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Isotherms in the Critical Regions of Carbon Dioxide and Sulfur Hexafluoride*†

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The p-v isotherms of carbon dioxide and sulfur hexafluoride have been measured in their critical regions at 0.02°C temperature intervals while the gases were observed and photographed. It was found that the liquid-vapor boundary curve has a nearly flat top; this renders the classical van der Waals picture of the critical region inadequate. Some slight evidence was found for an anomalous critical region as predicted by Mayer, but this region could be only 0.04°C high for sulfur hexafluoride and less than 0.02°C high for carbon dioxide. It was found that constant pressure is rapidly achieved in the critical region, but that constancy of fluid structure requires five or more hours. The results of these experiments agree well with those of MacCormack and Schneider for sulfur hexafluoride and those of Michels for carbon dioxide. The influence of gravity upon critical phenomena was found to be large. A brief discussion of its effects and corrections to be made on account of it are given.

INTRODUCTION

THERE are two ways to define the critical temperature of a pure substance: either as the temperature of meniscus disappearance, when the densities of liquid and vapor become equal, or, as the highest temperature for which $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ are simultaneously zero. (Here T is temperature, p is pressure, and v is the volume per gram.) The present study sought to determine whether these two methods of determining the critical temperature are equivalent. In many real systems the densities of liquid and vapor remain quite different until the fluid is within a few hundredths of a degree of the critical; with a further increase of temperature the densities suddenly approach each other rapidly. Thus the critical density and also $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ are difficult to determine accurately.[1–3]

A theoretical explanation of critical phenomena was proposed by J. E. Mayer and co-workers,[4] who suggested that an anomalous critical region existed between the temperature of meniscus disappearance and the simultaneous vanishing of $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$. Between these temperatures the critical fluid was regarded as consisting of giant clusters of molecules. Zimm and Mayer later criticized this theory.[5,6] Much

of the experimental critical data is imperfect because improper corrections were made for the effects of gravity; these are important because of the high compressibility of critical fluids. Recently Lorentzen,[7] and Weinberger and Schneider[8] have done some careful studies of the critical region, and Palmer[9] has turned gravity to his account in a sensitive examination of critical fluids by schlieren methods.

PRESENT EXPERIMENTAL WORK

In order to obtain accurate p-v-T data in the critical region and at the same time make visual observations on the confined substance, a heavy cylindrical steel cell was constructed bearing large plane glass windows permitting a field of view two inches in diameter. The volume of the cell was about 65 ml. The cell was supported in an oil thermostat by evacuated viewing tubes extending beyond the thermostat insulation. The thermostat fluctuated at most 0.002°C for 30 seconds away from the control temperature. Its average temperature could be held to 0.001°C for 24 hours and was measured with a platinum resistance thermometer. Mercury, supplied from a calibrated steel tube volumeter equipped with a moveable, insulated probe, transmitted the pressure of the substance in the cell and also afforded a measure of volume accurate to one part in 5000. Pressures were measured with a relative error of 1 mm of mercury on a piston and cylinder dead weight gauge. The gauge was calibrated using the vapor pressure data of carbon dioxide of Meyers and van Dusen.[10] A known weight of substance was loaded into the cell from a lightweight loading bomb. A solenoid actuated stirrer permitted stirring of the cell contents.

Drawings of the apparatus are shown in Figs. 1, 2, and 3.

The carbon dioxide used in this work was generated from reagent grade sulfuric acid and boiled sodium

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[1] Tapp, Steacie, and Maass, Can. J. Research **9**, 217 (1933); Winckler and Maass, *ibid.*, p. 613. Mason, Naldrett, and Maass, Can. J. Research **B18**, 103 (1940); Naldrett and Maass, *ibid.*, p. 118.

[2] Maass and Geddes, Phil. Trans. Roy. Soc. **A236**, 303 (1937). Dacey, MacIntosh, and Maass, Can. J. Research **B17**, 206, 241 (1939).

[3] Michels, Blaisse, and Michels, Proc. Roy. Soc. (London) **A160**, 358 (1937).

[4] Mayer and Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940); Mayer and Harrison, J. Chem. Phys. **6**, 87 (1938).

[5] B. H. Zimm, J. Chem. Phys. **19**, 1019 (1951).

[6] J. E. Mayer, J. Chem. Phys. **19**, 1024 (1951).

[7] Lorentzen, Acta Chem. Scand. **7**, 1335 (1953).

[8] Weinberger and Schneider, Can. J. Chem. **30**, 422 (1952).

[9] Palmer, J. Chem. Phys. **22**, 625 (1954).

[10] Meyers and van Dusen, J. Research Natl. Bur. Standards **10**, 381 (1933).
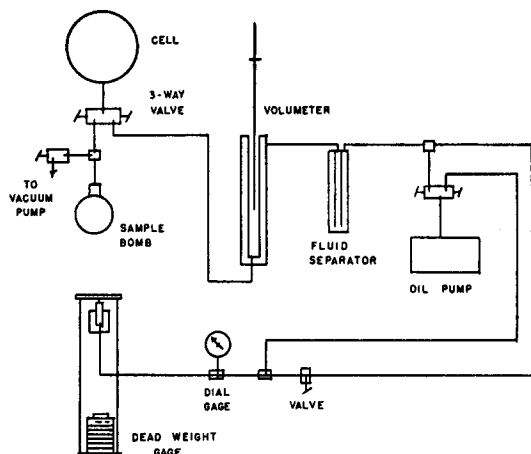
FIG. 1. Schematic diagram of apparatus.

bicarbonate solution, dried, and condensed into a steel storage cylinder. By absorbing 500 ml of the gas in 6N KOH the impurities were estimated to be 0.003%. This carbon dioxide gave a vapor pressure change of less than 1 mm of mercury between 10% liquid and 90% liquid at 16, 23, and 30°C. It was found that 99.9% medical carbon dioxide could not be further purified by repeated sublimation, presumably because impurities are adsorbed too tightly on the frozen gas.

