THERMOPHYSICAL PROPERTIES OF SUBSTANCES

TRANSPORT PROPERTIES OF MIXTURES OF RAREFIED GASES. HYDROGEN–METHANE SYSTEM

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An analysis and generalization of experimental data on transport properties based on the relations of molecular-kinetic theory and three-parameter interaction potentials of the Lennard-Jones (m–6) family have been performed for the mixture of rarefied neutral gases "hydrogen–methane." Nine parameters of the potentials have been restored in joint data processing using the weight nonlinear least-squares method. Tables of reference data for viscosity, the interdiffusion coefficient, and the thermal diffusion factor have been calculated in the temperature interval 200–1500 K. Errors of reference data in the entire interval of concentrations, including those of pure components, have been evaluated using the matrix of parametric errors.

Keywords: *gas, gas mixtures, viscosity, interdiffusion coefficient, thermal diffusion factor, molecular-diffusion theory, collision integrals, interaction potentials, generalization of data, hydrogen, methane.*

Introduction. This paper is a continuation of publications on transport properties of mixtures of rarefied neutral gases [1–3]. The place occupied by gaseous mixtures in nature and technology and the fundamental principles of analysis and generalization of the transport properties of these mixtures have been considered earlier. The hydrogen–methane mixture is the starting component of numerous combustion processes, one composition of the CVD processes of growth of diamond films, etc.

The basic propositions of the procedure of analysis and generalization of data are as follows:

(1) calculation of the properties is based on the relations of the molecular-kinetic theory of rarefied gases within the framework of pair elastic collisions of atoms and molecules [4];

(2) when the viscosity, the interdiffusion coefficient (IDC), and the thermal diffusion factor (TDF) of the components are calculated, it is assumed that the collision integrals involved in the relations of molecular-kinetic theory can be determined using unified orientation-averaged interaction potentials;

(3) three pair potentials — $U_{11}(R, \mathbf{a}_{11})$ and $U_{22}(R, \mathbf{a}_{22})$ for homogeneous interactions and $U_{12}(R, \mathbf{a}_{12})$ for heterogeneous ones — are considered as applied to a binary mixture of gases;

(4) generalization of experimental data and restoration of the potentials parameters are carried out using the weight nonlinear least-squares method (LSM). All experimental points of the minimized LSM potential are independent.

We emphasize that for a rarefied mixture of gases H_2–CH_4, it is only the individual properties that have independently been generalized: viscosity [5] and IDC [6, 7]. Little is known of the 1996 NASA Report in which the parameters of the potential and the procedure of calculation of the properties of this mixture from the relations of the Mason–Kestin similarity theory [8] were given for the considered components without indication of details.

In the present step of investigation, in generalizing the properties of the H_2–CH_4 mixture, we do not consider data on its heat conduction, whose analysis and matching require information on the relaxation characteristics of colliding molecules.

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TABLE 1. Initial Data on the Viscosity η of Gaseous Methane

No.	Literature source	Temperature interval, K	Number of points	Notes
1	Barua, Flynn, and Ross, 1964 [16]	273–423	6	Capillary method, $\delta_\eta = 1.5\%$
2	Kestin and Yata, 1968 [17]	293–303	2	Disk method, $\delta_\eta = 0.5\%$
3	Clarke, Maitland, Rigby, and Smith, 1969 [18]	113–374	9	Capillary method, $\delta_\eta = 2–1.5\%$
4	Dawe, Maitland, Rigby, and Smith, 1970 [19]	293–1050	9	Capillary method, $\delta_\eta = 0.5–1.5\%$
5	Kestin, Ro, and Wakeham, 1971 [20]	298	1	Capillary method, $\delta_\eta = 0.3\%$
6	Hellemans, Kestin, and Ro, 1973 [21]	298–468	5	Disk method, $\delta_\eta = 0.5\%$
7	Maitland and Smith, 1974 [22]	293–873	5	Capillary method, $\delta_\eta = 0.75–1\%$
8	Timrot, Serednitskaya, and Bespalov, 1975 [23]	296–675	9	Disk method, $\delta_\eta = 0.75–1\%$
9	Gough, Matthews, and Smith, 1976 [24]	120–320	10	Capillary method, $\delta_\eta = 1\%$
10	Kestin, Khalifa, and Wakeham, 1977 [25]	298–468	7	Disk method, $\delta_\eta = 0.5\%$
11	Abe, Kestin, and Wakeham, 1978 [26]	248–468	5	Disk method, $\delta_\eta = 0.5\%$
12	Vogel, Wilhelm, and Kirchenmeister, 2000 [27]	260–360	5	Oscillatory viscometer, $\delta_\eta = 0.3\%$
13	Evers, Losch, and Wagner, 2002 [28]	233–529	8	Rotating-cylinder method, $\delta_\eta = 0.75\%$
14	Schley, Jaeschke, Kirchenmeister, and Vogel, 2004 [29]	260–360	5	Oscillatory viscometer, $\delta_\eta = 0.3\%$ (repetition of [27]
15	May, Berg, and Moldover, 2007 [15]	210–391	13	Double-capillary method, comparison to the helium strandard, $\delta_\eta = 0.2\%$
16	Trengove and Wakeham, 1987 [30]	200–1050	18	Reference data, $\delta_\eta = 1.5–2\%$
17	SSSRD 94-86, 1986 [31]	200–1000	22	Reference data, $\delta_\eta = 1.5–2\%$
18	Hellmann, Vogel, Dickinson, and Vesovic, 2008 [32]	200–1500	22	Nonspherical potential, trajectory method, $\delta_\eta = 1.5–2\%$

