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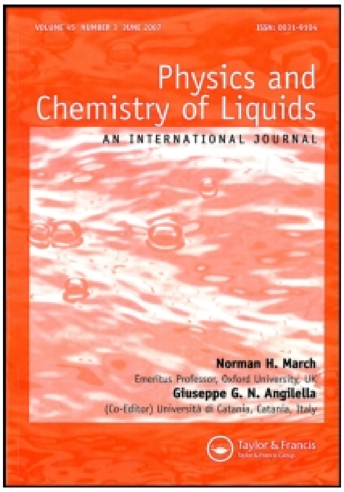

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Critical Properties of Argon*

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Abstract—Measurements of P-V-T properties of argon in the critical region are reported. Isothermal compressibilities have been calculated from the data for liquid and vapor along the coexistence curve and for the gas above the critical temperature at the critical denstiy. Densities of the liquid and vapor along the coexistence curve were measured, and the critical temperature, pressure and density of argon were redetermined. These data are compared with those of other workers; in addition critical indices which represent the manner in which these properties vary as one approaches the critical point were determined and compared with the predictions of several theoretical estimates of these quantities.

1. Introduction

Recently, there has been a considerable resurgence of interest in critical phenomena, primarily on the part of theoreticians.[1-5] In the course of this work, it has been pointed out that theoretical results frequently cannot be tested against experiment because of lack of suitable data. This problem seems to be particulary noticable with regard to values for the so-called "critical indices" for simple one-component fluids at the gas-liquid critical point. In general, a critical index for some property P is defined by:

$$\lim_{T=T_c} \ln P = \xi \ln |T - T_c| + A \tag{1}$$

where ξ is the critical index, T_c is the critical temperature and A is a constant. A single property may have more than one value of ξ, depending upon whether the critical temperature is approached from above or below, and upon what thermodynamic variables are held constant (if any) along the path of approach. For example, the isothermal compressibility is one such parameter, and one has at least three different values

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of interest for the critical exponent in this case: (1) approach from above T_c at constant density; (2) approach from below T_c along the gas-liquid coexistence curve in the gas phase. (3) same conditions as (2), but in the liquid phase. Recent theoretical work has been concerned not only with estimates of the values of these indices (usually based on Ising model calculations) but also on the relationships between various indices. Adequate tests of the predicted relationships are particularly hard to carry out because of the need for accurate data for several different properties of some simple substance in the neighborhood of its critical point. The work reported in this paper was undertaken in the hope of obtaining data suitable for comparisons with theory.

The apparatus was designed[6] and built to make precise measurements of P-V-T data of dense fluids at low temperature, and had been used previously in a comparative study of the properties of methane and perdeutero methane[7]. Critical indices were determined for these substances in the earlier work, but the values obtained were not as precise as one might wish, mainly because the experiments covered the whole temperature range from the melting points to the critical points and the data in the critical region were not as closely spaced nor as carefully measured as is desirable for a study of critical indices. In the present investigation, measurements were made of the P-V-T properties of argon at several closely spaced temperatures within seven degrees above and below the critical temperature. From these data and the known vapor pressures of argon in this region,[8,9] the isothermal compressibilities were determined on the gas and liquid sides of the gas-liquid coexistence curve; in addition, the isothermal compressibilities were determined above the critical point at a constant density very nearly equal to the critical. From these data, the critical temperature was determined; with the aid of this parameter and the values of the density along the gas-liquid coexistence curve, the critical density and pressure were redetermined. Finally, the difference in density between gas and liquid was measured in the critical region. These data were then used to obtain values of γ and β, the critical indices defined by:

$$\log \varkappa_T = -\gamma \log |T - T_c| + A \qquad (2)$$

$$\log (\varrho_g - \varrho_l) = \beta \log (T_c - T) + A' \qquad (3)$$

where $\varkappa_T$ denotes the isothermal compressibility and ϱ_g and ϱ_l denote the densities of the gas and liquid respectively along the coexistence curve.

Finally, our values for the indices were combined with the results of Voronel *et al.*[11,12] to test the equality

$$\gamma + 2\beta + \alpha = 2.00 \tag{4}$$

where the index α is defined by

$$(C_v - C_v^0) = \frac{A''}{\alpha}\left[\left|1 - \frac{T}{T_c}\right|^{-\alpha} - 1\right] \tag{5}$$

where C_v, C_v^0 are the total heat capacity and the kinetic contributions to the heat capacity of the fluid at the critical density.

