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Comparison of Lorentz–Berthelot and Tang–Toennies Mixing Rules Using an Isotropic Temperature-Dependent Potential Applied to the Thermophysical Properties of Binary Gas Mixtures of CH_4, CF_4, SF_6, and $C(CH_3)_4$ with Ar, Kr, and Xe

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In this paper the isotropic temperature-dependent potential (ITDP) approach and the concepts introduced in our previous papers have been used to calculate equilibrium and transport properties of low-density gas mixtures. The twelve binary mixtures considered here are: Ar–CH_4, Ar–CF_4, Ar–SF_6, Ar–$C(CH_3)_4$, Kr–CH_4, Kr–CF_4, Kr–SF_6, Kr–$C(CH_3)_4$, Xe–CH_4, Xe–CF_4, Xe–SF_6 and Xe–$C(CH_3)_4$. The $(n-6)$ Lennard–Jones potential parameters n (repulsive parameter), R_m (equilibrium distance), and ε (potential well depth) of the pure noble gases Ar, Kr, and Xe are obtained by a minimization of the sum of squared deviations between experimental and calculated viscosity (η), and second pVT (B) and acoustic (β) virial coefficients normalized to their relative experimental error a_{exp}. The number of included experimental points for B, β, η was $N = 305$, 210, and 167 for Ar, Kr, and Xe, respectively. For the pure globular gases the potential parameters were taken from previous publications. The calculations of B, η, and ρD_{12} of binary mixtures were compared with experimental data by using two different mixing rules (Lorentz–Berthelot and Tang–Toennies). Recommended sets and fitting formulae for the potential parameters that can be used for the calculation of low-pressure thermophysical properties of these mixtures are provided.

KEY WORDS: binary mixtures; binary diffusion coefficient; isotropic temperature-dependent potential; mixing rules; noble and molecular gases.

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1. INTRODUCTION

Thermophysical properties such as the binary diffusion coefficient ρD[4] are needed for modeling and optimization of technological processes and equipment in a wide range of temperatures. In general, they could be measured but the variety of mixtures is not restricted and, apparently, it is not possible to have measured data for each particular case. The theory of gas mixtures [1] presents binary mixture properties as a result of interactions between "*equal*" (of the same sort A or B) and between "*unequal*" particles (of two different sorts A and B). In the case of diffusion in a binary gas mixture, we consider this process as self-diffusion of an artificial gas containing only qual molecules of mass $M = m_1 m_2/(m_1 + m_2)$ and calculate the diffusion coefficient by means of a standard formula,

$$\rho D = \frac{3}{8}\left(\sqrt{\frac{\pi MkT}{\pi\sigma^2\Omega^{(1,1)*}}}\right), \tag{1}$$

where at σ the potential energy U(σ)=0, $\Omega^{(1,1)*}$ is the reduced collision integral at temperature T , and k is the Boltzmann constant. In the case of an $(n-6)$ Lennard–Jones potential, $\sigma = \sqrt[n-6]{(6/n)}R_m$, with R_m being the equilibrium distance.

If the viscosity η is known, it might be simpler to use [1]

$$\rho D = \frac{6}{5}A^*\eta, \tag{2}$$

where $A* = \Omega^{(1,1)^*}/\Omega^{(2,2)^*}$.

Here we consider binary gas mixtures of the noble gases Ar, Kr, and Xe with the molecular gases methane (CH_4), carbon tetrafluoride (CF_4), sulphur hexafluoride (SF_6), and neopentane ($C(CH_3)_4$). The thermophysical properties B and η of the pure molecular gases were determined previously with the use of the potential parameters (PP) of Ref. 2. Later on, improved PP for methane and neopentane were obtained in our systematic study on the thermophysical properties of small alkanes [3].

In our present study, we focus on the procedure for obtaining PP for noble gases. In addition to our elaborate tabulations on the interaction pVT-virial coefficient $B_{12}(T)$ and the mixture viscosity $\eta_{\mathrm{mix}}(T)$ given in Ref. 4, we examine the effect of an alternative set of mixing rules on the thermophysical properties of the binary mixtures of noble gases with other globular (quasi-spherical or nearly quasi-spherically symmetric) molecules. In extending our previous tabulations, we have refined some of the PP

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[4] In the following the term $\rho D \equiv \rho D_{12}$, ρ = density, is called diffusion coefficient.

based on more recent experimental data and we also include a study of the binary diffusion coefficient.

Generally, the ITDP between two globular particles A and B is given by

$$U_{AB}(R,T)=\frac{\varepsilon_{AB}(T)}{n_{AB}-6}\left[6\left(\frac{R_{mAB}(T)}{R}\right)^{n_{AB}}-n_{AB}\left(\frac{R_{mAB}(T)}{R}\right)^{6}\right]. \tag{3}$$

For pure gases we have $A=B.R$ is the center-of-mass distance, $R_{mAB}(T)$ is the equilibrium distance, $\varepsilon_{AB}(T)$ is the potential well-depth, and n_{AB} is the repulsive parameter. As already discussed in detail [3, 5], the temperature dependence of $R_{mAB}(T)$ and $\varepsilon_{AB}(T)$ is due to the vibrational excitation of the molecules. Therefore, in our model the PP of the noble gases argon, krypton, and xenon do not show any temperature dependence.

In the following, the index "A" is used for the noble gases whereas "B" denotes the molecular gases. The repulsive parameters n_{AA} and n_{BB} are supposed to be independent of the temperature. The separation between equal molecules is

$$R_{mBB}(T)=R_{mBB}(T=0\,K)+\delta_0 f(T), \tag{4}$$

where the product $\delta_0 f(T)$ is the effective enlargement of molecular size caused by the vibrational excitation. δ_0 is a constant (independent of temperature) fit parameter, whereas the function $f(T)$ can be calculated from the vibrational partition function (see Refs. 3 and 5 for details). Assuming that the attractive dispersion-interaction does not depend on the temperature, the well-depth is given by

$$\varepsilon_{BB}(T)=\varepsilon_{BB}(T=0)(R_{mBB}(T=0)/R_{mBB}(T))^{6}. \tag{5}$$

The $(n-6)$ Lennard–Jones (LJ) parameters for the noble gases $(n_{AA}, R_{mAA}, \varepsilon_{AA})$ have been determined by the same procedure as was used for the molecular gases (see, for example, Refs. 2 and 3). However, in accordance with our physical model, we set $\delta_0=0$ and $f(T)=0$ in Eq. (2). This leads to constant R_{mAA} and ε_{AA} and to a temperature independent potential $U_{AA}(R)$ for the noble gases.