Initial Data. For molecular hydrogen, we have included into processing mainly the same initial data as in the previous publications [2, 3, 9]. They contain the high-temperature (1100–2130 K) experimental data of Guevara et al. [10] and results of generalization of the set of data on the molecular-hydrogen viscosity, heat conduction, and self-diffusion on the basis of the Lennard-Jones (L-J) m–6 potential (the generalization was performed by V. E. Lyusternik and L. R. Fokin in 1983 (100–2000 K) [11]) and also the reference data of the State Service of Standard and Reference Data (SSSRD) (100–1200 K) [12, 13].

At the present time, there is a transition to a new level of accuracy of measurements of the viscosity of rarefied gases. It is proposed that the gaseous-helium viscosity calculated in the wide temperature range 4–3000 K from the quantum-mechanical interaction potential be used as a primary standard [14]. The viscosity of a large group of gases, in particular hydrogen and methane, compared to the viscosity of standard helium has been measured in [15] by the double-capillary method with a claimed error of <0.1% in the temperature range 210–400 K. Up to now, there have been no independent measurements of the viscosity of gases compared to the viscosity of standard helium; corresponding data for hydrogen and methane were included in further processing with an error of 0.2%.

Table 1 gives the list of data on methane viscosity which are used in the processing. The notes in the table contain the estimates of errors based on the critical analysis. We can single out three groups of experimental data in this list. Kestin et al. (Brown University, USA) carried out measurements by the disk method in the temperature range 298–468 K [17, 20, 25, 26]. As a result the data of Trautz et al., which had been obtained as far back as the 1930s [33] were refined for methane and a number of other gases. In due time, it was shown in generalizing experimental data on the transport properties of gaseous nitrogen [34] that the experimental data of Kestin's group in the temperature range 150–200°C were overstated to 0.8%. Moreover, it was reported in [35] (1983) that recalibration of the unit yielded a result on viscosity, at 200°C, 0.3% lower than the previous one. Subsequently, in generalizing the data of

Kestin et al. (1968–1978) for methane, we did not correct measurement results and took the total error $\delta \sim 0.5\%$ (except the data of the year 1971 at 298 K [20]).

The viscosity of methane was measured by Smith et al. [18, 19, 22, 24] in the temperature interval 113–1050 K. The authors used the relative version of a capillary viscometer when comparing to the viscosity of nitrogen and argon whose data were gradually refined. The error of these data on methane was estimated at 1.5–0.75–1.5%. New precision experimental data for methane were published after the year 2000 [27–29]. An oscillatory viscometer was used for measurements of the viscosity of gases in the temperature interval 260–360 K [27, 29]: the data obtained for the viscosity of a rarefied gas were included in processing with an error of 0.3%. As has already been noted, after the development of the viscosity standard for helium [14], the viscosities of a number of gases, in particular of hydrogen and methane, were measured by the double-viscometer method in the temperature interval 210–390 K [15]; these data were included in processing with an error of 0.2%.

The experimental data in Table 1 have been obtained at atmospheric pressure or in extrapolating experimental isotherms to a zero density. In the considered temperature range for methane, the correction is $[\eta(1 \text{ atm}) - \eta^0]/\eta < 0.1\%$, i.e., is smaller than the characteristic errors of experimental data. We included in the processing the reference data of [30, 31] in addition to the direct experimental data.

In [30], the Mason and Kestin similarity method was used in preparing the reference tables for methane. When the SSSRD reference tables were developed, data on the viscosity of methane in the state of a rarefied gas were generalized on the basis of the spherical-shell potential [31].

Of fundamental interest are two new works [32, 36] in which first the anisotropic interaction potential of two methane molecules was calculated by the quantum-mechanics method [36], and then calculations of collisions were done with it and the integrals of the collisions, viscosity, the self-diffusion coefficient, and a number of relaxation characteristics were determined after the corresponding averaging [32]. The accessibility of the [E-JCPSA-109-607830] archives on the Internet enabled us to use these data, and the corresponding values of $\eta(T)$ in the temperature interval 100–1500 K with an error $\delta_\eta \sim 0.5$–1.5% were included in the procedure of further processing. Of fundamental interest was the issue of matching of the experimental and calculated data [32] on methane viscosity.

