HEAT CAPACITY IN THE CRITICAL REGION OF XENON*

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New results are reported for the equilibrium constant-volume heat capacity of xenon measured isothermally under completely static (unstirred) conditions at critical average density. The shift of the heat-capacity singularity to slightly below the reported phase-transition temperature is observed here as it has been for argon and oxygen. An explanation of this effect is suggested.

Recent testing of theoretical models for critical-region condensation, models based upon either (a) scaling theory[1,3] or (b) extensions of classical-fluctuation theory[4,5], have led to renewed interest in experimental data on heat capacities in critical regions. For theories of type (a) the indices α and α' giving the order of the singularity in the constant-volume anomalous-configurational heat capacity,

$$\Delta C_v \propto \epsilon^{-\alpha}, \quad T > T_c; \tag{1}$$

$$\Delta C_v \propto (-\epsilon)^{-\alpha'}, \quad T < T_c; \tag{2}$$

$$\epsilon = (T - T_c)/T_c, \tag{3}$$

enter into several of the important simple sum rules believed to hold among singularity indices. Direct or indirect measurements of the heat capacity are the only routes to the determination of α and α' and are among the weaker links in verifying the rules for physical, as opposed to lattice-model, systems. Theories of type (b) predict $\alpha = 0.5$ and predict a constant of proportionality in (1) which can be related to the range of intermolecular forces.

We have improved the Bunsen ice-calorimetric method in order to make measurements of relative enthalpy in the critical region for systems which may be equilibrated using any thermostating program of arbitrary time length without disturbing the system by stirring and without introducing experimental uncertainties inherent in drift corrections for long-duration adiabatic measurements. The method is being used for both liquid-liquid and liquid-vapor systems.

The calorimeter is similar to one described previously[6] except that the improvements envisioned there have been incorporated into the present model. The xenon sample was generously furnished by Linde Air Products Company with a rated purity of better than 99.99%; our mass-spectrographic analysis showed no impurity to a limit of detectability of less than 0.03%. The stainless-steel sample bomb was a 1:10 tapered cylinder approximately 10 cm high and 2.5 cm at its lowest (bottom) diameter. It held about 59 g of fluid at a density of 1.1010 ± 0.0008 g/cm^3. (Habgood and Schneider[7] report a critical density of 1.099 ± 0.002 g/cm^3 based upon extrapolations of compressibility data from above T_c. Weinberger and Schneider's value of 1.105 g/cm^3 from a rectilinear diameter extrapolation in the two-phase region has recently been shown to be consistent with the compressibility data extrapolated using scaling theory.[1] Our sample was made up before that explanation was given.) The bomb valve was an integral part of the cap welded to the cylinder top. All parts were made of 17-4PH steel as thin as possible, consistent with negligible uncertainty in elastic expansion at the critical pressure, and were hardened by heat treatment after assembly. The coarse stainless-steel heat-exchange screens ran vertically in the cylinder so as not to obstruct phase separation or convection. There has been no significant change in the weight of the loaded bomb since it was made up in 1961.

The probable error in individual relative enthalpy determinations was about ±3 mg Hg displaced (0.9 J) during the first set of runs with an earlier calorimeter model and less than ±1.5 mg Hg for the second series, based upon precision of the method and scatter of replicated runs. Thermostatting of the sample and precision of the temperature readings were to $\pm 1 \times 10^{-3}$ and 0.5×10^{-3} °C probable error for the first and second series, respectively. Run sets were spaced as close as 0.03°C near the anomaly. Heat-capacity features for the two sets of runs were similar; the data shown in Fig. 1 are for the second, more extensive and precise set. The probable errors lead to uncertainties of the molar heat capac-

