EXPERIMENTAL INVESTIGATION OF THERMAL CONDUCTIVITY
AND THE TEMPERATURE JUMP IN NONREACTIVE GASES AT
LOW PRESSURES

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The thermal conductivities of inert gases, air, and sulfur hexafluoride in the low-pressure region are investigated with measurement cells having different geometries.

In recent years much attention has been paid to experimental investigation of the thermal conductivities of metal vapors at high temperatures. As a rule, these research subjects, with the exception of alkali metals and mercury, have a low vapor curve. This means that the majority of measurements of the thermal conductivities of vapors will necessarily be made in the low-pressure region.

The correction for the temperature jump at the boundary between the gas and the surface of the measurement cell is important in the investigation of the thermal conductivities of gases in the low-pressure region. The size of this correction depends on the structure of the gas molecules, the thermal accommodation of the gas at the surface, and its mode of flow, i.e., the relation between the mean free path of the molecules and the characteristic (least) size of the measurement cell.

A large number of articles have been devoted to the study of the temperature jump in a pure rarefied gas in a wide range of pressures, including the transitional region. For a hot-filament measurement cell the connection between the measured coefficient of thermal conductivity λ_{exp} and the true one λ_{true} given by kinetic theory is determined by the equation

$$\frac{1}{\lambda_{exp}} = \frac{1}{\lambda_{true}} + 8 \left(\frac{2 - \xi \alpha_1}{2 \alpha_1} \right) \left(\frac{\gamma - 1}{\gamma + 1} \right) \frac{T}{\overline{V}(T)} \frac{A}{P}, \tag{1}$$

where $A = (r_1 + r_2)/r_1 r_2 \ln(r_2/r_1)$; α_1 is the energy accommodation coefficient at the surface of the filament (it should be noted that by virtue of the condition $r_2 \gg r_1$, the temperature jump at the second surface is slight compared with the jump at the filament, and the possible difference in the accommodation coefficients plays no significant role); ξ is a multiplier, the relative size of which is not fully clear at present. One group of theoretical and experimental articles gives ξ as a variable quantity, ranging from $\xi_0 \cong 0.827$ to 0 in the transition from the temperature-jump regime to the free-molecule regime [1-4]. In the second group of articles $\xi = 0$ is obtained regardless of the regime [5-7].

When λ_{true} is calculated from (1), the maximum systematic error in the transitional regime due to the indicated uncertainty in ξ for a monatomic gas is about 9%. It should be mentioned that the error actually will be larger, since an extrapolation procedure is usually used to determine λ_{true} in the treatment of experimental data.

An experimental solution to the problem of the value of ξ in various regimes directly in the vapors of high-boiling substances is difficult because of the complexity of the experiment and the limited operating times of the measurement cells. Model investigations of well-studied gases, making it relatively easy to study features of the formation of the temperature jump in different regimes of gas flow and to generalize the conclusions, are of definite interest in this connection.

Developing the conclusions obtained by us in [8] on the basis of the experimental investigation of [9], we can show that for a pure gas the multiplier ξ depends on the flow regime,
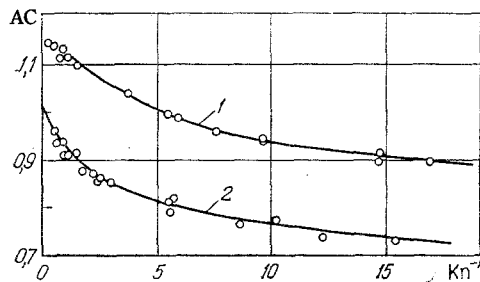

Fig. 1. Dependence of the accommodation complex on the inverse Knudsen number: 1) air; 2) xenon.

$$\xi = \frac{8(\gamma + 1)}{10\,\varepsilon}\left(\frac{a}{\varkappa} + \mathrm{Kn}\right)^{-1},$$

(2)

where the parameter Kn represents the "translational" Knudsen number and equals $\mathrm{Kn} = \overline{l}_{tran}/L(r_1, r_2)$; $\overline{l}_{tran}$ is the mean free path of the molecules; $L(r_1, r_2) = r_1\ln(r_2/r_1)$. The cofactor a in Eq. (2) characterizes the depth of the wall layer in which the investigated processes develop. The theoretical dependence of a on Kn is unknown. The relation

$$a = \sum_{n=0}^{n>1} a_n \mathrm{Kn}^n,$$

(3)

in which all the coefficients are positive, was proposed in [8]. The parameter $\varkappa$ in (2) allows for the difference in the relaxation times of the rotational—vibrational degrees of freedom of gas molecules and is defined as the ratio of the effective relaxation time of a polyatomic molecule to the relaxation time of the translational degrees of freedom ($\varkappa = \tau_{rel.ef}/\tau_{rel.tran}$). For inert gases, in particular, $\varkappa \equiv 1$. The cofactor ε represents the Eucken factor, $\varepsilon = (9\gamma - 5)/4$.