The sulfur hexafluoride was purified by repeated distillation of the liquid, supplied as 99.9% by the Pennsylvania Salt Company. An infrared analysis of this material revealed no contamination. The purified product showed no detectable change of vapor pressure between 10% liquid and 90% liquid at 16 and 45.5°C.

PROCEDURE

The data were taken in the form of isotherms, always in the general direction of compression, since dibutyl phthalate adhering to the inner walls of the volumeter tube beneath the mercury could cause error in the volume readings if the data were taken in the expansion direction (mercury rising in the tube). When moving from one volume to another, the substance was slightly overcompressed and about ten minutes later slightly expanded. This hastened the attainment of equilibrium. About 50 minutes was usually allowed for the attainment of equilibrium at constant volume before measuring the pressure. (Constant pressure was usually reached in 30 minutes, but constant fluid structure was often attained only after as long as five hours near the critical volume and temperature.) The slight expansion usually formed a liquid phase; its remaining or disappearing helped determine the liquid-vapor boundary curve. It was found that stirring caused a slight pressure increase on account of the heating of the stirrer case by eddy currents. Pressure measurements made within 15 minutes after stirring were ignored. Photographs and visual observations of the cell contents were made at will. The determination of the maximum temperature

of meniscus disappearance was made after the isotherms had been determined. The substance was slightly expanded (to form a meniscus) to likely critical volumes at various temperatures, and the behavior of the system observed. Usually the meniscus would begin to blur in one hour if it were unstable.

ERRORS

The thick walls of the pressure cell reduced any short time (5 minutes) 0.002°C fluctuations in the thermostat fluid to less than 10^{-4}°C in the cell contents.

The average error in volumeter reading was about 0.003 ml as exhibited by its calibration curves; the error in the temperature corrections to the volume averages about 0.004 ml. Thus the volume is known on the average to about 1 part in 5000.

Errors in the measurement of pressure arise in the barometer reading, the reading of the heights of the liquid columns between the cell and the dead weight gauge, the temperature variation of the piston area of the gauge, and the sensitivity of the gauge. All these together give an uncertainty of about 1 mm of mercury.

Another error in pressure measurement arises from the extreme compressibility of the critical fluid.[11] Its density may vary by 20% between top and bottom of the cell, but to plot the isotherm one needs to know the pressure at that height in the fluid where the local density equals the average density of all the fluid in the cell.
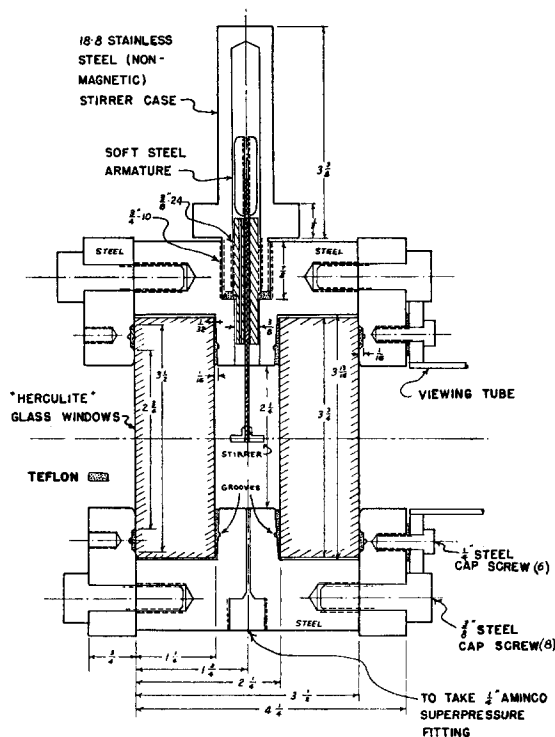

FIG. 2. Cell, center section.

[11] Schneider and Habgood, J. Chem. Phys. 21, 2080 (1953).

A general method for correcting for the effect of gravity on a compressible fluid is given here.

In a cell of height h whose cross-sectional area at height y is $A(y)$, let there be a fluid at uniform temperature in a gravitational field g. The pressure p depends on y by:

$$dp/dy = -g\rho(y) = -g\rho(p),$$

where $\rho(p)$ is the density, a function of p.

From the form

$$\int_{p_0}^{p} (dp/\rho_0(p)) = -gy, \qquad (1)$$

where $p = p_0$ at $y = 0$, and $\rho_0(p)$ is known approximately from experiment, one determines $p(y)$ and thence $\rho(y)$.

One would like to know the pressure at the point in the fluid where the local density equals the average density.

The average density is $\bar{\rho} = M/V$, where M is the total mass of the fluid and V is the volume of the cell.

Let the local density equal the average density at height $\bar{y}$.

In order to redistribute the fluid so that all the fluid would have the same density $\bar{\rho}$, one would remove a mass $(\rho_1 - \bar{\rho})A_1(\bar{y} - y_1)$ from the height interval under $\bar{y}$ and transfer it to the volume $A_1^1(y_1^1 - \bar{y})$ above $\bar{y}$. y_1^1 is determined by the equation

$$(\rho_1 - \bar{\rho})A_1(\bar{y} - y_1) = (\rho_1^1 - \bar{\rho})A_1^1(\bar{y} - y_1^1).$$

Similarly one could match the region $(y_1 - y_2)$ below $\bar{y}$ with the region $(y_2^1 - y_1^1)$ above $\bar{y}$.

