NOTATION

u(T, t), content of liquid phase, kg/kmole; ρ, density, kg/m^3; c, heat capacity, J/kg·K; λ, thermal conductivity, W/m·K; x, coordinate, m; t, time, sec; T(x, t), temperature, °K; τ, relaxation time, sec; ε, thermal activity, J/m^2·K·sec$^{1/2}$. Indices: 1) substrate; 2) test medium.

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DETERMINATION OF THE TRUE THERMAL CONDUCTIVITIES OF HELIUM AND NITROGEN AT ATMOSPHERIC PRESSURE AND TEMPERATURES FROM THE NORMAL BOILING POINTS TO 6700°K

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True values of the thermal conductivity of helium are calculated and the data obtained is compared with theoretical values and available generalized data on thermal conductivity.

The studies [1-64]* present data on the thermal conductivity of helium measured in the temperature range 3.3-6700°K at atmospheric pressure (Table 1). There is a substantial difference among the experimental results obtained both by different methods and by the same methods with identical state parameters of the gas. The goal of the present study is to obtain generalized data on the thermal conductivity of helium measured by steady-state methods — plane layer, hot-wire, and column — and by transient methods — shock tube and hot-wire.

The first four methods belong to the same group, which is characterized by the fact that a density gradient occurs in the measuring device while the pressure of the test gas remains constant.

The transient hot-wire method belongs to another group which is characterized by the occurrence of a pressure gradient in the measuring device while the density remains constant. It should be noted that this method has not yet come into wide use because it can be used to measure thermal conductivity only within a narrow temperature range (300-400°K) at high pressures.

As was shown in [67], energy transfer occurs under the conditions of experiments conducted by methods of the first group as a result of temperature and density gradients. In this case, the relationship between the true thermal conductivity (the value which character-

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*The first studies of the thermal conductivity of helium were reported in [65, 66].

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TABLE 1. List of Sources for Empirical Determination of the Thermal Conductivity of Helium

Author	Literature source	T, K	P, bar
Eucken	[1, 2]	20,9—373,1	1
Weber	[3]	273; 373,16	1
Curie, Lepape	[4]	273	1
Dickins	[5]	273—285	1
Ubbink and De Haas	[6, 7]	2,78—89,4	1
Johnston and Grilly	[8]	80—380	1
Lenoir, Commings	[9]	316	1—208
Kannuluik, Carman	[10]	90—579	1
Thomas, Golike	[11]	310—330	1
Rothman	[12]	959	1
Waelbroek, Zyckerbrodt	[13]	313	1
Tsederberg, Popov	[14]	273—673	10—500
Zaitseva	[15]	347—804	1
Ubisch	[16]	302—793	1
Blais, Mann	[17]	1200—2100	1
Wilson	[18]	256—1145	1—544
Johanin, Wilson, Vodar	[19]	303—629	1—200
Cheung et al.	[20]	373—588	1
Tarmy, Vonilla	[21]	293—653	1
Leidenfrost	[22]	290	1
Vargaftik, Zimina	[23]	310—1238	1
Peterson, Bonnila	[24]	306—1268	1
Timrot Totskii	[25]	715—1288	1
Timrot, Umanskii	[26]	400—2400	1
Carmichael, Reamer, Sage	[27]	277,6—445,2	0,105—0,126
V. Saxena, S. Saxena	[28]	313—388	1
Collins et al.	[29]	1600—6700	1
Golubev, Shpagina	[30]	21—273	1—500
Golubev, Rychkova	[31]	77,96—373,2	0—500
Mukhopadhyay	[32]	90—473	1
Gandi, S. Saxena	[33]	303—363	1
Srivastava, Gupta	[34]	314—473	1
Freud, Rothberg	[35]	296	1—3300
Tree, Leidenfrost	[36]	283—303	1—20
Van Dael, Cauwenbergh	[37]	296,8	1
V. Saxena, S. Saxena	[38]	400—1350	1
Burge, Robinson	[39]	297; 317	1
Kerrisk	[40]	1,5—3,95	1
Roder	[41]	20—40	1
Briggs et al.	[42]	312; 368	3—10
Ho, Leidenfrost	[43]	290—398	1—304
Leidenfrost	[44]	298; 303	0,2—15
Le Neindre	[45]	303; 778	1—250
Haarman	[46]	350—430	1
Desmond, Ibele	[47]	793—1198	1
Tufeu et al.	[48]	303—610	1—950
Adamov, Gasanov	[49]	323—623	100—1000
Sashkov, Kamchatov	[50]	309,59—390,59	1
Zemlyanykh	[51]	500—6000	1
Varfaftik, Vinogradov, Khludnevskii	[52]	308—1208	1
Faubert, Springer	[53]	800—2100	1
Shashkov, Marchenkov	[54]	407—1413	1
Jody, Jain, Saxena	[55]	400—2500	1
De Groot, Kestin, Sookiazian	[56]	298	10—355
Shashkov	[57]	90—280	1
Jody et al.	[58]	400—2500	1
Acton, Kellner	[59]	20	0,65—2.5
Kestin et al.	[60]	300	1
Clifford et al.	[61]	300	10—350
Popov, Tsarev	[62]	7,76—273,77	
Acton, Kellner	[63]	5,1—5,6	2—5
Zhuze	[64]	4,5—20	1—20