From Eq. (2) it follows that the multiplier ξ varies from $\xi = \xi_0 = 8\varkappa(\gamma + 1)/10\,\varepsilon a_0$ for $\mathrm{Kn} = 0$ to $\xi = 0$ as $\mathrm{Kn} \to \infty$.

The above-noted circumstances allow us to formulate the problem of the present article:

1) to clarify the dependence of ξ on the Knudsen number; it is very desirable to do this for several measurement cells with different characteristic parameters and for a number of gases of strictly identical molecular structure, such as inert gases;

2) to investigate the influence of the internal structure of the gas, characterized by the different relaxations of the rotational—vibrational degrees of freedom of the molecules, on the function $\xi(\mathrm{Kn})$;

3) to determine the role of $\xi(\mathrm{Kn})$ in estimates of λ_{true} from experimental data obtained at different low pressures.

In choosing the geometry of the measurement cells for this work we were guided by the fact that, first, the hot-filament method is used most often to investigate the thermal conductivities of gases at moderate and high temperatures, and second, the number of corrections to be taken into account rather precisely is minimal in this method.

The measurements of λ_{exp} for different gases at low pressures were made simultaneously in three cells with tungsten filaments of radii $r_1 = 0.054$, 0.025, and 0.0154 mm. The filaments were placed in molybdenum tubes of diameter $7.00/6.80$ mm, serving as the outer resistance thermometers. Thus, the cells had temperature—jump geometrical factors $A_1 = 4.541$, $A_2 = 8.202$, and $A_3 = 12.086$ mm^{-1} and characteristic parameters $L(r_1, r_2)_1 = 0.2237$, $L(r_1, r_2)_2 = 0.1228$, and $L(r_1, r_2)_3 = 0.0831$ mm, respectively. As the investigated substances we chose inert gases (argon, krypton, and xenon), air, and sulfur hexafluoride. Such a choice was conditioned by the considerably different internal structures of molecules of these substances.

The cells were filled with the investigated gas to a certain pressure using a special dispensing valve. The pressure was measured with mercury manometers: compression manometers

TABLE 1. Experimental Values of λ_{exp} and AC Obtained on Three Measurement Cells at a Temperature of 326°K

