MEASUREMENT OF THE THERMAL DIFFUSIVITY AND CONDUCTIVITY OF CARBON-DIOXIDE IN THE CRITICAL REGION BY HOLOGRAPHIC INTERFEROMETRY

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ABSTRACT

The thermal diffusivity and conductivity of carbon dioxide have been evaluated from the transient temperature field under a horizontal heated plate. The temperature distribution was made visible and photographed by holographic interferometry. Measurements were done on the isotherms of 25; 31.2; 32.1 and 34.8°C in the density range of $0.1<\varrho<1$ g/cm³. The results compare well with the measurements by Michels, Sengers and van der Gulik, obtained with a conventional parallel plate apparatus and show that the thermal conductivity has a pronounced maximum at the critical density. In the present work, however, convection, which has often been supposed to have caused the maximum, can be excluded as a result of the optical method used.

NOMENCLATURE

a	thermal diffusivity
A	$2\sqrt{a}$
B	$\lvert\partial n/\partial T\rvert\ q_{cd}\,\ell/\lambda\Lambda$
c_p	specific heat capacity
k	interference order
ℓ	length of the glass plate (heater)
n	refractive index
p	pressure
q_{cd}	heat flux density into the carbon dioxide
q_t	total heat flux density
t	time elapsed since starting the experiment
T	temperature
x	distance from the heating plate

Greek symbols

α	thermal expansion coefficient
ϑ	temperature rise compared with the homogeneous state at the beginning of the experiment
λ	thermal conductivity
Λ	wave length of the light
ϱ	density

Subscript

c	or kr for critical values

INTRODUCTION

Several measurements of the thermal conductivity of various gases in the critical region have been published during the last 20 years. These have all shown a pronounced maximum in the thermal conductivity at the critical density. Fig.1 shows the famous results of Michels, Sengers and van der Gulik for carbon dioxide (1). Table 1 gives a survey of the most important literature. The two oldest papers on this subject date from 1934 (2, 3) and from that time there have been doubts about the reliability of measurements in the critical region. The chief argument against the existence of a maximum is that it is caused by an additional heat transfer due to convection.

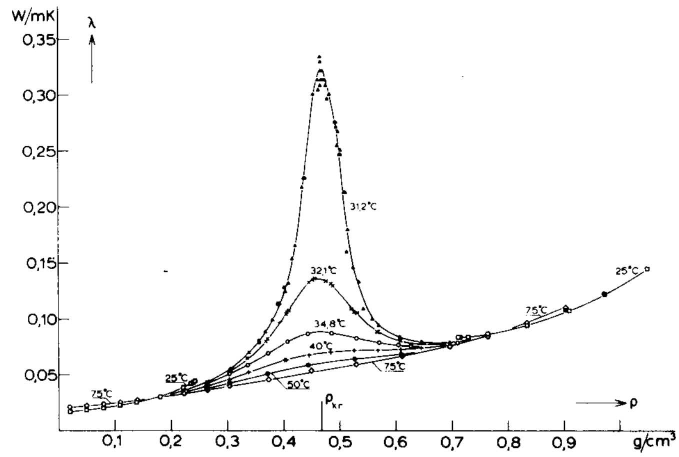

Fig.1 The thermal conductivity λ of CO_2 as measured by Michels, Sengers and van der Gulik (1).

Convection is induced by extremely small temperature differences in the critical region because the thermal expansion coefficient $\alpha=-(1/\varrho)(\partial\varrho/\partial T)$ tends to infinity as the critical point is approached (fig.2). Similarily the Grashof- and Rayleigh-numbers also tend to infinity at the critical point, although at different rates. The Grashof-number being a measure for the intensity of convection increases in proportion to 'α' whereas the Rayleigh-number being a measure for the transported heat increases quadratic in 'α'.