The intermolecular interaction potentials $U_{AB}(R,T)$ for unlike interactions between a noble gas A and a molecular gas B are obtained by two different empirical combination rules for binary mixtures. We have applied the Lorentz–Berthelot (LB) (Eqs. (6b), and (6c)) as well as the physically more reasonable Tang–Toennies (TT) mixing rules (Eqs. (6d), and (6e)) [6] for the potential parameters $R_{mAB}(T)$ and $\varepsilon_{AB}(T)$.

$$n_{AB} = (n_{AA} + n_{BB})/2, \tag{6a}$$

$$R_{mAB}(T) = [R_{mAA} + R_{mBB}(T)]/2, \tag{6b}$$

$$\varepsilon_{AB}(T) = \sqrt{\varepsilon_{AA} \times \varepsilon_{BB}(T)}, \tag{6c}$$

$$(R_{mAB}(T))^6 = \frac{\left\{0.5\left[(\varepsilon_{AA})^{1/13}(R_{mAA})^{12/13} + (\varepsilon_{BB}(T))^{1/13}(R_{mBB}(T))^{12/13}\right]\right\}^{13}}{(\varepsilon_{AA}\varepsilon_{BB}(T))^{1/2}(R_{mAA}R_{mBB}(T))^3}, \tag{6d}$$

$$\varepsilon_{AB}(T) = (\varepsilon_{AA}\varepsilon_{BB}(T))^{1/2}\frac{(R_{mAA}R_{mBB}(T))^3}{(R_{mAB}(T))^6}\frac{2\alpha_A\alpha_B(C_6^{AA}C_6^{BB})^{1/2}}{C_6^{AA}\alpha_B^2 + C_6^{BB}\alpha_A^2}, \tag{6e}$$

where α is the dipole-polarizability of the atom or molecule and C_6 is the constant in the leading term $-C_6R^{-6}$ of the dispersion interaction energy.

2. PROCEDURE

The calculation of the mixture and interaction properties is performed following the formulae given by the molecular theory of gases [1]. It requires a knowledge of the interaction potential between *equal* ($U_{AA}(R)$ and $U_{BB}(R, T)$) and *unequal* $U_{AB}(R, T)$) particles as a function of their distance R.

In Table I the PP of the atoms and globular molecules are shown. In the first row the present results for the PP are given. They are calculated after the data sets used in our previous studies [2, 4] are extended with additional experimental data.

We have to clarify that the potential parameters of the interactions Ar–Ar, Kr–Kr, and Xe–Xe used in Ref. 4 were defined in an earlier unpublished version of the present paper. In the course of revising the present manuscript, however, additional measurements were included into the minimization procedure, and our recommended PP now are not essentially different from those published in Ref. 4 which are given in brackets in the second row of Table I. For instance, in the case of the Ar–Ar interaction we have included experimental data on the acoustic virial coefficient β [31–34] and additional data for B [28–30] and η [37, 39]. Altogether, this causes a slight change in the potential parameters.

One can also notice the difference of the PP for CH_4–CH_4 and $C(CH_3)_4$–$C(CH_3)_4$ between our present investigation and those published in Ref. 4, which resulted from using the B measurements compiled recently by Dymond et al. [76] and by adding new η, β, and ρD [3].

Table I. Atomic Constants and Potential Parameters of Binary Interactions of Noble and Molecular Gases. (The numbers in parentheses are taken from Refs. 2 and 4)

No	Interaction	Mass (a.u.)	α (a.u.)	C_6 (a.u.)	n	ε/k_B (K)	R_m (10^{-10}m)	RMS (a_{exp})
1	Ar–Ar	39.95	11.08	64.30	17.10	155.0	3.600	0.938
			[77]	[78]	(17.99)	(158.8)	(3.590)	
2	Kr–Kr	83.8	16.79	129.6	17.80	221.0	3.860	0.908
			[77]	[78]	(17.83)	(220.1)	(3.869)	
3	Xe–Xe	131.3	27.16	285.9	18.76	310.9	4.204	0.873
			[77]	[78]	(17.90)	(299.5)	(4.060)	
4	CH_4–CH_4	16.04	17.50	129.6	21.63	220.8	3.868	0.997
			[77]	[79]	(22.8)	(226.8)	(3.815)	
5	CF_4–CF_4	88.005	19.10	254.0	52.71	328.40	4.329	0.701
			[77]	[80]				
6	SF_6– SF_6	146.1	30.04	585.8	34.76	417.80	5.041	0.657
			[77]	[81]				
7	$C(CH_3)_4$–$C(CH_3)_4$	72.14	66.22	1656.0	37.28	619.02	5.697	0.958
			[77]	[82]	(28.02)	(586.3)	(5.779)	

Therefore, the whole procedure is composed of the following steps:

1. Defining the interaction potentials $U_{AA}(R)$ and $U_{BB}(R,T)$ for the pure components of the mixture.
2. Calculating the ITDP potential parameters $\varepsilon_{AB}(T)$, $R_{mAB}(T)$, and n_{AB} for interactions between unequal particles by means of combination rules for mixture (see Eqs. (6a)–(6d)).
3. Calculating the properties of the mixtures (interaction second virial coefficient B_{12}, mixture viscosity η_{mix}, and binary diffusion ρD) by using the already known potential parameters for interaction between equal and unequal particles.
4. Comparing the resulting values with the available measured ones.
5. Giving fitting formulae for $R_{mBB}(T)$, from which $R_{mAB}(T)$ and subsequently $\varepsilon_{AB}(T)$ can be calculated according to Eqs. (5), (6c) and (6e).

3. INTERATOMIC POTENTIALS OF THE PURE GASES

The $(n-6)$ potentials $U_{AA}(R)$ for Ar, Kr, and Xe were determined in order to calculate the thermophysical properties of some binary mixtures containing these gases. For this purpose we collected all available experimentally obtained B, η, and β (see Tables II, III, and IV for Ar, Kr,

