NOTATION

 V_c , V, V_d , initial volume of sample, volume at moisture content u, and volume of absolutely dry material, respectively; ΔP , change in mass of the moist material; ρ_w , density of water; N/N_0 , ratio of the current value of the radioactivity at the surface of the sample to the maximum value at the end of drying; i/i_0 , ratio of the moisture flux through the sample surface to its initial value; ϕ , relative moisture content of air.

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TEMPERATURE DEPENDENCE OF THE TRANSPORT

COEFFICIENTS OF MONATOMIC GASES

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We study the range of applicability of the power-function approximation for the

temperature dependence of viscosity and thermal conductivity of monatomic gases.

The temperature dependence of the transport coefficients of gases and their mixtures is often described by the power function

$$\mu(T) = \mu_0 \left(\frac{T}{T_0}\right)^n,\tag{1}$$

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where the exponent n is different for different gases, and μ_0 is the value of the so-called reference point at temperature T_0 . The quantity n, generally speaking, varies with temperature according to

$$n = \frac{d \ln \mu}{d \ln T},$$
 (2)

but in restricted temperature intervals one can, with some accuracy, use the value n = const. This dependence is used in theoretical modeling of a variant of the shock-tube method [1-4] in the measurement of the thermal conductivity of gases at temperatures 1000-6000°K (Table 1).

It was shown in [5-7] that the experimental results concerning the thermal conductivity of monatomic gases are described satisfactorily by the function (1) with n = const at high temperatures. As the temperature is lowered, however, the results deviate from this function towards higher values of thermal conductivity. From the point where this deviation starts, the limit of applicability of the function (1) was determined in [5-7] for each gas. In [8], these results were generalized to the viscosity of monatomic gases in order to obtain data at high temperatures at which no experimental investigations have been carried out. The temperatures of the reference point T_0 and the exponents n which were found in [5-7] are shown in Table 1. It should be noted that the experimental results concerning the high-temperature thermal conductivity are characterized by a large error. Consequently, the scatter of these data can affect the accuracy of determination of the parameter T_0 for the function (1).

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Gas	Determin conducti tube met	Analy perim therm	sis of ental al cond	the ex- data on luctivity	Analysis of the data [9] on the transport coefficients		Average values of the exponent		
	<i>T</i> ₀ , K	n	source	<i>T</i> 0, K	ħ	source	<i>T</i> ₀, K	n	ñ
He	320 300	0,69	[3]	300	0,710	[5]	150	0,697	0,699
Ne	300	0,637	121	600	0,630	[6]	350	0,662	0.643
Ar	300	0,703	[2]	500	0,675	i6i	600	0,680	0,690
	300	$0,68\pm0,01$	[1]						
	300	0,71	[4]	1					
Kr	303	0,695	[2]	700	0,690	[7]	900	0,680	0,688
\mathbf{Xe}	303,15	0,72+0,01	1 [1]	800	0,690	1 71	1100	0,692	0,701

TABLE 1. Empirical Parameters of the Power Function (1) Which Approximates the Temperature Dependence of the Transport Coefficients at Temperatures $T > T_0$

* In the measurements of thermal conductivity by the shocktube method, the exponent in the dependence (1) was determined in [1-4] from the experimental material obtained at temperatures above 1000-1600°K. The values of the reference point T_0 were chosen in [1-4] arbitrarily in the room-temperature range.



Fig. 1. Dependence of the transport coefficients of monatomic gases [1) He; 2) Ne; 3) Ar; 4) Kr; 5) Xe] on the temperatures (T,°K) from the standard handbook data [9]: a) viscosity (η , Pa·sec); b) thermal conductivity (λ , W/ ($m^{-1} \cdot K^{-1}$).

The viscosity of gases is, at present, measured with higher accuracy than thermal conductivity. Vagraftik and Vasilevskaya [9] used the experimental material on viscosity and thermal conductivity of monatomic gases to determine the temperature dependence of the so-called real collision integral. Hence, they obtained standard handbook data about the transport coefficients in the temperature range from the normal boiling points to 2500 °K. Figure 1 shows the temperature dependences of viscosity and thermal conductivity of monatomic gases from the data of [9]. It is seen that the exponent n in the dependence (1) increases with decreasing temperature; only at very low temperatures one observes an anomaly for He. Analogously to the results of [5-8] on thermal conductivity, the data of [9] at high temperature can be described by the function (1) with n = const and, with increasing molecular mass of the gases, the deviations from this formula are observed at increasingly higher temperatures. Table 1 shows the values of the exponent in the dependence (1) which can be used to reproduce the data [9] with an error not exceeding 1% in a region bounded from below by the parameter T₀. This is considerably less than the error given by Vagraftik and Vasilevskaya [9] for the handbook data.