2. Experimental

In these experiments, densities were measured by determining the changes in buoyancy of a magnesium sphere immersed in the fluid at a

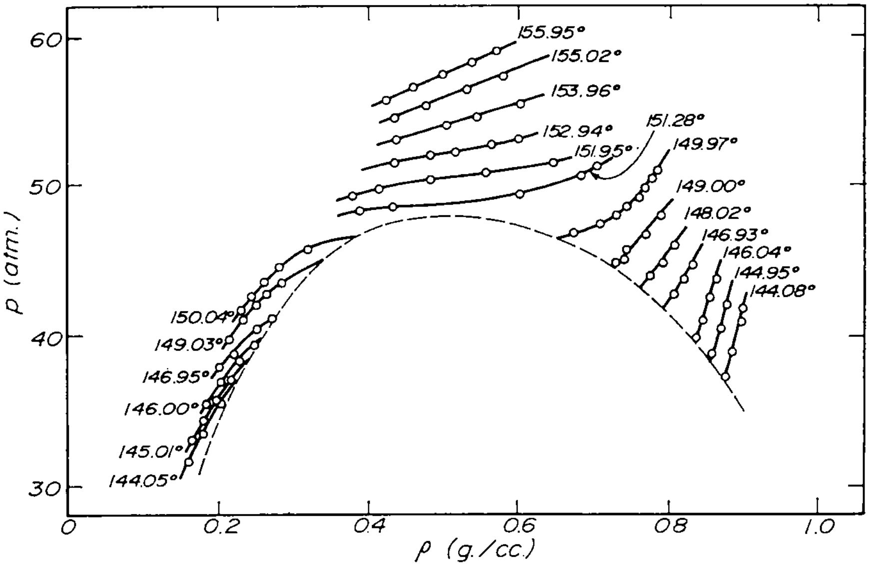

Figure 1. A portion of the isotherm data for argon is shown here. The points indicate the measured data; the solid lines drawn through the points represent the isotherms. Below the critical temperature, the isotherms terminate on either side of the two phase region at a pressure equal to the vapor pressure. The dashed curve shows the coexistence curve constructed in this way from the isotherms and the vapor pressure data of van Itterbeek, *et al.*[8]

given temperature and pressure.[6,7] Since the sample was enclosed in a heavy copper block, it was not possible to observe a meniscus visually; for this reason, measurements of the pressures along the coexistence curve were impractical, especially at temperatures very near the critical. However, a number of separate investigations[8-10] of the vapor pressure

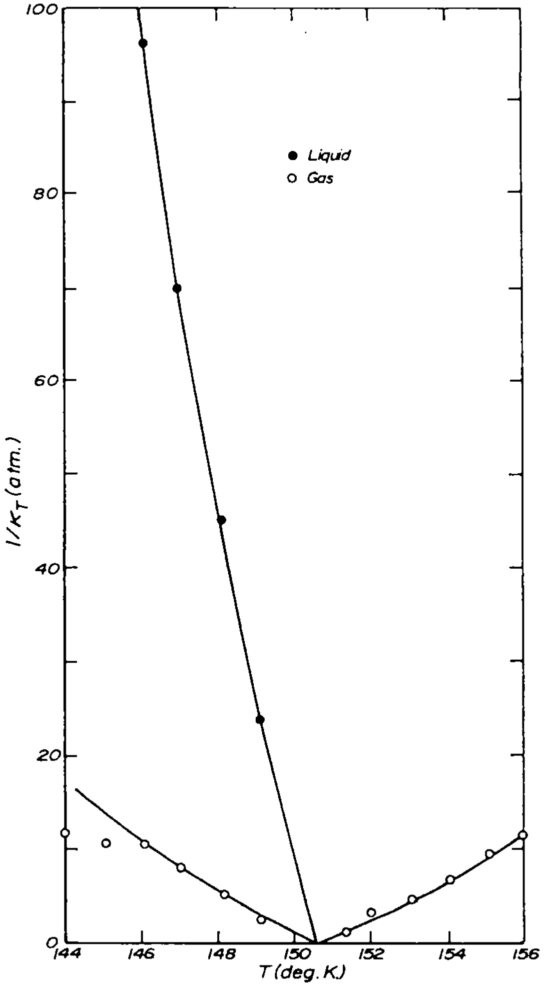

Figure 2. The reciprocal of the isothermal compressibilities of argon are plotted as a function of temperature. The three branches of the curve represent: liquid phase data along the coexistence curve; gas phase data along the coexistence curve; gas phase data above the critical point at the critical density.