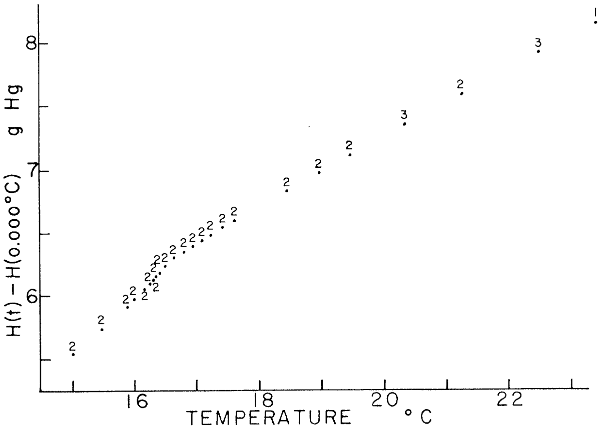

FIG. 1. Enthalpy difference $H(t)-H(0.000°C)$ for xenon bomb in g Hg displaced (much compressed plot, 1 g Hg = 270.45 J). Numbers indicate run replications.

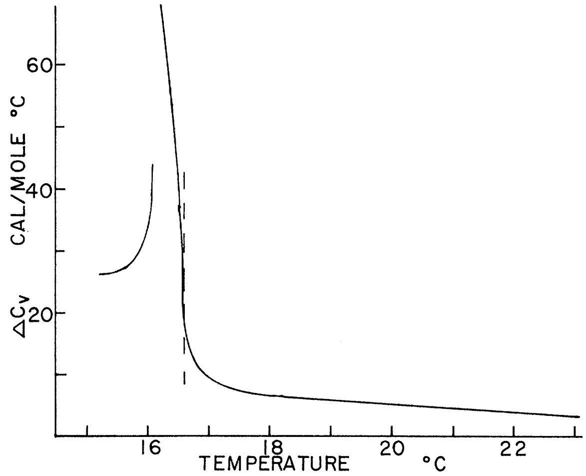

FIG. 2. Molar configurational heat capacity at constant volume for xenon. Anomaly peak at $T_c = 16.27 \pm 0.02°C$. Curve made from slopes of enthalpy curve smoothed within probable limits of error.

ity C_v from smoothed enthalpy curves ranging from less than 10% over most of the range to about 16% within 0.1° of the peak of the curve. Projected further analysis of the data may lead to a considerable reduction of the C_v error limits.

The sample was always raised to 31°C with agitation for at least an hour before it was lowered into the thermostat. Runs with varying thermostatting times at the same temperature indicated that a constant enthalpy was reached after 6 h. This equilibration time is consistent with 5 h reported by Wentorf[8] as necessary for other liquid-vapor systems but is less than the longest period reported as necessary for complete gravitational equilibrium by Wilcox and Balzarini[9] at temperatures which were probably closer to T_c than we were able to establish.

In Fig. 1 the enthalpy curve is shown on a compressed scale appropriate only to show the distribution and number of runs. The anomalous configurational heat capacity which was obtained from the enthalpy data smoothed within the limits of error is shown in Fig. 2.

Fisher[10] has pointed out that for both argon and oxygen heat-capacity measurements by Voronel', the peak of the anomaly was some 0.2°C lower than the critical temperature reported from careful visual observation or gravity-corrected *PVT* data. Figure 3 shows early work of Voronel' on xenon as a function of density.[11] These measurements were done in a stirred adiabatic calorimeter. Again there appear to be points on the $T > T_c$ portion of the curve which extend below the (dashed) reported T_c. The resolution of the plot presented by Voronel' does not allow detailed analysis. Our data indicate a shift of −0.32°C for the xenon peak. There is a wealth of *PVT* data on xenon thin samples in the critical region and there are three independent measurements of the form of the density gradient in the grav-

