
**THERMOPHYSICAL PROPERTIES
OF MATERIALS**

The Viscosity and Self-Diffusion of Rarefied Steam: Refinement of Reference Data

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Abstract—New experimental data on the viscosity of rarefied steam [1] confirm the prediction potentialities of the calculations of steam properties using the modified m -6-3 Stockmayer potential. Repeated processing is performed of experimental data on the viscosity and self-diffusion coefficient of steam in the temperature range from 280 to 1400 K, and refined tables of reference data for the properties under consideration are calculated.

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INTRODUCTION

The possibility and adequacy of description of the transport properties of polar gases, first of all, steam, based on the pair semiempirical potential of molecular interaction present the subject of studies into present-day molecular physics.

In [2], we analyzed and generalized the experimental data on the viscosity and self-diffusion coefficient of rarefied steam in the temperature range from 300 to 2000 K. The generalization was performed using relations of molecular kinetic theory and the modified four-parameter m -6-3 Stockmayer potential. The m -6 Lennard-Jones (LJ) function with variable rigidity m of the repulsive branch (as distinct from the traditional value of $m = 12$) was considered as the spherically symmetric core of potential,

$$U(R, \varphi) = U_{LJ}(R, \varepsilon, \sigma, m) - \mu^2/R^3 f(\varphi), \quad (1)$$

where R is the spacing between the centers of mass of interacting molecules; ε and σ denote the well depth and collision diameter of LJ potential, respectively; μ is the dipole moment of H_2O molecule; and φ is the vector of angular variables. The orientation-averaged corrections to collision integrals $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ for nonspherical dipole-dipole interactions of molecules were conditionally taken by the data of Monchick and Mason for 12-6-3 potential [3]; this is one of the basic assumptions in the procedure employed in [2].

The transport properties of rarefied gases are of great practical importance. The region of pair interactions, which corresponds to this state, takes a significant place in the phase diagram of substances.

Unlike a number of previous papers, two series of data corrected in view of new information were included into the array of experimental data on viscosity in [2], namely, 1) data from the dissertation of

Aleshin [4] (399–1377 K, 21 points with an error $\delta\eta = 1.5$ –2%; the experimental setup was described in [5]) and 2) data of Bonilla et al. [6] (473–1773 K, 14 points, $\delta\eta = 3$ –5%). As a result of LSM approximation of experimental data, potential (1) was found with soft repulsion $m = 9 \pm 0.7$ and the well depth of spherically symmetric core $\varepsilon \approx 690 \pm 20$ K. Given in [2] are detailed tables of viscosity in the temperature range from 300 to 2500 K with estimates of confidence errors.

In compiling tables of reference data on the viscosity of steam, the main problems arise at low (<400 K) temperatures and at temperatures above ~1400 K. In the high-temperature region, on the one hand, no representative experimental data are available on the transport properties of steam. In addition, the extrapolation of reference data using the theoretical relations and the potential found using the data at $T < 1400$ K appears problematic because of the active population of the vibrational and rotational levels of H_2O molecule, which causes a variation of the characteristics of intermolecular interaction. At temperatures below the normal boiling point of water, which is extremely important in considering numerous processes occurring in nature and engineering, few experimental data are available on the kinetic coefficients of steam, and the accuracy of their determination decreases abruptly. At the same time, in the region of reduced temperatures $T^* = T/\varepsilon < 0.5$ –0.6, the importance and indeterminacy of inclusion of various approximations employed in the kinetic theory in describing collisions of nonspherical and, the more so, dipole molecules increase [7], and this sends one in search of additional arguments for substantiating the foregoing scheme of calculation of properties and the reliability of reference data [2].

NEW EXPERIMENTAL DATA

Results of precision measurements of the viscosity of low-density steams in a very important temperature range from 298 to 438 K were published in 2005 (University of Rostock, Germany) [1]. This caused a significant change of the data base of the problem under consideration.

The measurements were performed by the oscillating disk method in an all-quartz viscometer on ten isochores (steam density of 0.0185–0.23 kg/m³) at fixed temperatures. The authors estimated the error of experimental data at $\delta\eta = 0.2\text{--}0.3\%$. The experimental data converted to isotherms were extrapolated to zero density; as a result, 11 values of $\eta^\circ(T)$ could be obtained. Table 1 gives the values of temperature and experimental data for $\eta^\circ(T)$ from [1], as well as the reference data on steam viscosity with confidence errors (the third column) calculated for our model of 2000 [2]. The estimates of errors of $\delta\eta^\circ$ [1] in the second column of Table 1 were obtained as a result of statistical processing of experimental data on isotherms.

