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*THE THERMAL CONDUCTIVITY OF CARBON DIOXIDE IN THE REGION OF THE CRITICAL POINT**

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Communicated by Frederick G. Keyes, September 15, 1958

Introduction.—Thermal conductivity phenomena very close to the critical point of CO_2 have not been determined. Reported attempts either have completely skipped the region of most interest or are obviously in error. A new effort based on extensive analysis of the problem was undertaken with equipment exceptionally well suited to the rigorous treatment of the data from which the thermal conductivity can be obtained.[1]

Equipment.—The cell was of the massive concentric cylinder type with a uniform conductivity gap, d, of 0.06955 cm. along the vertical axis and at the bottom. Heat was supplied in a center well of the inner cylinder, and temperature differences were measured by Chromel-P Alumel thermocouples placed at the top and center of the cylinders. A heat guard at the top was brought to the same temperature as the inner cylinder, and thus heat loss along the thermocouple and heater wires was avoided. The thermocouples were calibrated in place against a platinum resistance thermometer contained in a thermostat bath regulated within ±0.001° C. All voltage measurements were made on an Eppley thermocouple potentiometer, which was carefully calibrated. Pressures were measured on a dead-weight gauge calibrated for the vapor pressure of CO_2 at 0° C., and they were controlled by a special regulator system to about 1 part in 100,000.

Theory.—The energy conducted across length, l, of the annulus, d, between two infinite concentric cylinders is

$$Q = \frac{2\pi K l \Delta T}{\ln r_2/r_1}.$$

The constant for the cell is obtained from this term and a similar term for the bottom,

$$Q = \frac{\pi r_1^2 K}{d}\Delta T,$$

together with two correction terms, one for the corner at the bottom, and another for the heat-guard gap. By the use of newly developed measurement techniques the cell dimensions were determined with such dependability that the cell constant can be specified within 0.1 per cent.

The problem of convection has been generally recognized by those measuring the thermal conductivity of dense gases. When a flat plate cell is used, it is assumed that no convection occurs if the hotter plate is placed horizontally above the colder, although data obtained in some cases suggest that this may not be true. In other cases, cells have been designed with very narrow annuli to reduce the effect of convection. There is also the criterion that the Grashof-Prandtl product, namely,

$$\text{Gr. Pr} = \frac{d^3 g \alpha \rho^2 c_p \Delta T}{\eta \quad K}, \text{ be less than 1,000.}$$

Here d is the annulus width, g is the acceleration of gravity, α is $-\left(\frac{1}{\rho}\frac{\partial \rho}{\partial T}\right)_p$, ρ is the specific gravity, c_p is the specific heat capacity at constant pressure, η is the viscosity, K is the thermal conductivity at low pressure, and ΔT is the temperature drop across the annulus.

In a more fundamental consideration of convection based on the work of Jones and Furry,[2] it can be shown that, for the annulus between two infinite coaxial cylinders, the ratio of heat transferred by convection to the conductivity is $(q/\Delta T)_{\text{conv}}/K = \frac{\pi \bar{r}}{720} \cdot \text{Gr. Pr}$ if $d/\bar{r} << 1$. The convection conduction takes place by laminar flow up to a value of Gr. Pr of about 12,000 and, if the temperature rise is not excessive so that the other factors are constant, is linear versus ΔT. Near the critical region, large convective effects are encountered, and they must be eliminated by extrapolation of the apparent thermal conductivity versus ΔT to zero ΔT. If the temperature rise becomes large enough, turbulent convection sets in, with a large increase in slope of the total conductivity versus ΔT, so that the extrapolation must be based on measurements made in the region below the onset of turbulence. As the critical temperature and density are approached closely, the allowable temperature rise becomes smaller. Ultimately, the conduction by laminar convection becomes very large, and the angle between the straight lines of the laminar and turbulent conductivities versus ΔT approaches 180°.

Experimental.—Duplicating the isotherms of the pVT measurements reported by Michels and Michels[3] (M and M) and Michels, Blaisse, and Michels[4] (M B and M), measurements were made on 99.99+ per cent pure CO_2 at average gas temperatures of 32.054°, 34.721°, 40,089°, and 75.260° C. at small density intervals around the critical point. Pressures corresponding to a given density were determined from the data of M and M, and M B and M. Two sets of triplicate measurements of the temperature drop for a preselected heat input were made for both the top and the middle thermocouple. Three different energy inputs were used, so that the temperature rises were in the ratio of 1:2:4. The total conductivities, corrected for asymmetric temperature distribution of the inner cylinder, were extrapolated to zero temperature rise. The loss of heat by radiation and through the supporting pins, determined by measurement of the heat transfer in a vacuum, was deducted to give the final net thermal conductivities.

