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DETERMINATION OF TRUE VALUES OF THE THERMAL CONDUCTIVITY OF INERT GASES AT ATMOSPHERIC PRESSURE AND TEMPERATURES FROM THE NORMAL BOILING POINT TO 6000°K

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True values of the thermal conductivity are calculated for neon, argon, krypton, and xenon over the temperature range from the normal boiling point to 6000°K at atmospheric pressure.

The thermal conductivity (λ) of gases and their mixtures is a fundamental physical constant. Knowledge of its precise value is of great practical and theoretical importance. The information available in the literature on the thermal conductivity of gases and their mixtures is not always of satisfactory quality, internally consistent, and free from errors related to various physical effects which distort the true value of the coefficient.

In experiment, no matter what method is used, one always measures an effective value of λ, which is not equal to the true value (by true we understand the quantity defining heat transfer due to a temperature gradient).

When the thermal conductivity of heavy inert gases is measured at low temperatures with the steady-state hot-wire method, elevated values of the coefficient are obtained, while determination of λ of inert gases by the shock-tube method gives reduced values (by up to 12%), and the thermal conductivity column method gives elevated (up to 3%) values compared to results of steady-state methods in overlapping temperature ranges.

In 1982 a table of standard reference data on transport properties of inert gases at atmospheric pressure for temperatures from the normal boiling point to 2500°K was developed in the USSR [1]. In our opinion, the thermal conductivity data presented in [1] require extension to a temperature of 6000°K.

In the temperature range from the normal boiling point to 1000°K the thermal conductivity of inert gases is usually measured by the steady-state plane layer or hot-wire methods, while from 1000 to 6000°K the nonsteady-state shock-tube method is used.

In processing the available experimental material on the thermal conductivity of inert gases obtained by the steady-state hot-wire and nonsteady-state shock-tube methods in overlapping temperature ranges, the authors of [2-4] observed that the data obtained with the second variant of the shock-tube method* are systematically low in comparison with the results of steady-state measurements (Table 1).

*The first variant of the shock-tube method is based on approximate solution of the nonlinear energy transport equation in a narrow temperature interval, based on the assumption that $\beta = (\lambda/\lambda_f)T_f/T$ is a constant quantity; the second variant consists of specifying the form of the temperature dependence of the thermal conductivity in the form $\lambda = \lambda_0(T/T_0)^b$, where b = const.

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TABLE 1. Reduction in Value of Thermal Conductivity of Inert Gases Measured by the Second Variant of the Shock-Tube Method Compared to Data of Steady-State Methods

Gas	T, K	Reduction, %
He	1000—2500	5
Ne	1500—2700	4
Ar	1500—2500	5—6
Kr	1500—2500	12
Xe	1500—2500	11

Those studies maintained that this divergence in the experimental results was the result of incorrect processing of experimental data for shock tubes and the high uncertainty of the experimental data. In connection with this it is of interest to compare data obtained with the various modifications of the shock-tube method. Such a comparison establishes that data obtained with the first variant of the shock-tube method are not low in value in the overlapping temperature range (1000-2000°K) relative to values obtained by the steady-state hot-wire method, since in the indicated temperature range this variant of the method is based on use of thermal conductivity results obtained by the latter methods, so that the new results agree well in this range. However, above 2000°K the results are lowered relative to the temperature dependence for the range 1000-2000°K.

Experimental data on the thermal conductivity of argon obtained with the first variant of the shock-tube method were presented in [5]. These results were evaluated in [3], which stated: "... Smiley's results agree completely satisfactorily with data obtained by steady-state methods up to 2000°K, while with further increase in temperature Smiley's data are low in value."

Thus, the experimental values of gas thermal conductivity obtained by the first variant of the shock-tube method also lead to depressed values, with the reduction starting after 2000°K.

As was shown in [6], the cause of this reduction for the shock-tube method as compared to steady-state methods is energy transport related to motion of the gas as a whole, which affects the thermal conductivity more intensely, the higher the gas density, since the non-isothermal gas diffusion coefficient decreases.