P	Cell 1		Cell 2		Cell 3	
	$\lambda_{exp}\cdot10^4$	AC	$\lambda_{exp}\cdot10^4$	AC	$\lambda_{exp}\cdot10^4$	AC
Argon	$\alpha_1 = 0{,}909$		$\alpha_2 = 0{,}922$		$\alpha_3 = 0{,}922$	
0,193	28,99	1,060	17,49	1,049	11,86	1,075
0,225	33,17	1,052	20,23	1,041	14,02	1,048
0,266	38,01	1,052	23,47	1,041	16,25	1,055
0,329	45,80	1,025	28,67	1,021	20,07	1,034
0,407	54,24	1,009	34,52	1,012	24,45	1,023
0,570	68,82	0,996	45,51	0,999	33,00	1,008
0,572	69,57	0,983	46,09	0,986	33,24	1,003
0,951	94,99	0,947	66,95	0,967	50,14	0,987
1,201	107,41	0,923	79,12	9,932	59,74	0,976
2,850	147,85	0,830	123,79	0,855	103,71	0,889
3,210	152,32	0,815	129,15	0,850	109,90	0,879
4,090	160,67	0,778	140,46	0,817	121,91	0,863
4,320	162,10	0,777	142,72	0,812	125,17	0,846
5,325	166,94	0,779	149,88	0,815	133,86	0,848
5,400	168,10	0,748	150,72	0,805	134,01	0,856
6,325	171,75	0,727	156,06	0,793	142,00	0,816
7,300	174,03	0,735	160,66	0,775	147,51	0,807
8,265	176,02	0,732	163,67	0,779	151,64	0,806
12,75	181,46	0,722	173,43	0,743	165,12	0,760
760	192,05		191,47		191,52	
Krypton	$\alpha_1 = 0{,}930$		$\alpha_2 = 0{,}948$		$\alpha_3 = 0{,}948$	
0,158	17,03	1,004	10,13	1,017	7,04	1,020
0,219	21,74	1,032	13,24	1,043	9,32	1,041
0,280	27,19	0,984	17,07	0,990	12,12	0,993
0,352	32,15	0,979	20,59	0,990	14,74	0,997
0,421	36,53	0,968	23,95	0,977	17,23	0,992
0,482	39,98	0,960	26,61	0,973	19,30	0,989
0,495	40,63	0,961	27,10	0,975	19,61	0,996
0,554	43,63	0,954	29,47	0,973	21,65	0,985
0,700	50,06	0,938	34,96	0,959	26,24	0,969
0,750	52,78	0,906	37,37	0,928	28,02	0,951
0,963	59,24	0,905	43,73	0,921	33,52	0,947
1,199	65,54	0,876	49,93	0,902	39,19	0,928
1,519	71,73	0,850	56,81	0,876	45,70	0,906
2,135	80,11	0,792	66,98	0,819	55,40	0,876
2,960	85,74	0,784	74,62	0,808	64,72	0,839
3,090	86,28	0,789	76,13	0,785	65,91	0,834
4,140	90,52	0,767	82,17	0,763	73,66	0,797
4,200	91,05	0,743	82,43	0,763	73,75	0,805
5,370	93,52	0,748	86,66	0,746	79,74	0,764
5,400	93,63	0,744	87,11	0,727	79,46	0,779
9,010	98,36		93,74		88,05	
13,74	99,88		97,24		93,53	
14,43	99,37		96,73		94,02	
20,77	100,83		98,99		97,02	
41,41	102,32		101,87		100,13	
112,4	103,06		103,01		102,98	
760	104,31		103,84		103,73	
Xenon	$\alpha_1 = 0{,}976$		$\alpha_2 = 0{,}990$		$\alpha_3 = 0{,}990$	
0,191	15,64	0,939	9,72	0,953	6,89	0,957
0,247	19,27	0,908	12,37	0,918	8,82	0,931
0,344	23,89	0,906	15,94	0,919	11,59	0,935
0,382	26,18	0,862	17,65	0,887	12,91	0,907
0,438	28,31	0,858	19,49	0,882	14,35	0,908
0,580	32,60	0,857	23,38	0,882	17,61	0,912
0,685	35,88	0,814	26,43	0,847	20,23	0,881
0,720	36,60	0,815	27,23	0,844	21,01	0,875
0,896	39,98	0,800	30,62	0,840	24,19	0,871
0,976	41,53	0,778	32,21	0,824	25,70	0,856
1,028	41,81	0,802	32,77	0,837	26,40	0,861
1,230	44,26	0,791	35,70	0,823	29,32	0,850
2,255	51,14	0,742	44,98	0,759	39,08	0,812
2,265	51,24	0,737	45,27	0,743	39,54	0,789
3,535	54,90	0,645	50,33	0,708	45,73	0,762
4,190	55,50		51,60		47,53	
5,010	56,21		53,38		49,79	
6,320	57,24		54,79		51,91	
8,580	58,02		56,34		54,24	
14,01	59,10		58,29		56,77	
20,59	59,69		59,25		58,74	
760	61,11		61,00		61,29	

TABLE 2 (continued)