Results.—Based on the work of M and M, M B and M, and Wentorf,[5] the value of $\rho = 0.474$ gm/cc was used for the critical density. The results in Table 1 are represented by the isotherms of Figure 1, giving the thermal conductivity versus density with special emphasis on the critical region. The values of the conductivity obtained from maximum temperature rises greater than $80\mu V$ (about 2° C.) are precise within 0.1 per cent, and extrapolate linearly within 0.1 per cent. It is expected that such extrapolated values have a total probable error of 0.2 or 0.3 per cent. However, the onset of turbulence occurs at low temperature rises (1–$8\mu V$, corresponding to 0.025°–0.20° C.) near the critical, and in fact, where a $1\mu V$ maximum temperature rise must be used, because of loss of precision and the merging of the two regions graphically, it is not clear that the turbulent region has been avoided. This is true in particular for the values at 32.054° C. and $0.400 < \rho < 0.550$. The maximum temperature rises used for the extrapolation are indicated in column 4 of Table 1. In column 5 the point at which turbulence arose is indicated.

TABLE 1

p (Atm.) (1)	ρ (gm/cc) (2)	$10^6 K$ I.T. cal cm^{-1} sec^{-1} deg^{-1} (3)	Max. ΔT (μV) (4)	Onset of Turb. ΔT (μV) (5)	Probable Error (Per Cent) (6)
		30.90° C. $dE/dT = 42.45\mu V$/deg			
2.18	0.0036	3.99	228	..	0.3
30.82	0.0651	4.60	128	..	0.3
57.62	0.161	6.37	67	80	0.4
		32.054° C. $dE/dT = 42.68\mu V$/deg			
72.51	0.300	12.6	6	7	1.5
74.29	0.400	31	1	..	5
74.49	0.450	57	1	..	5
74.56	0.476	70	2.3	..	5
74.62	0.500	49	1	..	5
74.99	0.550	28	1.7	2	5
75.90	0.600	21.5	2.6	3.5	3
79.67	0.650	19.4	7	..	2
		34.721° C. $dE/dT = 42.79\mu V$/deg			
78.18	0.400	20	4	5.3	5
79.13	0.474	25	4	..	5
80.46	0.550	19.6	8	..	2
		40.087° C. $dE/dT = 42.99\mu V$/deg			
85.81	0.400	15.1	6	..	1.5
88.91	0.474	16.5	2	..	3
91.85	0.550	17.5	9	10.5	1
		40.107° C. $dE/dT = 42.99\mu V$/deg			
124.9	0.737	19.7	32	40	0.5
195.2	0.840	23.14	95	..	0.3
		75.26° C. $dE/dT = 43.22\mu V$/deg			
150.7	0.474	13.00	40	45	0.5
178.2	0.575	15.48	38	50	0.3
300.0	0.770	20.68	..	..	..*

* Tentative.

By the development of special measuring techniques and extreme experimental precautions, it was possible even on the lowest temperature rises of $0.25\mu V$ to obtain a precision of ± 5 per cent (i.e., ± 0.0003° C.), and thus the data while not as good as could be wished, are significant. The uncertainty about the existence of turbulent convection for these measurements is unfortunate, but if there is error for this source, it is to cause the highest values of each isotherm to be too low.

Discussion.—Sellschopp,[6] Lenoir and Comings,[7] and Timrot and Oskolkova[8] have reported measurements of the thermal conductivities of dense CO_2 covering the range of densities considered in this research. However, only Lenoir and Comings have any measurements in the region of ρ_{crit}. Sellschopp's results, which agree quite well for $0 < \rho < 0.3$ and $0.7 < \rho < 0.9$, appear to reflect unextrapolated