Table II. Experimental Data for Ar

Reference	N	ΔT (K)	a_{exp}(%)
1. Holborn and Otto (1925) [7]	9 (B)	173–673	1.5–86
2. Tanner and Mason (1930) [8]	7 (B)	298–447	6.1–139
3. Michels et al. (1949) [9]	7 (B)	273–423	5–93
4. Whalley et al. (1953) [10]	9 (B)	273–873	5–80
5. Cottrell et al. (1956) [11]	3 (B)	303–363	14–51
6. Michels et al. (1958) [12]	12 (B)	133–248	2–3.5
7. Lecocq (1960) [13]	6 (B)	573–1223	5–10
8. Fender and Halsey Jr., (1962) [14]	11 (B)	85–124	1.5–2
9. Crain Jr. and Sonntag (1966) [15]	4 (B)	143–273	1.6–7
10. Weir et al. (1967) [16]	16 (B)	80–190	1–3.5
11. Kalfoglou and Miller (1967) [17]	6 (B)	303–773	1.5–4
12. Byrne et al. (1968) [18]	18 (B)	84–271	2–5
13. Lichtenthaler and Schäfer (1969) [19]	5 (B)	288–323	6–9
14. Blancett et al. (1970) [20]	3 (B)	223–323	2–2.6
15. Provine and Canfield (1971) [21]	3 (B)	143–183	1–3
16. Pope et al. (1973) [22]	3 (B)	101–138	0.5–1
17. Bellm et al. (1974) [23]	10 (B)	300–550	13–200
18. Hahn et al. (1974) [24]	5 (B)	200–273	4–9
19. Schramm and Hebgen (1974) [25]	3 (B)	77–90	2
20. Rentschler and Schramm (1977) [26]	6 (B)	326–713	25–670
21. Schramm et al. (1977) [27]	11 (B)	202–500	8–500
22. Ewing and Trusler (1992) [28]	14 (B)	75–700	1–11
23. Gilgen et al. (1994) [29]	27 (B)	110–340	1–4
24. Estrada-Alexanders and Trusler (1996) [30]	17 (B)	110–450	1–15
25. Ewing et al. (1985) [31]	7 (β)	251–330	4–300
26. Ewing et al. (1989) [32]	9 (β)	100–304	1–4
27. Ewing and Trusler (1992) [33]	8 (β)	90–373	1–3
28. Estrada-Alexanders and Trusler (1995) [34]	21 (β)	110–450	7–19
29. Kestin et al. (1971) [35]	1 (η)	298.15	1
30. Rakshit et al. (1973) [36]	4 (η)	238–308	2
31. Clifford et al. (1975) [37]	9 (η)	321–1300	1–2
32. Kestin et al. (1977) [38]	8 (η)	298–673	1
33. Kestin et al. (1978) [39]	9 (η)	298–773	0.3
34. Vogel (1984) [40]	3 (η)	298–423	1
35. Kestin (1984) [41]	5 (η)	200–600	1
36. Aziz and Slaman (1990) [42]	3 (η)	298–423	2
37. Wilhelm and Vogel (2000) [43]	3 (η)	298–423	1
all B data	215	77–1223	
all η data	45	200–1300	
All β data	45	90–450	
All B+β+ηdata	305	77–1300	

Table III. Experimental Data for Kr

Reference	N	ΔT (K)	$a_{\mathrm{exp}}(\%)$
1. Glockler (1933) [44]	2 (B)	329–369	13.5–20
2. Beattie et al. (1952) [45]	13 (B)	273–573	2–90
3. Whalley and Schneider (1954) [46]	9 (B)	273–873	1–100
4. Thomaes and van Steenwinkel (1962) [47]	9 (B)	110–270	0.2–2
5. Fender and Halsey, Jr., (1962) [14]	10 (B)	108–138	0.2–2
6. Trappeniers et al. (1966) [48]	14 (B)	273–423	2–6
7. Brewer (1967) [49]	4 (B)	123–223	0.1–0.2
8. Weir et al. (1967) [16]	13 (B)	111–224	0.9–2.7
9. Byrne et al. (1968) [18]	12 (B)	117–252	0.6–2
10. Pollard and Saville (1971) [50]	15 (B)	167–274	1.3–3.1
11. Santafe et al. (1976) [51]	6 (B)	273–323	5–7.5
12. Rentschler and Schramm (1977) [26]	6 (B)	300–715	8–200
13. Schramm et al. (1977) [27]	13 (B)	202–497	3.4–53
14. Dillard et al. (1978) [52]	3 (B)	223–323	0.1–0.2
15. Schmiedel et al. (1980) [53]	12 (B)	213–475	1.9–20.4
16. Perez et al. (1980) [54]	5 (B)	300–500	3.9–30.8
17. Zamojski and Stecki (1982) [55]	3 (B)	304–306	105–13.6
18. Patel et al. (1988) [56]	3 (B)	223–323	3–4.9
19. Ewing et al. (1985) [31]	3(β)	285–320	7
20. Rankine (1910) [57]	3 (η)	273–373	3
21. Nassini and Rossi (1928) [58]	2 (η)	288–373	3
22. Kestin and Leidenfrost (1959) [59]	1 (η)	293.15	3
23. Clifton (1963) [60]	10 (η)	298–690	3
24. Rigby and Smith (1966) [61]	15 (η)	293–972	3
25. Kestin et al. (1978) [39]	9 (η)	298–778	1
26. Van den Berg (1979) [62]	2 (η)	298–348	0.5
27. Vogel (1984) [40]	2 (η)	298–348	0.5
28. Kestin et al. (1984) [41]	6 (η)	100–600	3
29. Aziz and Slaman (1990) [42]	2 (η)	298–348	0.5
30. Wilhelm and Vogel (2000) [43]	2 (η)	298–348	0.5
all Bdata	152	108–773	
all βdata	3	285–320	
all η data	55	100–972	
all B+β+η data	210	100–972	

and Xe, respectively), and minimized the sum of the squared deviations between them and those calculated by means of the parameterized potentials, normalized to their relative experimental error a_{exp}.

$$F=\sum_{1}^{N_\eta}\frac{\ln(\eta_{\mathrm{exp}}/\eta_{calc})^2}{a_{\eta\,\mathrm{exp}}}+\sum_{1}^{N_B}\frac{\ln(B_{\mathrm{exp}}/B_{calc})^2}{a_{B\,\mathrm{exp}}}+\sum_{1}^{N_\beta}\frac{\ln(\beta_{\mathrm{exp}}/\beta_{calc})}{a_{\beta\,\mathrm{exp}}}. \tag{7}$$

Table IV. Experimental Data for Xe.

Reference	N	ΔT (K)	A_{exp} (%)
1. Beattie et al. (1951) [63]	13 (B)	290–573	3–17
2. Michels et al. (1954) [64]	8 (B)	273–423	1.5–2
3. Reeves and Whytlaw-Gray (1955) [65]	5 (B)	273–313	10–12.5
4. Whalley et al. (1955) [66]	10 (B)	273–973	1–200
5. Greenlief and Constabaris (1966) [67]	1 (B)	298	1
6. Brewer (1967) [49]	3 (B)	173–223	0.1–8.8
7. Pollard and Saville (1971) [50]	17 (B)	160–301	1.2–3
8. Hahn et al. (1974) [24]	5 (B)	201–273	1–1.3
9. Rentschler and Schramm (1977) [26]	7 (B)	309–713	3.3–54
10. Schramm et al. (1977) [27]	11 (B)	231–491	1.9–10
11. Schmiedel et al. (1980) [53]	12 (B)	213–475	0.8–4.4
12. Perez et al. (1980) [54]	5 (B)	300–500	2–5.2
13. Schramm and Mueller (1982) [68]	8 (B)	213–450	1.9–7
14. Hurley et al. (1997) [69]	10 (β)	210–400	3
15. Nassini and Rossi (1928) [58]	2 (η)	290–373	1
16. Trautz and Heberling (1934) [70]	5 (η)	293–550	1
17. Naldrett and Maass (1940) [71]	1 (η)	298	1
18. Watts et al. (1955) [72]	4 (η)	273–373	1–2
19. Rigby and Smith (1966) [61]	14 (η)	293–972	1
20. Clarke and Smith (1968) [73]	4 (η)	176–299	1–3
21. Dawe and Smith (1970) [74]	3 (η)	1200–1600	3
22. Kestin et al. (1972) [75]	4 (η)	373–973	3
23. Kestin (1984) [41]	6 (η)	100–600	2
24. Kestin et al. (1978) [39]	9 (η)	298–778	1
all B data	105	201–973	
all β data	10	210–400	
all η data	52	100–1600	
all B+β+η data	167	100–1600	

Altogether we put into the minimization procedure 305 experimentally measured values of B, β, and η from 37 sources. [7–43] for Ar, 210 from 30 sources [14, 16, 18, 26, 27, 31, 39–62] for Kr, and 167 from 24 sources for Xe [24, 26, 27, 39, 41, 49, 50, 53, 54, 58, 63–75]. The obtained LJ $(n-6)$ potential parameters and the root-mean-square deviations $RMS=\sqrt{F/M}$ of the "best" solutions are shown in Table I.