P	Cell 1		Cell 2		Cell 3	
	$\lambda_{exp} \cdot 10^4$	AC	$\lambda_{exp} \cdot 10^4$	AC	$\lambda_{exp} \cdot 10^4$	AC
Air	$\alpha_1 = 0{,}858$		$\alpha_2 = 0{,}873$		$\alpha_3 = 0{,}870$	
0,145	36,55	1,142	21,83	1,130	14,97	1,140
0,148	37,07	1,147	22,13	1,137	15,19	1,146
0,303	67,97	1,119	42,32	1,122	29,61	1,137
0,610	111,82	1,089	74,57	1,109	54,03	1,131
0,709	123,01	1,076	83,60	1,099	61,61	1,114
0,988	148,32	1,046	105,76	1,075	79,83	1,098
2,525	213,44	0,959	175,54	1,000	145,21	1,038
3,730	234,64	0,896	201,30	0,977	174,80	0,995
4,020	238,66	0,871	207,07	0,950	180,24	0,986
5,160	246,77	0,883	220,50	0,939	197,42	0,956
6,610	254,64	0,858	232,93	0,909	212,24	0,934
10,10	264,20	0,838	248,09	0,901	233,36	0,894
11,70	267,59	0,785	252,42	0,894	238,84	0,893
15,23	271,37	0,760	260,16	0,834	249,38	0,829
19,24	273,80		263,16		254,39	
29,61	277,22		270,27		263,25	
760	282,91		281,51		279,71	
Sulfur hexafluoride	$\alpha_1 = 0{,}971$		$\alpha_2 = 0{,}985$		$\alpha_3 = 0{,}985$	
0,086	26,09	0,995	15,57	1,006	10,84	1,006
0,134	37,18	0,996	23,21	0,995	16,32	1,003
0,173	45,57	0,974	28,90	0,986	20,59	0,993
0,739	101,11	0,929	78,99	0,931	63,41	0,942
0,937	109,14	0,932	88,09	0,933	72,41	0,945
1,168	115,74	0,940	96,65	0,926	81,37	0,935
1,590	124,46	0,931	107,40	0,927	93,41	0,931
2,125	130,68	0,950	116,77	0,918	104,27	0,922
2,920	136,93	0,936	124,99	0,929	115,22	0,904
2,980	138,01	0,893	126,46	0,892	116,05	0,897
4,945	142,40		135,07		128,15	
5,900	145,47		139,11		133,24	
7,310	147,08		142,05		136,82	
8,930	148,41		143,83		140,09	
9,460	147,54		143,41		139,33	
12,74	150,74		147,51		144,37	
14,69	149,54		147,48		145,92	
19,28	152,49		149,93		148,32	
760	155,77		155,64		156,10	

in the pressure range of 0.05–1.5 mm Hg and U-shaped manometers in the pressure range of 1.5–300 mm Hg. Filling of the cells to atmospheric pressure was monitored with a vacuum manometer. The temperature difference in the tests was about 10°K.

The results of measurements of λ_{exp} for the gases enumerated above, obtained using cells 1, 2, and 3, are presented in Table 1. Data on the viscosities of the investigated gases of [10, 11] were used to calculate the Knudsen numbers. In the treatment of the measurement results the corrections for emission and heat losses were introduced through calculation. Equation (1), converted to the form

$$\frac{2 - \xi\alpha}{2\alpha} = \left(\frac{1}{\lambda_{exp}} - \frac{1}{\lambda_{true}} \right) \left(\frac{\gamma + 1}{\gamma - 1} \right) \frac{\bar{V}(T)}{8T} \frac{P}{A}, \tag{4}$$

served as the main expression in the further treatment of the test data. The values of the accommodation complex AC = $(2 - \xi\alpha)/2\alpha$ for each cell at a concrete pressure were determined from this equation. The values of λ_{exp} obtained on the cells at atmospheric pressure were taken as λ_{true} in the calculations. This enabled us to eliminate to a certain extent the possible unaccounted-for remnants of the systematic measurement errors. The energy accommodation coefficient for each cell was determined by extrapolation of the AC–Kn^{-1} curve into the region of the free-molecule regime, $Kn^{-1} = 0$, where $\xi = 0$ according to theory [2-8]. A typical graph of the AC–Kn^{-1} dependence, obtained for xenon and air on a cell with $r_1 = 0.0154$ mm, is presented in Fig. 1. The values of the energy accommodation coefficient and the accommodation complex for all the investigated gases are presented in Table 1.
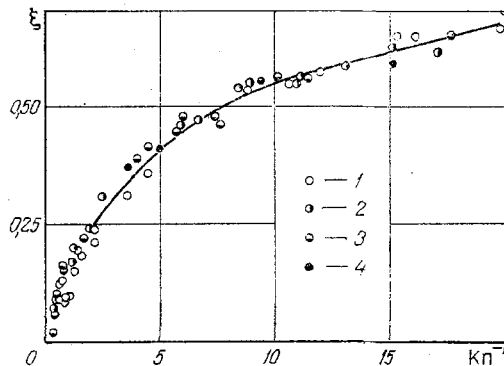
Fig. 2. Dependence of the factor ξ on the inverse Knudsen number for argon: 1, 2, 3) cell numbers; 4) from data of [3].

