EQUATION FOR CALCULATING THE THERMAL CONDUCTIVITY OF A GAS IN THE CRITICAL REGION

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UDC 536.23

An equation that describes the experimental data on the thermal conductivity of a gas in the critical region $|T/T_{cr}-1| < 0.03$ and $|\rho/\rho_{cr}-1| < 0.4$, is presented.

It has often been noted (see [1-4] among others) that the thermal conductivity of gases increases anomalously as the critical point is approached. Recently, Sengers and Keyes [5] suggested that one should express the anomalous part of the thermal conductivity in terms of its value on the critical isochor, this to be determined on the basis of experimental data in accordance with the formula obtained by Kadanoff and Swift [6] by means of the scaling theory of critical phenomena. By analogy with the thermodynamic behavior of a gas near the critical point, it was assumed in [5] that the dependence between these variables is

$$\sqrt{\omega}\,\Delta\lambda(\rho, T) = \Delta\lambda(\rho_{cr}, T) f(x), \tag{1}$$

where

$$\Delta\lambda(\rho_{cr}, T) = A|\tau - 1|^{\varphi}. \tag{2}$$

Sengers and Keyes analyzed Eq. (1) qualitatively, constructing for this the function $f(x) = \sqrt{\omega}\Delta\lambda(\rho, T)/\Delta\lambda(\rho_{cr}, T)$ of the argument $x\beta$ for smoothed values of λ for carbon dioxide [1]. According to Sengers and Keyes [5], the empirically introduced function $\sqrt{\omega}$ must reflect the displacement of the maxima of $\Delta\lambda(\rho, T)$ to the region of subcritical densities when $T > T_{cr}$. Since only some of the points plotted on the graph can be represented by a single curve, Sengers and Keyes concluded that the data on the thermal conductivity of carbon dioxide are described satisfactorily by Eq. (1) in the restricted parameter range $|\tau-1| < 0.065$ and $|\omega-1| < 0.4$. In [5] an analytic expression was not obtained for the function f(x) nor was any estimate made of the accuracy of description of the thermal conductivity of a gas in the critical region by means of Eq. (1).

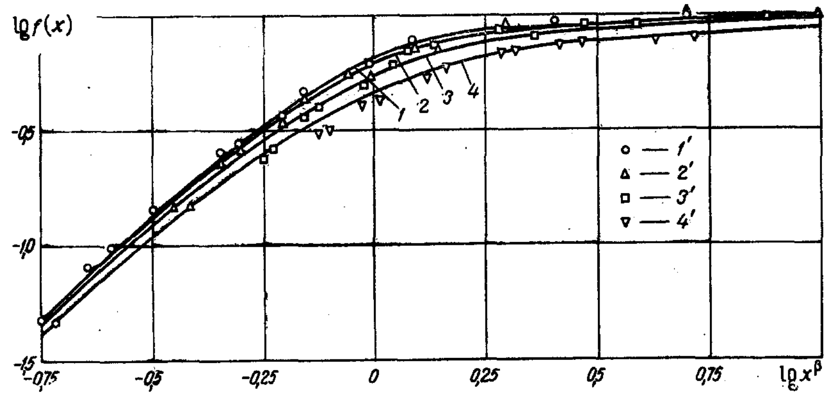

Fig. 1. The function $f(x) = \sqrt{\omega}\Delta\lambda(\rho, T)/\Delta\lambda(\rho_{cr}, T)$ of x^β in the interval τ = 1.000493-1.029421 and ω = 0.63-1.39: 1) and 1') T = 304.35°K; 2) and 2') 305.25; 3) and 3') 307.95; 4) and 4') 313.15.

Odessa Institute of Nautical Engineering. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 26, No. 5, pp. 839-843, May, 1974. Original article submitted September 26, 1973.

TABLE 1. Relative Deviations of the Thermal Conductivity Calculated in Accordance with Eq. (1) from the Data of [1]: $\delta\lambda = [(\lambda_{calc} - \lambda_{exp})/\lambda_{exp}] \cdot 100$, %