Thus there would arise the set of equations

$$(\rho_n - \bar{\rho})A_n(y_{n-1} - y_n) = (\rho_n^1 - \bar{\rho})A_n^1(y_{n-1}^1 - y_n^1).$$

As we made the intervals $(y_{n-1} - y_n)$ smaller, the sum of each side of the equation would approach a limit and

$$\int_{\bar{y}}^{0} (\rho(y) - \bar{\rho})A(y)dy = \int_{\bar{y}}^{h} (\rho(y) - \bar{\rho})A(y)dy. \qquad (2)$$

Thus $\bar{y}$ is determined from (2), knowing $\rho(y)$ from (1). $p(\bar{y})$ is the pressure sought. Knowing $p(\bar{y})$, one can construct a first corrected isotherm, $\rho_1(p)$. From $\rho_1(p)$ one constructs a second corrected isotherm using (1) and (2). When $\rho_i(p) = \rho_{i+1}(p)$, the true isotherm is $\rho_i(p)$.

As h increases, each side of (2) increases, and the determination of $\bar{y}$ will be more uncertain, for $\bar{y}$ is determined by the difference between two large numbers. If h is large enough, the uncertainty in $p(\bar{y})$ will exceed the experimental uncertainty of $\rho_0(p)$, and no correction to the measured pressure is possible; i. e., the true isotherm is out of reach.

In the present work the effective cell height [where $A(y)$ is large] is about 5 cm, and the gravity pressure correction is at most 0.2 cm of mercury.
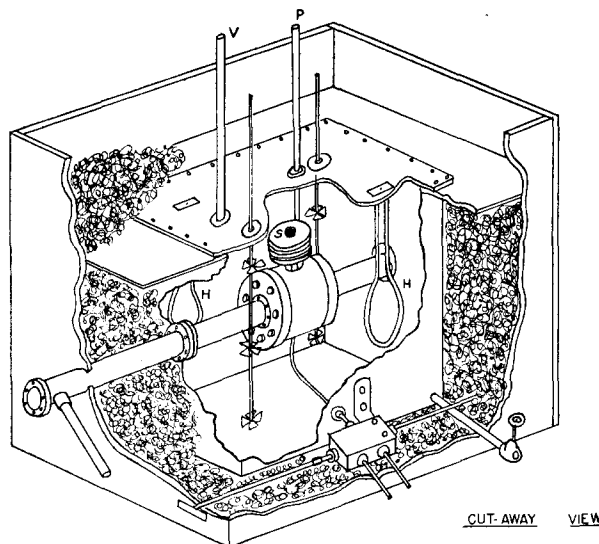

FIG. 3. Cut-away view of thermostat.

Dr. W. G. Schneider of the National Research Council, Ottawa, has called attention to the fact that oily substances can be dissolved from Teflon by critical fluids. The Teflon gaskets in this pressure cell were exposed to a wide variety of solvents as well as two fillings of liquid carbon dioxide in a period of nearly two months before the data of this paper were taken. Further, no traces of oil were found when the cell was dismantled after the experiments, so that it is not likely that the fluids studied were seriously contaminated.

PHENOMENA COMMON TO BOTH CARBON DIOXIDE AND SULFUR HEXAFLUORIDE

Perhaps the most striking property of critical fluids is their opalescence. The color of the confined gas, when viewed by transmitted light varies from a deep, smoky brown at volumes and temperatures very near to that of meniscus disappearance to a pale yellow at volumes and temperatures somewhat removed from the critical. Usually the gas is only faintly yellow at volumes corresponding to that of saturated liquid or saturated vapor at temperatures about 0.05°C above or below the temperature of meniscus disappearance. The intensity of the color is always enhanced by stirring. The color is the result of small-scale density fluctuations in the material which scatter the blue light more than the red.

It was found that the equilibrium pressure was usually reached in 30 minutes, but that equilibrium of fluid structure was achieved only after many hours near the temperature of meniscus disappearance. This is illustrated in the photographs. Stirring the substance by any method is not conducive to the attainment of equilibrium because any stirring adds energy to some parts of the fluid and not to others. It was found that a

TABLE I. Isotherms of carbon dioxide.