curve have been reported for argon in the critical region, and it was assumed in the present work that the data of van Itterbeek, *et al.*[8] were correct. At fixed temperatures below the critical, densities of the liquid were measured at several pressures in excess of the reported vapor pressure; in addition, densities of the gas were measured at several pressures below the vapor pressure. Care was taken to obtain data points at pressures as close as possible to the coexistence pressure. A portion of the data are shown in Fig. 1. By extrapolating the subcritical isotherms back to the coexistence curve, values for ϱ_g and ϱ_l, the densities of the liquid and gas along this curve, were calculated. In addition, the limiting slopes of the isotherms at the points where they meet the coexistence curve were calculated. These slopes were then used to calculate isothermal compressibilities $\varkappa_T$. Figure 2 shows the reciprocal compressibilities plotted versus temperature, together with a plot of the reciprocal compressibility of the super-critical vapor at $\varrho = 0.530$ g/cc. Since the three curves should intersect the axis at the critical temperature, one can use these data to obtain an estimate of the critical temperature which does not depend upon a visual observation of the disappearance of the

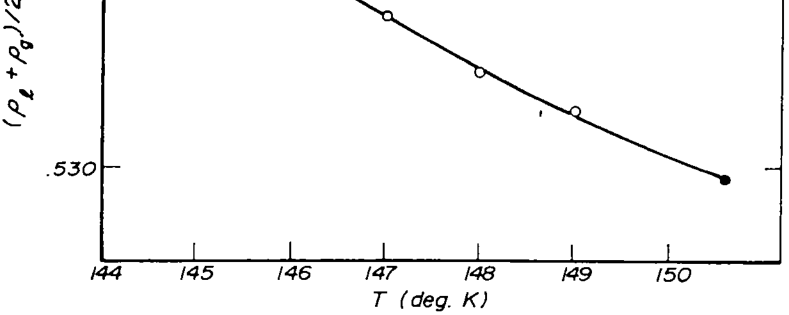

Figure 3. The average of the densities taken from either side of the coexistence curve are shown here as a function of temperature. By extrapolating to the critical point, an accurate value of the critical density is obtained; this point is indicated by the solid circle.

meniscus in a two phase system. The value of T_c calculated in this way is shown in Table I together with some of the other reported measurements of this quantity. The values of ϱ_l and ϱ_g were used in two ways; the curve of $(\varrho_l + \varrho_g)/2$ versus temperature shown in Fig. 3 was extrapolated to the critical point to determine the critical density ϱ_c shown in Table I (note that Fig. 3 is actually a rectilinear diameter plot; however, on the scale of the figure, this quantity is not the linear function of temperature which it is frequently assumed to be). In addition, the logarithmic plot of $\varrho_l - \varrho_g$ versus temperature was constructed as shown in Fig. 4. The largest source of error in these data as one approaches the critical point is of course due to the uncertainty in the critical temperature. The value of the critical index β given by the slope of the straight line through these points is shown in Table II. Finally, logarithmic plots of the three branches of the χ_T versus temperature curve are shown in Fig. 5; values of the critical index γ obtained from the slopes of the straight lines drawn through the data points are listed in Table II together with the estimated uncertainties in these parameters.

TABLE I Critical Constants for Ar

	T_c (deg. K)	P_c (atm)	ϱ_c (g/cc)
Crommelin, *et al.*[13]*	150.72	48.00	0.5308
Michels, *et al.*[14]*	150.87	48.34	0.5365
Voronel, *et al.*[11], [12]†	150.50±.05		0.533
McCain, *et al.*[10]	150.65±.02	47.92±0.05	
This work	150.6±0.1	48.0±0.15	0.5295±0.0010

* No error estimates given by these authors.

† Estimated from the data; explicit values not given in the original papers.