ω	T=304,35 °K τ=1,000493			T=305,25 °K τ=1,003452			T=307,95 °K τ=1,012327			T=313,15 °K τ=1,029421		
	I	II	III	I	II	III	I	II	III	I	II	III
0,63371	3,2	—4,4	2,2	4,0	—3,4	3,2	5,0	—1,5	6,3	5,3	0,7	11,2
0,71821	—4,3	—10,8	—5,6	—0,6	—7,1	—1,8	1,4	—4,0	3,1	2,8	—0,6	9,4
0,80270	—6,2	—12,0	—8,3	—1,6	—7,5	—3,8	—1,0	—5,0	1,1	0,9	—1,4	6,7
0,84495	—4,4	—10,1	—7,4	—0,3	—5,9	—3,3	—2,0	—5,3	0,1	0,2	—1,5	5,1
0,88720	0,7	—5,0	—4,1	0,3	—4,4	—2,7	—3,0	—5,3	—1,5	0,1	—1,1	4,0
0,92945	4,6	—1,2	—3,3	—3,6	—6,5	—5,6	—3,1	—4,5	—3,8	0,6	0	3,5
0,97169	—1,7	—4,2	—5,5	—5,9	—7,1	—6,9	—2,0	—3,1	—1,4	1,8	1,7	3,7
1,01394	—5,1	—5,3	—7,3	—4,2	—4,1	—5,0	—0,6	—0,7	—0,1	2,7	3,2	4,1
1,05619	—4,5	—4,8	—11,1	—0,9	0	—2,5	—0,8	0,4	0,1	1,5	2,6	3,8
1,09844	—3,0	—1,7	—8,2	4,1	5,7	1,3	0,4	2,3	1,6	0,9	2,7	3,9
1,14068	—0,3	2,4	—3,3	4,7	6,9	2,0	1,5	3,9	3,0	0,9	3,0	4,4
1,22518	—3,6	—0,5	—4,8	—0,1	2,8	—1,3	1,4	4,2	2,7	1,0	3,6	5,0
1,30968	—2,2	0,7	—2,8	—0,8	1,9	—1,4	0,6	3,2	1,4	1,2	3,7	4,4
1,39417	0	2,4	—0,4	0,3	2,7	0	1,6	3,9	2,1	1,6	3,8	3,7
$\delta\lambda_{av}$, %	3,6	5,9	6,0	3,0	5,2	3,4	2,1	3,7	2,6	2,0	2,4	5,7

In this paper we derive an equation for calculating the thermal conductivity of a gas in the form (1) from the same data [1] as were used in [5]. The anomalous part of the thermal conductivity is defined by means of the equation

$$\Delta\lambda(\rho,\ T) = \lambda - \lambda_{id}. \tag{3}$$

The quantity λ_{id} was found by means of the equations

$$\lambda_{id} = \lambda_0(\tau) + \tilde{\lambda}(\omega), \tag{4}$$

$$\lambda_0(\tau) \cdot 10^6 = -0.348 + 7.623\tau + 13.49\tau^2 - 4.352\tau^3 + 0.4367\tau^4 \ (\mathrm{kW \cdot m^{-1} \cdot deg^{-1}}) \tag{5}$$

$$\tilde{\lambda}(\omega) \cdot 10^6 = 14.32\omega + 41.12\omega^2 - 36.63\omega^3 + 15.60\omega^4 - 1.634\omega^5 \ (\mathrm{kW \cdot m^{-1} \cdot deg^{-1}}) \tag{6}$$

For calculations in accordance with Eqs. (5) and (6) we adopted the following values of the critical parameters of CO_2 [1]: T_{cr} = 304.2°K and ρ_{cr} = 236.7 amagat (467.8 kg · m³). We derived Eq. (5) on the basis of the smoothed values of the thermal conductivity [7] in the temperature range 200–900°K, and it describes them with an error up to 1.5%. In obtaining the generalized dependence (6), we used the experimental data of [1, 8–10], which together cover the range of temperatures 293–373°K and pressures $(0.1\text{–}210) \cdot 10^6$ N/m² (ω = 0–2.5). The error in this range of parameters for calculating λ_{id} does not exceed 3%.

The values of A and φ in Eq. (2) were found from the graph of the function $\lg\Delta\lambda(\rho_{cr},\ T) = f(\lg|\tau - 1|)$. A straight line in these coordinates was drawn from the conditions of best satisfaction of the values of $\lambda(\rho_{cr},\ T)$ at the temperatures 304.35, 305.25, and 307.95°K, since at higher temperatures the points depart appreciably from a straight line, i.e., from the power law (2) dictated by scaling theory. As a result, we obtained the following values of the parameters: $A = 2.85 \cdot 10^{-6}$ kW · m^{-1} · deg^{-1} and $\varphi = -0.6$, and we described the values of $\lambda(\rho_{cr},\ T)$ for temperatures 304.35–307.95°K with error from −2.4 to +1.6%. At 313.15°K the error reaches 5.5%, and when T = 348.15°K the thermal conductivity is more accurately determined by Eq. (4).

The function f(x) was calculated in accordance with Eq. (1) and plotted as a function of x^β in logarithmic coordinates (Fig. 1). We took the value of the critical index β = 0.35 in accordance with the data of [11]. The points for the temperature range 304.35–313.15°K (τ = 1.000493–1.029421) and the reduced densities ω = 0.63–1.39 exhibit a stratification with respect to isotherms, this being particularly noticeable at the temperature T = 313.15°K. However, as $x \to \infty$ and as $x \to 0$ the points collapse onto a single curve in such a way that f(x) = 1 on the critical isochor, and on the critical isotherm the tangent of the slope of the curve is 1.71, i.e., f(x) vanishes here as $(x^\beta)^{-\varphi/\beta}$. Each of the limits of the function satisfies the condition $\Delta\lambda(\rho_{cr},\ T_{cr}) = \infty$. The points lying outside the given range of parameters depart appreciably from the generalizing curve for all x and are not shown in Fig. 1.