Experimental works on the viscosity of methane that were performed before the year 1964 are not included in Table 1. The list of these works and the corresponding data can be found, e.g., in [5]. Now these data are mainly of historical interest, if we take into account accuracy of new viscosity measurements. In addition to the data on the viscosity of methane, we have included, in the processing, the results of measurements of the self-diffusion coefficient of a rarefied gas $D_{11}(T)$, referred to a pressure of 1 atm; they include the experimental data of [37] (195–353 K, four points, $\delta_{D_{11}} = 5\%$, the data of [38] (298, 353, and 382 K, these points, $\delta_{D_{11}} = 3\%$), the data of [39] (154–354 K, nine points, $\delta_{D_{11}} = 3\%$), and the data of [40] (273–382 K, four points, $\delta_{D_{11}} = 2\%$).

A priori generalizations of the parameters of the L-J cross potential $U_{12}(R, \mathbf{a}_{12})$ have also been included in the procedure of joint data processing. They are $d_{11} \approx 3.58$ Å, $\varepsilon_{11} \approx 200$ K, and $m_{11} \approx 20$ for methane and $d_{22} \approx 3.15$ Å, $\varepsilon_{22} \approx 25$ K, and $m_{22} \approx 9$ for molecular hydrogen [2, 3]. Hence using the simple rules of combination we obtain the following values of the parameters $\mathbf{a}_{12}$ and tentative estimates of the errors: $d_{12} \approx 3.4 \pm 0.4$ Å, $\varepsilon_{12} \approx 72 \pm 10$, and $m_{12} \approx 11 \pm 2$.

The works on the viscosity, IDC, and thermal diffusion of the H_2–CH_4 mixture are listed in Table 2. Experimental data for the mixture cover a limited interval of temperatures (130–523 K). Data on the mixture's viscosity have been given in [33, 41–46]. The data of Trautz et al. are known to be understated for most gases at high temperatures; at 500 K, deviations amount to ~1%. Therefore, these data were included in the processing with an error of 1% at room temperature and of 1.5% at 523 K (see Table 2). Kestin et al. [45] have modified the disk method for measuring the viscosity of gases and the estimated error of the data (~0.3%) at room temperature seems justified. The isotherms of viscosity of the H_2–CH_4 mixture have the characteristic form: first, with growth in the share of hydrogen, the viscosity changes only slightly or passes through the maximum, but thereafter it sharply drops once the 50% content of hydrogen has been exceeded. Table 2 does not contain Adzumi's results [64] on the mixture's viscosity on isotherms of 20, 60, and 100°C, which have systematically been overstatated by nearly 3% compared to the basis data array. These data on the 298 K isotherm have a weak maximum. The experimental data of Graham obtained in the year 1846 (!) for the viscosity of the H_2–CH_4 mixture at 286 K also have a maximum; they are reproduced in ICT [65].

TABLE 2. Initial Data for the Viscosity η of the Interdiffusion Coefficient D_{12} and the Thermal Diffusion Factor α_T for the Mixture of Gases H_2–CH_4 at $p = 1$ atm

No.	Literature source	T, K	$x(CH_4)$	Number of points	Notes
1	Trautz and Sorg, 1931 [33]	293, 373, 473, 523	0–1	24	η, capillary method, $\delta_\eta = 1$–1.5%
2	Golubev (with participation of V. A. Petrov) [41]	282, 326, 374	0.335	3	η, capillary method, $\delta_\eta = 2\%$
3	Iwasaki and Takahasi, 1961 [42]	298, 323, 348	0.36–0.80	9	η, capillary method, $\delta_\eta = 2\%$
4	Golubev and Gnezdilov [43]	273–523	0.3, 0.54	21	η, capillary method, $\delta_\eta = 2\%$
5	Chuang, Chappelear, and Kobayashi, 1976 [44]	273, 223, 198, 173	0.76	24	η, capillary method, $\delta_\eta = 0.7\%$
6	Kestin, Ro, and Wakeham, 1983 [45]	295, 303	0.3, 0.6	2	η, disk method, $\delta_\eta = 0.3\%$
7	Kobayashi, Korokawa, and Hirata, 2007 [46]	293, 333	0–1	22	(two isotherms out of the six, points from the plots)
8	Obermayer, 1983 [47]	298	0.5	1	D_{12}, open-tube method, $\delta_{D_{12}} = 5\%$
9	Boyd, Stain, et al., 1951 [48]	298	0.5	1	D_{12}, two-bulb method, $\delta_{D_{12}} = 5\%$
10	Fejes and Czaran, 1961 [49]	298	0.5	1	D_{12}, two-bulb method, $\delta_{D_{12}} = 5\%$
11	Arnold and Toor, 1967 [50]	298	0.5	1	D_{12}, chromatographic method, $\delta_{D_{12}} = 7\%$
12	Gotoh, Manner, et al., 1974 [51]	298, 378, 438	0.5	3	D_{12}, Loschmidt method, $\delta_{D_{12}} = 5\%$
13	Chu and Kobayashi, 1974 [52]	248–323	0.5	4	D_{12}, Loschmidt method, $\delta_{D_{12}} = 3\%$
14	Zhavrin, Kosov, and Novosad, 1975 [53]	298	0.5	1	D_{12}, chromatographic method, $\delta_{D_{12}} = 7\%$
15	Amoroux, Sancez, and Saint-Yrieix, 1978 [54]	305, 319, 343	0.5	3	D_{12}, two-bulb method, $\delta_{D_{12}} = 5\%$
16	Shister, 1986 [55]	130–190	0.5	5	D_{12}, chromatographic method, $\delta_{D_{12}} = 7\%$
17	Bogatyrev, Dzhamankulova, Karpushin, et al., 1990 [7]	130–300	0.5	6	D_{12}, two-bulb method, $\delta_{D_{12}} = 5\%$ (in addition to [54], Karpushin's data at 300 K)
18	Bogatyrev and Karpushin, 2002 [56]	297	0.5	1	D_{12}, two-bulb method, $\delta_{D_{12}} = 5\%$
19	Nezovitina, 2011 [57]	260–500		7	D_{12}, two-bulb method, $\delta_{D_{12}} = 3$–5%
20	Schmahl and Schewe, 1940 [58]	372, 419, 451	0.41	3	α_T, two-bulb method, $\delta_{\alpha_T} = 10\%$ (T is the logarithmic mean temperature of experiments)
21	Drickamer, Downey, and Pierce, 1949 [59]	236, 262, 383, 391, 445	0.5	5	α_T, two-bulb method, $\delta_{\alpha_T} = 10\%$
22	Devyatykh, Vlasov, and Tsinovoi, 1968 [60]	237	0.1–0.9	9	α_T, two-bulb method, $\delta_{\alpha_T} = 10\%$
23	Korzun and Sapronov, 1985 [61]	380	0.6	1	α_T, two-bulb method, $\delta_{\alpha_T} = 10\%$
24	Bogatyrev and Belavov, 2005 [62]	380	0.5	1	α_T, two-bulb method, $\delta_{\alpha_T} = 10\%$
25	Zolotukhina, 1989 [63]	100–900 300	0.5 0.14, 0.9	9 2	α_T, generalization of data, similarity method, $\delta_{\alpha_T} = 10\%$