izes heat transfer due to the temperature gradient) and the effective thermal conductivity when measured in the experiment by standard methods is determined by the equation

$$\lambda_{\mathrm{tru}}=\frac{3}{5}\lambda_{\mathrm{ef}}\left(1-0.216a\frac{\rho D}{\eta}\right)^{-1}, \tag{1}$$

while the relationship between the true value and the effective value when measured by means of the transient shock-tube method is determined by the equation

$$\lambda_{\mathrm{tru}}=\frac{3}{5}\lambda_{\mathrm{ef}}\left[1+0.384a\frac{\rho D}{\eta}(1-\alpha)^{-1}-0.6a\frac{\rho D}{\eta}\right]^{-1}, \tag{2}$$

where $aD=\tilde{D}$ is the isothermal coefficient of diffusion caused by the density difference; α is a characteristic of the transience of the energy transfer process; $\alpha=\frac{3}{5}\frac{D_{ef}T^2}{L_{12}}$; $0<\alpha<1$. In the steady-state, $D_{ef} = 0$ and $\alpha = 0$.

The relationship between the true thermal conductivity and the effective value when measured by the transient hot-wire method is determined by the expression [67]:

$$\lambda_{tru}=\lambda_{ef}\left[1-\frac{3}{5}b\frac{\rho D}{\eta}(1-\alpha)^{-1}\right]^{-1}, \tag{3}$$

where $bD=\tilde{D}$ is the nonisothermal coefficient of diffusion caused by the pressure difference: $\alpha = D_{ef}T^2/L_{12}$; $\rho D/\eta = (6/5)A^*$.

Equations (1)-(3) can be used to correct empirical data on the thermal conductivity of gases. To do this, it is necessary to know the values of the nonisothermal coefficients of diffusion due to either the density difference or the pressure difference. Such data is not available in the literature, so empirical results on thermal conductivity must be corrected with Eqs. (1-3) by indirect means.

For steady-state methods (plane layer, column, and hot-wire), we seek the value of the coefficient a in relation to (1) on the basis of the condition $\lambda_{tru} = \lambda_{ef}$, from which

$$a = 1.852(\rho D/\eta)^{-1}. \tag{4}$$

This value of a corresponds to the case of energy transfer only as a result of the temperature gradient: if $a<1.852\left(\frac{\rho D}{\eta}\right)^{-1}$, then $\lambda_{tru} < \lambda_{ef}$; if $a>1.852\left(\frac{\rho D}{\eta}\right)^{-1}$, then $\lambda_{tru} > \lambda_{ef}$.

We rewrite (1) in the form

$$\lambda_{tru}=0.6\lambda_{ef}+0.216a\frac{\rho D}{\eta}\lambda_{tru}. \tag{5}$$

In the right side of (5) we replace λ_{tru} by the expression $\lambda_{teor} = f\eta c_v$, $f = 5/2$ (we should note that $\lambda_{ef} = \bar{f}\eta c_v$, where $\bar{f}\neq 5/2$) and insert the value of a from (4):

$$\lambda_{tru}=0.6\lambda_{ef}+1.5\eta\frac{k}{m}. \tag{6}$$

In reality, for the conditions of an experiment conducted by the steady-state methods, the value of a will differ from $1.852(\rho D/\eta)^{-1}$.

