AN EQUATION FOR CALCULATION OF THE THERMAL CONDUCTIVITY OF GASES AND LIQUIDS

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A unified equation is proposed for calculation of the thermal conductivity of gases and liquids. The procedure for formulation of the equation is illustrated in the example of nitrogen.

As more and more experimental data are gathered on the thermal conductivity coefficient of compressed gases and liquids the need becomes more urgent for an analytical description of those data. Unfortunately, there is no generally acceptable form of equation for calculating the thermal conductivity of gases and liquids.

The most widely used equation for gases represents the excess thermal conductivity $\Delta\lambda = \lambda - \lambda_0$ as a function of the density [1]. However, in the analysis of reliable experimental data on the thermal conductivity of compressed gases [2, 3] the isotherms in the coordinates $\Delta\lambda$, ρ are found to separate, and the gap widens with increasing density. The separation is relatively small and ordinarily falls within the limits of the discrepancies between the data of different researchers, so that it is neglected in the application of the dependence $\Delta\lambda = f(\rho)$ and a general curve is drawn through the majority of the experimental points. Nevertheless, a valid equation for the thermal conductivity of a real gas over a wide range of parameters ought to take into account the influence of the temperature on the excess thermal conductivity.

Equations have been proposed recently [4, 5] in which the thermal conductivity of superheated steam is represented as a function of the pressure and temperature. These equations are well suited to practical calculations, but they are valid only in a relatively narrow range of reduced parameters due to the complexity of the thermal conductivity isobar configurations.

An equation has also been formulated in [5] for calculations of the thermal conductivity of water and steam in the critical region; this equation takes the form $t = f_1(\lambda) + pf_2(\lambda)$. The equation was derived with reliance on the fact that the constant-thermal conductivity lines in the coordinates p, t are practically linear near the elasticity curve. The author of [5] himself remarks that this correspondence is observed only in a limited range of temperatures and pressures. A check of our own has shown that the lines $\lambda = \text{const}$ curve appreciably and pass through a maximum over a wide range of the reduced parameters.

The experimental data on the thermal conductivity of liquids, as shown in [6], are described most accurately by the equations $\lambda = F(\rho)$ and $\Delta\lambda = f(\rho)$, where the values of λ_0 for a gas are used in the calculation of the quantities $\Delta\lambda$. Although the first of the indicated equations was in fact obtained for the liquid phase [7], their accuracy is practically identical, because λ_0 yields only a small contribution to the thermal conductivity of a liquid.

The equation set forth in the present article is derived on the basis of an analysis of the dependence of the thermal conductivity on the thermal parameters. An examination of various sections of the λ-surface reveals that the simplest curves are the isochors in the coordinates λ, T, which have the same configuration as the thermal conductivity curve at atmospheric pressure: $\lambda_0(T)$.

The foregoing is illustrated by Fig. 1, which was plotted from the experimental data of [2, 8, 9] for nitrogen.* The density values required in order to plot the isochors are taken from the data of [2, 6, 10].

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*We note that these data do not disclose an increase of the thermal conductivity in the critical region.

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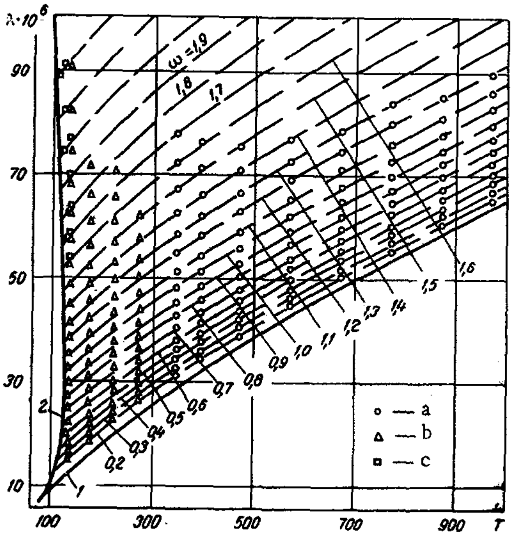

Fig. 1. Isochoric sections of the thermal conductivity surface for nitrogen ($\lambda \cdot 10^6$ kW/m · deg; T, °K). a) Data of [2]; b) [8]; c) [9]; 1) curve of $\lambda_0(T)$; 2) saturation curve.

The accuracy of the experimental values of λ_0 is generally higher than that of the thermal conductivity–pressure data, so that the isochors can be plotted on the basis of the most reliable data, using the configuration of the $\lambda_0(T)$ as a guideline.