Noteworthy is the new series of works on the viscosity of the H_2–CH_4 mixture [46] which have been carried out on the subject of hydrogen power for promising fuel compositions "hythane." Similar in content is the work on measurement of the viscosity of the mixture hydrogen–natural gas where the composition of the latter is close to the content of methane ($CH_4 \sim 95\%$, $C_2H_6 \sim 3.5\%$, $N_2 \sim 1.5\%$, 298–400 K, and 0.1–7 MPa) [66].

The few data on the IDC of the H_2–CH_4 mixture obtained before the year 1969 were generalized in [6]. The table of reference data of D_{12} from this review in the temperature interval 293–673 K was used in analyzing our calculations. We know of the SSSRD tables of recommended reference data [7] based on the results of IDC measure-

TABLE 3. Parameters of the L-J (m–6) Potentials for the Components of the H$_2$–CH$_4$ Mixture

Potentials	$d_{ij} \pm \Delta^*$, Å	$\varepsilon_{ij} \pm \Delta^*$, K	$m_{ij} \pm \Delta^*$
U_{11}(CH$_4$–CH$_4$)	3.586 ± 0.027	200.7 ± 10.6	17 ± 1.6
U_{12}(H$_2$–CH$_4$)	3.390 ± 0.032	72.7 ± 3.9	9 ± 0.6
U_{22}(H$_2$–H$_2$)	3.150 ± 0.020	24.96 ± 1.7	8 ± 0.1

*Here the estimates of the errors are $\Delta_{ij} = \sqrt{\mathbf{D}_{ij}}$, where $\mathbf{D}_{ij}$ are the diagonal elements of matrix of parametric errors.
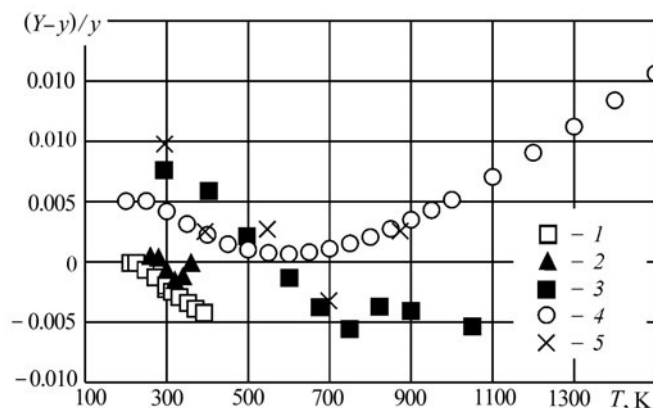

Fig. 1. Deviations $(Y-y)/y$ of the basic initial data from approximation for the viscosity of methane vs. its temperature: 1) May et al [15]; 2) Vogel et al. [27, 29]; 3) Dawe et al. [19]; 4) Hellman et al. [32]; 5) Maitland et al. [22].

ments by the two-bulb method in the temperature interval 130–297 K at pressures of to 5 MPa [55]. With account taken of the scatter in the experimental IDC data indicated in Table 2, we included the latter in processing mainly with an error of ~5%.