Specific volume ml/gram	Observed pressure cm Hg	Corrected pressure cm Hg	Corrected pressure atmos	Specific volume ml/gram	Observed pressure cm Hg	Corrected pressure cm Hg	Corrected pressure atmos
31.020°C				**31.040°C**			
2.554	5527.0	5526.9	72.723	2.095	5535.7	5535.6	72.837
2.504	5529.4	5529.3	72.754	2.087	5535.8	5535.7	72.838
2.447	5531.5	5531.4	72.782	2.056	5535.6	5535.5	72.837
2.394	5532.7	5532.6	72.798	2.026	5535.6	5535.5	72.835
2.355	5533.2	5533.1	72.804	1.989	5535.8	5535.6	72.837
2.308	5533.4	5533.4	72.807	1.982	5535.9	5535.7	72.839
2.267	5533.4	5533.4	72.808	1.981	5535.8	5535.6	72.837
2.230	5533.5	5533.4	72.808	1.916	5536.2	5536.1	72.844
2.185	5533.4	5533.3	72.807	1.906	5536.7	5536.6	72.850
2.142	5533.4	5533.3	72.807	1.878	5538.1	5538.0	72.869
2.080	5533.5	5533.4	72.808	1.873	5537.5	5537.4	72.861
2.019	5533.4	5533.3	72.807				
2.003	5533.6	5533.4	72.808	**31.060°C**			
1.926	5533.6	5533.4	72.808	2.479	5535.0	5534.9	72.828
1.925	5533.3	5533.1	72.805	2.388	5537.0	5536.9	72.854
1.881	5533.8	5533.7	72.812	2.324	5537.5	5537.4	72.861
1.853	5535.4	5535.3	72.833	2.249	5537.8	5537.7	72.865
1.850	5535.2	5535.1	72.831	2.248	5537.7	5537.6	72.864
				2.227	5537.6	5537.5	72.863
31.030°C				2.212	5537.9	5537.8	72.866
2.551	5528.7	5528.6	72.745	2.164	5538.1	5538.1	72.870
2.490	5530.9	5530.8	72.774	2.121	5538.1	5538.1	72.869
2.483	5531.7	5531.6	72.785	2.112	5538.0	5538.0	72.868
2.470	5532.0	5531.9	72.788	2.109	5538.3	5537.9	72.871
2.416	5533.3	5533.2	72.806	2.056	5538.2	5538.2	72.870
2.389	5533.8	5533.7	72.812	2.052	5538.2	5538.1	72.870
2.366	5534.3	5534.2	72.819	2.022	5538.1	5538.0	72.868
2.316	5534.3	5534.3	72.820	1.986	5538.2	5538.1	72.870
2.272	5534.5	5534.5	72.822	1.927	5539.2	5539.1	72.883
2.250	5534.4	5534.4	72.821	1.898	5539.9	5539.8	72.892
2.230	5534.6	5534.5	72.822	1.875	5541.7	5541.6	72.916
2.191	5534.3	5534.2	72.819				
2.172	5534.6	5534.5	72.822	**31.080°C**			
2.102	5534.8	5534.7	72.825	2.361	5538.8	5538.7	72.878
2.087	5534.7	5534.6	72.824	2.297	5539.5	5539.4	72.887
2.071	5534.8	5534.7	72.825	2.255	5539.6	5539.5	72.888
2.062	5534.7	5534.6	72.824	2.212	5539.9	5539.8	72.892
2.032	5534.8	5534.7	72.824	2.204	5539.8	5539.7	72.891
2.003	5534.5	5534.4	72.820	2.145	5540.2	5540.1	72.896
1.999	5534.7	5534.6	72.823	2.093	5540.4	5540.3	72.899
1.946	5534.7	5534.5	72.823	2.090	5540.6	5540.5	72.901
1.904	5534.8	5534.6	72.824	2.037	5540.6	5540.5	72.901
1.864	5536.7	5536.6	72.850	1.987	5540.9	5540.8	72.906
				1.953	5541.2	5541.1	72.910
31.040°C				1.865	5546.1	5546.0	72.974
2.615	5527.6	5527.5	72.731				
2.505	5532.3	5532.2	72.792	**31.100°C**			
2.485	5532.6	5532.5	72.796	2.401	5540.2	5540.1	72.896
2.391	5535.0	5534.9	72.828	2.320	5540.6	5540.5	72.902
2.384	5535.2	5535.1	72.831	2.268	5541.3	5541.2	72.911
2.332	5535.5	5535.5	72.836	2.224	5541.7	5541.6	72.916
2.324	5535.5	5535.5	72.836	2.165	5542.1	5542.0	72.921
2.278	5535.6	5535.6	72.837	2.116	5542.3	5542.2	72.924
2.267	5535.5	5535.5	72.836	2.097	5542.4	5542.3	72.925
2.257	5535.7	5535.7	72.838	2.037	5542.7	5542.6	72.929
2.204	5535.8	5535.8	72.839	1.994	5543.0	5542.9	72.933
2.172	5535.7	5535.6	72.837	1.945	5544.1	5544.0	72.948
2.110	5535.9	5535.8	72.840	1.919	5545.5	5545.4	72.966

meniscus formed several hundredths of a degree below the meniscus disappearance temperature can be easily obliterated by mild stirring; it is then several hours before the meniscus is again formed.

Lorentzen[7] has measured the rate of approach to equilibrium fluid structure of critical carbon dioxide.

Another property common to both gases is the persistence of density gradients above the temperature of meniscus disappearance. This is to be expected from the shape of the isotherms. Photographs reveal that these gradients are stable and reproducible. In several cases two photographic negatives could be exactly superimposed if they were both taken at the same volume and temperature, though the substance had undergone volume and temperature changes between the exposing of the two.
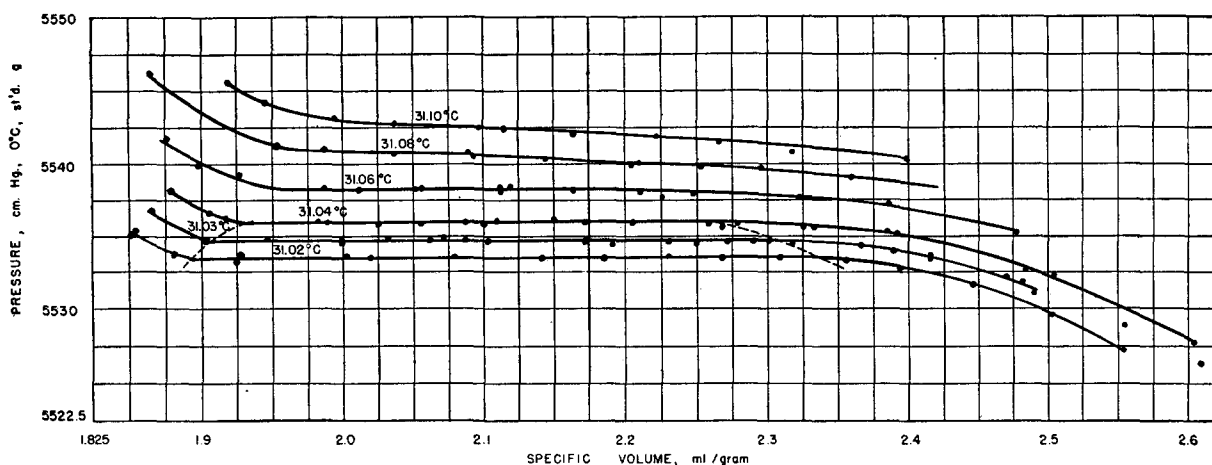
Fig. 4. Isotherms of carbon dioxide.

