, "Liquid–Vapour Phase Equilibria in Binary Systems at Low Temperatures: I. Argon–Methane System," *Russ. J. Phys. Chem.*, **50**, 298 (1976).

Somait, F. A., and A. J. Kidnay, "Liquid–Vapour Equilibria at 270.00 K for Systems Containing Nitrogen, Methane, and Carbon Dioxide," *J. Chem. Eng. Data*, **23**, 301 (1978).

Sowers, G. M., and S. I. Sandler, "Computer Simulation of Molecular Fluid Mixtures: Results and Two New One-Fluid Models," *AIChE J.*, **39**, 663 (1993).

Stryjek, R., P. S. Chappelear, and R. Kobayashi, "Low Temperature Vapor–Liquid Equilibria of Nitrogen–Ethane System," *J. Chem. Eng. Data*, **19**, 334 (1974a).

Stryjek, R., P. S. Chappelear, and R. Kobayashi, "Low Temperature Vapor–Liquid Equilibria of Nitrogen–Methane System," *J. Chem. Eng. Data*, **19**, 340 (1974b).

Tillner-Roth, R., and A. Yokozeki, "An International Standard Equation of State for Difluoromethane (R-32) for Temperatures from the Triple Point at 136.34 K to 435 K and Pressures up to 70 MPa," *J. Phys. Chem. Ref. Data*, **23**, 731 (1997).

Vrabec, J., A. Lotfi, and J. Fischer, "Vapour Liquid Equilibria of Lennard-Jones Model Mixtures from the *NpT* Plus Test Particle Method," *Fluid Phase Equilib.*, **112**, 173 (1995).

Weingerl, U., and J. Fischer, "Test of a Mixing Rule for the Quadrupolar Contribution to the Helmholtz Energy," *Fluid Phase Equilib.*, **171**, 59 (2000).

Weingerl, U., and M. Wendland, "Description of Binary and Ternary Mixtures of R125a, R134a, and R143a with BACKONE Equations," *Proc. Int. Conf. of Refrigeration*, IIR/IIF, Sydney 1999, CD-Rom paper No. 538, Int. Inst. Refrigeration, Paris (2000).

Wichterle, I., and R. Kobayashi, "Vapor–Liquid Equilibrium of Methane–Propane System at Low Temperatures and High Pressures," *J. Chem. Eng. Data*, **17**, 4 (1972a).

Wichterle, I., and R. Kobayashi, "Vapor–Liquid Equilibrium of Methane–Ethane System at Low Temperatures and High Pressures," *J. Chem. Eng. Data*, **17**, 9 (1972b).

Wichterle, I., and R. Kobayashi, "Vapor–Liquid Equilibrium of Methane–Ethane–Propane System at Low Temperatures and High Pressures," *J. Chem. Eng. Data*, **17**, 13 (1972c).

Widiatmo, J., H. Sato, and K. Watanabe, "Bubble-Point Pressures and Liquid Densities of Binary R-125 + R-143a System," *Int. J. Thermophys.*, **16**, 801 (1995).

Wisotzki, K. D., and G. M. Schneider, "Fluid Phase Equilibria of the Binary System N_2 + Ethane and N_2 + Pentane Between 88 K and 313 K and at Pressures up to 200 MPa," *Ber. Bunsenges. Phys. Chem.*, **89**, 21 (1985).

Younglove, B. A., and J. F. Ely, "Thermophysical Properties of Fluids: II. Methane, Ethane, Propane, Isobutane, and Normal Butane," *J. Phys. Chem. Ref. Data*, **16**, 577 (1987).

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