The error of few experimental data on the TDF of the mixture with account of the experimental difficulties and scatter in α_T values was taken to be $\delta_{\alpha_T} \sim 10\%$. The procedure of estimating the TDF on the basis of two-parametric similarity in the group of binary mixtures has been developed and published at the A. V. Luikov Heat and Mass Transfer Institute [62]. The TDF values obtained for the H$_2$–CH$_4$ mixture in the temperature interval 100–900 K according to this procedure were included in the procedure of joint processing with an error of ~10%, too.

The special properties of hydrogen-containing mixtures are due, in particular, to the fact that for the interacting pairs of the components with molecular weights M_i, the reduced mass $\mu_{ij} = M_i M_j / (M_i + M_j)$ tends to two. For example, μ_{ij} (H$_2$–CH$_4$) = 1.778. The value of the de Buhr parameter $\Lambda^* = h/[d_{ij}(2\mu_{ij}\varepsilon_{ij})^{1/2}]$ using which one conventionally expresses corrections to the classical collision integrals due to quantum effects [6] tends to unity, and the issue of quantum corrections to the classical collision integrals becomes topical. An analysis has shown that we have $\Lambda^* \sim 0.75$ for the H$_2$–CH$_4$ mixture. For the lowest temperature of the experimental data of Table 2, the reduced temperature is $T^* = 130/71 \sim 2$ and the error estimated using the tables of $D^q/D^{cl}(T^*, \Lambda^*)$ for the L-J potential (12–6) [6] is equal to 1.015. The considered error can be disregarded against the background of the errors of the experimental data from Table 2 for the mixture.

Results of Approximation of the Data and Their Analysis. As a result of approximation of the data for hydrogen, methane, and a mixture of these gases with minimization of the LSM functional, we have obtained the sum of the weighted deviations squared $S = 141$ (for a number of points of 422), the parameters of the L-J potentials, and the estimates of their errors (Table 3). In Table 3, the indices m_{ij} are rounded off to the nearest integers.

As far as the potential U_{22}(H$_2$–H$_2$) is concerned, its characteristics and the quality of description using experimental data for molecular hydrogen were discussed earlier [2, 3]. The results of measurements of differential cross sections of scattering of molecular beams at three energies, 1180, 745, and 445 K, were published for methane [67]. Data on the beam scattering combined with information on the second virial coefficient of methane (to the year 1980) and

TABLE 4. Versions of Indices of Different Potentials for the H_2–CH_4 Mixture

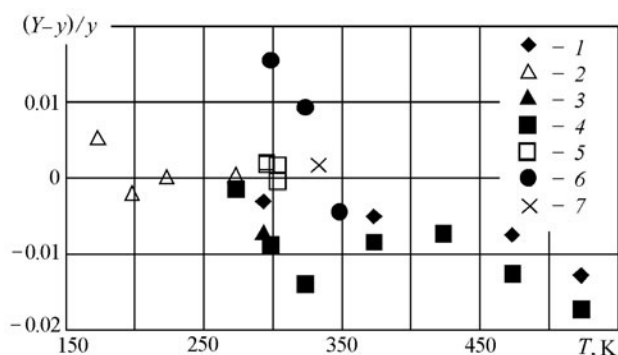| Potential	S	d_{12}, Å	ε_{12}, K	U_{12} (2.4 Å), K	D_{12} (1500 K), cm^2/s
L-J, $m_{12} = 8.5$	142.2	3.425	69.4	6200	11.88
L-J, $m_{12} = 8.8$	141.0	3.406	71.1	6770	11.81
L-J, $m_{12} = 9$	141.8	3.395	72.7	7200	11.78
L-J, $m_{12} = 10$	143	3.342	79.3	8584	11.60
L-J, $m_{12} = 11$	145	3.288	86.2	9922	11.47
L-J, $m_{12} = 12$	152	3.25	93.5	11 914	11.36
11–6–γ (8) [66]		3.275	87	13 105	
Born–Mayer potential at $T^* > 10$ [8]				6800	

Fig. 2. Deviations $(Y - y)/y$ of experimental data from calculated ones for the viscosity of the H_2–CH_4 mixture of equipolar composition vs. its temperature: 1) Trautz, Sorg [33]; 2) Chuang et al. [44]; 3) Iwasaki [42]; 4) Golubev and Gnezdilov [43]; 5) Kestin et al. [45]; 6) Kobayashi [46]; and 7) Golubev (with participation of V. A. Petrov) [41].

its viscosity (to the year 1972) were used in [67] to restore the effective spherically symmetric potential representing a combination of Morse and van der Waals potentials. The parameters of this potential (well depth $\varepsilon_{11} = 200 \pm 2$ K and collision diameter $d_{12} = 3.61 \pm 0.03$ Å) agree with the values given in Table 3.