By analogy with the isochroic sections of the thermodynamic surface the thermal conductivity isochors can be divided into a rectilinear and a curvilinear part. Following the procedure of [11, 12], we represent the linear part of the equation for the $\lambda(\rho, T)$-surface in the form $F_1(\rho) + F_2(\rho)T$, and the curvilinear part as the product of functions in separated variables $F_3(\rho)\varphi(T)$. Then the equation for the given surface assumes the form

$$\lambda(\rho, T) = F_1(\rho) + F_2(\rho)T + F_3(\rho)\varphi(T). \tag{1}$$

The product of the temperature function $\varphi(T)$ and the value of $F_3(\rho)$ at a fixed density is the curvilinear part of the isochoric equation. Owing to the invariance of the equation in the form (1) under linear transformations of the temperature function [10], we can adopt the isochoric equation as the function $\varphi(T)$, and, in turn, the similarity of the configurations of the isochors and the function $\lambda_0(T)$ enable us to use the latter as a the temperature function. A strong argument in favor of this choice of $\varphi(T)$ is the fact that the values of λ_0, as mentioned, are fairly reliably determined in experiments.

For the generalization of the thermal conductivity data for various substances it is helpful to form the equation for the λ-surface in reduced coordinates: $\omega = \rho/\rho_{cr}$, $T = T/T_{cr}$. Then the equation for the thermal conductivity of a gas or liquid can be written in the form

$$\lambda(\omega, \tau) = \alpha(\omega) + \beta(\omega)\tau + \gamma(\omega)\lambda_0(\tau), \tag{2}$$

where $\alpha(\omega)$, $\beta(\omega)$, and $\gamma(\omega)$ are polynomials in the reduced density.

It must be stressed that the kinetic theory developed for real gases by Bogolyubov [13] and his successors [14, 15] yields the following virial equation for the thermal conductivity:

$$\lambda = \lambda_0(1 + B_\lambda \rho + C_\lambda \rho^2 + \ldots). \tag{3}$$

Unfortunately, it is impossible on the basis of the experimental data to make a reliable determination of the virial coefficients past the second one, and the theory only permits one to calculate the first virial coefficients for extremely simplified models of a gas.

Equation (2) agrees with the theoretical equation (3) on the supposition that the virial coefficients B_λ, $C_\lambda, \ldots$, when multiplied by λ_0, have a linear part and a curvilinear part that is proportional to the function $\lambda_0(\tau)$. This supposition is fairly well borne out by the results of the theoretical studies [16, 17].

We illustrate the procedure for the formulation of Eq. (2) in the example of nitrogen, whose thermal conductivity has been investigated over a wide range of parameters, including the liquid-state region. Initially the values of λ_0 taken in the temperature interval from 240 to 1300°K were described analytically

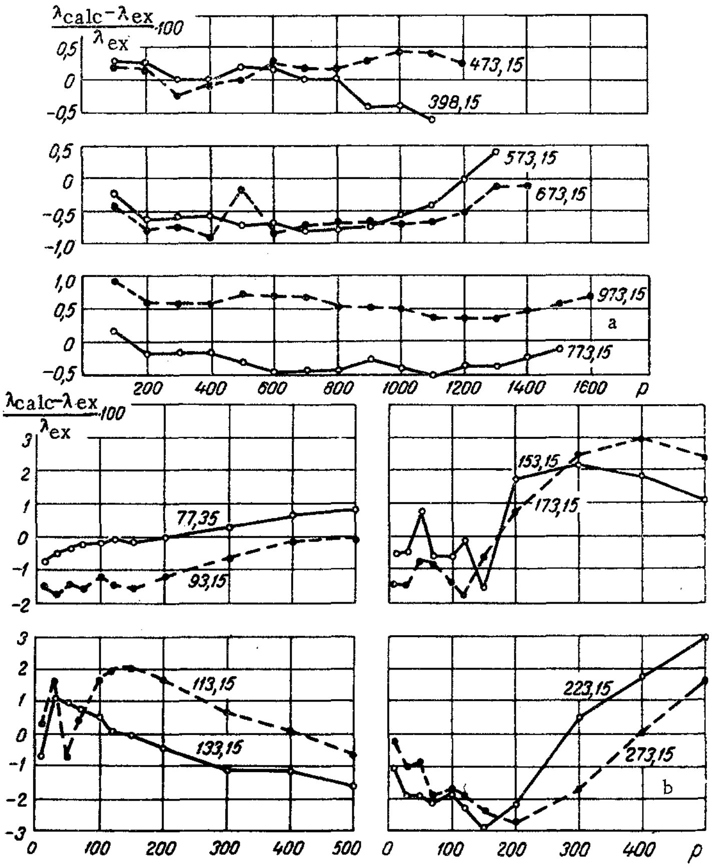

Fig. 2. Deviations of the calculated values of the thermal conductivity of nitrogen from the experimental data (p in atm; numbers alongside the curves in °K). a) From [2]; b) [8].