Comparison of theoretical and experimental data on the thermal conductivity of inert gases shows that, except for low temperatures, the theoretical values will be higher than the experimental values, i.e.,

$$a>1.852(\rho D/\eta)^{-1}, \text{ or } a>1.852\left(\frac{6}{5}A^*\right)^{-1}.$$

The expression for $f\eta c_v$ can be represented in the form $f\eta c_v=f\left(\frac{6}{5}A^*\right)^{-1}\rho Dc_v$. For the true value of thermal conductivity

$$\lambda_{tru}=f\eta c_v=f\frac{a}{1.852}\rho Dc_v.$$

For the case $a>1.852(\rho D/\eta)^{-1}$, $\lambda_{teor}>\lambda_{tru}=f\frac{a}{1.852}\rho Dc_v$. In actuality, the value of a entering into this expression should be less than $1.852(\rho D/\eta)^{-1}$, so that the second term in (5)

$$0.216a\frac{\rho D}{\eta}\lambda_{tru}=0.216\cdot 1.852\left(\frac{\rho D}{\eta}\right)^{-1}\frac{\rho D}{\eta}f\left(\frac{\rho D}{\eta}\right)^{-1}\rho Dc_v$$

will be equal to $1.5\eta\frac{k}{m}$. In the low-temperature region, the theoretical values of thermal conductivity will be lower than the experimental values [68]. In this case, $a < 1.852(\rho D/\eta)^{-1}$ and $\lambda_{teor} < \lambda_{tru} = f\frac{a}{1.852}\rho Dc_v$. The value of $a = 1.852(\rho D/\eta)^{-1}$ used in writing (5) will be greated than its actual value, so that the term $0.216a(\rho D/\eta)\lambda_{tru}$ in (5) is equal to $1.5\eta\frac{k}{m}$.

TABLE 4. Deviations of Theoretical (I), Standard (II) [71], and Standard [72] (III) [73] (IV) Data from Correlated True Values of the Thermal Conductivity of Helium

T, K	I	II	III	IV
5	—2,81	—0.7		
10	—0,56	—0,78		
20	+3,39	—0,64		
50	+1,57	—4,42		
100	+1,19	—0,59		—1,19
200	+1,16	+0,73		—1,82
300	+0,5	+1,52	—1,15	—1,84
500	—0,63	+3,04	+0,9	—1,24
1000	—4,38	+2,99	+1,13	+0,43
2000	—6,86	+2,62	+0,58	+2,34
2500	—7,14	+3,29	+3,12	+2,59
3000	—7,16		+3,7	+2,6
4000	—7,24		+4,38	+2,26
5000	—7,59		+4,95	+2,41
6000	—8,21		+5,87	+2,96
6700	—9,05			+2,87

TABLE 5. Theoretical Values of the Thermal Conductivity of Helium Shown in [70]

T, K	$\lambda\cdot10^3$, W/m·K	T, K	$\lambda\cdot10^3$, W/m·K
100	78,0	800	297,1
120	87,8	900	320,6
160	105,6	1000	343,2
200	121,9	1200	386,3
240	137,0	1400	427,0
280	151,2	1600	465,8
300	158,0	1800	502,9
320	164,7	2000	538,7
360	177,6	2200	573,3
400	190,0	2400	606,8
500	219,4	2600	639,4
600	246,7	2800	671,1
700	272,5	3000	702,1

Having rewritten (2) in the form

$$\lambda_{\mathrm{tru}} = 0.6\lambda_{\mathrm{ef}} - \left(\frac{0,384}{1-\alpha} - 0.6\right) a \frac{\rho D}{\eta} \lambda_{\mathrm{tru}} \tag{8}$$

and having written $\lambda_{\mathrm{tru}} = f\eta c_v$, $f = 5/2$, $\alpha = 0.76$ and $a = -0.4\left(\frac{\rho D}{\eta}\right)^{-1}$, we obtain

$$\lambda_{\mathrm{tru}} = 0,6\lambda_{\mathrm{ef}} + 1.5\eta\frac{k}{m}. \tag{9}$$

Comparing (6) and (9), we are convinced of their identity.