Year	Subst.	Authors	Apparatus
1934	CO_2	Kardos (2)	Hot wire
1934	CO_2	Sellschopp (3)	Cylinder
1958/62	CO_2	Guildner (4,5)	Cylinder
1962	CO_2	Michels, Sengers, van der Gulik (1)	Plates
1963	CO_2	Simon, Eckert (6)	Interferometer
1965	NH_3	Needham, Ziebland (7)	Cylinder
1965	SF_6	Lis, Kellard (8)	Cylinder
1967/68	Ar	Bailey, Kellner (9,10)	Cylinder
1968	He	Kerrisk, Keller (11)	Plates
1970	CO_2	Murthy, Simon (12)	Plates
1970	H_2	Roder, Diller (13)	Plates
1971	Xe	Tufeu, Le Neindre, Bury (14)	Cylinder
1973	H_2O,CO_2	Le Neindre, Tufeu, Bury, Sengers (15)	Cylinder
1974	Xe	van Oosten (16)	Plates
1976	H_2O	Sirota, Latunin, Beljaeva (17)	Plates

Table 1 Survey of the measurements of the thermal conductivity in the critical region.

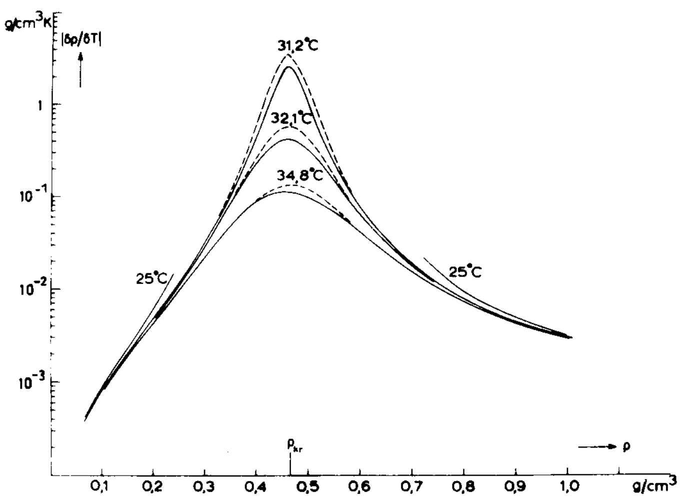

Fig.2 $\partial\varrho/\partial T$ of CO_2, solid lines: calculated from the equation of state of Meyer-Pittroff and Grigull (36, 37), broken lines: calculated according to the equation of Sengers et al. (27-30).

The different amplitudes of the maxima of several thermal conductivity measurements could be explained most easily by the assumption that convection had disturbed all the measurements but to different extents and that the thermal conductivity had no extremum at all (18). This argument could not be refuted experimentally by any of the previous workers in this field, because none of the classical measuring methods offers the opportunity of a direct check for convection.

THE OPTICAL METHOD

For our measurements we chose an optical method, which was initially used for the measurement of the thermal diffusivity and conductivity of water under normal pressure (19, 20) and which was refined so that it could be used in the critical region. Carbon dioxide was used for the experiments because very reliable thermodynamic data are available and because many of the earlier measurements were made on this substance.

The apparatus is described in detail elsewhere (21) and especially (22). The central part of it was a square horizontal heating-plate made of glass, the lower surface of which was polished flat to 0.5 μm and coated with a thin metallic film serving as a resistance-heater. The electric current was supplied via two evaporated gold strip electrodes.

One part of the heat delivered by the metallic layer after starting the electric current goes into the glass, the other goes into the carbon dioxide under the glass plate. Fig.3 shows the ratio of the heat flux going into the carbon dioxide to the total heat flux along the measured isotherms.

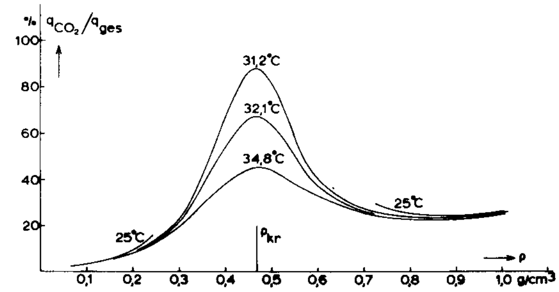

Fig.3 Ratio of the heat flux into the CO_2 to the total heat flux.