Using an analysis of the experimental data on thermal conductivity of monatomic gases, Vagraftik and Vasilevskaya [5-7] and Shashkov et al. [10] showed that, in the temperature range 90-6000°K, it is unsuitable to use the function (1) with a constant value of the expo-

δΩ^(2,2)*, % Potential " theor T * b а function $\substack{0,684\pm0,007\\0,652\pm0,007\\0,652\pm0,005}$ 0,184+0,007 0.190 0,20 10-100 -6) 0,20 0,169 $(11-6-8), \gamma=3$ 10 - 200 $0,152\pm0,007$ 0,14 $(12-6-8), \gamma=0$ (12-7) 0,152+0,0050,160 11 - 200 $0,644 \pm 0,004$ 0.144 ± 0.004 0,138 0,12 11,5-110 $0,648\pm0,003$ $0,573\pm0,002$ 0.148 ± 0.003 0,157 0.09 (12-6) 18 - 4000,06 0,076 0,073 + 0,002 *(*28--7) 20-100

TABLE 2. Parameters Which Characterize the Dependence (4a)

for Different Potential Functions



Fig. 2. Dependence of the collision integral $\Omega^{(2.2)*}(a)$ and of the quantity $E^* = \Omega^{(2.3)*}/\Omega^{(2.2)*}(b)$ on the reduced temperature for the potential functions: 1) (9-6) [14]; 2) (11-6-8) [15]; 3) (12-6) [11]; 4) (12-7) [16]; 5) (28-7) [14]; 6) (exp-6) [17, 18] [a) $\alpha = 12.3$ (Kr), $\alpha = 12.4$ (He); b) $\alpha =$ 13.0 (Xe); c) $\alpha = 14.0$ (Ar); d) $\alpha = 14.5$ (Ne)].

nent in [1-4] in a wide temperature range. For example, the approximation of the results of measurements using the shock-tube method [1-4] by the power function at temperatures from 300-320 to 5000-6000°K (Table 1) gives thermal conductivity too low by 5-12%. They were corrected in [10] by restricting the region of applicability of the power law by the temperature range of the measurements in shock tubes $(T_0 = 1000-1600°K)$.

Thus, it is not completely clear in what temperature range it is correct to approximate the data on viscosity and thermal conductivity of monatomic gases by a power function with a constant exponent. The data concerning the parameter T_0 in Table 1 differ from each other and, as a result, must be tested and confirmed. This should not be done by a direct analysis of the experimental values of the transport coefficients, but by some other independent method.

We consider the temperature dependences of thermal conductivity and viscosity of monatomic gases within the framework of the Chapman-Enskog calculation. According to [11, 12], in the first approximation for the two-parametric potentials of the intermolecular interaction

$$[\mu(T)]_1 = f[T, M, \varepsilon, \sigma, \Omega^{(2,2)*}(T^*)]_1$$

The effect of force parameters on the magnitude of viscosity and thermal conductivity is indeterminate: They are more sensitive to the variation of σ than to the variation of ε . Despite the imperfection of the available model potentials for which the values of the collision integrals are tabulated, it is possible to use them to describe satisfactorily individual properties of gases in specific temperature intervals by choosing appropriate values of the force parameters. The ratio

$$\frac{\mu}{\mu_0} = \sqrt{\frac{T}{T_0}} \frac{\Omega^{(2,2)*}(T_0^*)}{\Omega^{(2,2)*}(T^*)}$$
(3)



Fig. 3. Coefficient of dynamic viscosity (a), the empirically determined exponent n (b), and the correction for the proper volume of molecules in the Van der Waals equation of state (c) as functions of the molecular mass. The quantity η is in Pa·sec, b in m³/kmol, and M in kg/kmol.

does not contain the parameter σ and depends only on the reduced temperature.

If the dependence $\mu(T)$ can be adequately described by a power function, it follows from (1) and (3) that

$$\frac{\Omega^{(2,2)*}(T^*)}{\Omega^{(2,2)*}(T^*_0)} = \left(\frac{T_0}{T}\right)^b$$
(4)

or

$$\ln \left[\Omega^{(2,2)*}(T^*)\right] = a - b \ln T^*, \tag{4a}$$

where

$$b = n - \frac{1}{2}, \ a = \ln \left[(T_0^*)^b \, \Omega^{(2,2)*}(T_0^*) \right].$$
 (4b)

Figure 2a shows the dependences of $\ln \Omega^{(2,2)}$ on $\ln T^*$ for a number of potential functions. It is seen that, with increasing temperature, they all approach a straight line.

