FORM OF THE EQUATION FOR CALCULATION OF THERMAL CONDUCTIVITY OF GASES AND LIQUIDS OVER A WIDE PARAMETER RANGE

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An equation developed from Vargaftik's equation [8] for description of experimental data on thermal conductivity of gases and liquids is presented. The effectiveness of the equation is demonstrated with the example of argon.

In an analytic description of experimental data on the coefficient of thermal conductivity of gases and liquids over a wide temperature and density range it is of primary importance to consider the character of the dependence of thermal conductivity on thermal properties. Analysis of much experimental data reveals that in the coordinates $\Delta\lambda = \lambda_{p,T} - \lambda_T$, ρ the separation of "excess" thermal conductivity isotherms is comparable to the experimental error and is observed only at supercritical densities over a wide temperature range [1-4], as well as in the critical region [2, 5-7]. Due to the insignificant effect of the temperature factor in the coordinates $\Delta\lambda$, ρ the equation for calculation of thermal conductivity is most often written in the form

$$\lambda_{p,T} = \lambda_T + f(\rho), \tag{1}$$

where $f(\rho)$ is usually represented by a polynomial. Equation (1), proposed by Vargaftik [8], has been employed for description of experimental data on thermal conductivity of many materials in both the gaseous and liquid phases, excluding the critical region ([2, 6, 8-10] and others). In using Eq. (1) the curve $\Delta\lambda = f(\rho)$ was extended between experimental points, while deviation of points from this curve in the high-density region was attributed to experimental error.

In recent years, in connection with the accumulation of sufficiently reliable data on thermal conductivity of gases and liquids over a wide parameter range, more complex equations have been proposed for calculation of thermal conductivity [11, 12], depicting the separation of isotherms in the coordinates $\Delta\lambda$, ρ. These equations contain 12 or 15 terms in various powers of the density, but the significant increase in number of coefficients over that of Eq. (1) did not lead to a noticeable increase in accuracy of approximation and, in particular, did not describe the sharp increase in thermal conductivity in the critical region, where a special form of the equation is required [13, 14]. It would thus be useful to slightly modify Eq. (1), which basically does describe thermal conductivity correctly, by introducing a correction to account for isotherm separation.

Since in Eq. (1) the function $f(\rho)$ is positive, the calculated values of the thermal-conductivity coefficient for a gas at atmospheric pressure prove to be systematically higher than experimental values of λ_T used in establishing the equation. This same shortcoming is inherent in the equations of [11, 12]. Thus it will be expedient to employ as an argument the quantity $\bar{\rho} = \rho(p, T) - \rho(1, T)$, thus ensuring strict satisfaction of the limit condition ($\lambda_{p,T} \to \lambda_T$ as $p \to 1$ atm).

Considering the above, in composing the empirical equation for calculation of thermal conductivity of a gas or liquid over a wide parameter range, excluding the critical region, it will be convenient to employ the quite flexible form

$$\lambda_{p,T} = \lambda_T + a_1\bar{\rho} + a_2\bar{\rho}^2 + a_3(T)\bar{\rho}^3 + \ldots + a_n(T)\bar{\rho}^n. \tag{2}$$

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TABLE 1. Mean Square Deviation of Experimental Thermal-Conductivity Values of Argon from Values Calculated by Eq. (5).

Authors	No. of points	Parameter range			$\delta\lambda_{mn}$, %
		T, K	ρ, g/cm³	pmax, bar	
Michaels, Sengers, and Van de Klundert [15]	110	273—348	0,001—1,212	2457	0,9
Ikenberry and Rice [16]	48	91—235	0,070—1,434	539	2,7
Bailey and Kellner [6]	193	89—299	0,031—1,467	490	1,4
Golubev and Shpagina [7]	70	97—366	0,027—1,437	491	1,2
Le Neindre [17]	140	298—977	0,048—0,972	1000	1,7
Amirkhanov, Adamov, and Gasanóv [18]	220	282—624	0,074—0,997	981	3,1
Tufeu [19]	76	302—607	0,008—0,918	952	0,9
Amirkhanov, Adamov, and Gasanov [20]	136	113—253	0,209—1,478	981	1,8
All data	993	89—977	0,001—1,478	2457	2,0
Data of [6, 7, 15, 17, 19]	589	89—977	0,001—1,467	2457	1,3

In Eq. (2) the coefficients of the lower powers of $\bar{\rho}$ are constant, as in Eq. (1), while the coefficients of the higher powers are temperature dependent, which allows them to reflect separation of isotherms of "excess" thermal conductivity at high densities.