One can see that new experimental data enter the corridor of errors of reference values of [2] and, at $T > 330$ K, lie systematically lower by 0.1–0.7%.

In view of significant indeterminacy of ~2–5% of the experimental data on steam viscosity at low temperatures, which were previously employed in generalizing, as well as the assumptions of molecular kinetic theory and the approximate character of the model of potential (1), the result of comparison of data in Table 1 is, in our opinion, indicative of the prediction capabilities of the procedure of fitting the data employed in [2].

At the same time, combining the previously employed [2] and new experimental data enables one to repeat their simultaneous processing and obtain updated reference data for the viscosity of rarefied steam with refined estimates of confidence errors. The error of $\delta\eta^\circ = 0.4\%$ was taken in the fitting procedure for data in [1]. The new prediction curve in this temperature range (see the last column of Table 1) is approximately 0.2% below the previous curve. It is important that the new corridor of errors in this range is approximately twice lower than that calculated previously.

The use of potential functions enables one, in principle, to simultaneously process the thermal properties of gases of different types within the present-day molecular kinetic theory. Model potentials of the type of (1) are approximate and, in solving the inverse problem, each property gives rise to its own effective potential [7]. However, the calculations of viscosity, as well as of the coefficients of self-diffusion and binary diffusion of rarefied gases, are associated with the calculation of close (in structure) triple integrals which describe the dynamics of collisions. Therefore, there is reason to believe that a unified potential of the type of

Table 1. Comparison of experimental [1] and reference data on the viscosity of rarefied steam

T , K	η° [1], $\mu\text{Pa s}$	η° [2], $\mu\text{Pa s}$	η° , $\mu\text{Pa s}$
298.39	9.703	9.65 ± 0.23	9.650 ± 0.11
311.50	10.151 ± 0.010	10.12 ± 0.21	10.118 ± 0.09
326.25	10.662 ± 0.002	10.65 ± 0.20	10.649 ± 0.08
339.20	11.122 ± 0.005	11.13 ± 0.19	11.121 ± 0.07
352.66	11.601 ± 0.003	11.63 ± 0.17	11.618 ± 0.07
366.89	12.120 ± 0.004	12.16 ± 0.16	12.149 ± 0.08
381.02	12.635 ± 0.004	12.70 ± 0.15	12.683 ± 0.08
394.91	13.151 ± 0.006	13.25 ± 0.15	13.214 ± 0.08
409.18	13.694 ± 0.006	13.79 ± 0.14	13.764 ± 0.08
423.15	14.237 ± 0.006	14.34 ± 0.12	14.308 ± 0.09
438.43	14.835 ± 0.007	14.94 ± 0.11	14.908 ± 0.10

(1) may be employed in fitting the experimental data on viscosity and self-diffusion of steam.

Previously, the experimental data on self-diffusion coefficient D_{11} [8] (363–517 K, five points, $\delta D_{11} = 3\text{--}5\%$ [2]) were involved, in addition to the viscosity data, in the procedure of finding the parameters of potential (1) for steam. These results were obtained in a two-flask apparatus with the recording of the signal of diffusing traces of HTO hydrogen-tritium molecules of steam. Each point in [8] is the average value obtained from five to seven measurements.

No description of the procedure of reducing the results of measurements of the diffusion coefficient of radioactive HTO molecules $D_{12}(\text{HTO}\text{--}\text{H}_2\text{O})$ to the self-diffusion coefficient of solvent $D_{11}(\text{H}_2\text{O})$ is given in the paper [8]. This conversion for low-density gases is usually performed using the relation $D_{11} = (\mu_{12}/\mu_{11})D_{12}$, where μ is the reduced mass of a pair of particles. In so doing, it is assumed that the interaction potentials $U(\text{HTO}\text{--}\text{H}_2\text{O})$ and $U(\text{H}_2\text{O}\text{--}\text{H}_2\text{O})$ are identical, and that the indeterminacy in the procedure of conversion of experimental data is lower than the instrumental error of the experiment.

Note that the product ρD_{11} on isotherms in a wide range of relatively low thermodynamic parameters is a weak function of density ρ ; thereby, the data on the coefficients of self-diffusion of rarefied gas D_{11}° provide the basis for simulating this property in a wide range of states. The coefficients D_{11}° appear in expressions for multicomponent diffusion of gases, in approximate dependences of thermal conductivity of gas mixtures, when simulating the processes of nucleation of droplets of liquid in steam, and so on [7].