The transient temperature field, caused by the constant heat flux is made visible by interferometry, therefore it can be photographed. In order to compensate for optical inhomogeneities of the cuvette windows which bent under the internal pressure in the cuvette, we used a holographic interferometer which is described in (23).

In our experiments any convection would have resulted in characteristic changes in the temperature field. Looking at the interferograms it is very easy to distinguish whether convection was present or not. Thus we can be sure that our measurements were not disturbed by convection because there was never any indication of convection on the interferograms.

Fig.4 shows an interferogram of an experiment far from the critical point in the fluid region, fig.5 at almost critical density.

The heating plate is situated directly over the interference fringes, where the fringe density is greatest. The right hand corner shows the time elapsed since starting the heater. In the lower section of the picture a part of a precision-5 mm-scale is visible.

The optical method used has one further advantage compared with conventional measuring techniques which makes it especially suitable for the critical region: this is the fact that the primary measuring quantity in interfero-

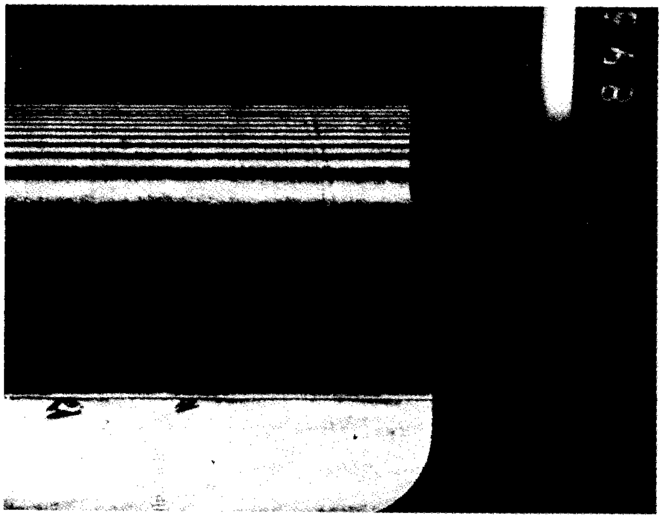

Fig.4 Interferogram of an experiment far from the critical point (T=32.112 °C, p=327.23 bar, ϱ =0.953 g/cm^3, t=8.96 s and q_t=13.45 mW/cm^2).

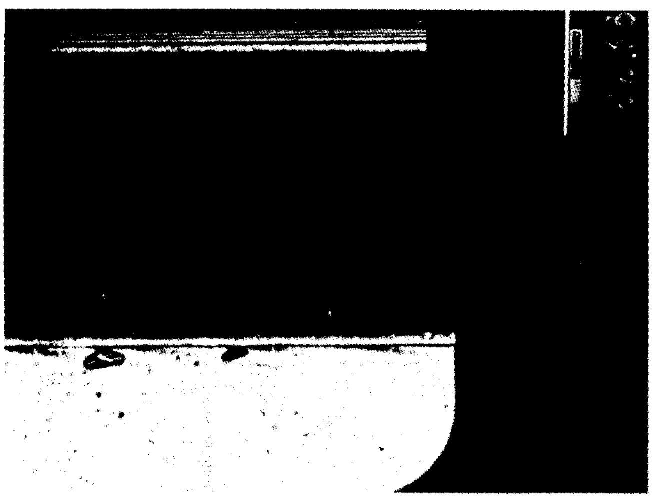

Fig.5 Interferogram of an experiment at almost critical density (T=32.081 °C, p=75.525 bar, ϱ =0.434 g/cm^3, t=22.36 s and q_t=0.113 mW/cm^2).

metry is a change in refractive index which is proportional to a change in density. Because $\partial\varrho/\partial T$ tends to infinity as one approaches the critical point (fig.2), the temperature difference between two neighbouring interference fringes becomes smaller and smaller. Fig.6 shows the temperature difference necessary to generate one fringe with our experimental set-up. The minimum temperature difference between two fringes is on the order of 10^{-5} K on the 31.2 °C-isotherm.