The treatment and analysis of the measurement results showed that, to within the errors of the experiment and subsequent calculations, the correction factor ξ for a specific gas depends on the Knudsen number for all three cells: $Kn = \overline{l}_{tran}/L(r_1, r_2)$. The ξ–Kn^{-1} dependence for argon, supporting this conclusion, is presented in Fig. 2 as an example. In their time Schafer et al. [3] made analogous investigations of λ_{exp} in a wide range of Knudsen numbers on a cell with a platinum filament of radius $r_1 = 0.0208$ mm. The radius of the outer cylinder was $r_2 = 2.94$ mm. Consequently, the characteristic parameter of the measurement cell was $L(r_1, r_2) = 0.1030$ mm. The results of [3] treated by us by the above scheme coincide with the discussed material to within the errors of the experiments and calculation. Here it must be noted that the energy accommodation coefficients of argon on tungsten and platinum are practically the same.

In Fig. 3 we present the ξ–Kn^{-1} dependences for argon, krypton, xenon, air, and sulfur hexafluoride, allowing one to judge the influence of the structure of the gas molecules on the form of $\xi(Kn)$. As one would expect, the dependence is the same for argon, krypton, and xenon, which have molecules of the same structure ($\varkappa = 1$). The $\xi(Kn)$ curves for air and sulfur hexafluoride differ considerably from $\xi(Kn)$ for the inert gases, which is evidently connected with the different contributions of the rotational—vibrational degrees of freedom of the molecules to the process of energy dissipation in the wall gas layer. At this stage the authors were forced to confine themselves to only recording this experimental fact, since more profound conclusions and the construction of a unified theoretical scheme for the dependence of ξ on the molecular structure are possible only after the accumulation of extensive experimental material.

With allowance for the $\xi(Kn)$ dependence, we can state that Eq. (1) in the λ_{exp}^{-1}–P^{-1} coordinates is mapped not by a straight line, as follows from [5, 6], but by a complicated curve which has the following characteristics (see Fig. 4): the asymptote to it is

$$\frac{1}{\lambda_{exp}} = \frac{1}{\lambda_{true}} + \frac{8}{\alpha} \left(\frac{\gamma-1}{\gamma+1}\right) \frac{T}{\overline{V}(T)} \frac{A}{P} \tag{5}$$

and the tangent at the point $(P_{atm}/P) = 1$ is

$$\frac{1}{\lambda_{exp}} = \frac{1}{\lambda_{true}} + 8 \left(\frac{2-\xi_0\alpha}{2\alpha}\right) \left(\frac{\gamma-1}{\gamma+1}\right) \frac{T}{\overline{V}(T)} \frac{A}{P}. \tag{6}$$

From the form of the curve and Eqs. (5) and (6) it follows that the entire region of pressures (or Knudsen numbers) can be divided into three clearly separated zones corresponding to different regimes of gas flow. Zone I corresponds to the regime of a weakly developed temperature jump, zone II to the transitional regime, and zone III to the free-molecule regime. Naturally, the boundaries between the regimes are individual and are determined by the $\xi(Kn)$ dependence for the specific gas.
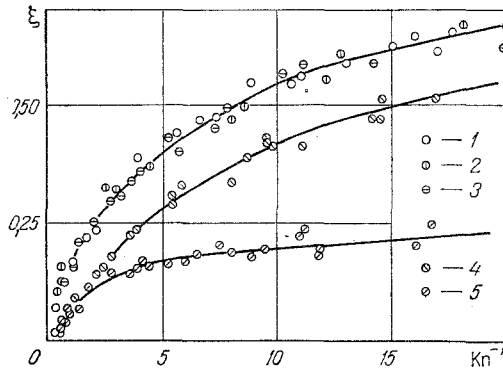
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Fig. 3. Dependence of the factor ξ on the inverse Knudsen number for different gases at a temperature of 326°K: 1) Ar; 2) Xe; 3) Kr; 4) air; 5) SF_6.
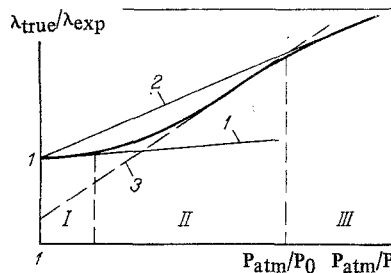

Fig. 4. Approximation of the experimental data in the $\lambda_{true}/\lambda_{exp}$–$P_{atm}/P$ coordinates: 1) tangent; 2) asymptote; 3) linear approximation.