TABLE 2. Expressions Characterizing Relationship between True and Measured Thermal Conductivity Values

Experimental method	Equation	Parameter measurement range
nonsteady-state hot-wire method	$\lambda_{tr}=\lambda_{ef}\left[1-\frac{3}{5}b\frac{\rho D}{\eta}(1-\alpha)^{-1}\right]^{-1}$,	$0<\alpha<1$, $b>0$
steady-state methods (plane layer, thermal conductivity column, hot wire)	$\lambda_{tr}=\frac{3}{5}\lambda_{ef}\left(1-0{,}216a\frac{\rho D}{\eta}\right)^{-1}$,	$a>0$
Nonsteady-state shock-tube method	$\lambda_{tr}=\frac{3}{5}\lambda_{ef}\left[1+0{,}384a\frac{\rho D}{\eta}(1-\alpha)^{-1}-0{,}6a\frac{\rho D}{\eta}\right]^{-1}$,	$0<\alpha<1$, $a<0$
	$\lambda_{tr}=\frac{3}{5}\lambda_{ef}\left(1+a\frac{\rho D}{\eta}\right)^{-1}$	$\alpha=0{,}76$

Note. $bD = D_1$ is the coefficient for gas diffusion caused by pressure difference: $aD = D_2$, that caused by density difference, $\rho D/\eta = (6/5)A^*$.

TABLE 3. Coefficients a_i of Polynomials Approximating Thermal Conductivity of Inert Gases as Functions of Temperature from Experimental Data

Gas	T, K	a_0, 10^{-2}	a_1, 10^{-4}	a_2, 10^{-7}	a_3, 10^{-10}	a_4, 10^{-13}	a_5, 10^{-16}	a_6, 10^{-20}	a_7, 10^{-20}
Ne	70—273	—0,29223	3,6487	—17,227	80,707	—239,67	307,03		
	273—5000	1,2837	1,3667	—0,59136	0,23825	—0,05654	0,0069964	—0,0034819	
Ar	90—273	6,5432	—26,192	442,94	—3754,4	17248,0	—40850,0	390850,0	
	273—6000	0,05037	0,67623	—0,38708	0,18354	—0,050542	0,007683	—0,0057849	0,15784
Kr	120—273	—0,91482	2,9695	—29,023	154,83	—405,14	416,67		
	273—5000	—0,09185	0,40647	—0,22815	0,1049	—0,028028	0,0040194	—0,0025582	0,031695
Xe	170—273	—1,2548	2,6570	—16,204	25,9	150,66	—688,10	8146,0	
	273—5000	—0,09482	0,2532	—0,129	0,052828	—0,011954	0,00136	—0,000609	

TABLE 4. Parameters of Potential Interaction Functions for Similar Molecules

Gas	Potential function	ε/k, K	σ, Å	m	γ	Reference
Ne	Lennard-Jones (12—6)	35,7	2,789			[64]
Ar	Klein-Henley (m — 6 — 8)	153,0	3,292	11	3	[65]
Kr		216,0	3,509	11	3	[65]
Xe		295,0	3,841	11	3	[65]

In measuring λ of heavy inert gases at atmospheric pressure and reduced temperatures by the steady-state hot-wire method, the effective thermal conductivity of the gas contains a contribution produced by the effect of the density gradient on energy transport, which leads to elevation of the measured coefficient as compared to its true value.

In the authors' opinion the above indicates the necessity of determining true thermal conductivity values for gases over a wide temperature range using the data obtained by various methods available in the literature.

A comparison of the effective thermal conductivity values measured by various methods (Table 2) shows that the variations among the values may be due to the nonidentical nature of diffusion processes occurring in the measurement apparatus realizing one or the other method.

In experimental determination of the thermal conductivity we must deal with the process of energy transport, since the existence of a temperature gradient in the measurement device produces a density (or pressure) gradient, which introduces its own contribution to the effective λ value. We note that in experiment it is practically impossible to create a temperature gradient per unit length of the normal of 1°, which would correspond to determination of the true λ [7].

For example, in the steady-state hot-wire method the temperature difference between the solid surfaces bounding the gas under study is approximately 10°. When the coefficient is measured by the shock-tube method, the temperature gradient between the cold tube wall and the heated gas region may reach 10^6-10^7 °K/m in a thin boundary layer (10^{-4} m) over the course of 10^{-4}-10^{-7} sec. It follows from this that the experimental method of determining the thermal conductivity is based on "transformation" of an energy flux into a heat flux, the characteristic of which is the effective thermal conductivity.

Using the technique of [6], the results of which are presented in Table 2, and data available in the literature [8-62] for a wide temperature range, true values of the thermal conductivity of neon, argon, krypton, and xenon were calculated, processed by the method of least squares, and represented by approximating functions of the form

$$\lambda_{\text{corr}} = \sum_{i=0}^{n} a_i T^i.$$

We will term these thermal conductivity values "correlated true." The values of the coefficients a_i are presented in Table 3.

