Coexistence Curve of Sulfur Hexafluoride*

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(Received 17 May 1972)

The coexistence curve of sulfur hexafluoride has been determined by interferometric measurements for the temperature range $10^{-5} < (T_c - T)/T_c < 10^{-1}$. The refractive index difference $n_l - n_v$ is fitted by a power law. The difference Δn is proportional to $(\Delta T)^{\beta}$, where $\beta = 0.346 \pm 0.001$ for the temperature range $10^{-2} < (T_c - T)/T_c < 10^{-1}$. The exponent β decreases to 0.339 ± 0.003 as $(T_c - T)/T_c$ decreases to the lower limit of the data at 10^{-5}.

Interest in phase transitions has increased in recent years. The critical behavior of a simple fluid is not completely understood despite much theoretical and experimental investigation. This paper reports research investigating the temperature dependence of the liquid-vapor coexistence curve of sulfur hexafluoride by measurements of the refractive index difference between the liquid and vapor.

The compressibility of a pure fluid diverges near the critical point, resulting in a large density variation near the critical density due to Earth's gravitational field. The fluid is compressed under its own weight, giving rise to a large density variation with height in a sample of fluid. Several optical techniques have been used to study static properties of a fluid near its critical point.[1-5]

The coexistence curve of sulfur hexafluoride has been determined by measurements of the Fraunhofer diffraction pattern produced by a thin slab of fluid near its critical density.[4,5] A laser beam, rendered uniphase and collimated by a beam-expanding telescope and pinhole filter, traverses a sample vessel and produces a Fraunhofer diffraction pattern in the focal plane of a lens. The sample vessel has plane parallel windows and is filled with SF_6 such that its average density is near the critical density. If the temperature is maintained slightly above the critical temperature, a large density variation with height results due to the gravitational field. A sigmoid density distribution is obtained with the density at the bottom of the cell being greater than critical and the density at the top being less than the critical density. The density and index of refraction are related by the Lorentz-Lorenz relation. Therefore, the refractive index has a sigmoid distribution.

The Fraunhofer diffraction pattern is easily understood. In the absence of any density variation in the cell, the laser beam is focused to a point in the focal plane of the lens. In the presence of density gradients in the cell, light is refracted as it traverses the cell and is not focused to the same point as in the case of uniform density in the cell. A ray traversing the sample vessel through the region where the density gradient is maximum is refracted through some maximum angle and is focused to a point at some maximum distance from the zero-angle point in the focal plane. Light rays traversing the cell where the gradient is less than the maximum are refracted through smaller angles. Consider two rays, one traversing above the maximum gradient region and one below, but traversing regions where the gradients are the same. These two rays are refracted through the same angle and are focused to the same position in the focal plane of the lens. The two rays have traversed regions of the cell where the gradients are equal, but where the optical thicknesses are not equal. In general, there is a phase difference between them. It is easy to see that the Fraunhofer pattern will exhibit maxima and minima. The most refracted maximum is due to light traversing the maximum gradient region; the most refracted minimum is due to rays differing by one-half wavelength, etc.; and the portion of the pattern nearest zero angle is due to light traversing the top and bottom of the sample cell.

A similar Fraunhofer pattern is observed if the sample is maintained at a temperature slightly below critical. In this case, however, there is an additional phase difference due to the liquid-vapor density difference at the meniscus. If the Fraunhofer pattern is recorded continually while the temperature is slowly decreased, the most refracted minima in the pattern are observed to diverge to "infinite" angle as the liquid-vapor density difference increases. A kymograph can be made by slowly transporting film across the

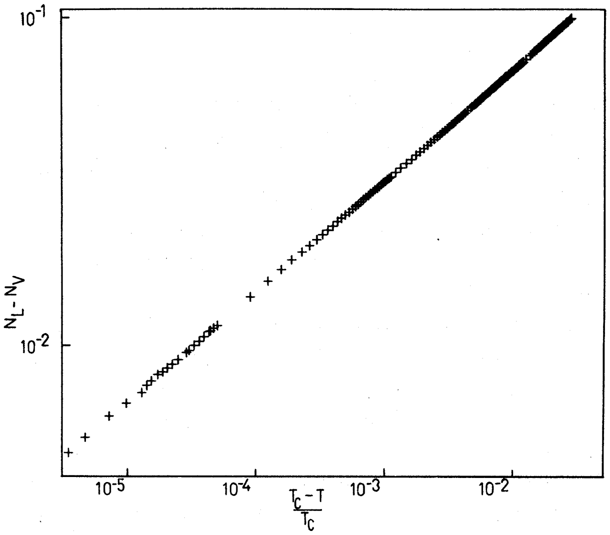

FIG. 1. Log-log plot of refractive index difference versus reduced temperature.