All the initial data are described, with rare exception, within the errors taken in Tables 1 and 2. Figure 1 shows the deviations of a number of experimental and calculated data on the viscosity of methane from the dependence obtained in approximating the data set. It can be seen that the precision experimental data of the year 2007 [15], obtained in the interval 211–391 K, lie somewhat lower (within 0.3%) than the calculated curve. The theoretical values of viscosity of methane [32] which are based on the results of quantum-mechanical calculation of the potential surface CH_4–CH_4 [36] and on further modeling of collision integrals agree with the calculated dependence within 0.5% to 1000 K, but thereafter, at 1500 K, they begin to appreciably deviate upward to 1.5%. On the whole, the results of theoretical calculations [32, 36] must be considered as the achievement of today's computational methods of quantum physics and statistical physics. The only high-temperature experimental data on methane viscosity, which have been obtained by the capillary method [19], lie lower by 0.5% than the calculated dependence at 1050 K. Other results of this group of researchers [34] also show such a trend.

The obtained index $m_{12} = 9$ of the repulsive branch of the cross potential (Table 3) is stably lower than the value $m_{12} = (m_{11} + m_{22})/2 \approx 12$, which can be expected when the combination rules are used. Table 4 gives a summary of indices which can be used for critical analysis of this result. We note that the experimental data on the IDC of the mixture in question, which are largely determined by the cross potential U_{12}, are limited by a narrow temperature interval.

Table 4 gives the values of the functional S at different fixed values of the index m_{12}. It is seen that the functional varies smoothly near the minimum, but markedly increases at $m_{12} = 12$. Furthermore, it can be seen that

TABLE 5. Viscosity η and Estimate of the Error in Its Determination δ for the H$_2$–CH$_4$ Mixture

T, K	η, μPa·s; δ, %	Mole fraction x(CH$_4$)						
		0	0.2	0.4	0.5	0.6	0.8	1
200	η	6.75	7.69	7.94	7.95	7.93	7.82	7.67
	δ	0.50	0.65	0.65	0.60	0.55	0.50	0.60
300	η	8.94	10.50	11.08	11.20	11.25	11.24	11.14
	δ	0.25	0.60	0.60	0.55	0.50	0.35	0.25
400	η	10.90	12.96	13.83	14.04	14.16	14.25	14.22
	δ	0.30	0.60	0.60	0.55	0.45	0.35	0.25
500	η	12.71	15.19	16.30	16.59	16.78	16.95	16.96
	δ	0.35	0.60	0.65	0.60	0.50	0.40	0.40
600	η	14.41	17.26	18.57	18.93	19.16	19.40	19.45
	δ	0.45	0.65	0.65	0.60	0.55	0.45	0.55
700	η	16.02	19.21	20.69	21.10	21.37	21.66	21.74
	δ	0.50	0.70	0.75	0.70	0.60	0.50	0.60
800	η	17.57	21.06	22.69	23.14	23.45	23.78	23.87
	δ	0.60	0.80	0.80	0.75	0.70	0.55	0.60
900	η	19.07	22.83	24.59	25.08	25.42	25.77	25.88
	δ	0.65	0.90	0.90	0.80	0.75	0.60	0.65
1000	η	20.52	24.54	26.41	26.94	27.29	27.67	27.78
	δ	0.75	1.0	1.0	0.9	0.8	0.65	0.70
1100	η	21.93	26.18	28.17	28.72	29.09	29.48	29.59
	δ	0.8	1.1	1.1	1.0	0.9	0.70	0.75
1200	η	23.30	27.78	29.86	30.43	30.82	31.22	31.32
	δ	0.9	1.2	1.2	1.1	1.0	0.80	0.80
1300	η	24.64	29.34	31.50	32.10	32.49	32.89	32.99
	δ	0.95	1.3	1.3	1.2	1.1	0.90	0.90
1400	η	25.96	30.86	33.10	33.71	34.11	34.51	34.60
	δ	1.0	1.4	1.4	1.3	1.2	1.0	1.0
1500	η	27.24	32.34	34.65	35.28	35.69	36.09	36.16
	δ	1.1	1.5	1.5	1.4	1.3	1.1	1.1

the calculated IDC value at 1500 K varies only slightly within 4%, as m_{12} changes from 8.8 to 12: within the error of D_{12}. The table gives the values of the potential energy U_{12} ($R = 2.4$ Å) for a certain arbitrary point $R = 2.4$ Å on the positive portion of the potential. The estimates of U_{12} (2.4 Å) from two independent works [8, 68] are also given there for comparison.

For analysis of the absorption spectra in the atmospheres of the planets, data on the broadening of the spectra have been analyzed and generalized for the H$_2$–CH$_4$ mixture in [68]. Information on the interparticle-interaction potential was used in the procedure of generalization of the data. Borysov et al. proposed, from the then known selected data on the scattering of H$_2$–CH$_4$ beams and the second cross virial coefficient, a potential of the L-J (m–6–γ(8)) type with parameters $m_{12} = 11$, $\gamma = 3$, $d_{12} = 3.275$, and $\varepsilon_{12} = 87$ K. A very high value of U_{12} (2.4 Å) calculated from this potential is given in Table 4. We note that the analysis of the data in [68] was oriented primarily to consideration of the potential's attractive branch. We have noted in the Introduction that the transport properties of hydrogen-containing mixtures of gases are not clearly understood. The extended Mason–Kestin similarity theory, widely recognized