As a consequence of this effect the Grashof- and even the Rayleigh-number do not increase in our experiments when approaching the critical point, so that convection is no longer a serious problem. On the other hand temperature-control does become a serious problem because the temperature has to be homogeneous and constant to within about 10^{-6}K if 10^{-5}K generates one interference fringe. If this temperature criterion is not fulfilled you do not get a zero fringe field of sufficient quality before starting an experiment.

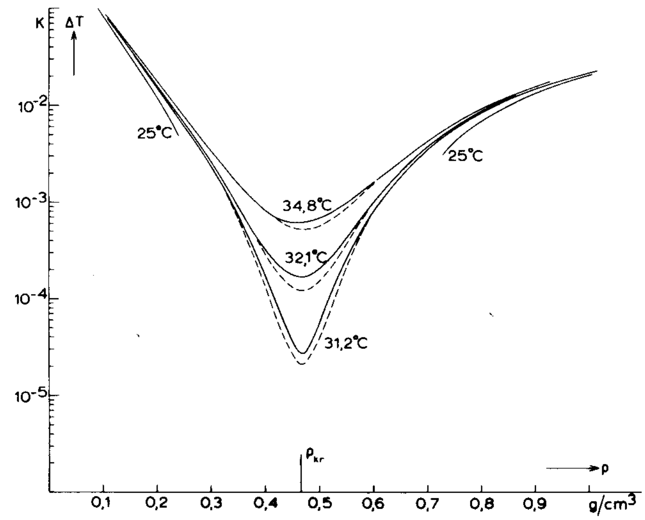

Fig.6 The temperature difference ΔT that caused one interference fringe with our experimental set up.

PROCESSING OF THE EXPERIMENTAL RESULTS

Transport properties such as thermal diffusivity and conductivity can be derived from interferograms only if a proper theory of the special transport process exists. If the heating times are sufficiently small one can regard our set-up as a combination of two semi-infinite bodies, one the glass plate and the other the carbon dioxide beneath it, separated by a heat source with constant flux density.The temperature field arising in the carbon dioxide is given by the theory of transient heat transport (24) as

$$\vartheta = (2q_{cd}/\lambda)\sqrt{at}\ \ \mathrm{ierfc}(x/2\sqrt{at}) \tag{1}$$

Several deviations from this ideal theory are discussed in (22).

The connection between the temperature rise and the observed interference fringe distribution is given by the so-called interferometer equation

$$k = |\partial n/\partial T|\vartheta \ell/\Lambda \tag{2}$$

Using the abbreviations

$$A = 2\sqrt{a} \tag{3}$$

and

$$B = |\partial n/\partial T|\ q_{cd}\ell/\lambda\Lambda \tag{4}$$

and inserting eq. (1) in (2)

$$k = AB\sqrt{t}\ \mathrm{ierfc}(x/A\sqrt{t}) \qquad (5)$$

As the maximum temperature differences were so small, the quantities A and B can be regarded as constants under all experimental conditions.

In order to obtain good statistics, several interferograms at different times were taken for each experiment. The distances x_i of the interference extrema from the heating plate were measured with a photometer with a precision of better than 1 μm. The two quantities A and B were then calculated by a least squares evaluation (25) from 100 to 250 pairs of k_i, x_i-values.

Equation (2) is derived on the assumptions of ideal interferometry which in principle can not be applied in our case, because the light rays are curved, especially in the critical region. To minimize the deviations from ideal interferometry we focussed on a special plane, the so-called ideal focussing plane which was calculated following (22,26). The remaining deviations and the density change with cuvette height (due to gravity) which occurs very close to the critical point were taken into account by calculating the light paths through the experimental cell and the optical path length for each extremum. This calculation procedure is also described in detail in (22, 26). It results in a correction of the observed interference field towards an ideal interference field, from which A and B were finally computed.