The effectiveness of Eq. (2) may be shown with the experimental data of [6, 7, 15-20] on thermal conductivity of gaseous and liquid argon, encompassing a temperature interval of 89-977°K and densities of 0.001-1.478 g/cm³ (up to 2.76 ρ_{cr}). Using a Minsk-32 electronic computer and considering experimental data weight $w_i = 1/(\lambda_i \delta\lambda_i)^2$ a number of equations with various numbers of constants all in the form of Eq. (2) were composed. The magnitude of the relative error $\delta\lambda_i$ was taken as 1% for the data of [6, 15, 17, 19] and 2% for the data of the other authors. Gas and liquid density values at the experimental temperature and pressure ρ(p, T) were calculated with the equation of state presented in [9, 10]. Gas density at atmospheric pressure ρ(1, T) was determined from the equation of state of an ideal gas, which is completely permissible in this case. Thermal conductivity of argon at atmospheric pressure was calculated from the equation, developed by the author,

$$\lambda_T = -0.226 + 7.21\theta - 0.475\theta^2 + 0.024040\theta^3 - 0.000494\theta^4, \tag{3}$$

where $\theta = T/100$. This equation describes the smoothed data of [2] in the temperature interval 90-1300°K with a mean square error of 0.9% and maximum error of 1.8%, and the data of [21] over the same temperature interval with errors of 0.3 and 1.1%.

The equation for calculation of thermal conductivity of gaseous and liquid argon with the maximum number of constants has the form

$$\lambda_{\rho,T} = \lambda_T + a_1\bar{\rho} + a_2\bar{\rho}^2 + (a_{30} + a_{31}\theta)\bar{\rho}^3 + (a_{40} + a_{41}\theta)\bar{\rho}^4 + (a_{50} + a_{51}\theta + a_{52}\theta^2)\bar{\rho}^5. \tag{4}$$

To reduce the number of constants, powers of θ and the term containing $\bar{\rho}^5$ were eliminated. Fifth- and fourth-order equations in $\bar{\rho}$ in which the higher or highest coefficients are temperature dependent describe the most reliable experimental data of [6, 7, 15, 17, 19] with a mean square deviation of 1.3%. Analogous equations with constant coefficients have lower accuracy ($\delta\lambda_{mn}$ = 1.6%), which indicates the necessity of considering temperature dependence of the coefficients of the higher powers. Detailed analysis of deviations at all experimental points revealed that for argon the equation

$$\lambda_{\rho,T} = \lambda_T + 23.49\bar{\rho} + 27.37\bar{\rho}^2 - 21.565\bar{\rho}^3 + (22.451 + 1.68318\theta)\bar{\rho}^4 \tag{5}$$

may be recommended, where the dimensions of λ are 10^{-3} W/(m·deg); ρ, g/cm³. Further increase in number of constants does not lead to significant increase in accuracy of approximation. Table 1 presents mean square deviations of experimental data of the various authors from values calculated with Eq. (5).

For analytic description of experimental data on thermal conductivity of other materials in other parameter ranges, a different number of parameters may be required, but the general form of Eq. (2) will be preserved. It should be noted that Eq. (2), like Eq. (1), is useful for extrapolation to high temperatures, since for a fixed maximum pressure the major contributions to calculated values of coefficient of thermal conductivity at high temperatures are produced by the function λ_T, which is usually defined over a wider temperature interval than the thermal conductivity of the compressed gas.

Thus, by using in Vargaftik's equation [8] coefficients of higher powers which are temperature dependent, it is possible to reflect separation of isotherms in the coordinates $\Delta\lambda$, ρ and to describe experimental data on thermal conductivity of gas or liquids over a wide parameter range within experimental accuracy with a quite simple equation.

NOTATION

λ and $\lambda_{p,T}$, thermal conductivity of compressed gas or liquids; λ_T, thermal conductivity of gas at atmospheric pressure; $\Delta\lambda = \lambda_{p,T} - \lambda_T$, "excess" thermal conductivity; ρ and $\rho(p, T)$, density of compressed gas or liquids; $\rho(1, T)$, density of gas at atmospheric pressure; $\bar{\rho} = \rho(p, T) - \rho(1, T)$; ρ_{cr}, critical density; a_i, coefficients of Eq. (2); w_i, weight of experimental data; $\delta\lambda$, relative error of data; $\theta = T/100$.

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