The correlated values were compared to results of formal molecular-kinetic theory, obtained with the Henley—Klein potential; for neon the theoretical λ values were calculated using the Lennard-Jones potential. Potential parameters for all the gases are presented in Table 4.

Table 5 presents correlated true, theoretical, and standard [1] values of the thermal conductivity. The values of λ_{corr} lie between the theoretical and generalized experimental values for all gases considered. Deviations between theoretical and correlated values lie within the range 2-4%; for neon and xenon the deviations do not exceed 3%, for krypton, 2.1%, while for argon they increase to 4% with increase in temperature.

The correlated true values λ_{corr} agree well with the standard data of [1]: for argon and krypton the divergence does not exceed 1.5%, and 2.5% for neon and xenon.

The generalized data of [2, 3] are basically higher than those we propose. For neon the divergence comprises 2.7% at T = 600°K and decreases with increase in temperature; in

TABLE 5. Temperature Dependence of Thermal Conductivity ($\lambda \cdot 10^3$, W/(m·K)) of Inert Gases

T, K	λ corr	λ theo	λ stand
1	2	3	4
Neon			
90	20,46	20,74	20,38
100	22,32	22,53	22,16
200	37,19	37,10	37,04
300	49,12	48,72	49,06
400	59,43	58,53	59,50
500	69,03	67,31	68,97
600	78,02	75,91	77,77
700	86,46	84,49	86,06
800	94,43	91,98	93,96
900	102,6	99,18	101,5
1000	109,2	106,3	108,9
1100	116,1	113,2	115,9
1200	122,8	119,6	122,8
1300	129,2	126,0	129,5
1400	135,4	132,3	136,1
1500	141,5	138,3	142,5
1600	147,4	144,1	148,7
1700	153,2	149,9	154,9
1800	158,9	155,6	160,9
1900	164,2	161,1	166,9
2000	169,9	166,5	172,8
2100	175,3	171,9	178,6
2200	180,6	174,5	181,4
2300	185,9	182,2	189,9
2400	191,1	187,3	195,5
2500	196,1	192,4	201,0
2600	201,2	197,3	
2700	206,1	202,1	
2800	211,0	206,9	
2900	215,8	211,7	
3000	220,6	216,3	
3100	225,2	221,0	
3200	229,8	225,6	
3300	234,4	230,1	
3400	238,8	234,5	
3500	243,3	239,0	
3600	247,6	243,3	
3700	251,9	247,3	
3800	256,2	251,3	
3900	260,4	255,3	
4000	264,5	259,3	
4100	268,6	263,2	
4200	272,73	267,1	
4300	276,8	271,9	
4400	280,8	274,9	
4500	284,8	278,8	
4600	288,8	282,6	
4700	292,7	286,4	
4800	296,7	290,3	
4900	300,6	294,1	
5000	304,5	297,9	
Argon			
90	5,91	5,79	5,92
100	6,55	6,40	6,54
200	12,46	12,49	12,47
300	17,76	17,88	17,76
400	22,41	22,57	22,42
500	26,64	26,72	26,61
600	30,51	30,49	30,43
700	34,08	33,97	33,98
800	37,39	37,23	37,31
1000	24,98	24,73	24,66
1100	26,65	26,41	26,36
1200	28,24	28,02	28,00
1300	29,78	29,58	29,57
1400	31,26	31,08	31,10
1500	32,70	32,54	32,59
1600	34,10	33,95	34,03
1700	35,48	35,33	35,44
1800	36,82	36,68	36,82
1900	38,15	38,01	38,16
2000	39,46	39,30	39,49
2100	40,74	40,57	40,78
2200	41,99	41,82	42,04
2300	43,22	43,05	43,27
2400	44,43	44,25	44,48
2500	45,61	45,43	45,67
2600	46,77	46,59	46,84
2700	47,91	47,72	47,98
2800	49,03	48,84	49,10
2900	50,13	49,94	50,20
3000	51,21	51,02	51,28
3100	52,27	52,08	52,34
3200	53,31	53,12	53,38
3300	54,34	54,14	54,40
3400	55,35	55,15	55,41
3500	56,34	56,14	56,40
3600	57,32	57,12	57,38
3700	58,28	58,08	58,34
3800	59,23	59,03	59,29
3900	60,16	59,96	60,22
4000	61,08	60,88	61,14
4100	61,98	61,78	62,04
4200	62,87	62,67	62,93
4300	63,75	63,55	63,81
4400	64,61	64,41	64,67
4500	65,46	65,26	65,52
4600	66,30	66,10	66,36
4700	67,13	66,93	67,19
4800	67,94	67,74	68,00
4900	68,74	68,54	68,80
5000	69,53	69,33	69,59
Krypton			
120	4,08	3,96	4,05
200	6,52	6,49	6,56
300	9,48	9,54	9,50
400	12,29	12,30	12,20
500	14,85	14,79	14,67
600	17,19	17,07	18,01
700	19,34	19,17	19,05
800	21,34	21,13	21,02
900	23,22	22,97	22,89
400	7,42	7,27	7,26
500	9,08	8,88	8,84
600	10,60	10,37	10,32
700	12,00	11,76	11,70
800	13,31	13,06	13,01
900	14,53	14,28	14,24
1000	15,69	15,44	15,42
1100	16,78	16,55	16,54
1200	17,83	17,60	17,62
1300	18,83	18,62	18,66
1400	19,80	19,60	19,66
1500	20,75	20,57	20,63
1600	21,68	21,50	21,57
1700	22,58	22,41	22,48
1800	23,46	23,29	23,37
1900	24,32	24,15	24,24
2000	25,16	24,99	25,09
2100	25,98	25,81	25,92
2200	26,78	26,61	26,73
2300	27,57	27,40	27,53
2400	28,34	28,17	28,31
2500	29,09	28,92	29,07
2600	29,83	29,66	29,81
2700	30,55	30,38	30,54
2800	31,26	31,09	31,25
2900	31,96	31,79	31,95
3000	32,64	32,47	32,64
3100	33,31	33,14	33,31
3200	33,97	33,80	33,97
3300	34,62	34,45	34,62
3400	35,26	35,09	35,26
3500	35,89	35,72	35,89
3600	36,51	36,34	36,51
3700	37,12	36,95	37,12
3800	37,72	37,55	37,72
3900	38,31	38,14	38,31
4000	38,89	38,72	38,89
4100	39,46	39,29	39,46
4200	40,02	39,85	40,02
4300	40,57	40,40	40,57
4400	41,12	40,95	41,12
4500	41,66	41,49	41,66
4600	42,19	42,02	42,19
4700	42,72	42,55	42,72
4800	43,24	43,07	43,24
4900	43,75	43,58	43,75
5000	44,25	44,08	44,25