The quantity A yields the thermal diffusivity a directly; it is determined purely from the interference fringe distribution without need for any further assumptions. In particular there is no necessity for any caloric measurements (these were nevertheless performed for control purposes). In principle the thermal conductivity could be evaluated from B using eq. (4), but we found it more precise and straightforward to use the relation

$$\lambda = a \varrho c_p \qquad (6)$$

PURITY OF THE CARBON DIOXIDE AND CRITICAL DATA

The CO_2 used in the experiments was purchased from Buse, Bad Hönningen. The manufacturer guaranteed a purity of better than 99.994 vol%, the remainder being 97% nitrogen and 3% oxygen, the water content was stated as less than 1.4 ppm. The meniscus disappearance was used to measure the critical temperature $T_c = 30.994 \pm 0.003$ °C and the critical pressure $p_c = 73.765 \pm 0.005$ bar.

THE RESULTS

Fig.7 shows the four measured isotherms of the thermal diffusivity plotted against the density (tabulated results are given in (21, 22)). These isotherms were chosen to allow a direct comparison with the thermal conductivity measurements published by Michels, Sengers and van der Gulik (1) which seemed to be the most reliable thermal conductivity measurements using steady state techniques.

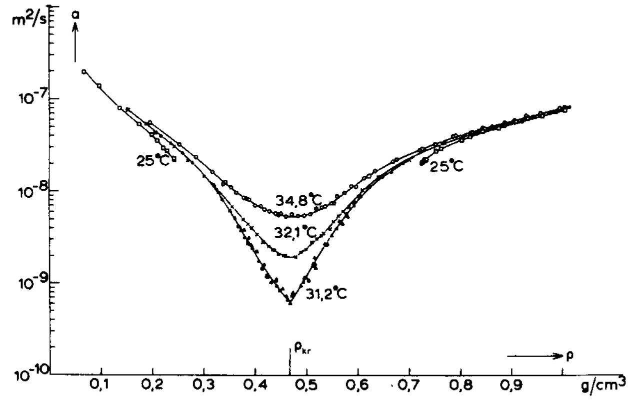

Fig.7 The measured isotherms of the thermal diffusivity of CO_2. The density in the critical region was calculated from the equation of Sengers et al. (27-30) outside of the critical region Meyer-Pittroff's equation (36, 37) was used.

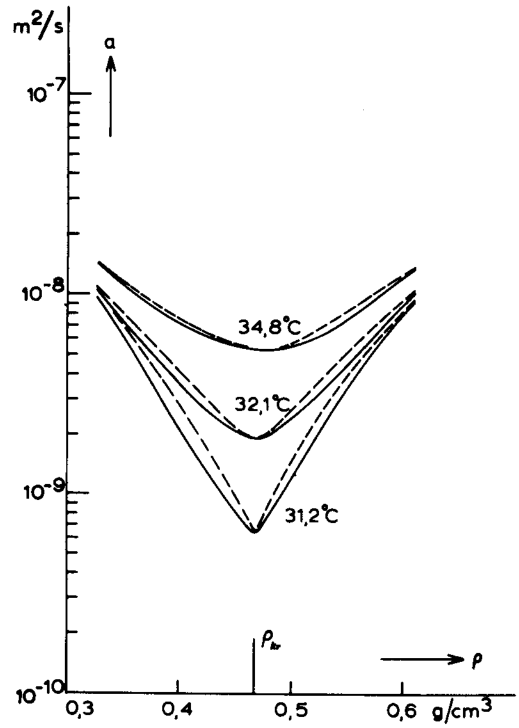

Fig.8 The thermal diffusivity of CO_2 in the critical region; Solid lines: density calculated from the equation of state of Sengers et al. (27-30), broken lines: density calculated from Meyer-Pittroff's equation (36, 37).

From our measured p,T-data (precision in p ±0.010 bar, in T ±0.003 K) we evaluated the density ϱ used to plot fig.7 by means of two equations of state. One was suggested by Sengers et al. (27-30) especially for the critical region. It is in accordance with the 'scaling laws' proposed by Widom (31) and Griffiths (32) and has a parametric formulation, proposed by Schofield, Ho and Litster (33-35). The range of validity is determined by $|\varrho-\varrho_c|/\varrho_c \leq 0.3$ and $|T-T_c|/T_c \leq 0.03$.