RESULTS

A. Carbon Dioxide

The observed and corrected pressures and volumes for the isotherms have been tabulated in Table I and the corrected pressures have been plotted against volume in Fig. 4. Pressures are expressed in centimeters of mercury at 0°C and standard gravity. The corrected pressure represents the pressure in the fluid where the local density equals the over-all measured density. Volumes are in milliliters per gram. The maximum temperature of meniscus disappearance was found to be 31.045°C. (See Table II.) The isotherm at 31.06°C seems to have a portion exhibiting $(\partial p/\partial V)_T$ zero or nearly zero in the volume range 1.96 to 2.16 ml per gram. The isotherms at 31.080 and 31.100°C definitely show no part having $(\partial p/\partial V)_T$ zero.

A plot of the minimum $(\partial p/\partial V)_T$ vs the temperature is shown in Fig. 5, where p is in centimeters of mercury and v is in milliliters per gram. The values of $(\partial p/\partial V)_T$ were estimated from the plots of the isotherms; the short bars indicate the probable range of error expected in the estimation of this quantity. The plot also shows a single point at 31.185°C which was estimated from the data of Michels, Blaisse, and Michels.[3] It is seen that it is possible to make a linear extrapolation to $(\partial p/\partial V)_T=0$ at 31.045°C, the temperature of meniscus disappearance, without exceeding the estimated errors. On the other hand, it is also possible to extra-

polate to $(\partial p/\partial V)_T=0$ at 31.055°C, as shown by the dashed line.

The critical density seems to be about 0.474 gram per ml at 31.045°C, and about 0.48 gram per ml at 31.060°C where $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ are both zero or nearly zero. The corresponding critical pressures are 5536.0 cm Hg (72.842 atmos) at 31.045°C, and 5538.1 cm Hg (72.870 atmos) at 31.060°C.

Some of the more interesting photographs are shown in Figs. 6 and 7. These are views through the fluid of a number of lines ruled at 45° on a piece of paper. A vertical displacement of an interline space corresponds to a density gradient of about 0.007 gram ml⁻¹ cm⁻¹.

B. Sulfur Hexafluoride

The observed and corrected pressures and volumes for the isotherms have been tabulated in Table III and plotted in Fig. 8. Pressures are expressed in cm of mercury at 0°C and standard gravity. Volumes are in ml per gram. The maximum temperature of meniscus disappearance was found to be 45.642°C. The isotherms at 45.662 and 45.682°C seem to have portions exhibiting $(\partial p/\partial V)_T=0$ over the volume ranges 1.24 to 1.5 and 1.26 to 1.4 ml per gram, respectively.

TABLE II. Comparison of critical constants obtained in this work with those of Michels[3] and Meyers and Van Dusen.[10]

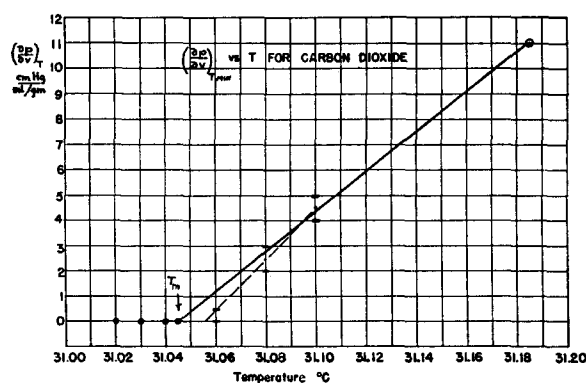| | Carbon dioxide | | |
	Critical temperature °C	Critical pressure atmos	Critical density grams/cm³
Michels	31.04₀	72.85	0.467
Meyers and Van Dusen	31.04₀	72.87	...
This work:			
meniscus disappeared	31.04₅	72.839⁺	0.474
$(\partial p/\partial V)_T=(\partial^2 p/\partial V^2)_T=0$	31.06₀	72.870	0.48

Fig. 5. Minimum $(\partial p/\partial V)_T$ vs T for carbon dioxide.

TABLE III. Isotherms of sulfur hexafluoride.