The ITDP potential parameters at $T=0\,\mathrm{K}$ of the molecular gases shown in the same Table I have been defined previously [2, 3]. Since for methane $f(T)\approx 0$ (Eq. (4)), in this case, the minimization procedure yields $\delta_0\approx 0$. This result confirms, that due to the high vibrational frequencies, the molecule does not show any noticeable vibrational excitation in the investigated temperature range.

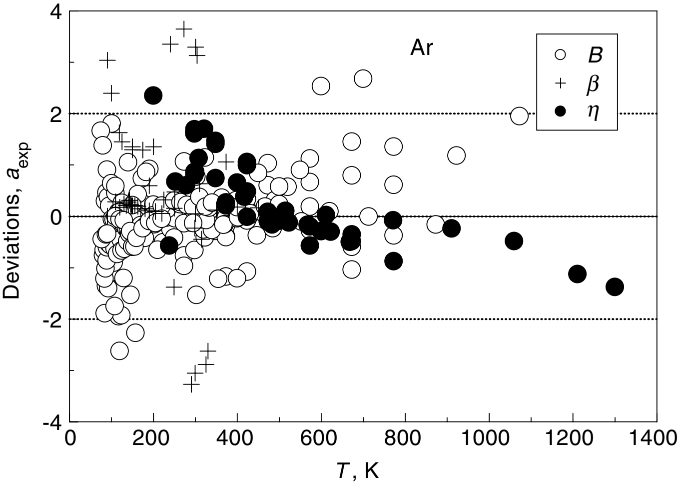

Fig. 1. Deviation plot for argon.

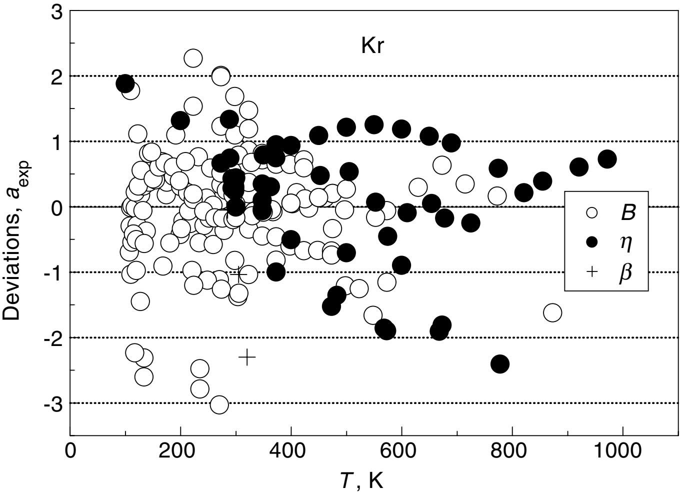

Fig. 2. Deviation plot for krypton.

The B, β, and η deviations between the experimental and calculated data for Ar, Kr, and Xe are shown in Figs. 1–3. In all cases the absolute deviations are situated symmetrically toward the reference line. The RMS deviation for each gas is less than one (see Table I) which means that the experimental data are reproduced within their stated experimental accuracy.

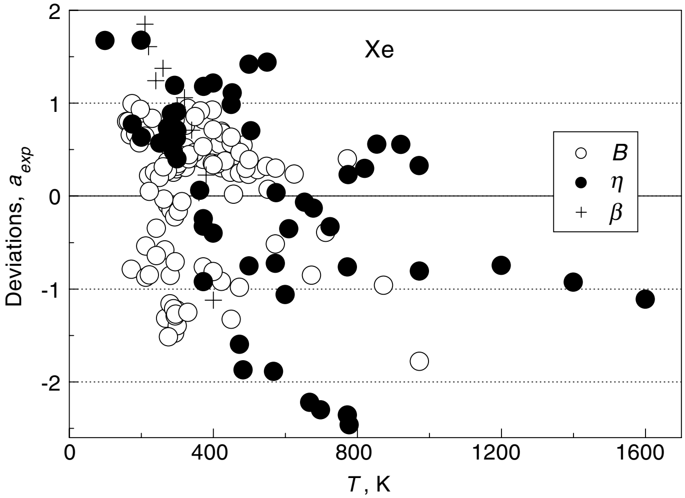

Fig. 3. Deviation plot for xenon.

4. BINARY MIXTURES

4.1. ITDP Potential Parameters for Interactions Between Unequal Particles

The potential parameters of binary mixtures at $T = 0$ K are shown in Tables V–VII. For comparison, the results of both mixing rules are displayed.

Additionally, we have fitted $R_{mBB}(T)$ to the function,

$$R_{mBB}(T) = R_{mBB}(0) + A_1 \exp(-B_1/T) + A_2 \exp(-B_2/T). \tag{8}$$

The fit parameters A_1, A_2, B_1, and B_2 for the molecular gases are given in Table VIII. They allow for a calculation of the potential parameters for each mixture according to Eqs. (6a)–(6e) in the temperature range between 200 and 900 K.

4.2. Comparison with the Available Experimental and Calculated Data

The available experimental data for binary mixtures for B_{12}, η_{mix}, and ρD given in the literature are presented in Table IX. The majority of them have been measured about 30 years ago. Our analysis has shown that in many cases they do not agree within the error bars given by the authors.