The possibility of obtaining λ_{true} from test data is of primary interest in an investigation of the thermal conductivity of a gas in the low-pressure region. Since it is often difficult to obtain the complete λ_{exp}^{-1}–P^{-1} curve, as in the case of metal vapors, for example, and the $\xi(Kn)$ dependence in (1) is unknown, one usually uses a linear approximation of the experimental points, which is equivalent to a linear approximation of the $\xi(Kn)$ dependence (see Fig. 3). In this variant of the treatment of experimental material the experimental points in zones I and III are well described by Eqs. (5) and (6), which yield an unbiased estimate of λ_{true}. In a linear approximation the true $\xi(Kn)$ dependence in zone II can be replaced by the function $\xi = (\partial\xi/\partial P)_{II}(P - P_0)$, where P_0 is the lower limit of the transitional regime for the specific gas and measurement cell. Then Eq. (1) is reduced to

$$\frac{1}{\lambda_{exp}} \approx \left\{ \frac{1}{\lambda_{true}} - 4\left(\frac{\overline{\partial\xi}}{\partial P}\right)_{II}\left(\frac{\gamma-1}{\gamma+1}\right)\frac{TA}{\overline{V}(T)}\right\} + 8\left\{\frac{1}{\alpha} + \left(\frac{\overline{\partial\xi}}{\partial P}\right)_{II}\frac{P_0}{2}\right\}\left(\frac{\gamma-1}{\gamma+1}\right)\frac{TA}{\overline{V}(T)\,P}, \qquad (7)$$

from which it follows that in zone II, i.e., the transitional regime, a linear approximation of the experimental data leads to a biased estimate of λ_{true}. This conclusion, in our view, is the most important in an analysis of the formation of the temperature jump in nonreactive gases, since it points directly to a possible source of systematic error in λ_{true} in planned measurements of the thermal conductivities of metal vapors and other high-boiling substances.

As follows from Fig. 3, the amount of bias in the estimate of λ_{true} in the transitional regime is determined by the properties of the gas.

The first term of Eq. (7) can be converted to the form

$$\frac{1}{\lambda_{true}} - 4\left(\frac{\overline{\partial\xi}}{\partial P}\right)_{II}\left(\frac{\gamma-1}{\gamma+1}\right)\frac{TA}{\overline{V}(T)} = \frac{1}{\lambda_{true}}\left\{1 - \left(\frac{\overline{\partial\xi}}{\partial Kn^{-1}}\right)_{II}\frac{10\,\varepsilon}{8\,(\gamma+1)}\right\}. \qquad (8)$$

The expression inside the curly brackets allows one to calculate the amount of bias in the estimate of λ_{true}, which for inert gases equals 0.86, for air 0.93, and for sulfur hexafluoride 0.97. The amount of bias of λ_{true} for a specific gas does not depend on the geometrical dimensions of the measurement cell, but the zone of a biased estimate of λ_{true} extends into the higher-pressure region with a decrease in the radius of the filament or in the characteristic parameter $L(r_1, r_2)$ in general.

NOTATION

λ_{exp}, λ_{true}, experimental and true coefficients of thermal conductivity, W/m·K; α, energy accommodation coefficient; r_1, r_2, radii of the filament and of the outer cylinder of the measurement cell; P, pressure, mm Hg; T, temperature; $\gamma = C_p/C_v$, ratio of isobaric and isochoric heat capacities; $\overline{V}(t)$, average thermal velocity of the molecules; ξ, correction factor, a dimensionless quantity; $\overline{l}(T)$, mean free path of molecules; $L(r_1, r_2)$, characteristic parameter of the measurement cell; d, dissipation parameter; Kn, Knudsen number; τ_{rel}, relaxation time; ε, Eucken factor; A, geometrical temperature–jump factor; AC, accommodation complex, a dimensionless quantity.

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