Equations (6-9) were used to correct available experimental data on the thermal conductivity of helium obtained by steady-state methods (plane layer, column, hot-wire) and the transient shock-tube method. The viscosity coefficient of helium, entering into (6-9), was calculated by means of the Legendre—Jones potential (12-6) at low temperatures at which quantum effects are significant [69] and by means of the potential (m-6-8) in the same temperature region where quantum effects can be ignored.

The mean deviation of the theoretical data from the empirical data for the viscosity of inert gases at high temperatures is no greater than 1.7% for xenon, 1% for krypton, 2.6% for argon, and 1.9% for helium according to [70].

The true values of the thermal conductivity of helium obtained from Eqs. (6)-(9) were analyzed by the least squares method and represented by approximating relations

$$\lambda_{\mathrm{corr}} = \sum_{i=0}^{n} a_i T^i,$$

the coefficients of which are shown in Table 2. We will call the values of λ_{corr} correlated true values of thermal conductivity.

TABLE 6. Deviations ($\Delta\lambda = \frac{\lambda - \lambda_{corr}}{\lambda_{corr}}$, %) of Experimental Data on the Thermal Conductivity of Helium from Correlated True Values ($\lambda \cdot 10^3$, W/m•K)

T, K	λ_{corr}	λ [51]	Δλ	λ[29]	Δλ
1000	353,3	346,1	—2,03		
2000	571,0	562,2	—1,54	563,1	—1,38
2500	664,2	657,3	—1,04	656,8	—1,11
3000	751,7	746,8	—0,7	744,8	—0,9
4000	916,1	913,4	—0,3	908,4	—0,8
5000	1067			1059	—0,7
6000	1205			1202	—0,3
6700	1294			1296	+0,2

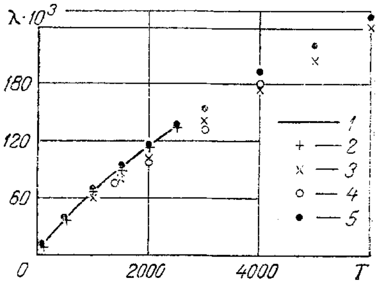

Fig. 1. Temperature dependence of the thermal conductivity of nitrogen: 1) standard data [76]; 2) data from [74]; 3) [51]; 4) data of V. Kmonichek in [51]; 5) correlated true values from the present work. λ, W/m•K; T, °K.

Table 3 shows correlated true values of the thermal conductivity of helium and theoretical values obtained from the formal molecular-kinetic theory.

Table 4 shows values of the deviation $\Delta\lambda = \frac{\lambda - \lambda_{corr}}{\lambda_{corr}} \cdot 100\%$ of the theoretical, standard [71], and generalized [72, 73] values from our proposed correlated true values of the thermal conductivity of helium. It is apparent that the deviation of the theoretical data from the correlated data reaches 9% at high temperatures. The theoretical values of the thermal conductivity of helium that we calculated agree with the data in [70] (Table 5).

Comparison of standard and generalized data with the correlated data showed that the difference between them increases with temperature and amounts to 3.3% at T = 2500°K for the standard data [71], 5.9% at T = 6000°K for the generalized data [72], and 3% for the generalized data [73].

Table 6 shows deviations of empirical values of thermal conductivity for helium from the correlated true values.

To illustrate the applicability of the method developed for the case of polyatomic gases, we calculated the true values of the thermal conductivity of nitrogen. Well-known generalizations of experimental results on the thermal conductivity of nitrogen in [74, 75] and the standard data in [76] were limited to the temperature 2500°K. The conductivity of nitrogen at high temperatures (1000-6000°K) was measured by the shock-tube method in [51, 77, 78]. As for the inert gases, the conductivities obtained for nitrogen by the standard methods agree poorly in the overlapping temperature range with the results obtained by the transient shock-tube method (see Fig. 1).

It was shown in [79] that the deviation of nitrogen conductivities measured by the shock-tube method [77] is 14-17% relative to the generalized data [75], 8-14% relative to [51], and 13-17% relative to [78] in the temperature range 1000-2500°K. It is indicated in [79] that this deviation is caused by a systematic error introduced by investigators in analyzing shock-tube measurements by means of the power law

$$\lambda(T) = \lambda_0 (T/T_0)^n \tag{10}$$

due to the use of a reference point λ_0 with a value of room temperature T_0.