on the basis of the smoothed data of [10], while those in the interval from 80 to 230°K were described on the basis of the data of [8, 18]. The following equation describes the reference of λ_0 with rms error 0.3% and maximum error 0.7%:

$$\lambda_0(\tau)\,[10^{-6}\ \mathrm{kW/m \cdot deg}] = -1.22 + 14.63\tau - 1.737\tau^2 + 0.1738\tau^3 - 0.00683\tau^4 \tag{4}$$

(the critical temperature of nitrogen was assumed to be 125.25°K).

As the reference values of the thermal conductivity of nitrogen at elevated pressures we choose the reliable experimental data of [2], which span the temperature interval from 75 to 750°C and the pressure interval from 1 to 1600 atm, and from lower temperatures up to the saturation curve we used a large portion of the data in [8, 9]. The data of other researchers either span a comparatively narrow range of the parameters or are not reliable enough and were therefore rejected for the development of the reference net. In particular, the well-known data of [19] turn out to be far too high in value for the construction of the isochors, as noted earlier [2, 10]. Fully satisfactory agreement between the reference values of λ and the experimental data of [2, 8, 9] on most of the isotherms and isochors is exhibited by Fig. 1. At high densities the isochors are drawn between the experimental data of [8, 9], which disclose discrepancies of 2 to 4%.

Equation (2) was formulated by the method of basis isotherms [10, 12]. According to this method, the functions $\alpha(\omega)$, $\beta(\omega)$, and $\gamma(\omega)$ are determined for known $\lambda_0(\tau)$ by solving the set of equations for three isotherms simultaneously with Eq. (2). For the reliable description of the thermal conductivity data for a liquid one of the basis isotherms must be chosen in the liquid-state region. Consequently, we adopted as our basis curves the 90, 348.15, and 873.15°K isotherms. The reference data on the 90°K isotherm in the interval of densities from ω'' to ω' were obtained by graphical extrapolation of the isochors. In order for the limiting conditions to be satisfied the isotherm equations were developed in the form

$$\lambda = \lambda_0 + \Sigma a_n \omega^n. \tag{5}$$

As remarked above, Eq. (5) can be used effectively to calculate the thermal conductivity of a liquid. All the basis isotherms were described correct to ±0.5% by fifth-degree polynomials in the density. The functions $\alpha(\omega)$, $\beta(\omega)$, and $\gamma(\omega)$ determined by solution of the indicated set of equations have the form

$$\begin{aligned}\alpha(\omega) &= 7.561\,\omega + 39.394\,\omega^2 - 42.296\,\omega^3 + 18.813\,\omega^4 - 2.375\,\omega^5,\\ \beta(\omega) &= -4.788\omega + 33.836\omega^2 - 47.755\omega^3 + 24.697\omega^4 - 4.479\omega^5,\\ \gamma(\omega) &= 1 + 0.4572\omega - 3.9749\omega^2 + 5.5543\omega^3 - 2.7079\omega^4 + 0{,}4559\omega^5.\end{aligned} \tag{6}$$

For the calculations the critical density of nitrogen was assumed to have a value $\rho_{cr} = 0.304$ kg/dm^3.

The unified thermal conductivity equation represented by expressions (2), (4), and (6) for nitrogen describe the experimental data for the gaseous and liquid phases in the temperature interval from 77.35 to 973.15°K and for reduced densities $\omega = 0$ to 2 (up to $\omega = 3$ for the liquid). A comparison of the calculated and experimental values (Fig. 2a and 2b) indicates that the deviations of the calculated values of the thermal conductivity from the experimental [2, 8] in the indicated range of the parameters, for the most part, does not exceed the experimental error. The calculated values of λ also agree with the majority of the experimental data of [9] within 1 or 2% error limits.

The advantage of the proposed form of the equation for calculating the thermal conductivity is its amenability of extrapolation into the region of higher temperatures, where data on the thermal conductivity of the compressed are lacking, but the values of the function $\lambda_0(\tau)$ are known.

NOTATION

λ	is the thermal conductivity coefficient of a compressed gas;
λ_0	is the thermal conductivity coefficient of the gas at atmospheric pressure;
ρ	is the density;
$\omega = \rho/\rho_{cr}$	is the reduced density;
$\tau = T/T_{cr}$	is the reduced temperature;
$B_\lambda, C_\lambda, \ldots$	are the second, third, etc., virial coefficients of the thermal conductivity.

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