Table V. Potential Well Depth ε_{AB} at $T = 0$ K According to the Lorentz–Berthelot, Eq. (4b), (first row) and Tang–Toennies Mixing Rules, Eq. (4e), (second row)

	Ar	Kr	Xe	CH_4	CF_4	SF_6	$C(CH_3)_4$
Ar	155.00	185.08	219.52	184.99	225.61	254.48	309.75
		182.19	203.85	181.35	205.46	198.65	194.59
	Kr	221.00	262.12	220.89	269.40	303.86	369.87
			256.53	220.70	255.98	259.95	269.95
		Xe	310.90	261.99	319.53	360.41	438.70
				257.25	305.84	328.84	366.43

Table VI. Equilibrium Distance R_{mAB} at $T = 0$ K According to the Lorentz–Berthelot, Eq. (4c), (first row) and Tang–Toennies Mixing Rules, Eq. (4d), (second row)

	Ar	Kr	Xe	CH_4	CF_4	SF_6	$C(CH_3)_4$
Ar	3.6000	3.7300	3.9020	3.7340	3.9645	4.3205	4.6485
		3.7362	3.9310	3.7404	4.0007	4.4353	4.8827
	Kr	3.8600	4.0320	3.8640	4.0945	4.4505	4.7785
			4.0404	3.8640	4.1057	4.5163	4.9381
		Xe	4.2040	4.0360	4.2665	4.6225	4.9505
				4.0442	4.2646	4.6488	5.0429

Table VII. Repulsive Parameter $n_{AB} = (n_{AA} + n_{BB})/2$

	Ar	Kr	Xe	CH_4	CF_4	SF_6	$C(CH_3)_4$
Ar	17.10	17.45	17.93	19.37	34.91	25.93	27.19
	Kr	17.80	18.28	19.72	35.26	26.28	27.54
		Xe	18.76	20.20	35.74	26.76	28.02

Table VIII. Coefficients of $R_{mBB}(T)$ According to Eq. (6)

Molecule	$A_1(10^{-10}\mathrm{m})$	$B_1(\mathrm{K})$	$A_2(10^{-10}\mathrm{m})$	$B_2(\mathrm{K})$
CH_4	0	–	0	–
CF_4	0.11546	720.414	0.25357	1748.917
SF_6	0.42385	785.083	0	–
$C(CH_3)_4$	0.18073	443.890	0.74702	1963.417

Table IX. Experimental Data for Mixtures

Mixture	Reference	N	ΔT (K)
Ar + CH4	Thomaes et al. (1962) [83]	2 (B_{12})	240–295
	Byrne et al. (1968) [18]	14 (B_{12})	107–274
	Lichtenthaler and. Schäfer (1969) [19]	5 (B_{12})	288–323
	Strein et al. (1971) [84]	11 (B_{12})	296–493
	Bellm et al. (1974) [23]	10 (B_{12})	300–550
	Hahn et al. (1974) [24]	5 (B_{12})	201–272
	Rakshit et al. (1973) [36]	20 (η_{mix})	238–308
	Dunlop and Bignell (1987) [85]	11 (ρD)	200–400
Ar + CF4	Dantzler-Siebert and Knobler (1971) [86]	1 (B_{12})	373
	Dunlop et al. (1986) [87]	3 (B_{12})	290–320
	Kestin et al. (1977) [38]	32 (η_{mix})	298–673
	Kestin et al. (1977) [38]	6 (ρD)	298–673
Ar + SF6	Bellm et al. (1974) [23]	10 (B_{12})	300–550
	Santafe et al. (1974) [88]	6 (B_{12})	273–323
	Martin et al. (1982) [89]	3 (B_{12})	290–320
	Kestin et al. (1977) [38]	10 (η_{mix})	298–473
	Kestin et al. (1977) [38]	5 (ρD)	298–483
	Trengove et al. (1984) [90]	3 (ρD)	280–320
	Ivakin and Suetin (1964) [91]	7 (ρD)	287–472
	Loiko et al. (1981) [92]	3 (ρD)	280–320
	Marrero and Mason (1972) [93]	6 (ρD)	328–472
	Santafé et al. (1978) [94]	1 (ρD)	315
Ar + $C(CH_3)_4$	Strein et al. (1971) [84]	11 (B_{12})	296–493
	Bellm et al. (1974) [23]	10 (B_{12})	300–550
	Baughman et al. (1975) [95]	7 (B_{12})	200–258
	Jescheck (1979) [96]	4 (ρD)	312–393
Kr + CH4	Byrne et al. (1968) [18]	13 (B_{12})	119–271
	Dunlop and Bignell (1987) [85]	11 (ρD)	200–400
Kr + CF4	Dunlop et al. (1986) [87]	3 (B_{12})	290–320
Kr + SF6	Martin et al. (1982) [89]	3 (B_{12})	290–320
	Schramm et al. (1984) [97]	10 (B_{12})	201–465
	Trengove et al. (1984) [90]	3 (ρD)	280–320
Xe + CH4	Dunlop and Bignell (1987) [85]	11 (ρD)	200–400
Xe + CF4	Dunlop et al. (1986) [87]	3 (B_{12})	290–320
Xe + SF6	Martin et al. (1982) [89]	3 (B_{12})	290–320

Deviation plots for B_{12} (Figs. 4–11), η_{mix} (Figs. 12–14), and ρD (Figs. 15–19) are presented as examples only for some reliable experimental data.

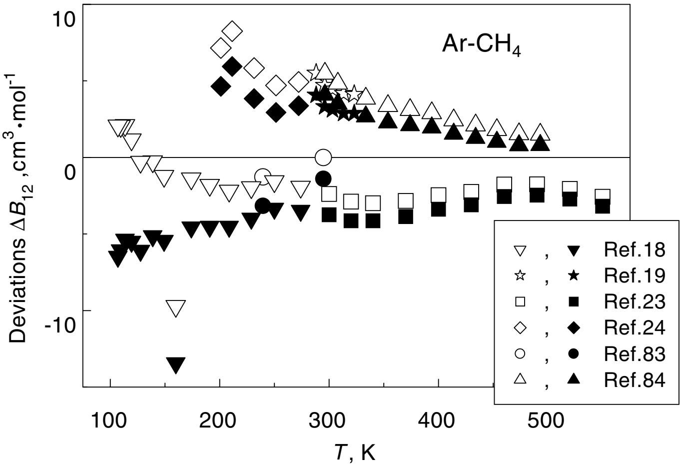

Fig. 4. Deviations between experimental and calculated interaction virial coefficients B_{12} of Ar–CH_4. Open symbols: LB mixing rules, full symbols: TT mixing rules.

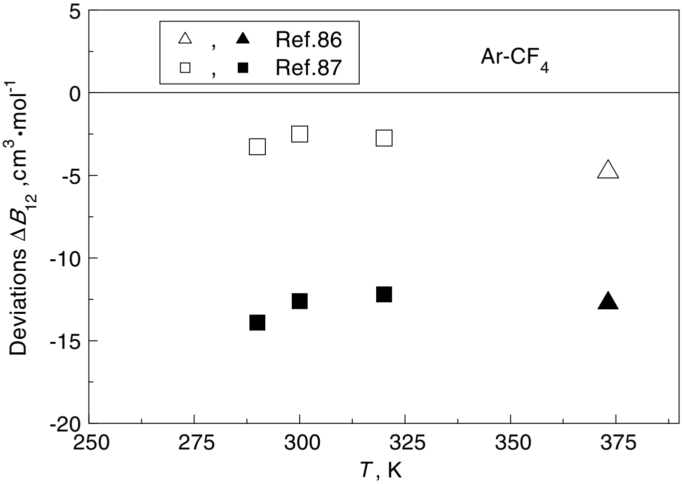

Fig. 5. Deviations between experimental and calculated interaction virial coefficients B_{12} of Ar–CF_4. Open symbols: LB mixing rules, full symbols: TT mixing rules.