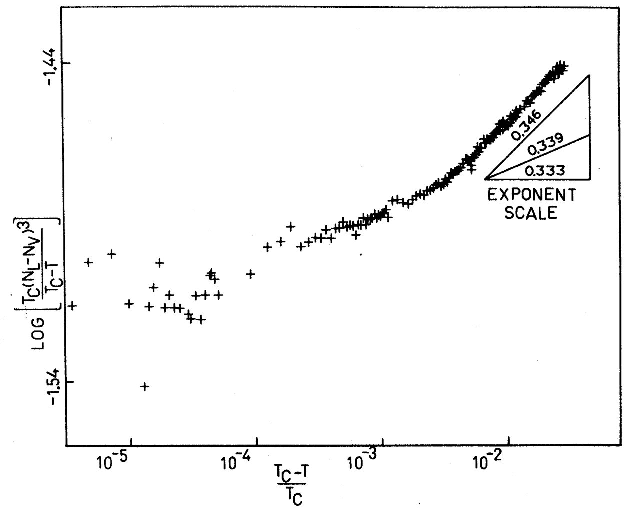

FIG. 2. Sensitive log-log plot of refractive index difference versus reduced temperature. The major temperature dependence has been divided out, yielding a sensitive log-log plot.

focal plane while the temperature is swept. The liquid-vapor difference can be obtained by studying the "vanishing" of the minima as a function of temperature. The same effect is observed if the temperature is swept in the opposite direction; minima are observed to form in the Fraunhofer pattern as the temperature is increased. This procedure has been used to make measurements down to temperatures of 40° below the critical temperature. In order to eliminate any nonequilibrium effects due to temperature sweeping, it is desirable to sweep temperature in steps. The data reported here have been obtained by this sweep-stop procedure. The stopping period is 30 min for temperatures far from critical and is several hours for temperatures within 0.01 deg of the critical temperature.

The results of studies of sulfur hexafluoride are presented in the figures. Figure 1 is a log-log plot of the refractive index difference between liquid and vapor and reduced temperature $(T_c - T)/T_c$. Temperatures are measured by a Dymec quartz-crystal thermometer and independently with a thermistor. The critical temperature is obtained by assuming that the refractive index difference is proportional to temperature,

$$\Delta n \propto (T_c - T)^\beta,$$

choosing a trial β, plotting $\Delta n^{1/\beta}$ versus T, and extrapolating the data to $\Delta n = 0$. This trial T_c is then used for plotting $\log\Delta n$ versus $\log(T_c - T)$, and a second trial β is obtained from the slope of this graph. The procedure is repeated as many times as necessary. It is not a difficult procedure because the range of possible T_c is small; the temperature at which the smallest Δn is measured is only a few millidegrees below the temperature at which definitely supercritical Fraunhofer patterns are observed. The uncertainty in T_c is ± 0.0002 K. The thermometers have not been calibrated with international standards; an absolute determination of T_c is not possible.

A "straight" line is observed in Fig. 1. In order to make the plot more sensitive, $T_c(\Delta n)^3/\Delta T$ versus $(\Delta T)/T_c$ curves are graphed on a log-log scale in Fig. 2. The major part of the exponent is thus divided out and the plot is very sensitive. If Δn were proportional to $\Delta T^{1/3}$, the data in Fig. 2 would lie in a horizontal line. The slope of any line in this graph corresponds to β being different from $\frac{1}{3}$. An "exponent scale" is illustrated.

No error bars have been plotted with the data. The points at the right of the graph are insensitive to errors in measurement, measurements of temperature, and choice of T_c. The effect of these errors becomes greater as $T_c - T$ decreases. The scatter of the points is a good illustration of the size of error bars on the points.

The value of β for the temperature range greater than 10^{-2} is 0.346 ± 0.001. The value of β decreases as the critical temperature is approached. There is some indication that β increases for $T/T_c < 10^{-4}$, but this possibility will be neglected here because of the limitations of the data. A fit of the data for $(T_c - T)/T_c < 3\times10^{-3}$ yields $\beta = 0.339$

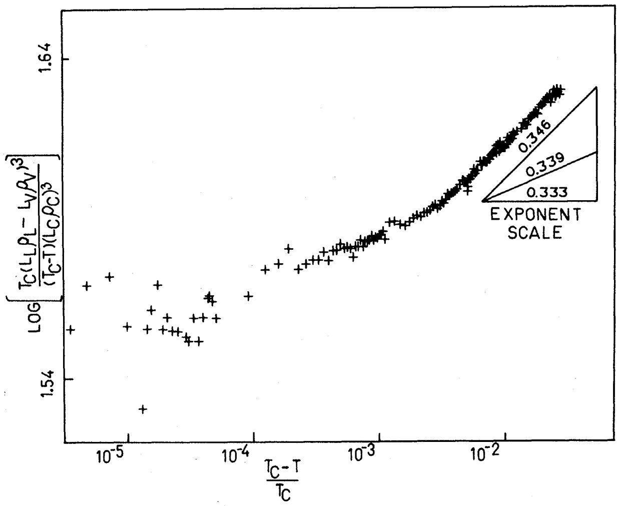

FIG. 3. Sensitive log-log plot of data reduced with the aid of the Lorentz-Lorenz relation.