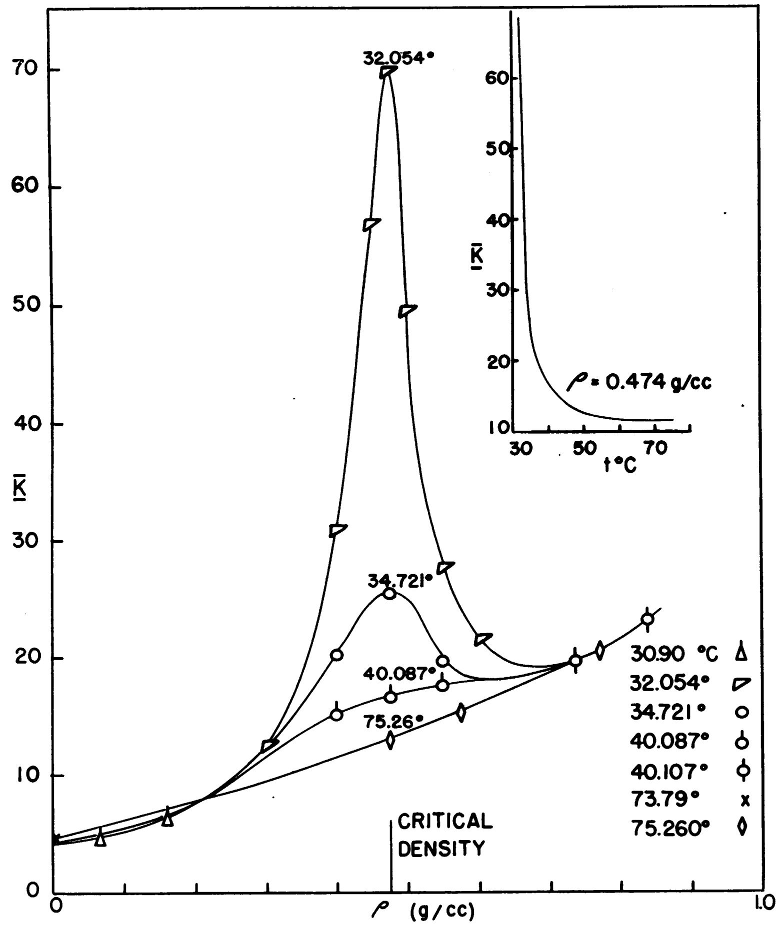

FIG. 1. Isotherms of the thermal conductivity of CO_2 versus density. $K = 10^5$ I.T. cal. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$, ρ = gm/cc.

convection in the range $0.575 < \rho < 0.7$ and at $\rho = 0.375$ and do not cover the region of higher interest, $0.375 < \rho < 0.575$. Lenoir and Comings measured the thermal conductivity at 41.11°, 56.67°, and 67.22° C. In the critical region their five points are scattered but are in approximate agreement with the 40.09° and 75.26° isotherms. Timrot and Oskolkova, measuring with a hot-wire cell having a very small surrounding tube (I.D. of 0.84 mm.), recognized the convection problem and made approximate corrections on certain of their density-temperature points.

As well as can be estimated, on their approach to the critical point (approximately 33° C. and 75 kg/cm², and 35.5° C. and 80 kg/cm²), they obtained a thermal conductivity of 11.1 cal cm^{-1} sec^{-1} deg^{-1} at $\rho = 0.28$ and 10.0 at $\rho = 0.33$. This agrees with the results obtained in this work within experimental error in the first case and is about 21 per cent low in the second case. No data fall within the range $32 < t < 40$ and $0.35 < \rho < 0.60$.

Summary.—By the control of convection through extremely careful experimental procedures, it has been shown that the thermal conductivity of carbon dioxide in the density range near the critical density of 0.474 gm/cc exhibits marked increases as the temperature of the critical point is approached from higher temperatures. The isotherms of thermal conductivity versus density are nearly symmetrical about the critical density, although some additional increase is observed on the low-density side. As can be seen in Figure 1 from the inset of the isometric of K versus t, the rate of increase of thermal conductivity with diminishing temperature at constant density, $-\left(\frac{\partial K}{\partial T}\right)_\rho$, suggests an extremely high, if not infinite, value of the thermal conductivity at the critical point itself. At temperatures higher than 40° C. above the critical temperature, the shape of the isotherm is nearly "normal," and at low and high densities the isotherms near the critical temperature behave in a normal fashion also.

A more extensive paper covering this material is in preparation and will be offered for publication shortly.

* This work was sponsored by Project SQUID, which is supported by the Office of Naval Research, Department of the Navy, under contract Nonr 1858(25) NR-098-038. Reproduction in full or in part is permitted for any use of the United States government.

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