For each mixture interaction potentials with two different data sets were considered. The first one is obtained by applying the LB mixing rules Eqs. (6a)–(6c); the second one uses the more elaborate TT mixing rules (6a), (6d), and (6e).

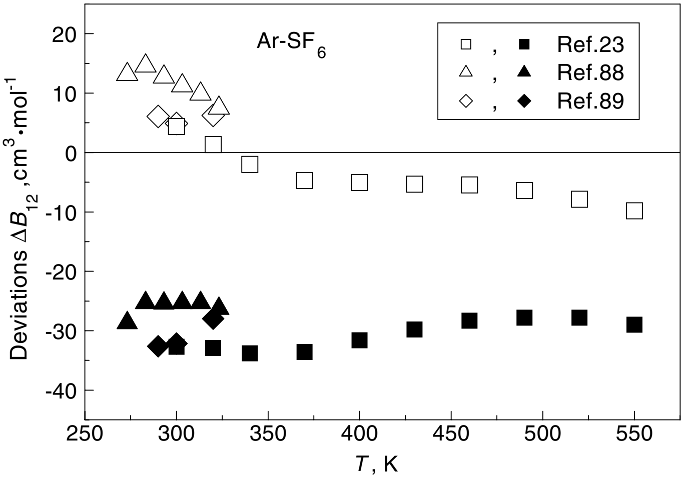

Fig. 6. Deviations between experimental and calculated interaction virial coefficients B_{12} of Ar–SF_6. Open symbols: LB mixing rules, full symbols: TT mixing rules.

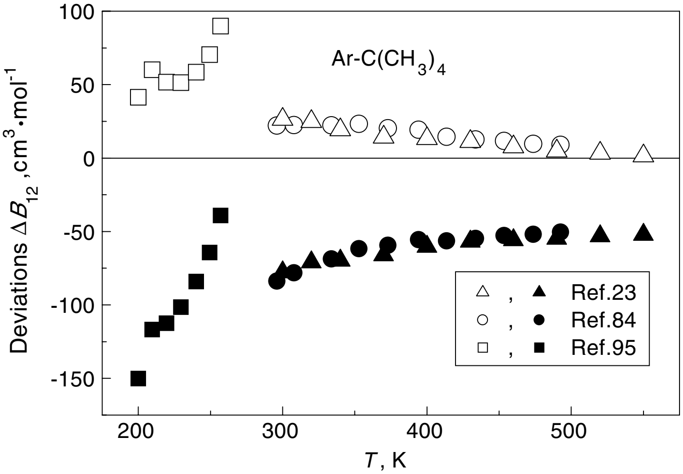

Fig. 7. Deviations between experimental and calculated interaction virial coefficients B_{12} of Ar–$C(CH_3)_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

In general, we found that the equilibrium property $B_{12}(T)$ is described better by using the LB than the TT mixing rules. For Ar–CH_4 (Fig. 4) a slight improvement by using the TT rules was detected. In the case of

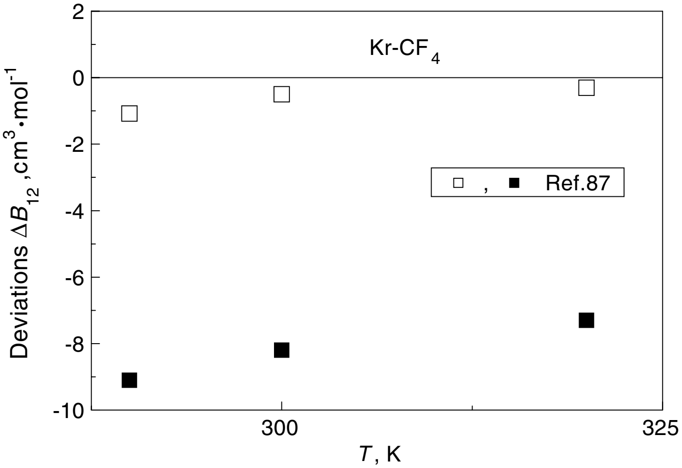

Fig. 8. Deviations between experimental and calculated interaction virial coefficients B_{12} of Kr–CF$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

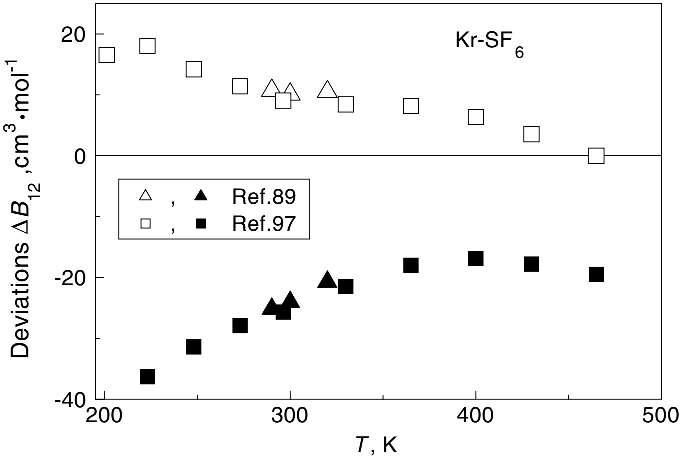

Fig. 9. Deviations between experimental and calculated interaction virial coefficients B_{12} of Kr–SF$_6$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

Xe–CF$_4$ (Fig. 10) and Xe–SF$_6$(Fig. 11), the TT rules give a better reproduction of the experimental interaction virial coefficient B_{12}(T). The transport properties show a somewhat different behavior. The viscosities η_{mix}

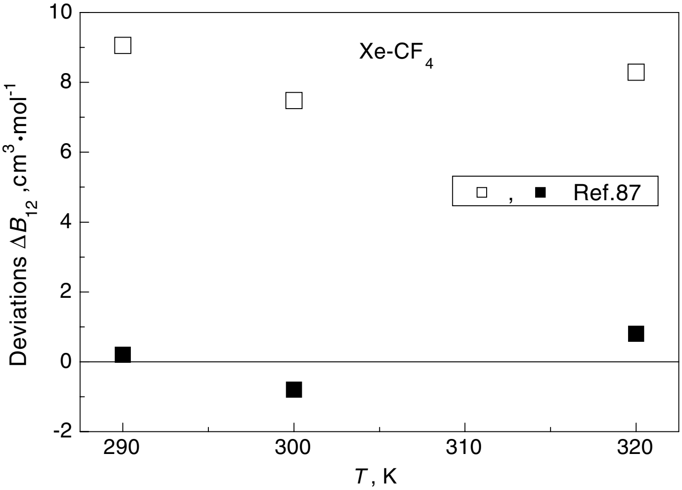

Fig. 10. Deviations between experimental and calculated interaction virial coefficients B_{12} of Xe–CF$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