TABLE 5 (continued)

	2	3	4	1	2	3	4
2200	42,01	41,81	42,06	1600	21,67	21,48	21,58
2300	43,27	43,03	43,31	1700	22,57	22,38	22,50
2400	44,51	44,24	44,54	1800	23,46	23,26	23,40
2500	45,73	45,42	45,76	1900	24,33	24,11	24,28
2600	46,93	46,59		2000	25,19	24,95	25,13
2700	48,12	47,74		2100	26,04	25,77	25,97
2800	49,30	48,88		2200	26,89	26,58	26,80
2900	50,46	49,99		2300	27,72	27,36	27,61
3000	51,61	51,10		2400	28,55	28,14	28,41
3100	52,74	52,19		2500	29,37	28,90	29,19
3200	53,86	53,27		2600	30,18	30,03	
3300	54,96	54,34		2700	30,98	30,39	
3400	56,06	55,39		2800	31,78	31,12	
3500	57,14	56,44		2900	32,56	31,84	
3600	58,22	57,47		3000	33,33	32,55	
3700	59,29	58,49		3100	34,09	33,24	
3800	60,36	59,51		3200	34,83	33,94	
3900	61,41	60,51		3300	35,57	34,62	
4000	62,47	61,50		3400	36,29	35,30	
4100	63,52	62,49		3500	37,00	35,97	
4200	64,57	63,47		3600	37,69	36,63	
4300	65,61	64,44		3700	38,37	37,28	
4400	66,65	65,39		3800	39,04	37,93	
4500	67,68	66,34		3900	39,69	38,57	
4600	68,69	67,29		4000	40,33	39,20	
4700	69,70	68,23		4100	40,95	39,84	
4800	70,68	69,16		4200	41,57	40,46	
4900	71,63	70,08		4300	42,18	41,08	
5000	72,55	71,00		4400	42,77	41,69	
	Xenon			4500	43,36	42,30	
				4600	43,94	42,90	
				4700	44,52	43,50	
170	3,30	3,19	3,27	4800	45,37	44,39	
200	3,80	3,73	3,81	4900	45,65	44,68	
300	5,62	5,54	5,58	5000	46,22	45,27	

the temperature range 2500-5000°K it does not exceed 0.1%. For argon the divergence does not exceed ±1.8% over the entire temperature range considered. For krypton and xenon the divergence increases with increase in temperature: at T = 5000°K it reaches 3.8% for Kr and 3.4% for Xe.

