THERMAL DIFFUSIVITY OF CARBON DIOXIDE IN THE NEAR CRITICAL REGION

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An interference method for measurement of thermal diffusivity of transparent media is described. Values of the thermal diffusivity coefficient for carbon dioxide in the near critical region are obtained.

At the present time there exists a great number of experimental studies on the coefficient of thermal diffusivity of various substances in the near critical region. But results obtained by various authors for one and the same substance are quite contradictory. This can be explained by the very difficulty of conducting experiments in the near critical region. Significant temperature instability of the substance studied in the critical state leads to rapid development of convection even with a low temperature gradient, while the absence of criteria to determine the conditions for development of convection complicates exclusion of convection effects from the measurements. It is thus necessary to employ new methods for studies in the near critical region, which permit reliable determination of the absence of convection in the layer studied.

The interference method employed in the present study makes possible visual control of the volume studied over the entire course of the experiment. The commencement of convection is determined from the form of the interference bands. The high sensitivity of the method permits measurements with very low temperature drops between the heater and the medium studied.

Using the shift of a polarization interferometer based on a Tepler IAB-451 shadow device [1, 2] measurements were made of the thermal diffusivity of carbon dioxide in the near critical region. The experimental technique proposed by Gustafsson [3] and employed earlier by the present authors [1, 2] was used.

The essence of the technique is that the substance to be studied, in which a planar heat source is situated, is located within a parallel light beam between the collimator and detector portions of the device. When the heater is switched on a nonstationary temperature field is formed about it, this field being depicted on the device screen in the form of interference bands parallel to the heater and moving away from it on both sides. If the band position is determined at various moments of time, the interferograms obtained (Fig. 1) may be used to calculate the coefficient of thermal diffusivity. The distances between three pairs of bands symmetric with respect to the heater are measured at various moments of time and a curve of the square of these distances versus time is constructed (Fig. 2). Each pair of bands forms a straight line in this diagram, which becomes curved when convection commences. All the straight lines intersect in one point, providing a time correction necessary because of lack of synchronization between the exposures and heater switch-on time. In the straight line segment $(2x)^2 = f(t)$ for a given moment of time the values x_1, x_2, x_3 are taken and substituted in the equation of [3]:

$$\operatorname{erfc}\left(\frac{x_1}{\sqrt{4at}}\right) + \operatorname{erfc}\left(\frac{x_3}{\sqrt{4at}}\right) - 2\operatorname{erfc}\left(\frac{x_2}{\sqrt{4at}}\right) = 0, \tag{1}$$

where x_1, x_2, x_3 are one half the distance between bands symmetric with respect to the heater (the indices denote the ordinal number of the band); t is time; and a is the coefficient of thermal diffusivity, determined from this equation.

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TABLE 1. Values of Coefficient of Thermal Diffusivity for Carbon Dioxide

P, bar	T, °K	$a \cdot 10^{-7}$, m^2/sec
$T = 304{,}33$ °K		
21,02	304,39	4,518
31,39	304,39	2,710
40,50	304,40	1,815
51,65	304,40	1,067
63,60	304,40	0,508
65,64	304,32	0,426
70,09	304,32	0,249
71,13	304,32	0,208
72,04	304,33	0,165
72,95	304,34	0,119
73,29	304,34	0,108
73,33	304,34	0,099
73,50	304,33	0,086
73,54	304,33	0,079
73,73	304,33	0,067
73,76	304,33	0,062
73,82	304,33	0,054
73,85	304,33	0,051
73,90	304,33	0,046
73,94	304,33	0,038
73,99	304,33	0,032
73,99	304,33	0,028
74,01	304,33	0,024
74,03	304,33	0,017
74,04	304,33	0,014
74,04	304,33	0,013
74,16	304,33	0,021
74,18	304,33	0,022
74,21	304,33	0,024
74,22	304,33	0,025
74,24	304,33	0,027
74,49	304,33	0,037
74,56	304,33	0,041
74,86	304,33	0,049
75,07	304,33	0,058
75,39	304,33	0,067
76,90	304,33	0,091
78,41	304,34	0,120
79,83	304,34	0,142
83,27	304,34	0,183
87,53	304,34	0.221
88,96	304,36	0,238
91,90	304,35	0,253
94,23	304,34	0,269
100,00	304,34	0,308
$T = 305{,}45$ °K		
32,04	305,39	2,675
40,68	305,39	1,852
49,99	305,40	1,204
52,88	305,43	1,046
57,62	305,44	0,804
64,30	305,46	0,513
69,43	305,44	0,319
71,59	305,43	0,238
72,11	305,43	0,217
81,94	313,14	0,250
83,24	313,14	0,218
85,08	313,15	0,167
86,46	313,15	0,138
89,41	313,14	0,101
73,19	305,44	0,165
73,82	305,45	0,138
74,18	305,45	0,120
74,78	305,47	0,083
74,96	305,45	0,070
75,14	305,44	0,061
75,63	305,45	0,040
75,44	305,45	0,031
75,49	305,45	0,026
75,54	305,45	0,020
75,58	305,45	0,019
75,64	305,45	0,021
75,71	305,45	0,025
75,84	305,46	0,030
75,96	305,45	0,035
76,15	305,45	0,041
76,30	305,45	0,047
76,63	305,44	0,052
77,12	305,45	0,064
78,00	305,43	0,082
78,88	305,44	0,104
80,47	305,44	0,131
$T = 307{,}87$ °K		
20,91	307,76	4,718
30,24	307,76	2,992
41,90	307,77	1,850
52,79	307,91	1,162
63,92	307,91	0,658
71,11	307,91	0,403
73,63	307,87	0.312
76,58	307,86	0,199
77,82	307,84	0,148
78,65	307,85	0,135
79,47	307,86	0,107
79,96	307,87	0,084
80,31	307,87	0,061
80,59	307,87	0,044
80,72	307,87	0,042
80,86	307,87	0,048
81,40	307,87	0,064
83,17	307,87	0,102
85,26	307,87	0,127
91,51	307,88	0,189
101,08	307,88	0,256
$T = 313{,}15$ °K		
22,45	313,18	4,528
31,65	313,18	3,004
40,61	313,18	2,102
49,36	313,18	1,503
62,18	313,17	0,897
71,12	313,17	0,565
73,33	313,16	0,498
76,61	313,15	0,406
78,58	313,13	0,348
91,28	313,15	0,087
93,65	313,16	0,092
97,02	313,14	0,117
99,64	313,14	0,145
103,51	313,18	0,183