Outside of the critical region we used the general equation proposed by Meyer-Pittroff and Grigull (36, 37) which is valid for $203K < T < 1274K$, $p < 600bar$ and $\varrho < 1.25 g/cm^3$. The results of using this equation in the critical region are shown by the broken lines in fig.8. It is readily apparent that the isotherms of a p,v-surface, calculated from Meyer-Pittroff's equation, are inclined too steeply. The expansion coefficient (refer to fig.2), compressibility and specific heat capacity c_p (fig.9) are consequently too small in the critical region. On our isotherms the

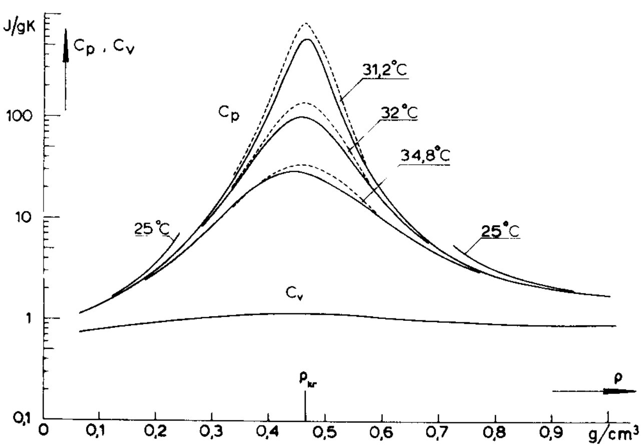

Fig.9 The specific heat capacity of CO_2. Solid lines: calculated from Meyer-Pittroff's eqation of state (36, 37), broken lines: according to the equation of Sengers et al. (27-30).

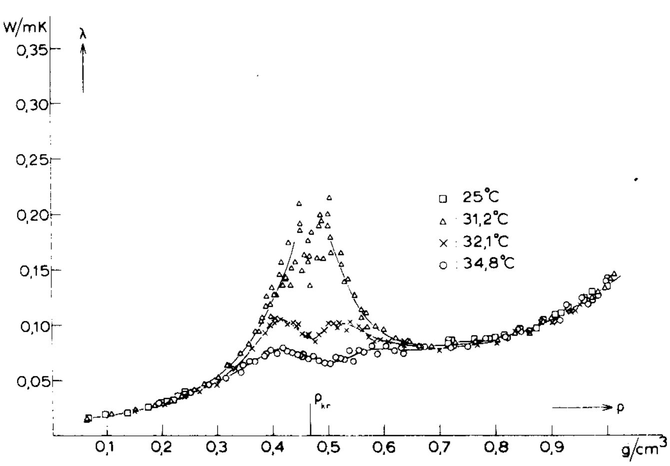

Fig.10 The thermal conductivity of CO_2 as calculated from our thermal diffusivity measurements using Meyer-Pittroff's equation of state (36, 37) for the evaluation of ϱ and c_p.

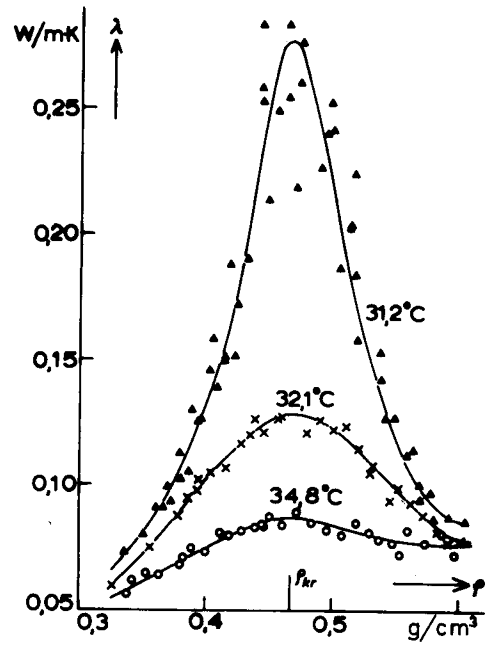

Fig.11 The thermal conductivity of CO_2 in the critical region as calculated from our thermal diffusivity measurements using the equation of state of Sengers et al. (27-30).