The divergence between the present values and those of [63] increases with increase in temperature and molecular mass of the gas: for neon it does not exceed 2% for the entire temperature range, increasing to 2.5% for argon, 4.2% for krypton, and 6.8% for xenon in the temperature range 4000-4600°K.

Tables 6 and 7 present deviations of the correlated true thermal conductivity of inert gases from the available experimental data. The values of λ_{corr} for heavy inert gases at lower temperatures agree with the data of [66].

The values of the corrections $\Delta\lambda$ presented in Tables 6 and 7 are equal to the uncertainties of theoretical data within the framework of Chapman—Enskog theory.

TABLE 6. Deviations $\left(\Delta\lambda = \frac{\lambda - \lambda_{corr}}{\lambda_{corr}} \cdot 100\%\right)$ of Experimental Data of [58] from Correlated True Values of Thermal Conductivity ($\lambda \cdot 10^3$, W/m·K)

Krypton				Xenon			
T, K	λ_{exp}	λ_{corr}	$\Delta\lambda$	T, K	λ_{exp}	λ_{corr}	$\Delta\lambda$
120	4,17	4,08	+2,2	170	3,4	3,3	+3,0
140	4,77	4,70	+1,5	180	3,57	3,47	+2,9
160	5,37	5,30	+1,3	190	3,73	3,63	+2,8
180	5,97	5,91	+1,0	200	3,89	3,80	+2,4
200	6,56	6,52	+0,6	220	4,22	4,12	+2,4
220	7,16	7,14	+0,3	240	4,55	4,45	+2,2
240	7,79	7,75	+0,5	260	4,88	4,77	+2,3
260	8,35	8,36	−0,1	280	5,21	5,24	−0,6
280	8,95	8,89	+0,7				

TABLE 7. Deviations $\left(\Delta\lambda = \frac{\lambda - \lambda\ \mathrm{corr}}{\lambda\ \mathrm{corr}} \cdot 100\%\right)$ of Experimental Data from Correlated True Values of Thermal Conductivity ($\lambda \cdot 10^3$, W/m·K)

Argon							
T, K	λ corr	λ [25]	$\Delta\lambda$	λ [45]	$\Delta\lambda$	λ [49]	$\Delta\lambda$
1000	43,43					41,61	—4,2
1500	56,40	54,87	—2,7	52,88	—6,2	55,49	—1,6
1600	58,79	57,42	—2,3	55,25	—6,0	58,10	—1,2
2000	67,97	67,17	—1,2	64,30	—5,4	68,07	+0,1
2500	78,86	78,58	—0,4	74,84	—5,1	79,75	+1,1
3000	89,15	89,32	+0,2	84,72	—5,0	90,78	+1,8
4000	108,1	109,3	+1,1	103,0	—4,7	111,3	+3,0
5000	126,7	127,9	+0,9			130,5	+3,0
6000	144,1					148,5	+3,1

	Neon			Krypton			Xenon		
T, K	λ corr	λ [25]	$\Delta\lambda$	λ corr	λ [45]	$\Delta\lambda$	λ corr	λ [45]	$\Delta\lambda$
1000				24,98	21,84	—12,6			
1400				31,27	27,60	—11,7	19,81	17,39	—12,2
1500	141,5	137,2	—3,0	32,70	28,95	—11,5	20,75	18,28	—11,9
2000	169,9	164,7	—3,1	39,46	35,36	—10,4	25,19	22,48	—10,8
2500	196,1	189,9	—3,2	45,73	41,29	—9,7	29,37	26,40	—10,1
3000	220,6	213,3	—3,3	51,61	46,87	—9,2	33,33	30,11	—9,7
4000	264,5	256,2	—3,1	62,47	57,24	—8,4	40,33	37,04	—8,2
5000	304,5	295,3	—3,0	72,55	66,85	—7,9	46,22	43,50	—5,9

NOTATION

λ, thermal conductivity; T, temperature; T_f, gas temperature at shock-tube wall; λ_f, thermal conductivity at temperature T_f; λ_o, thermal conductivity at temperature T_o; λ_{tr}, true thermal conductivity; λ_{ef}, effective thermal conductivity, measured by one or the other experimental method; ρ, density; η, viscosity; D, self-diffusion coefficient; $A^* = \Omega^{(2,3)*}/\Omega^{(1,1)*}$; $\Omega^{(i,j)*}$, collision integrals; $\alpha = D_{ef}T^2/L_{12}$ [6]; L_{12}, phenomenological coefficient.

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