The exponent in the dependence (4)

$$b = -\frac{d \ln \Omega^{(2,2)}}{d \ln T^*}$$
(5)

can be determined from a recurrence formula for the collision integrals [11, 12]

$$T \frac{d\Omega^{(l,r)}}{dT} + \left(r + \frac{3}{2}\right)\Omega^{(l,r)} = \Omega^{(l,r+1)},$$

which, for the reduced integrals, gives the relation

$$\frac{d\ln\Omega^{(l,r)*}}{d\ln T^*} = (r+2) \left[\frac{\Omega^{(l,r+1)*}}{\Omega^{(l,r)*}} - 1 \right].$$
 (6)

From (5) and (6) we obtain, for r = l = 2,

$$b = 4(1 - E^*), \ n = \frac{9}{2} - 4E^*, ^{\dagger}$$
 (7)

where $E^* = \Omega^{(2,3)}/\Omega^{(2,2)}$ * (Fig. 2b).

Table 2 shows, for a number of potential functions, the regions of reduced temperatures in which the dependences $E^{*}(T^{*}) = \text{const}$ (collision integrals, respectively) are approximated, with a certain accuracy, by a straight line of the form (4a). Also shown are the values of the coefficients a, b, and n_{theor}. From the lower bound of these regions T_0^{*} , one can determine for each gas the temperature of the reference point $T_0 = T_0^{*} \epsilon/k$. However,

⁺ We note in passing that the exponent in the dependence (1) for the diffusion coefficient is determined from the formula $n = 9/2 - C^*$, where $C^* = \Omega^{(1,2)*}/\Omega^{(1,1)*}$.



Fig. 4. Dependence of the function $z = \ln[(T^*)n^{-1/2}$. $\Omega^{(2,2)*}(T^*)]$ on ln T* and parameter n_{exp} obtained using the potential functions (12-7) (a) and (m-6-8) (b) for the following gases: 1) Xe; 2) He; 3) Ar; 4) Kr; 5) Ne.

the values of T_0 for the most often used potentials (12-6), (12-7), and (m-6-8) are in the temperature intervals 100-180°K for He. 520-630°K for Ne, and exceed 1500°K for Ar, 2100°K for Kr, and 2900°K for Xe, which contradicts the data in Table 1 for heavy inert gases. We therefore turn to an analysis of the values of the exponent n.

Since, at high temperatures, the transport coefficients are determined mainly by the repulsion forces, the exponent n in the dependence (1) clearly should also be associated with these forces. It follows from Fig. 2a and Table 2 that the quantity n_{theor} is due to the slope of the repulsive branch of the potential function: the "softer" the potential, the higher the value of n. According to (4), n = 1/2 in the limiting case of hard-sphere model, and n = 1 for the model of point repulsion center for Maxwellian molecules. It was noted in [13] that the greatest possibilities occur for the potential functions (m-6-8) and (12-7) since, in contrast with the (n-6) and (exp-6) models, they make it possible to describe systematically (for identical values of the force parameters) the experimental values of a number of properties of gases in a wide temperature range. It is seen from Table 2 that the values of the exponent determined using models (m-6-8) and (12-7) agree within 1.2%.

The data in Table 1 show that the deviations of the empirically determined values of n_{exp} (from the viscosity and thermal conductivity measured by stationary methods and by the nonstationary shock-tube method) are approximately 3% for He, 5% for Ne, \pm 5% for Ar, 2% for Kr, and 4% for Xe. Below, we use the average empirical values of n_{exp} which are given in Table 1. It should be noted that the quantity n_{exp} for Ne has a much lower value than for other gases. In accordance with the above discussion, the neon molecules are "harder" at high temperature than the molecules of other inert gases. Consequently, in the temperature range T > T₀, neon is closer to the ideal-gas model than other inert gases. Figure 3a, b shows a clear relationship between the magnitude of viscosity of inert gases and the average empirical value of the exponent of the dependence (1). The correction for the proper volume of molecules in the Van der Waals equation of state, taken from [19] (Fig. 3c), shows a qualitatively analogous dependence on the molecular mass of the gas as the parameter n_{exp} .

A comparison of the experimental and theoretical values of the exponent n (Tables 1 and 2, respectively) obtained using the potential curves (m-6-8) and (12-7) shows a good agreement (within 1.4%) only for Ne; for other gases, $n_{theor} < n_{exp}$. It is therefore possible to estimate for Ne the temperature of the reference point T_0 from the lower bound of the region of the reduced temperature in which the dependence $\ln \Omega^{(2,2)*}$ on $\ln T^*$ can be approximated in the form of a straight line (4a). This agreement is probably a reason for the good agreement of the theoretical and experimental values of thermal conductivity and viscosity which is, as a rule, observed for Ne.

⁺ This deviation for Ne is due to a difference between the results of [6] and [2], which are in very good agreement, and the value obtained from the data of [9] on the viscosity and thermal conductivity. The relatively high value of n in the latter case is explained by the fact that, in the determination of the temperature dependence of the actual collision integrals in [9], argon was used as the base substance. This leads to leveling of the values of the exponent for other gases.