TABLE 6. Interdiffusion Coefficient D_{12} at $p = 1$ atm and Estimate of the Error in Its Determination δ for the H_2–CH_4 Mixture

T, K	D_{12}, cm^2/s; δ, %	Mole fraction $x(CH_4)$						
		0	0.2	0.4	0.5	0.6	0.8	1
200	D_{12}	0.75	0.36	0.36	0.36	0.36	0.36	0.10
	δ	1.0	1.9	1.9	1.9	1.9	1.9	—
300	D_{12}	1.50	0.74	0.75	0.75	0.75	0.75	0.22
	δ	0.65	2.05	2.05	2.05	2.05	2.05	1.15
400	D_{12}	2.44	1.23	1.24	1.24	1.24	1.24	0.38
	δ	0.65	2.35	2.35	2.35	2.35	2.35	1.40
500	D_{12}	3.57	1.81	1.82	1.82	1.83	1.83	0.56
	δ	0.75	2.70	2.70	2.70	2.70	2.70	1.60
600	D_{12}	4.88	2.48	2.49	2.50	2.50	2.51	0.77
	δ	0.85	3.1	3.1	3.1	3.1	3.1	1.80
700	D_{12}	6.34	3.22	3.24	3.25	3.25	3.26	1.01
	δ	0.95	3.5	3.5	3.5	3.5	3.5	2.00
800	D_{12}	7.96	4.04	4.07	4.08	4.08	4.10	1.26
	δ	1.0	3.8	3.8	3.8	3.8	3.8	2.25
900	D_{12}	9.73	4.94	4.97	4.98	4.99	5.01	1.54
	δ	1.1	4.1	4.1	4.1	4.1	4.1	2.5
1000	D_{12}	11.64	5.90	5.94	5.95	5.96	5.98	1.84
	δ	1.2	4.4	4.4	4.4	4.4	4.4	2.7
1100	D_{12}	13.70	6.93	6.98	7.00	7.01	7.03	2.16
	δ	1.3	4.7	4.7	4.7	4.7	4.7	2.9
1200	D_{12}	15.89	8.03	8.08	8.10	8.12	8.15	2.50
	δ	1.35	5.0	5.0	5.0	5.0	5.0	3.1
1300	D_{12}	18.22	9.20	9.26	9.28	9.30	9.33	2.85
	δ	1.4	5.3	5.3	5.3	5.3	5.3	3.3
1400	D_{12}	20.68	10.42	10.49	10.52	10.54	10.57	3.22
	δ	1.5	5.5	5.5	5.5	5.5	5.5	3.5
1500	D_{12}	23.27	11.71	11.79	11.82	11.84	11.88	3.61
	δ	1.5	5.8	5.8	5.8	5.8	5.8	3.7

recently, did not include hydrogen at all in its original version for gases of commercial importance; information for the H_2–CH_4 pair (mixture) appeared only in the 1987 SADIA Report [8]. If we calculate the cross-interaction energy for this mixture with the parameters from [8] for the distance $R = 2.4$ Å, we obtain the value $U_{12} = 6800$ K, which is close to the corresponding estimate for the potential L-J (m–9). Taking into account the data of Table 4 on the inter-action potential of the H_2–CH_4 pair, we dwell on the approximation results presented in Table 3. Deviations of few experimental data on the viscosity of the mixture from the calculated data in the range of concentrations $x \sim 0.5$ are shown in Fig. 2. As could be expected, the experimental data of [33, 43] deviate from the calculated dependence, as the temperature grows.

From the found parameters of the potentials (Table 3), and using the relations of the molecular-kinetic theory of a binary mixture of rarefied gases [69], we have calculated the values of viscosity (Table 5), the IDC (Table 6),

TABLE 7. Thermal Diffusion Factor α_T and Estimate of the Error in Its Determination δ for the H_2–CH_4 Mixture

T, K	α_T; δ, %	Mole fraction $x(CH_4)$						
		0	0.2	0.4	0.5	0.6	0.8	1
200	α_T	0.45	0.27	0.22	0.20	0.19	0.16	0.12
	δ	6.0	3.8	3.7	3.7	3.6	3.6	—
300	α_T	0.47	0.35	0.29	0.27	0.25	0.22	0.25
	δ	3.1	5.5	5.0	4.8	4.6	4.4	10.0
400	α_T	0.47	0.39	0.33	0.30	0.28	0.24	0.34
	δ	2.4	7.4	6.7	6.5	6.3	5.9	6.0
500	α_T	0.47	0.41	0.34	0.32	0.29	0.26	0.41
	δ	2.4	8.7	8.0	7.7	7.4	7.0	5.7
600	α_T	0.47	0.43	0.35	0.33	0.30	0.27	0.46
	δ	2.6	9.8	8.9	8.6	8.3	7.8	6.3
700	α_T	0.47	0.43	0.36	0.33	0.31	0.27	0.49
	δ	2.7	10.7	9.7	9.3	9.0	8.5	7.0
800	α_T	0.47	0.44	0.37	0.34	0.31	0.27	0.52
	δ	2.8	11.0	10.3	10.0	9.5	9.0	7.6
900	α_T	0.46	0.44	0.37	0.34	0.32	0.28	0.54
	δ	3.0	12.0	11.0	10.4	10.0	9.5	8.3
1000	α_T	0.46	0.45	0.37	0.34	0.32	0.28	0.55
	δ	3.1	13.0	11.5	11.0	10.5	9.8	8.8
1100	α_T	0.46	0.45	0.37	0.34	0.32	0.28	0.56
	δ	3.2	13.0	12.0	11.3	10.8	10.0	9.3
1200	α_T	0.46	0.45	0.37	0.35	0.32	0.28	0.57
	δ	3.2	13.7	12.2	11.6	11.2	10.5	10.0
1300	α_T	0.46	0.45	0.37	0.35	0.32	0.28	0.58
	δ	3.3	14.0	13.0	12.0	11.5	10.7	10.0
1400	α_T	0.46	0.45	0.38	0.35	0.32	0.28	0.59
	δ	3.3	14.5	13.0	12.5	12.0	11.0	10.5
1500	α_T	0.45	0.45	0.38	0.35	0.32	0.28	0.59
	δ	3.4	15.0	13.0	13.0	12.0	12.0	11.0