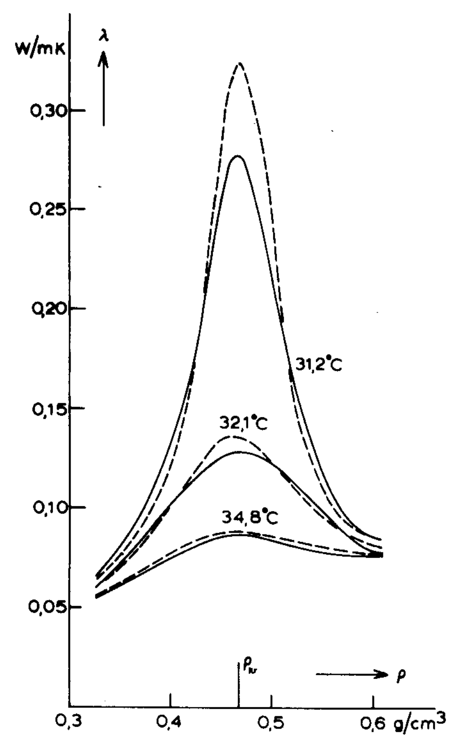

Fig.12 The thermal conductivity of CO_2 in the critical region. The solid lines represent our measurements (taken from fig.11), broken lines those of Michels, Sengers and van der Gulik (1) taken from fig.1.

maximum-deviations of these quantities range up to 50 %. In the critical region such deviations are characteristic for all 'analytic' equations of state with a wide range of validity. The defect of the Meyer-Pittroff equation in the critical region becomes especially distinct, if the thermal conductivity is calculated from our thermal diffusivity data via eq. (6). There is no physically reasonable explanation for the double maximum on the 32.1 and on the 34.8 °C-isotherms near the critical density (fig.10). There would also be a double maximum on the 31.2 °C-isotherm, but it is hidden by the scatter of the data points.

If the equation of Sengers et al. is used to convert the diffusivity data to thermal conductivity in the critical region a plot such as fig.11 results. The physically unreasonable double maximum has disappeared and a marked single maximum is formed. This shows that the peculiar aspect of fig.10 is caused by the shortcomings of the Meyer-Pittroff equation especially for the specific heat capacity in the critical region.

For the purpose of comparison, the isotherms of the thermal conductivity of fig.1 (Michels, Sengers and van der Gulik) and own results of fig.11 are redrawn together in fig.12. Bearing in mind that the thermal properties and in particular the specific heat capacity c_p, are not well known in the critical region, there is excellent agreement between the two sets of results. Furthermore we can be absolutely sure that our measurements were not disturbed by convection. We can therefore state that the maxima in the thermal conductivity at the critical point actually do exist.

All other measurements of the thermal conductivity of carbon dioxide cited in table 1 yield greater maxima than the ones of Michels, Sengers and van der Gulik. We believe this is due to convection and we will therefore not discuss these results further here.

Our values of the thermal diffusivity also compare well with light scattering measurements on the critical isochore (38) (fig.13). This not only verifies our results but also validates the assumptions and approximations used in their technique.