Gas	He		Ne		Ar		Kr		Xe	
Potential function	т <mark>*</mark>	<i>т</i> , к	τ *	<i>Τ</i> ο, Κ	<i>T</i> [*] ₀	<i>T</i> 0, K	τ <mark>*</mark>	<i>T</i> 0, K	<i>T</i> [*] ₀	T _e , K
(12-6-8) (11-6-8) (12-7) (12-6)	4,7 4,3 4,7	48,0 43,9 48,0	12,0	540	4,7 4,6 5,2	719 699 645	4,9 4,7 5,2	1058 1005 988	4,2 4,2 4,6	1239 1239 1053

TABLE 3. Value of the Temperature Parameter of the Reference Point in the Dependence (1) Determined for Monatomic Gases Using Different Models of Intermolecular Interaction

To take into account the disagreement between the empirical and theoretical values of n we introduce the function

$$z(n, T^*) = \ln \left[(T^*)^{n - \frac{1}{2}} \Omega^{(2,2)*}(T^*) \right].$$

It follows from Eq. (4b) that $z(n_{\text{theor}}, T_0^*) = a$. Figure 4 shows the dependences of the function z on ln T* and the parameter n_{exp} obtained from the data on the collision integral for potentials (12-7) and (m-6-8). It is seen that they have a minimum which is shifted towards higher temperatures with decreasing parameter n. Table 3 shows the values of T_0^* determined from the condition of minimum of the dependence $z(n_{\text{exp}}, T^*)$:

$$E^*(T_0^*) = \frac{1}{4} \left(\frac{9}{2} - \bar{n}_{exp} \right).$$

Since the methods for the determination of the force parameters of the potential functions are based mainly on the experimental information concerning the thermophysical properties of gases,† the obtained values of T_0 are not exact. However, on average, they confirm the results of [6] for Ne and the results of analysis of the data [9] for Ar, Kr, and Xe. Only for He the interval of the application of the power function was extended towards lower temperatures.‡ The values of the reference point $\lambda_0(T_0)$ which were used in [10] in the correction of the results of measurements of thermal conductivity by the shock-tube method are, for all gases, within the limits shown in Table 3.

Thus, the results of the present work confirm that the power function with a constant exponent can be used for the description of transport coefficients of monatomic gases in a certain range of temperatures which is reduced on the high-temperature side with increasing molecular masses of the gas. Hence it follows that it is expedient to use a power function as a component of a polynomial which approximates the temperature dependence of viscosity and thermal conductivity of monatomic gases and their mixtures in the generalization of experimental data in a wide temperature range. The presence of this term makes it possible to describe reliably the available experimental data and, possibly, by extrapolating the generalized dependence, obtain the values of viscosity of inert gases in the temperature range above 2000°K where there are no experimental data.

The second aspect of the present work refers to the particular features in the temperature dependences of viscosity and thermal conductivity of He and Ne in comparison with other inert gases. The analysis of the temperature dependence of the transport coefficients using the experimental and generalized data [1-9], carried out with the power-function approximation, shows that each of the gases under consideration has an individual value of the exponent of the function in (1). For He, Ar, Kr, and Xe, the values of n in the region of high temperatures differ within 2%. For Ne, the difference is considerable (7.5%). When the temperature is decreased, the change of the quantity n is qualitatively identical for all gases with the exception of He for which n decreases in the temperature range below 150°K.

⁺For the (12-7) potential, we used the improved values of the parameter ε [13] determined from the multitude of experimental data on the properties of inert gases. ‡ An analysis of the dependence (4a) for the quantum collision integrals for the (12-6) potential leads to the value $T_0 = 50^{\circ}$ K.

A study of the temperature dependence of viscosity and thermal conductivity using a number of potential functions (relation (7), Table 2) showed that the magnitude of exponent n is due to the character of intermolecular interaction. Within the framework of each two-parameter model of the interaction, the quantity n is identical for the entire group of inert gases. The derivation of the exponent n which is observed for Ne at temperatures $T > T_0$ indicates that the true interaction potential between the molecules of this gas in the repulsive region increases more steeply than for other inert gases. An anomalous behavior of the quantity n for He is caused by the quantum-mechanical nature of the intermolecular interaction forces at low temperature. Consequently, viscosity and thermal conductivity of helium and neon in these temperature ranges obey the principle of corresponding states with much lower accuracy, and this should be taken into account in the analysis of the experimental results concerning the properties of inert gases and their mixtures.

NOTATION

T, temperature; μ , thermal conductivity (λ) or viscosity (η); M, molecular mass; σ , ε , α , potential parameters of the intermolecular interaction function; k, Boltzmann constant; $\Omega^{(2,2)*}(T^*)$, reduced collision integral; $T^* = kT/\epsilon$, reduced temperature; and b, correction for the proper volume of the molecules in the Van der Waals equation of state.

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