TABLE 7. Temperature Dependence of the Thermal Conductivity of Nitrogen ($\lambda \cdot 10^3$, W/m·K)

T, K	λ_{corr}	λ_{teor}	λ [76]	λ [80]	$\Delta\lambda_1$, %	$\Delta\lambda_2$, %	$\Delta\lambda_3$, %
100	10,02	10,28	9,665	9,69	+2,59	—3,54	—3,29
140	13,55	14,06	13,42	13,36	+3,76	—0,96	—1,40
180	16,92	17,64	16,95	16,84	+4,26	+0,18	—0,47
220	20,12	20,99	20,22	20,15	+4,32	+0,5	+0,15
260	23,18	24,09	23,25	23,27	+3,93	+0,3	+0,39
300	26,11	26,98	26,09	26,20	+3,33	—0,08	+0,34
400	32,99	33,63	32,65	32,91	+1,94	—1,03	—0,24
600	45,30	45,91	44,78	45,18	+1,34	—1,15	—0,26
800	56,49	57,94	56,45	57,02	+2,57	—0,07	+0,94
1000	67,09	69,60	67,72	68,36	+3,74	+0,94	+1,89
1400	87,34	91,06	88,18	89,0	+4,26	+0,96	+1,9
1800	106,3	110,1	106,65	107,1	+3,57	+0,33	+0,75
2200	123,7	127,6	123,51	123,4	+3,15	—0,15	—0,24
2600	139,6	146,1		138,4	+4,66		—0,86
3000	154,8	158,7		152,2	+2,52		—1,68
4000	193,3	192,7			—0,31		
5000	221,6	222,4			+0,36		
6000	251,1	250,1			—0,4		

Note. $\Delta\lambda_1 = \dfrac{\lambda_{teor} - \lambda_{corr}}{\lambda_{corr}} \cdot 100\%$, $\Delta\lambda_2 = \dfrac{\lambda_{[80]} - \lambda_{corr}}{\lambda_{corr}} \cdot 100\%$,

$\Delta\lambda_3 = \dfrac{\lambda_{[76]} - \lambda_{corr}}{\lambda_{corr}} \cdot 100\%$.

The correction made in [79] consisted of limiting the approximation of thermal conductivity by a power relation to the range of measurements on shock tubes (1000-6000°K) by means of a reference point $\lambda_0^!$, corresponding to the lower boundary T_0 of the investigated temperature range.

After the correction, the discrepancy between the results [51, 78] and those recommended in [75] did not exceed 4 and 6%, respectively, i.e., the correction made in [79] did not make it possible to obtain complete agreement between data obtained by standard and transient methods.

The method described above was used to calculate true values of the thermal conductivity of nitrogen from empirical values obtained by both the standard and transient shock-tube methods.

In the case of a polyatomic gas, Eqs. (5) and (8) become

$$\lambda_{tru} = 0{,}6\lambda_{ef} + 0.4 f^E \eta c_v,$$

where f^E is the Eucken factor for a polyatomic gas; c_v is the heat capacity of the polyatomic gas.

Table 7 presents true values of nitrogen conductivity calculated from the results in [51, 74] in the temperature ranges 80-2500°K and 1000-6000°K. Also shown is data from V. Kmonichek [51] (1400-4000°K). Comparison of the true values of thermal conductivity calculated from values obtained by standard and transient methods shows their good agreement in the temperature range 1000-2000°K.

Table 7 also shows deviations of experimental conductivities for nitrogen from correlated true values.

The errors corresponding to the corrections Δλ shown in Tables 6 and 7 are equal to the errors of theoretical data obtained within the framework of the Chapman–Enskog theory.

NOTATION

λ_{tru}, true value of the thermal conductivity of the gas; λ_{teor}, thermal conductivity of the gas calculated by the methods of formal molecular-kinetic theory; λ_{ef}, effective value of thermal conductivity; λ_{corr}, correlated value of thermal conductivity of the gas; c_v, heat capacity of the gas; ρ, density; D, self-diffusion coefficient; D_{ef}, effective self-diffusion coefficient; η, viscosity; k, Boltzmann constant; L_{12}, phenomenological coefficient; $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$; $\Omega^{(i,j)*}$, collision integrals; m, molecular weight.

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