The experimental apparatus, aside from the interferometer, consists of a measurement cell, precision thermostat, thermocompressor, gas purification system, and devices for measurement of temperature and pressure. The measurement cell is a brass cylinder with rectangular inner cavity through the center of which there extends a thin metallic foil which serves as a heater. Foil thickness is 0.01 mm, width 4 mm, length 160 mm. The height of the layer studied is 5 mm. The measurement cell is located within a brass cylinder whose end faces are formed of plano-parallel optical glass.

To maintain the required temperature a precision multilayer thermostat was constructed, as described in [4]. This thermostat permits maintenance of a constant temperature to an accuracy of $\pm 0.0005°$. In order to reduce the influence of the hydrostatic effect the tubes supplying gas to the measurement cell are installed horizontally within the range of the thermostat.

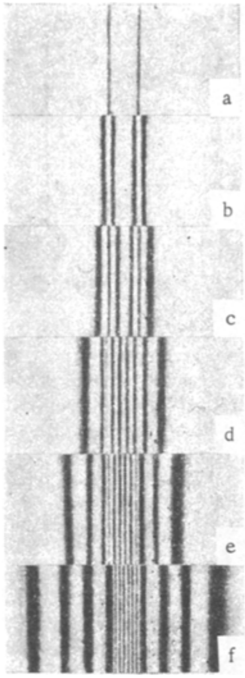

Fig. 1. Interferograms of time variation of temperature field: a) t = 0 sec; b) 0.3 sec; c) 0.6; d) 1.2; e) 1.8; f) 3 sec.

The carbon dioxide supplied to the cell was dried and purified by the method described in [5], which ensures a CO_2 content no less than 99.9%. Before final filling the entire system is washed several times with the gas to be studied.

The temperature of the gas was measured with a resistance thermometer made of type PL-1 chemically pure platinum, 0.1 mm in diameter.

Pressure was measured by a loaded piston manometer, type MP-600, accuracy class 0.05. All necessary corrections were made to the manometer reading.

The temperature field changes were recorded by a "Konvas" (KSR-1) motion picture apparatus, at a rate of three frames/sec.

Using this apparatus, control measurements were made of the thermal diffusivity of n-heptane, toluol, benzol [1], and carbon dioxide [2] far from the critical point. Comparison of the experimental data with that obtained from known λ, ρ, C_p taken from [6, 7] showed good agreement.

Thermal diffusivity of CO_2 in the near critical region was studied at isotherms of 304.33, 305.45, 307.87, 313.15, and 323.15°K in a pressure range of ~20 to ~125 bar. On the 304.33°K isotherm between 74.04 and 74.16 bar we did not succeed in determining the diffusivity because of convection, which developed practically instantaneously after heater switch-on. This is evidently due to the large height of the layer (5 mm). The value of ΔT in the minimum region did not exceed 0.03°. Upon approach to the critical point each experimental point was measured twice with different ΔT (temperature differences in the ratio 1.00:1.25). No significant discrepancies in thermal diffusivity coefficients were observed.