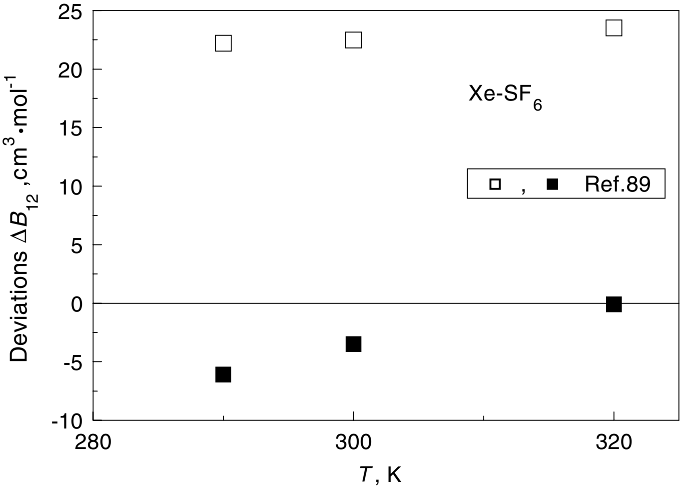

Fig. 11. Deviations between experimental and calculated interaction virial coefficients B_{12} of Xe–SF$_6$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

of the three mixtures Ar–CH$_4$ (Fig. 12), Ar–CF$_4$ (Fig. 13), and Ar–SF$_6$ (Fig. 14) as a function of composition and temperature are equally well described by both of the mixing rules. In the case of the binary diffusion

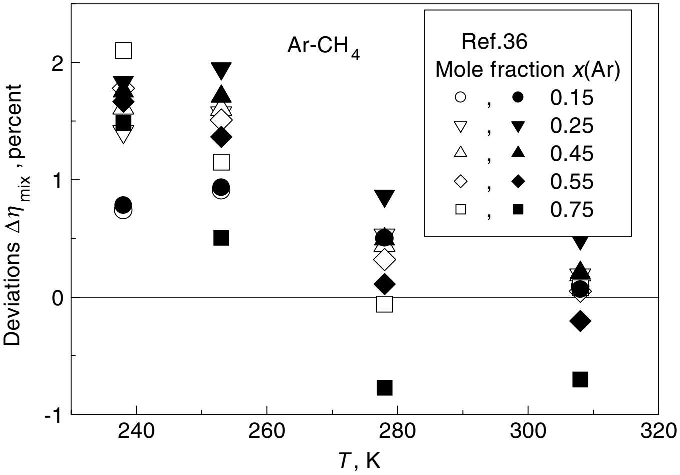

Fig. 12. Relative deviations between experimental and calculated mixture viscosities η_{mix} of Ar–CH$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

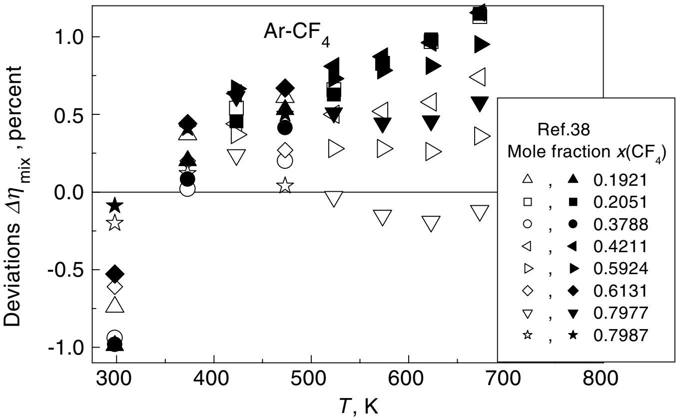

Fig. 13. Relative deviations between experimental and calculated mixture viscosities η_{mix} of Ar–CF$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

coefficients ρD for Ar–SF$_6$ and Kr–SF$_6$, Figs. 15 and 16, we found the TT rules to be superior to the LB mixing rules. For the interaction between methane and the noble gases both mixing rules yield approximately the same deviation between calculated and experimental values (Fig. 17). In contrast to this, the experimentally determined binary diffusion coefficient

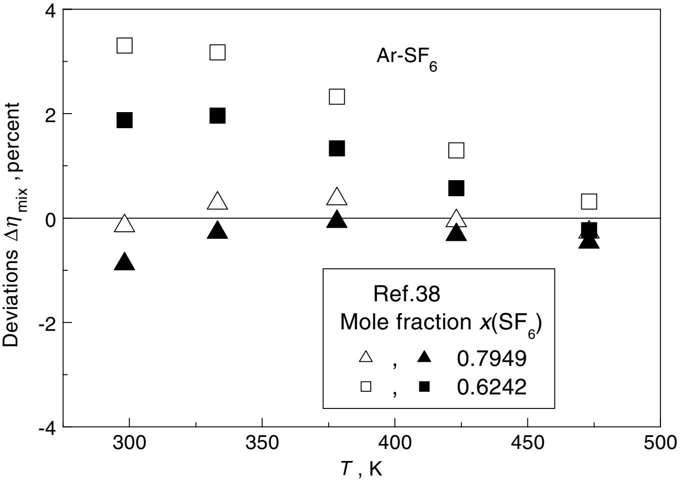

Fig. 14. Relative deviations between experimental and calculated mixture viscosities η_{mix} of Ar–SF$_6$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

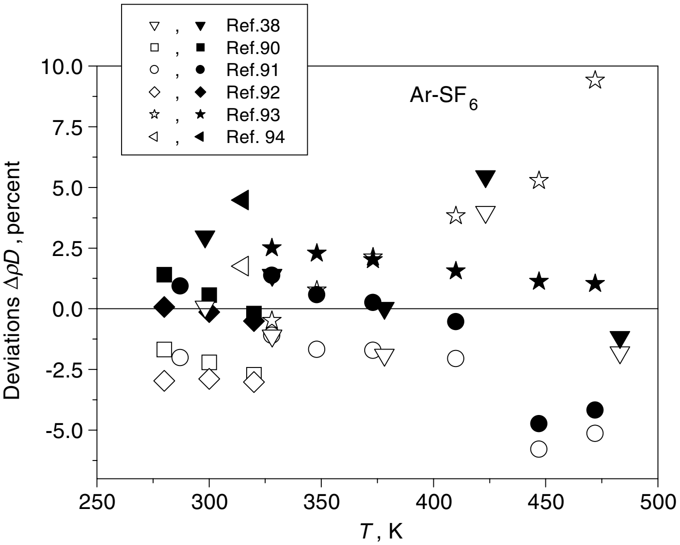

Fig. 15. Relative deviations between experimental and calculated binary diffusion coefficients ρD_{12} of Ar–SF$_6$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

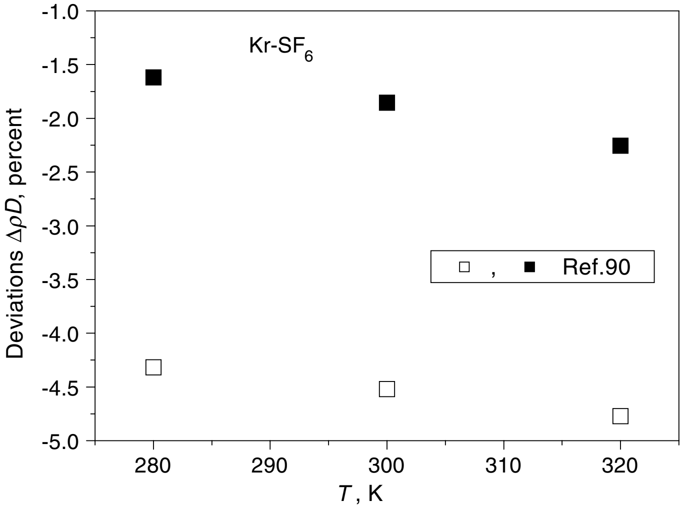

Fig. 16. Relative deviations between experimental and calculated binary diffusion coefficients ρD_{12} of Kr–SF_6. Open symbols: LB mixing rules, full symbols: TT mixing rules.