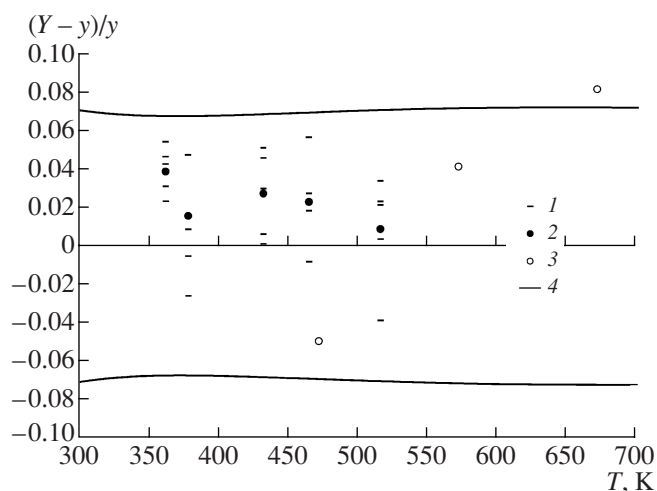


Fig. 1. The deviation of experimental data on self-diffusion coefficient Y from calculated values y : (1) experimental points [8], (2) average values [8] employed in the calculations, (3) [11], (4) limits of confidence errors.

The self-diffusion is an important property of matter associated with the process of motion of own particles without variation of the chemical potential of the system. In view of extensive uses of water at near-critical and supercritical parameters as the working medium for performing chemical reactions, extraction of harmful impurities, and so on [9], interest has grown recently in the structure of water and its kinetic characteristics. Numerous publications exist, which are devoted to experimental and theoretical investigations of self-diffusion in water, in particular, at high parameters [10]. Publications appeared recently, which give the results of measurements of self-diffusion coefficients in dense and rarefied steam by the spin echo method on the isotherms of 200, 300, and 400°C at pressures from 2 to 140 bar [11]. The extrapolation of the complex ρD_{11} on isotherms to zero density produced three values of D_{11}° which, after reduction to standard pressure (1 atm), were equal to 0.44, 0.73, and 1.07 cm²/s, respectively. These three points were also included in the procedure of fitting the experimental data with the error estimates of 10, 5, and 5%. The overall array of experimental data on viscosity and self-diffusion coefficient of steam contains 182 points.

EXTENDED PROCESSING OF DATA

The coefficient D_{11}° in a first approximation of theory [7] is calculated by the relation

$$[D_{11}^{\circ}]_1 = 2.628 \times 10^{-3} \times (T^3/M)^{0.5} / [p\sigma^2 \Omega^{(1,1)*}(T^*, m, \delta)], \text{ cm}^2/\text{s}, \quad (2)$$

where M is the molecular mass, p is the pressure in atmospheres, and $T^* = T/\varepsilon$ is the reduced tempera-

ture. The reduced collision integral for potential (1) $\Omega^{(1,1)*}(T^*, m, \delta)$ is calculated by the scheme of [2] with approximate correction to dipole-dipole interaction,

$$\Omega^{(1,1)*}(T^*, m, \delta) = \Omega_{\text{LJ}}^{(1,1)*}(T^*, m) + 0.19\delta^2/T^*,$$

where $\Omega_{\text{LJ}}^{(1,1)*}(T^*, m)$ is the collision integral for m -6 LJ potential [12]¹, and $\delta = 3662\mu^2/(\varepsilon\sigma^3)$; here and above, ε is in K, σ —in Å, and $\mu = \text{D}$.

The approximation of extended array of experimental data resulted in finding the following values of parameters of potential (1):

$$\varepsilon = 706.9 \text{ K}, \sigma = 2.481 \text{ \AA}, m = 9, \mu = 1.8 \text{ D}$$

and the corresponding covariance-variance matrix

	σ	ε	m	μ
σ	0.0039931	0.7979483	-0.0851025	-0.0129360
ε	0.6035087	437.7992068	-20.9413288	-3.2649146
m	-0.9814954	-0.7294007	1.8827867	0.2862534
μ	-0.97994	-0.7469469	0.998632	0.0436404.

The upper triangular part of matrix (3) contains estimates of dispersions $D(a_i)$ (on the diagonal) and of covariances $\text{cov}(a_i, a_j)$ of the errors of parameters. Given below the diagonal are the respective correlation coefficients $r_{ij} = \text{cov}(a_i, a_j)/[D(a_i)D(a_j)]^{0.5}$ by which one can judge the interference between the parameters in finding the potential. The LSM functional has a very gently sloping maximum in the region of parameters $m \sim 8.5$ – 9.5 and $\mu \sim 1.6$ – 2 D ; for convenience, further calculations are performed for “round” values of $m = 9$ and $\mu = 1.8 \text{ D}$. Note that the obtained value of dipole moment is close to the reference magnitude of free molecule of H₂O.