Specific volume ml/gram	Observed pressure cm Hg	Corrected pressure cm Hg	Corrected pressure atmos	Specific volume ml/gram	Observed pressure cm Hg	Corrected pressure cm Hg	Corrected pressure atmos
45.52₂°C				45.68₂°C			
1.6658	2816.0	2815.8	37.051	1.6449	2827.0	2826.8	37.195
1.6040	2818.2	2818.1	37.080	1.6159	2828.0	2827.8	37.209
1.5850	2818.5	2818.5	37.086	1.5812	2828.7	2828.5	37.218
1.5477	2818.4	2818.3	37.083	1.5510	2828.9	2828.7	37.220
1.4998	2818.5	2818.4	37.085	1.5224	2829.0	2828.8	37.222
1.3250	2818.5	2818.3	37.084	1.4882	2829.3	2829.2	37.226
1.2155	2818.6	2818.3	37.084	1.4570	2829.2	2829.1	37.225
1.1657	2819.6	2818.7	37.098	1.4266	2829.4	2829.3	37.226
				1.3893	2829.4	2829.2	37.227
45.62₂°C				1.3595	2829.4	2829.2	37.227
1.6659	2822.4	2822.2	37.135	1.3286	2829.4	2829.2	37.227
1.6326	2823.7	2823.5	37.152	1.2986	2829.4	2829.2	37.227
1.5977	2824.6	2824.4	37.164	1.2642	2829.4	2829.2	37.226
1.5632	2825.5	2825.4	37.176	1.2351	2829.5	2829.3	37.228
1.5182	2825.5	2825.4	37.176	1.2064	2829.9	2829.7	37.234
1.4934	2825.5	2825.4	37.177	1.1778	2830.7	2830.5	37.244
1.3447	2825.5	2825.3	37.176				
1.2470	2825.6	2825.4	37.176	45.70₂°C			
1.1944	2825.8	2825.6	37.180	1.6550	2827.2	2827.0	37.198
1.1751	2826.2	2826.1	37.185	1.6256	2828.8	2828.6	37.209
1.453	2827.8	2827.6	37.206	1.5954	2829.7	2829.5	37.231
1.1185	2831.2	2831.0	37.251	1.5665	2830.3	2830.1	37.238
				1.5307	2830.3	2830.1	37.239
45.64₂°C				1.4995	2830.4	2830.2	37.240
1.6587	2824.0	2823.8	37.156	1.4672	2830.4	2830.2	37.240
1.6190	2825.3	2825.1	37.173	1.4348	2830.5	2830.3	37.241
1.5772	2826.2	2826.0	37.185	1.4005	2830.6	2830.4	37.243
1.5483	2826.7	2826.7	37.193	1.3676	2830.6	2830.4	37.243
1.5142	2826.7	2826.6	37.193	1.3345	2830.7	2830.5	37.244
1.4892	2826.7	2826.6	37.192	1.3021	2830.8	2830.6	37.245
1.4593	2826.6	2826.5	37.191	1.2695	2830.9	2830.7	37.247
1.4261	2826.7	2826.6	37.192	1.2349	2831.1	2830.9	37.249
1.3912	2826.7	2826.6	37.191	1.2049	2831.6	2831.4	37.256
1.3577	2826.7	2826.5	37.191	1.727	2832.7	2832.5	37.270
1.2872	2826.8	2826.6	37.192	1.1445	2833.6	2833.4	37.282
1.2536	2826.8	2826.6	37.192				
1.2278	2826.8	2826.5	37.192	45.77₂°C			
1.1987	2826.9	2826.7	37.194	1.6605	2829.2	2829.0	37.224
1.1679	2827.9	2827.7	37.207	1.6257	2830.0	2829.8	37.235
				1.5915	2831.2	2831.0	37.251
45.66₂°C				1.5565	2831.6	2831.4	37.256
1.6713	2824.6	2824.4	37.164	1.5228	2831.8	2831.6	37.258
1.6372	2826.0	2825.8	37.182	1.4877	2831.9	2831.7	37.260
1.5806	2827.5	2827.3	37.202	1.4537	2832.1	2831.9	37.262
1.5497	2828.0	2827.8	37.209	1.4190	2832.3	2832.1	37.265
1.5178	2827.9	2827.8	37.208	1.3852	2832.4	2832.2	37.266
1.4889	2828.0	2827.9	37.210	1.3512	2832.4	2832.2	37.266
1.4632	2828.0	2827.9	37.210	1.3156	2832.4	2832.2	37.266
1.4331	2828.0	2827.9	37.210	1.2939	2832.6	2832.4	37.269
1.3725	2828.0	2827.8	37.209	1.2590	2832.8	2832.6	37.271
1.3549	2827.9	2827.8	37.208	1.2180	2833.2	2833.0	37.277
1.3256	2827.9	2827.7	37.208	1.1896	2834.0	2833.8	37.287
1.2937	2828.1	2827.9	37.210	1.1573	2835.8	2835.6	37.311
1.2611	2828.1	2827.8	37.209				
1.2197	2828.2	2828.0	37.210				
1.1907	2828.7	2827.5	37.218				
1.1564	2829.8	2829.6	37.232				

A plot of the minimum $(\partial p/\partial V)_T$ versus the temperature is given in Fig. 9, where p is in cm of mercury and v is in ml per gram. The values of $(\partial p/\partial V)_T$ were estimated from the plots of the isotherms; the short bars indicate the probable range of error expected in the estimation of this quantity. The plot also shows a single point at 45.800°C estimated from the data of MacCormack and Schneider[12] after correcting their

measured pressures for the effect of the vapor head as described later. It is seen that a straight line extrapolation to $(\partial p/\partial V)_T=0$ intersects the temperature axis at about 45.68°C, in agreement with the appearance of the isotherms.

The critical density seems to be about 0.725 gram/ml at 45.64°C and 0.74 gram/ml at 45.68°C where $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ are both zero. The critical pressure at 45.64°C is 2826.7 cm Hg (37.193 atmos) and at 45.68°C is 2829.4 cm Hg (37.229 atmos).

[12] MacCormack and Schneider, Can. J. Chem. 29, 699 (1951).

FIG. 6. Carbon dioxide at 31.049°C and 2.15 ml/gram. Constant p,v,T for 17 hours. This is just 0.004°C above the meniscus disappearance temperature.
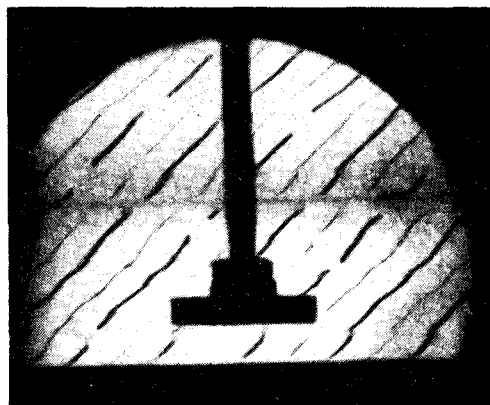

FIG. 7. Carbon dioxide at 31.042°C and 2.15 ml/gram. Constant p,v,T for 10 hours. This is just 0.003°C below the meniscus disappearance temperature. Note the opalescent fuzziness above and below the meniscus.

Some of the photographs of sulfur hexafluoride are presented in Figs. 10 and 11.