We described the function f(x) satisfying the limit conditions on the critical isochor and the critical isotherm by the dependence

TABLE 2. Comparison of Experimental Values of the Anomalous Part of the Thermal Conductivity $\Delta\lambda(\rho, T)$ with the Values Calculated in Accordance with Variants I and II near the Critical Isochor

ω	T=304,35 °K			T=305,25 °K			T=307,95 °K			T=313,15 °K		
	expt.	I	II	expt.	I	II	expt.	I	II	expt.	I	II
0,88720	109,4	110,5	101,6	68,3	68,7	63,3	36,8	34,3	32,4	19,5	19,6	18,8
0,92945	183,5	194,0	180,7	82,1	77,5	73,7	38,8	36,1	34,9	20,1	20,5	20,1
0,97169	261,3	256,0	248,4	89,6	81,5	79,8	39,2	37,4	36,4	20,1	21,4	21,3
1,01394	276,4	259,8	259,1	87,1	81,3	81,5	37,9	37,3	37,3	19,6	21,5	21,8
1,05619	224,4	212,0	211,2	76,1	74,9	76,1	35,3	34,6	35,6	18,6	19,7	20,5
1,09844	126,3	120,9	123,3	60,9	65,6	67,4	31,4	31,7	33,3	17,3	18,0	19,3

$$\lg f(x) = \frac{\varphi}{2\beta}\left(\sqrt{\lg^2 x^\beta + c^2} - \lg x^\beta\right), \qquad (7)$$

where $\varphi = -0.6$ and $\beta = 0.35$. The dependence (7) holds for values of x for the range $\tau = 1.00$–1.03 and $\omega = 0.6$–1.4. The values of the fitting parameter c^2 on the isotherms were found by averaging the values calculated for each experimental point in the given range of densities and temperatures. It was found that the average values of c^2 on the isotherms increase with increasing temperature. Since it was not established in [5] by how much the accuracy of the approximation of the thermal conductivity is increased by the introduction into Eq. (1) of the function $\sqrt{\omega}$, we calculated the thermal conductivity of CO_2 in the critical region both with and without allowance for this function (variants I and II). The corresponding dependences of c^2 on the temperature are

$$c_{\mathrm{I}}^2 = -2.886 + 2.9203\tau, \qquad (8)$$

$$c_{\mathrm{II}}^2 = -2.240 + 2.2815\tau. \qquad (9)$$

In Fig. 1 we have plotted the curves f(x) calculated in accordance with formula (7) with allowance for the dependence (8), and in Table 1 we give the relative deviations of the calculated values of the thermal conductivity from the smoothed data of [1]. In connection with the error of Eqs. (8) and (9), the deviations in the neighborhood of the critical isochor for both variants differ from the deviations obtained on the critical isochor itself in the calculation of $\Delta\lambda(\rho_{cr}, T)$ in accordance with Eq. (2). Comparison of the experimental [1] and calculated values of the anomalous part of thermal conductivity shows (Table 2) that the slight displacement of the maxima of $\Delta\lambda(\rho, T)$ into the region of subcritical densities when the temperature is increased is not completely reflected when the function $\sqrt{\omega}$ is used. However, it can be seen from Table 1 that on all the isotherms the rms deviations $\delta\lambda_{av}$ for variant I are less than for variant II. Thus, the introduction of the function $\sqrt{\omega}$ increases the accuracy of the calculation of the thermal conductivity of carbon dioxide in the critical region. Although the limit condition $\Delta\lambda \to 0$ as $\omega \to 0$ is violated when the function $\sqrt{\omega}$ is used, this occurs in a region in which Eq. (1) does not hold.

Since it is difficult to determine from Fig. 1 the extent to which allowance for the stratification of the isotherms in the coordinates $\lg f(x)$ and $\lg x^\beta$ increases the accuracy in the description of the thermal conductivity data in the critical region, we also calculated the values of λ for a constant (for all isotherms) average value of the parameter $c_{\mathrm{III}}^2 = 0.057$. The corresponding deviations $\delta\lambda$ are given in the third column of Table 1, from which it can be seen that in this case the accuracy of the approximation is lower than for variant I.

On the basis of our analysis we can recommend Eq. (1) for the calculation of the thermal conductivity of a gas in the critical region for $|\tau-1| < 0.03$ and $|\omega-1| < 0.4$; in it the function f(x) is represented by the expressions (7) and (8) with $\varphi = -0.6$ and $\beta = 0.35$.

NOTATION

$\Delta\lambda(\rho, T)$	is the anomalous part of the thermal conductivity;
$\Delta\lambda(\rho_{cr}, T)$	is the anomalous part of the thermal conductivity on the critical isochor;
$\omega = \rho/\rho_{cr}$	is the reduced density;
$\tau = T/T_{cr}$	is the reduced temperature;
f(x)	is the function of the parameter x;
$x = \lvert\tau-1\rvert/\lvert\omega-1\rvert^{1/\beta}$	is the scaling parameter;
A	is the coefficient of proportionality;
φ	is the critical index of the thermal conductivity on the critical isochor;

β is the critical index of the coexistence line;

λ_{id} is the "ideal" thermal conductivity in the absence of anomaly;

c^2 is the fitting parameter.

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