In 1974 Amirkanov, Usmanov and Norden published interferometric measurements of the thermal diffusivity of carbon dioxide (40). They used a differential interferometer (41) which required much greater temperature differences (minimum value: 0.03 K) than ours did and also used a vertical arrangement of the heater. Fig. 14 is taken from the original paper. Already at first glance it does not compare very well with our measurements. As the data table published in (40) did not contain any density data, we evaluated the density from the given p,T-data using the Meyer-Pittroff equation of state and generated the plot of fig.15. As is shown by fig.8 this plot would not look much different if the equation of state of Sengers et al. was used. We are not able to explain the differences between fig.14 and fig. 15. If the differences were caused solely by the use of a different equation of state to calculate

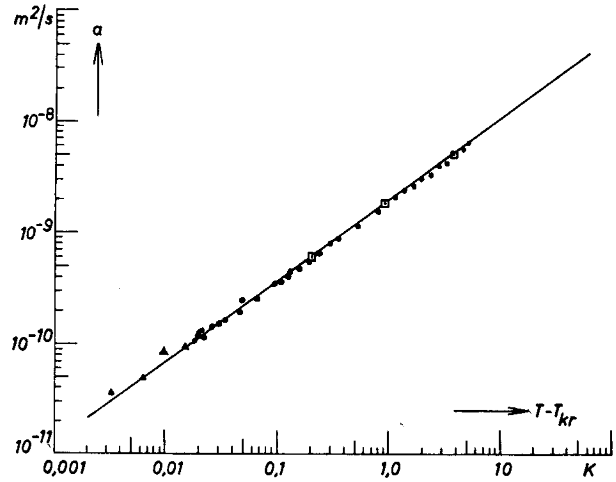

Fig.13 The thermal diffusivity of CO_2 along the critical isochore. •: light scattering measurements of Swinney and Cummins (38); ▲: light scattering measurements of Seigel and Wilcox (39) ◫: own experiments.

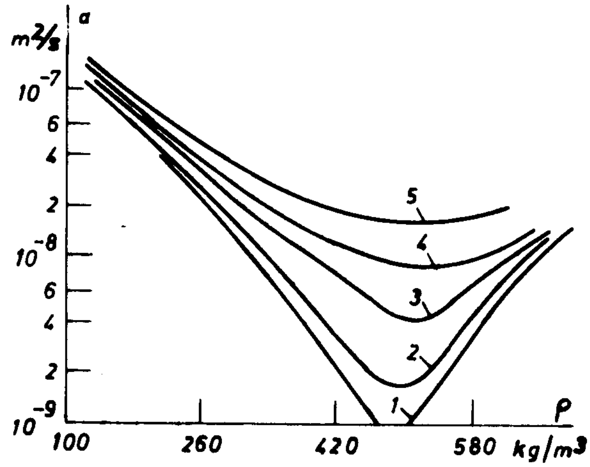

Fig.14 The thermal diffusivity of CO_2 as measured by Amirkanov, Usmanov and Norden (40). 1:31.18°C, 2:32.3°C, 3:34.72°C, 4:40°C, 5:50°C. This picture was taken from the original paper directly.

densities from measured p,T-data, the minima of the thermal conductivity would be expected to be shifted to one side or the other of the critical density ρ_c (ρ_{kr} in fig.15), but not to both sides. Furthermore the deviations of the minima from the critical density would be expected to increase as the critical temperature was approached. The data of the table in (40) seem to be smoothed and perhaps errors arose during their data evaluation.

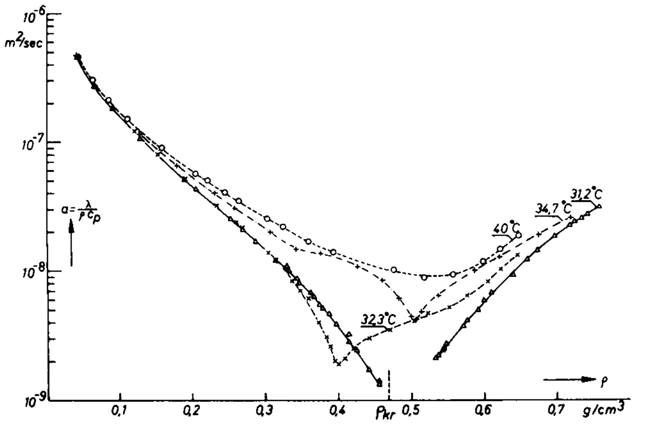

Fig.15 The thermal diffusivity of CO_2 as measured by Amirkanov et al. (40) after recalculation of the density.

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