TABLE II Critical Indices for Ar

Index	Value
β	0.380 ± 0.020
γ (liq.)	1.24 ± 0.04
γ (gas above and below T_c)	1.22 ± 0.04

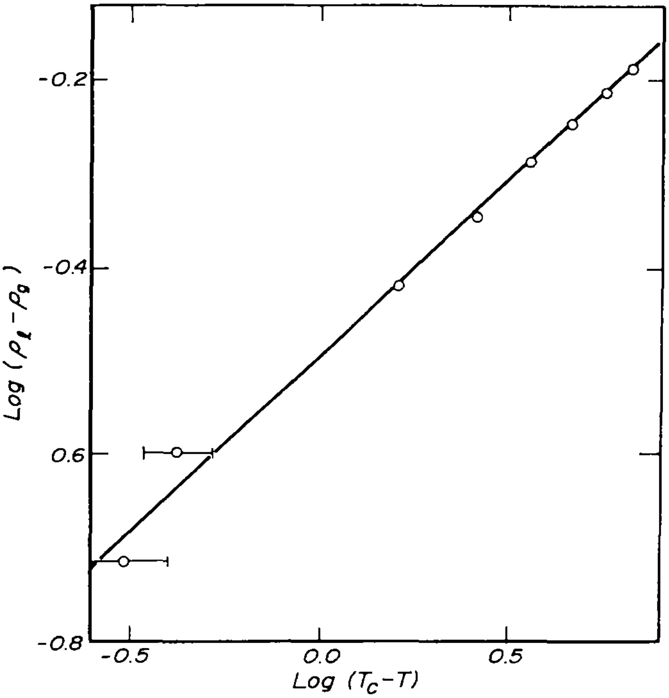

Figure 4. The logarithm of the difference in density between liquid and gaseous argon along the coexistence curve is plotted as a function of the logarithm of the difference between the temperature of measurement and the critical temperature. The critical temperature was taken to be 150.60°C., and the horizontal lines show the error limits which are produced in the points close to the critical temperature by an uncertainty of 0.10° in T_c. A straight line with a slope of 0.376 is drawn through the points.

From Fig. 1, it is evident that no data were taken in the immediate vicinity of the critical point (that is, within 0.6°K. of T_c). Of course, such data would be highly desirable, both to extend the ranges of the compressibility measurements and the density difference, and to obtain the critical isotherm. Attempts at such experiments were not successful, mainly because the temperature of the sample could not be accurately controlled for the very long time periods required for equilibrium in this region. An automatic temperature controller is now being constructed which is designed to hold the temperature of the system constant to better than 0.01°K. for indefinite time periods. This modification, com-

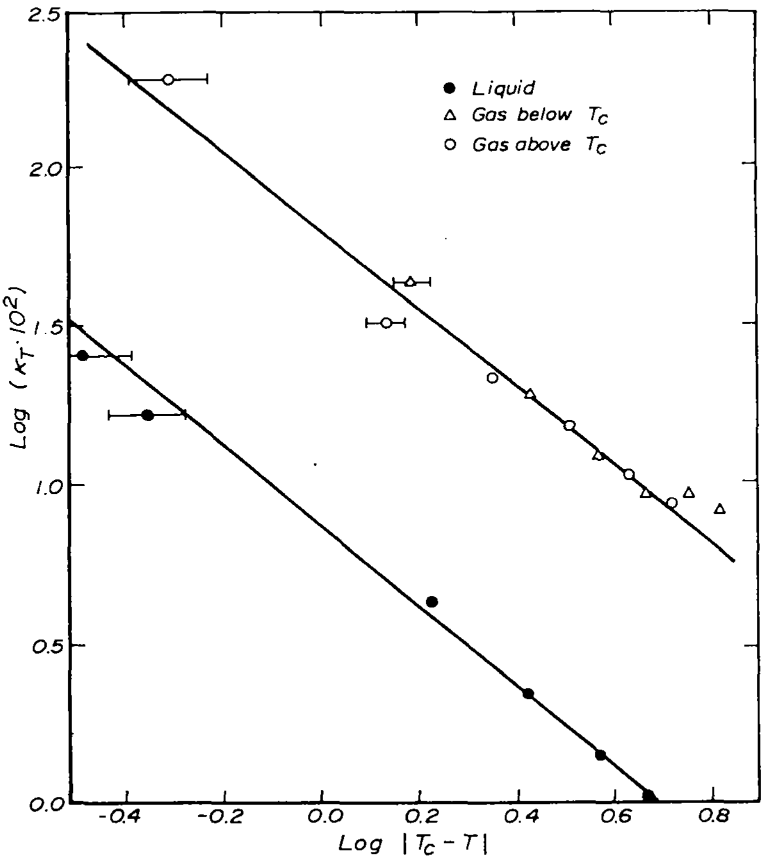

Figure 5. Logarithmic plots of three branches of the isothermal compressibility curves (shown in Fig. 2) are given here as functions of the logarithm of the absolute value of the temperature difference. Horizontal lines show the limits of uncertainty which result when the critical temperature is taken to be 150.60 ± 0.10°K. Straight lines with slopes −1.22 (upper line) and −1.24 (lower line) are drawn through the points.