Figures 1 and 2 give the deviations of experimental data on self-diffusion coefficient and viscosity from the calculated values.

Table 2 gives the reference data for the coefficients under consideration, which include estimates of errors; as regards the self-diffusion coefficient, such data are apparently given for the first time. Confidence estimates of errors of properties were obtained using the relation

$$\Delta y = t_p \sum_i \sum_j (\partial y / \partial a_i) (\partial y / \partial a_j) \text{cov}(a_i, a_j), \quad (4)$$

where $\text{cov}(a_i, a_j)$ denotes elements of matrix (3). The relative error is $\delta y = \Delta y/y$.

In approximating the experimental data, the LSM functional was conventionally formed as the weighted sum of squares of deviations of independent random

¹ Formula (4b) for the calculation of collision integrals in [12] must have the sign of minus instead of plus before the term $(a_{i4}/m \ln(1/m))$. We are grateful to Dr. A. Laesecke (NIST, Boulder) who called our attention to this inaccuracy.

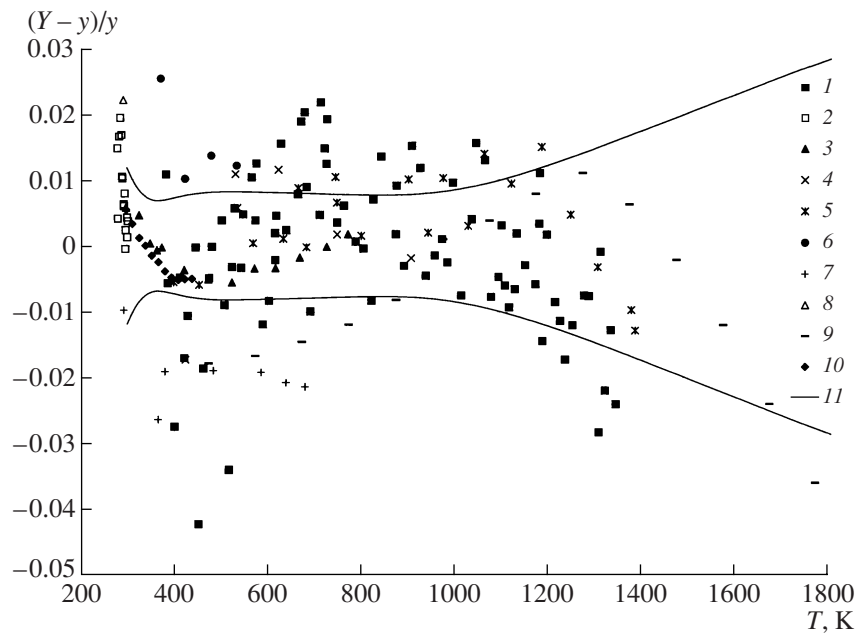


Fig. 2. The deviation of experimental data on viscosity Y from calculated values y : (1) [13], (2) [14], (3) [15], (4) [16], (5) [4], (6) [17], (7) [18], (8) [19], (9) [6], (10) [1], (11) limits of confidence errors.

quantities. One can see in Figs. 1 and 2 that the individual series of experimental data systematically deviate from smoothing curves; thereby, the basic principle of the procedure of fitting of data is violated. It is important that this fact must be taken into account, first of all, in estimating the error of the results. Therefore, in view of the reasoning given in [2], the value of $t_p = 6$ is assumed for the coefficient of proportionality t_p between the confidence and mean-square errors in Eq. (4) with confidence probability $P \sim 0.9$.

The calculation results enable one to use potential (1) for estimating the viscosity and self-diffusion coefficient of isotope modifications of H_2O molecule in replacing hydrogen atoms by deuterium and tritium or a ^{16}O atom of oxygen by its isotopes, i.e., for D_2O , T_2O , TDO , etc. In so doing, in a first approximation, molecular masses are to be replaced in calculated dependences of the type of (2). For rarefied steam of heavy D_2O and light water, the ratio of molecular masses is $\sim 20/18$, and the rough estimate of viscosity ratios will be $\eta(D_2O)/\eta(H_2O) \sim 1.05$. Timrot et al. [20] used the experimental data for the viscosity of rarefied steam of heavy-water in the temperature range from 370 to 770 K to obtain the ratio $\eta(D_2O)/\eta(H_2O) \sim 1.037-1.027$. One can assume that the approximate estimates of viscosity and coefficients of self-diffusion and binary diffusion of isotopes of light water will exhibit an additional error of $\sim 2-3\%$, and the investigation of individual potentials of interaction of isotope modifications of water will make possible significant refinement of values of the properties under consideration.