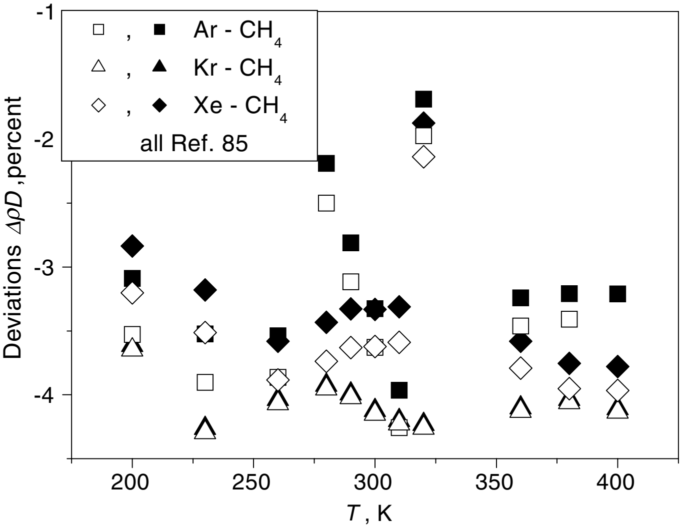

Fig. 17. Relative deviations between experimental and calculated binary diffusion coefficients ρD_{12} of noble gas – CH_4. Open symbols: LB mixing rules, full symbols: TT mixing rules.

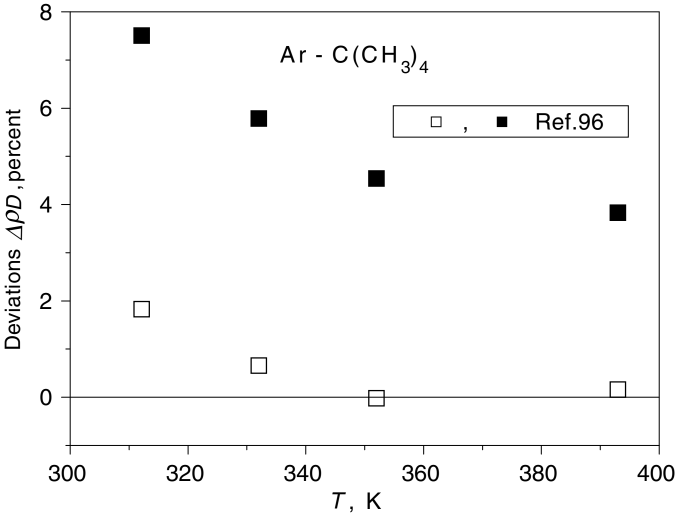

Fig. 18. Relative deviations between experimental and calculated binary diffusion coefficients ρD_{12} of Ar–C(CH$_3$)$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

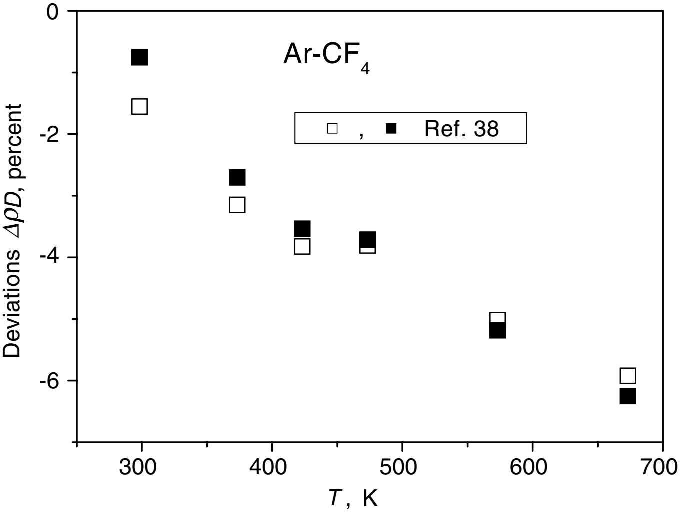

Fig. 19. Relative deviations between experimental and calculated binary diffusion coefficients ρD_{12} of Ar–CF$_4$. Open symbols: LB mixing rules, full symbols: TT mixing rules.

for the Argon–Neopentane system, Fig. 18, is better reproduced by the LB mixing rule. In the case of the Ar–CF_4 system, Fig. 19, we found that with increasing temperature the agreement between calculated and experimental data gets worse independent of the applied mixing rule.

Calculated thermophysical properties of more than 50 binary mixtures were published by Bzowski et al. [98]. In that paper the binary mixtures of Ar, Kr, and Xe with CH_4, CF_4, and SF_6 were included. In general, the comparison of our results with those of Ref. 98 shows that the agreement for η_{mix} and B_{12} is satisfactory good. In some cases, our deviations for B_{12} obtained with the LB mixing rules are smaller than those of Bzowski et al. (Ar–SF_6, Kr–CF_4, Kr–SF_6, and Xe–CF_4, presented in Figs 6, 8, 9, and 10, respectively). Our calculated diffusion coefficients for the binary systems Ar–SF_6 and Kr–SF_6 are of the same quality as those given in Ref. 98 as long as the TT mixing rules are applied. The deviation again gets larger if we use the LB mixing rules. In the case of methane–noble gas systems, our calculated ρD-values are slightly worse than the results given by Bzowski et al. [98].

5. CONCLUSION

The ITDP potential parameters are defined for the noble gases Ar, Kr, and Xe. They approximate reasonably well available experimental data for equilibrium (second virial coefficients B and β) and transport (viscosity η) properties.

The potential parameters for all of the explored mixtures have been updated to reflect the most recent determinations of the pure fluid potentials. The parameters given in this paper are to be preferred over those previously given in Ref. 4.

The influence of the mixing rules on the calculations of the thermophysical properties of the mixtures has been studied. We have observed that the simple Lorentz–Berthelot mixing rules give better results for the interaction virial coefficient $B_{12}(T)$. On the other hand, the results for the binary diffusion coefficients ρD are generally better when the more elaborate Tang–Toennies mixing rules are applied. Both mixing rules reproduce acceptably well the viscosities η_{mix} of the investigated binary mixtures.

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