bined with more precise temperature measurements, should allow us to work to within a few hundredths of a degree of T_c and to measure the critical isotherm to good accuracy. The inherent accuracy in the density measurements is more than adequate for this purpose; furthermore, precise determinations of the pressure changes in this region can be made to much greater accuracy than the absolute pressure by means of differential measurements.

3. Discussion

The critical constants for argon determined in this work are in excellent agreement with the recent precise measurements of McCain and Zeigler.[10] In as much as the data reported by Michels, *et al.*[15] show appreciable differences from the other data in Table I, it seems likely that their experiments were subject to systematic error in the critical region. Michels, *et al.* also reported vapor pressures which disagree with those of McCain and Zeigler and van Itterbeek and coworkers;[8] furthermore, a comparison of our measurements with their values for gas and liquid densities along the existence curve showed consistent discrepancies of 0.1–0.2% in the measured densities within 7° of T_c.

The critical indices calculated from our data are clearly different from those predicted by classical theories of critical behavior[1,2] which give $\beta = 0.5$, $\gamma = 1.0$. Furthermore, our value of β is larger than the empirical value of 0.333 given by Guggenheim [15] and than the estimates of 0.357 and 0.345 obtained from analysis of the extensive data for CO_2 and Xe[1]. Careful computations of the properties of the three dimensional Ising lattice give $\beta = 0.313$, $\gamma = 1.250$ below T_c and $\gamma = 1.313$ above T_c(1,16). Thus, although our value for the index γ is in agreement with the Ising model below T_c, the results obtained for γ above T_c and β are clearly not those expected from the theory.

It is generally conceded that the Ising model is capable of yielding specific results for the critical indices only because it includes a number of unrealistic simplifying assumptions. Thus, one should not be too surprised when discrepancies are found between experiment and theory. A less specific approach to the theory of the critical point has recently been proposed[4] which results in the so-called scaling-law equation of state.[17] The scaling-law approach predicts that the Rushbrook-Griffiths inequalities[5] are equalities, and that the critical indices for a given quantity are the same above T_c as below. It is evident that our value for γ above T_c is essentially equal to its value below T_c, and is the same both for liquid and gas along the coexistence curve below T_c. With respect to the Rushbrook-Griffiths expressions, only the one shown in Eq. (4) can be tested here. The data of Voronel *et al.*[11,12] for the constant volume heat capacity of argon indicate that the coefficient α is small and may well be zero. If the values of γ and β given in Table II are used together with

$\alpha = 0$, one finds that the experimental data for argon give

$$\gamma + 2\beta + \alpha = 1.98 \pm 0.06 \tag{6}$$

which may thus be considered to be a confirmation of the equality in Eq. (4). A second scaling-law expression can be written as

$$\delta - \frac{\gamma}{\beta} = 1.00 \tag{7}$$

where δ is the degree of the critical isotherm:

$$(P - P_c) = a\,(\varrho - \varrho_c)^{\delta} \text{ at } T = T_c \tag{8}$$

Previous analyses of the critical isotherms for xenon, carbon dioxide and hydrogen[18] have given $\delta = 4.2$; however, Green and coworkers[17] have recently argued that a value of ~ 5 is more nearly correct for this parameter. Our results satisfy Eq. (7) if $\delta = 4.3$, which is in good agreement with the earlier estimates. Clearly, accurate measurements of the critical isotherm for argon are necessary before Eq. (7) can be critically tested.

Note added in Proof: R. K. Teague and C. J. Pings have recently reported (J. Chem. Phys., to be published) extensive measurements of the refractive index of argon in the critical region. These data were used to define the gas-liquid coexistence curve in the critical region.

Precise values of the critical temperature, pressure and exponent β were obtained from this curve. Their results are in good agreement with ours, amounting to 150.704 ± 0.015°K, 48.18 ± 0.03 atm and 0.3609 ± 0.0045 for the three quantities.

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