and the TDF in the temperature interval 200–1500 K for the concentration interval $x = 0$–1 of the H_2–CH_4 mixture. For the limiting values $x = 0.1$, Tables 5–7 contain the properties of pure components, which have been calculated in the second approximation of the theory for the viscosity and the IDC and in the first nonvanishing approximation for the TDF. The isotopic TDF has been calculated for pure components.

Approximation of the data within the framework of the LSM yields, in addition to the parameters, their error matrix; this enables us to propose, in a linearized version (for $\Delta a_{ij} \ll a_{ij}$), estimates of the errors of the calculated properties, which are reproduced in Reference Tables 5–7 in the temperature interval 200–1500 K. The upper bound of the tables indicates that an CH_4 molecule which has characteristic vibration frequencies of >1300 cm^{-1} in the ground electron state [70] begins to experience marked excitations of vibrational levels at $T > 1500$ K.

The estimates of the errors are referred to a 90% confidence level and take account, as has been demonstrated in [2, 3], of the normalization of the functional and a number of assumptions made in the realized LSM functional. In particular, as experience of processing of large arrays of thermophysical data shows, modeling of systematic errors of individual groups of data gives rise to an augmented parametric-error matrix twice as high as the original one [71, 72]. As a result the coverage factor, which relates the estimates of the mean square and confidence $\Delta_{0.9} y(T, x)$ errors of the reference data, is $t_{0.9} \sim 3$ in the first approximation. Taking into account the problems of substantiation of the parameter $m_{12} = 9$, in calculating the reference tables in the final version we took the value $t_{0.9} \sim 4.5$.

It should be remembered that experimental data are limited by a temperature of 1050 K for the CH_4 viscosity and by a temperature of 523 K for the IDC. Therefore, in a wide range of temperatures, the reference data in Tables 5–7 represent extrapolation based on the relations of the theory and the interaction potentials. This circumstance should especially be kept in mind as applied to the statistical estimates of confidence errors.

In calculating the TDF, one must, in principle, make a correction for inelastic collisions of molecules. In [40, 73], estimates of this kind of corrections to the TDF have been obtained in joint analysis of the data on the IDC and the TDF of methane isotopes in the temperature range 100–300 K. Therefore, estimates of errors for the isotopic TDF of methane should only be referred to the elastic component of the corresponding data.

CONCLUSIONS

The developed system of reference data (potentials and tables of properties) for the H_2–CH_4 system is currently the most representative, as fas as the completeness of the initial information, the composition of the tables, and the possibility of reproducing them are concerned. Experimental and theoretical investigations of this important system require extension.

NOTATION

$\mathbf{a}_{ij}$, vector of the parameters of the potential function; D_{ii} and D_{ij}, self-diffusion and interdiffusion (binary diffusion) coefficients respectively at 1 atm, cm^2/s; $\mathbf{D}_{ij}$, diagonal elements of the matrix of parametric errors; d_{ij}, collision diameter of the potential function, Å; h, Planck constant, J·s; M_i, molecular wight, kg·kmole^{-1}; m_{ij}, index of the repulsive branch of the Lennard-Jones potential; p, pressure; R, distance between the centers of mass in the interaction potential; S, sum of weighted squares; T, temperature, K; T^*, reduced temperature; t_d, quantile of the composite distribution function of errors; U_{ij}, interparticle-interaction potential; x, mole fraction of the component in the mixture; Y and y, experimental and calculated point respectively; α_T, thermal diffusion factor; γ, parameter of the L-J m–6–γ(8) potential; δ, relative error, %; Δ, absolute error; $\Delta_d(y)$, total error at the confidence level P; ε, parameter of the potential function, K; η, viscosity, μPa·s; Λ^*, parameter characterizing the role of quantum effects; μ, reduced molecular weight. Subscripts and superscripts: i and j, mixture components; q, quantum; cl, classical; *, reduced; d, distribution.

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