Note that systematic tables of self-diffusion coefficients of 19 technically important gases in rarefied state in the temperature range from 50 to 1000°C were apparently first published in 1969 in the well-known reference book [21]. The tables of data were calculated using the empirical dependence of the form $D_{11}(T)/D_{11}(273) = (T/273)^n$ with the exponent $n(T)$. The value of $D_{11}(273) = 0.276 \text{ cm}^2/\text{s}$ was taken in the reference book [21] for steam as the basic value (this was done before relevant experimental data were available). This value appears to be clearly overstated compared to the experimental data for self-diffusion coefficient, which were published at a later date [8, 11], and to the correlations performed using relations of molecular kinetic theory and interaction potentials.

A table of data on self-diffusion coefficient of rarefied steam in the temperature range from 273 to 2000 K was further given in [22]. The data are accompanied by estimates of error of $\delta D_{11} = 8-6\%$. In this latter study, the values of $D_{11}(T)$ were obtained within the molecular kinetic theory in fitting with the data on the viscosity of steam. The latter data were in turn obtained as a result of simultaneous processing of experimental data on viscosity using the empirical dependence at $T < 800 \text{ K}$ and the collision integrals for the 12-6-3 Stockmayer potential at higher temperatures. Although the deviation of viscosity values calculated in [22] from the new reference data of Table 2 may be as high as 2-3%, the data on self-diffusion coefficient in Table 2 and in [22] agree within 1%. In interpreting this fact, one must bear in mind that

Table 2. Reference data on viscosity and self-diffusion coefficient (1 atm) of rarefied steam

T, K	$\eta, \mu\text{Pa s}$	$\delta\eta, \%$	$D_{11}^\circ, \text{cm}^2/\text{s}$	$\delta D_{11}^\circ, \%$
300	9.71	1.2	0.17	7.1
350	11.52	0.7	0.24	6.8
400	13.41	0.7	0.32	6.8
450	15.37	0.8	0.42	6.9
500	17.37	0.8	0.52	7.0
600	21.47	0.8	0.77	7.2
700	25.59	0.8	1.08	7.2
800	29.70	0.8	1.42	7.1
900	33.75	0.8	1.82	6.9
1000	37.72	0.85	2.26	6.6
1100	41.61	1.0	2.7	6.4
1200	45.42	1.2	3.3	6.1
1300	49.13	1.5	3.8	5.8
1400	52.76	1.7	4.4	5.5
1500	56.31	2.0	5.1	5.3
1600	59.77	2.3	5.7	5.0
1700	63.17	2.6	6.4	4.8
1800	66.48	2.8	7.2	4.6
1900	69.73	3.1	7.9	4.4
2000	72.92	3.3	8.8	4.3

the error of the self-diffusion coefficient data being compared is estimated at 6–8%.

CONCLUSIONS

The International Association for Properties of Water and Steam (IAPWS) is active in compiling reference data, in particular, on the viscosity of steam. The correlations of 1985 [23] are used at present, which entered GSSSD 6-89 and GSSSD R-776-98 tables (GSSSD – State Service of Standard and Reference Data). In these publications, the viscosity of steam is represented in the temperature range from zero to 800°C by a polynomial of the form $\eta^\circ = \tau^{0.5}/\Sigma H_i \tau^{-i}$ ($i = 0-3$, $\tau = T/647.226$). The reference data are accompanied by error estimates (tolerances) of $\delta\eta = 2\%$ at $t < 475^\circ\text{C}$ and less than 3%. The IAPWS along with the International Association for Transport Properties are working on a new set of data on the viscosity of water and steam.

The refined alternative version of reference data considered above differs from the IAPWS correlations in two respects. Firstly, the use of model potential (1) in generalizing the data enables one to extrapolate the results to the region of high and low temperatures and consider a consistent system of transport properties.

Secondly, and this is of primary importance, a different strategy is employed for estimating the errors of the results. In [23], the errors are non-formalized expert estimates which always exceed or are equal to the errors of selected precision data. This approach involves the proposition that the error of the average of many results may be less than the errors of individual groups of data, and the error estimation procedure proper meets the requirement of reproducibility.

The problem of accumulation of experimental data for steam at temperatures above 1000 K retains its urgency.

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