± 0.002. The value of $\beta = 0.339$ agrees with the value of β for xenon in the temperature range less than 3×10^{-3} K.[5] The larger value of 0.346 is less than the value of 0.355 for xenon in the corresponding temperature range.[5,6] A good fit to the xenon coexistence curve has recently been obtained by Estler by fitting with a power series in $(\Delta T)^\beta$.[6] A fit to the SF_6 data of the form

$$\Delta n = A(\Delta T)^{\beta 1} + B(\Delta T)^{\beta 2}$$

yields a value of $\beta_2 = 0.75 \pm 0.10$. Theoretical investigation of the form of the higher-order terms would be valuable for fitting these data.

Figure 3 is essentially the same as Fig. 2, except the Lorentz-Lorenz relation

$$(n^2-1)/(n^2+2) = L\rho,$$

has been used to relate the data to a density difference. The Lorentz-Lorenz coefficient L is nearly constant. In order to relate Δn to $\Delta\rho$, it is possible to expand the relation in a power series about n_c and ρ_c, or if $n_l + n_v$ is known as well as $n_l - n_v$, it is possible to calculate the quantities $L_l\rho_l$ and $L_v\rho_v$. The latter can be carried out easily if n_c is known and $n_l + n_v$ as a function of temperature is known. The quantities n_c and $n_l + n_v$ need be known to somewhat less precision than $n_l - n_v$ in order to use the Lorentz-Lorenz relation to calculate $L_l\rho_l$ and $L_v\rho_v$ separately. These quantities have been measured in this laboratory.[7] The value of n_c for sulfur hexafluoride is 1.093 ± 0.002.

Figure 3 illustrates a sensitive plot of the quantity

$$(L_l\rho_l - L_v\rho_v)/L_c\rho_c.$$

If the Lorentz-Lorenz coefficient is constant, then Fig. 3 is a sensitive plot of $(\rho_l - \rho_v)/\rho_c$. There have been studies indicating a variation in L, but the density dependence is small.[8] It seems that the variation in L is not enough to account for the shape of the coexistence curve being other than a single power law.

The density information plotted in Fig. 3 has been obtained with the Lorentz-Lorenz relation using data from Ref. 7 for the coexistence-curve diameter. The data in Ref. 7 were fitted with a diameter $\frac{1}{2}(n_l - n_v) = n_c + 0.000\,223(T_c - T)$. Any form for the temperature dependence of the diameter (compatible with the data) leads to a negligible change in Fig. 3. It has been called to the attention of the authors that the data can be compared with that of Benedek *et al.*[9] In order to compare the data of Fig. 3 with the preliminary data reported by Benedek *et al.*, it is useful to approximate the data of Fig. 3 by an equation. A least-squares fit gives $(\rho_l - \rho_v)/\rho_c = (3.66 \pm 0.08) \times (\Delta T/T_c)^{0.3463}$ for $T/T_c > 7\times10^{-3}$, and $(3.5 \pm 0.1) \times (\Delta T/T_c)^{0.339}$ for $T/T_c < 5\times10^{-3}$. The uncertainty in the coefficient is due to the uncertainty in $n_c - 1$.

The advice of R. Burgess, W. Opechowski, and L. Sobrino is greatly appreciated.

*Work supported by the National Research Council of Canada.

[1]H. L. Lorentzen, Acta Chem. Scand. 7, 1335 (1953).

[2]E. H. W. Schmidt and K. Traube, in *Progress in International Research on Thermodynamics and Transport Properties, Papers Presented at the Second Symposium on Thermophysical Properties*, edited by J. F. Masi and D. H. Tsai (Academic, New York, 1962), p. 193.

[3]M. H. Edwards, Can. J. Phys. 34, 898 (1956).

[4]L. R. Wilcox and D. Balzarini, J. Chem. Phys. 48, 753 (1968).

[5]D. Balzarini, Ph. D. thesis, Columbia University, 1968 (unpublished).

[6]W. Estler, Ph. D. thesis, State University of New York at Stony Brook, 1972 (unpublished).

[7]K. E. Ohrn, M. A. Sc. thesis, The University of British Columbia, 1972 (unpublished).

[8]J. M. Lucas and B. L. Smith, Phys. Lett. 19, 22 (1965).

[9]G. B. Benedek, J. B. Lastovka, M. Giglio, and D. Cannell, in *Critical Phenomena*, edited by R. E. Mills and R. I. Jaffee (McGraw-Hill, New York, 1971).