An extensive study of the critical region of sulfur hexafluoride has recently been made by MacCormack and Schneider.[12] The results of their experiments are compared with the results of this work in Table V. They confined various weights of the substance in a long (20 cm) vertical thermostatted glass tube and measured the pressure at the top of the tube. The substance was vigorously stirred by means of a solenoid and glass-encased armature. Temperature was measured with a platinum thermometer; pressure with a dead-weight gauge. The results of their experiments are tabulated in Table IV A. They found the temperature of meniscus disappearance to be 45.55°C, with stirring, contrasted to the 45.64°C of this paper (no stirring). On account of the rather long tube which they used, the effect of gravity is to make $(\partial p/\partial V)_T$ more negative for the observed isotherm than for the true isotherm. MacCormack and Schneider corrected for the effect of gravity in one of two ways, depending upon whether one or two phases were present in their

tube. Below the meniscus disappearance temperature they applied a correction to the measured pressures proportional to half the height of the tube times the average density of the fluid when only one phase was present, and proportional to the height of the vapor column times its density when both liquid and vapor were present. Above the meniscus disappearance temperature they applied a correction proportional to half the height of the tube times the average fluid density. The pressures corrected in this manner appear beside their observed pressures in Table IV A.

We took the liberty of applying the same pressure correction to their isotherms from 45.500 to 45.800°C as was applied to their liquid-vapor isotherm at 45.500°C. These corrected pressures are tabulated in Table IV B. It is seen that these corrected isotherms display parts having $(\partial p/\partial V)_T$ zero for 45.550 and 45.600°C, with 45.680°C doubtful, and $(\partial p/\partial V)_T$ definitely nowhere zero at 45.800°C. This is in good agreement with the results of our experiments. The value of $(\partial p/\partial V)_T$ at 45.800°C as thus obtained is plotted with our values in Fig. 9. We found that it
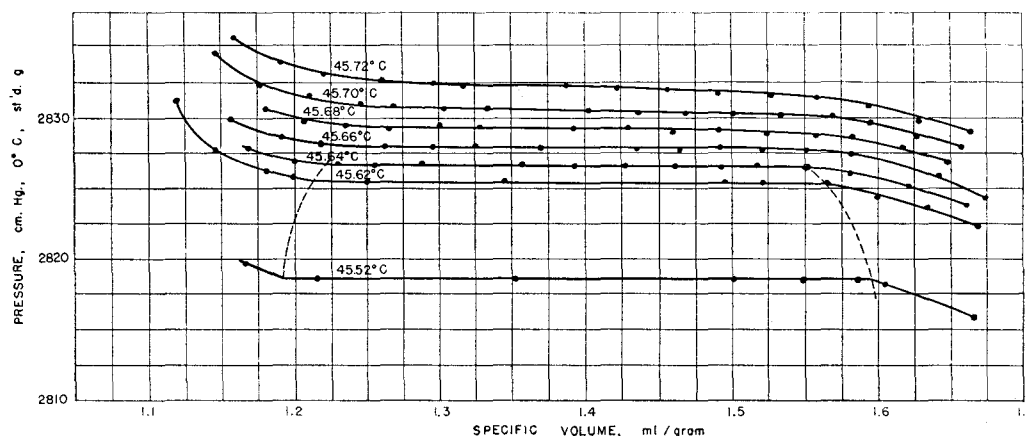
FIG. 8. Isotherms of sulfur hexafluoride.

TABLE IV A. Partial tabulation of the data of MacCormack and Schneider in the critical region
of sulfur hexafluoride.[12]

Specific volume cm³/gram	45.500°C Pressure, atmos		45.550°C Pressure, atmos		45.600°C Pressure, atmos	
	Measured	Corrected	Measured	Corrected	Measured	Corrected
1.183	37.095	...	37.142	37.157	37.188	37.203
1.188	37.088	...	37.137	37.152	37.180	37.195
1.221	37.073	...	37.118	37.133	37.164	37.179
1.221	37.070	...	37.116	37.131	37.162	37.177
1.263	37.064	37.070	37.107	37.121	37.147	37.161
1.318	37.064	37.073	37.105	37.119	37.147	37.161
1.379	37.059	37.072	37.099	37.112	37.141	37.154
1.438	37.059	37.074	37.099	37.111	37.139	37.151
1.490	37.058	37.075	37.096	37.108	37.135	37.147
1.556	37.049	...	37.086	37.097	37.124	37.135
1.604	37.038	...	37.073	37.084	37.110	37.121

Specific volume cm³/gram	45.680°C Pressure, atmos		45.800°C Pressure, atmos		46.000°C Pressure, atmos	
	Measured	Corrected	Measured	Corrected	Measured	Corrected
1.183	37.262	37.277	37.375	37.390	...	...
1.188	37.254	37.269	37.366	37.381	...	...
1.221	37.234	37.249	37.342	37.357	...	...
1.221	37.231	37.246	...	...	37.517	37.532
1.263	37.219	37.233	37.322	37.336	37.496	37.510
1.318	37.213	37.227	37.313	37.327	37.481	37.495
1.379	37.208	37.221	37.304	37.317	37.469	37.482
1.438	37.201	37.213	37.297	37.309	37.455	37.467
1.490	37.196	37.208	37.289	37.301	37.444	37.456
1.556	37.184	37.195	37.273	37.284	37.421	37.432
1.604	37.166	37.177	37.252	37.263	37.397	37.408

TABLE IV B. Data of MacCormack and Schneider, corrected to apparent meniscus height as described in the discussion.