The experimental results presented in Table 1 reveal that the thermal diffusivity drops sharply upon approach to the critical point. The minimum diffusivity in the region studied occurs on the 304.33°K isotherm. With removal from the critical point in the direction of higher isotherms, the depth of the minima decreases, and the minimum points are displaced in the direction of higher pressures. Also, the decrease in the diffusivity value to the left of the minimum point is sharper than the increase to the right. On the 313.15 and 323.15°K isotherms this assymetry is less noticeable.

Figure 3 shows thermal diffusivity isotherms as a function of density. There exist several experimental studies of CO_2 density in the near critical region. The most detailed measurements were made in the Van der Waals laboratory by Michels et al. [8, 9]. These data were also used to construct the diffusivity curves in coordinates a–ρ. As is evident from the curves, the diffusivity minima on the isotherms studied do not coincide with the critical isochore, but are displaced in the direction of lower specific volume, with the amount of displacement increasing with removal from T_{cr} toward higher temperatures. The thermal diffusivity values obtained on the critical isochore are described by the function

$$a = (19.3 \pm 0.5) \cdot 10^{-10} (T - T_{cr})^{0.77 \pm 0.03} \text{ m}^2/\text{sec}. \tag{2}$$

Swinney and Cummins [10] measured the coefficient of thermal diffusivity of carbon dioxide at the critical isochore in the temperature range $0.02° \leq (T - T_{cr}) \leq 5.3°$ and obtained the function

$$a = (18.1 \pm 0.5) \cdot 10^{-10} (T - T_{cr})^{0.73 \pm 0.02} \text{ m}^2/\text{sec}. \tag{3}$$

It was also reported in [10] that Osmundsen and White measured the width of the Rayleigh line for CO_2 and obtained an exponent for Eq. (2) of 2/3, while Zeigel and Wilcox found the exponent to be 0.70 ±0.1.

It is known that not only the coefficient of thermal diffusivity, but certain other thermophysical parameters in the critical region are described by simple power expressions. Thus, for example, along the critical isochore the isothermal compressibility K_T for $T > T_{cr}$ is described by the function $K_T \sim [(T - T_{cr})/T_{cr}]^{-\gamma} \equiv \varepsilon^{-\gamma}$. The isochoric heat capacity C_V is described by the function $C_V \sim \varepsilon^{-\psi}$. Above the critical temperature on the critical isochore C_p varies in the same fashion as the isothermal compressibility, i.e., $C_p \sim \varepsilon^{-\gamma}$. Comparing data on λ and C_V, Sengers arrived at the conclusion that in the first approximation, on the critical isochore λ varies as does the isochoric heat capacity. The coefficient of thermal diffusivity then varies as $\varepsilon^{\gamma - \psi}$.

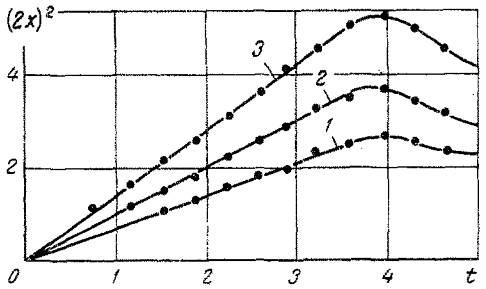

Fig. 2

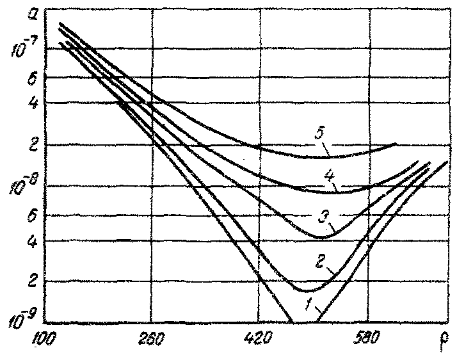

Fig. 3

Fig. 2. Interband distance versus time: 1) $(2x_1)^2 = f(t)$; 2) $(2x_2)^2 = f(t)$; 3) $(2x_3)^2 = f(t)$. x, mm; t, sec.

Fig. 3. Thermal diffusivity isotherms of CO_2 in the near critical region: 1) T = 304.33°K; 2) 305.45; 3) 307.87; 4) 313.15; 5) 323.15°K. a, m^2/sec; ρ, kg/m^3.

Sengers and Keyes [11], by processing experimental data for CO_2, arrived at a value $\psi = 0.60 \pm 0.05$, while theoretical considerations give 0.59 ± 0.10 [12]. For water, Sirota et al. obtained $\psi = 0.58$ [12]. Green et al. [13] analyzed experimental data on compressibility for various gases and concluded that $\gamma = 1.4$. Heller [14] found $\gamma = 1.35 \pm 0.15$ on the basis of a series of experiments with CO_2. From the data of these authors $0.75 \leq \gamma - \psi \leq 0.82$, which agrees with sufficient accuracy with the exponent obtained here of 0.77.

Thus, the results of the present measurements confirm that in carbon dioxide in the near critical region there is a significant increase in thermal conductivity.

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