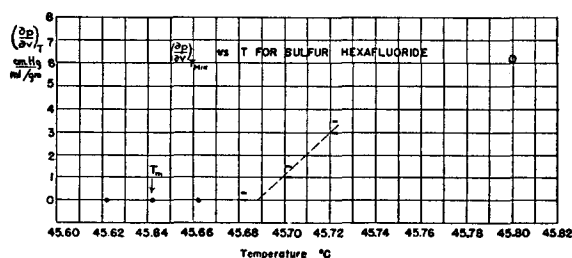| Specific volume cm³/gram	Pressure, atmos, corrected					
	45,500°C	45.440°C	45.600°C	45.680°C	45.800°C	46.000°C
1.183	37.100	37.157	37.203	37.277	37.390	...
1.188	37.093	37.152	37.195	37.269	37.381	...
1.221	37.088	37.133	37.179	37.249	37.357	...
1.221	37.085	37.131	37.177	37.246	...	37.532
1.263	37.070	37.113	37.153	37.225	37.328	37.502
1.318	37.073	37.114	37.156	37.224	37.322	37.490
1.379	37.072	37.112	37.154	37.221	37.317	37.482
1.438	37.074	37.114	37.154	37.216	37.312	37.470
1.490	37.075	37.113	37.152	37.213	37.306	37.461
1.556	37.061	37.097	37.135	37.195	37.284	37.432
1.604	37.049	37.084	37.121	37.177	37.263	37.408

was easy to destroy the meniscus of SF_6 by stirring at 45.60°C, and believe that the slow return to equilibrium of systems in the critical region caused MacCormack and Schneider to interpret 45.55°C as the meniscus disappearance temperatures in their stirred system. This fact also helps explain the discontinuity at the

meniscus disappearance temperature which they found in their plot of $(\partial p/\partial V)_T$ versus the temperature.

TABLE V. Comparison of critical constants obtained in this work with those of MacCormack and Schneider,[12] and Atack and Schneider.[a]

	Sulfur hexafluoride				
	Critical tempera- ture °C	Critical pressure atmos	Critical density grams/cm³	Vapor pressure Tempera- ture °C	Atmos
McCormack and Schneider	45.547	37.113	0.73	45.500	37.073
Atack and Schneider	45.555	...	0.7517		
This work: meniscus disappeared	45.64₂	37.193	0.725	45.500	37.065
$(\partial p/\partial V)_T = (\partial^2 p/\partial V^2)_T = 0$	45.68₂	37.229	0.74		

FIG. 9. Minimum $(\partial p/\partial V)_T$ vs T for sulfur hexafluoride.

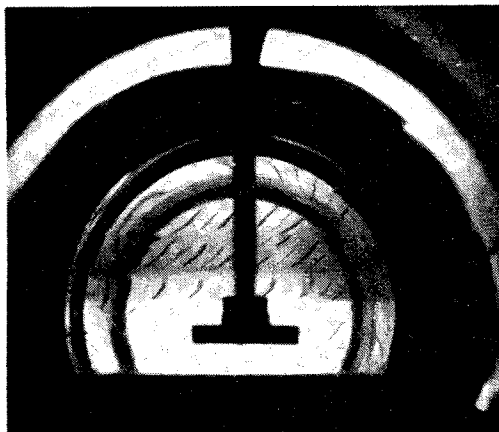[a] Atack and Schneider, J. Phys. & Colloid Chem. 55, 532 (1951).

FIG. 10. Sulfur hexafluoride at 45.640°C and 1.4 ml/gram. Constant p,v,T for 12 hours. The meniscus is in the center, with density gradients above and below it.
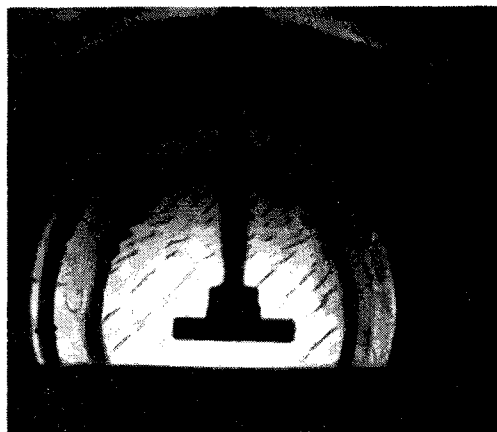

FIG. 11. Sulfur hexafluoride at 45.662°C and 1.4 ml/gram. Constant p,v,T for 3 hours. No meniscus visible.

CONCLUSIONS

For carbon dioxide and sulfur hexafluoride the difference in density between liquid and vapor remains about 20% in the temperature interval starting several degrees below to within 0.01 degree of the critical temperature. But a few hundredths of a degree higher this large density difference vanishes and only a single phase exists; i.e., the liquid-vapor boundary curves have relatively flat tops.

It is possible that the densities of liquid and vapor really approach each other uniformly, not abruptly, as the temperature rises to the critical. At the meniscus disappearance temperature the thermal agitation of the molecules may be sufficient to blur the meniscus, even though $(\partial p/\partial V)_T=0$, i.e., even though two phases are still present. In this way the anomalous critical region predicted by Mayer et al. could exist.

There is good evidence against the existence of such an anomalous region. First of all, the plots of $(\partial p/\partial V)_T{}^{min}$ versus T show that the anomalous region is at most 0.04°C high, if it exists at all. (We do not know if the true plot of $(\partial p/\partial V)_T{}^{min}$ versus T is really linear like the extrapolation.) From the shape of the liquid-vapor boundary curve, one would expect an anomalous region to be about 0.3°C high in order to give the liquid-vapor boundary curve a more rounded top.

Secondly, the extremely narrow temperature interval between a stable and a blurred meniscus is evidence against an anomalous critical region. The meniscus will disappear by increasing the absolute temperature of the system by only one part in 30 000; if two phases were still present, this temperature change would have reduced their density difference by less than 10%. Thus the disappearance of the meniscus is a sharp transition, and hints of a cooperative phenomenon similar to melting. The liquid has structure, even near its critical point. At the temperature of meniscus blurring, this structure "melts" or disintegrates, just as a strained rope breaks when a few important fibers are torn. Above the meniscus disappearance temperature only a single phase is present, and $(\partial p/\partial V)_T$ cannot be zero, according to the phase rule.

Michels and Strijland have measured the specific heat of carbon dioxide near the critical region.[13] They have found that at temperatures near but not beyond the critical the constant volume specific heat showed a sharp rise about the critical density. This can be interpreted as evidence that the liquid possesses some structure just below the critical temperature.

[13] Michels and Strijland, Physica 18, 652 (1952).