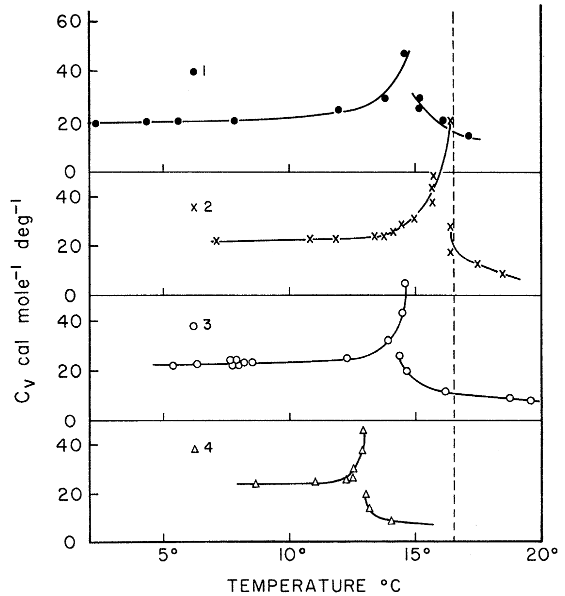

FIG. 3. Heat capacity of xenon as a function of temperature and density from Voronel' (Ref. 11). (1) $\rho = 1.14$ g/cm^3, (2) $\rho = 1.09$ g/cm^3, (3) $\rho = 0.98$ g/cm^3, and (4) $\rho = 0.85$ g/cm^3. Dashed line is drawn at $T_c = 16.590°C$.

itational field by *PVT*,[7] tracer,[12] and optical[9] methods which agree within experimental error. The form of this gradient at $\langle\rho\rangle = \rho_c$ and T_c is shown in Fig. 4. These curves, and those at temperatures up to 0.05° higher, all indicate a steep gradient in the first 1 cm of sample above and below the center critical density region going over into slowly varying density of about $\rho_c \pm 5\,\%$, respectively, in the lower and upper parts of the sample comprising most of the material. The density variation with height in the calorimetric samples is about an order of magnitude larger than uncertainties in ρ_c mentioned above or in the deviation of the average density of our sample from ρ_c. Our sample average density can therefore be considered to be at the critical density for purposes of these arguments.

The calorimeter of Voronel'[13] appears to be about 10 cm high as is our sample. It is difficult to estimate the extent to which his stirring of the system disturbed the gravitational equilibration. Equilibration times of 3 to 4 h which he reported in spite of stirring would indicate a slow relaxation such as a gravitational one. A comparison of Figs. 3 and 4 would indicate that less than 20% of the sample in our case, and perhaps in his, was within a few percent of the critical density, and that most of the rest of the sample, both near the top and near the bottom, had a heat-capacity maximum lower than T_c by a degree or more. Of course, the 1.09-g/cm^3 "isochore" of Fig. 3 is itself a composite of contributions by a sample with a range of densities so that changes in the anomaly with density will be even more pronounced than indicated in that family of curves. The anomalous heat capacity at the thin slab T_c of 16.590°C for our data is some 20 or 30% of the apparent anomaly-peak height. This observation compares favorably with the postulate that only that fraction of the sample is within a few percent of the critical density. Much of the slow decay of the anomaly with T, particularly below T_c, should probably be attributed to contributions of sample at other than critical density. This would mean that the true α' of Eq. (2), and possibly α, would be larger than previous analyses would indicate. For a sample of the height used in these measurements we would expect the heat capacity to rise very sharply at $T \gtrsim T_c$ but then to "lean over" with a lower slope at T slightly less than T_c as the shifted peak maximum is approached. There is a slight hint of such "leaning" in expanded plots of our data, but much closer analysis, and perhaps better experiments, will be necessary to determine if the effect will be observable in any more detail than just as an apparent over-all peak shift.

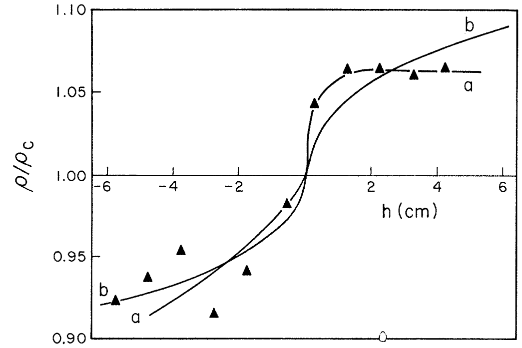

FIG. 4. Density variation with position in a xenon sample at T_c. (a) Tracer study by Weinberger and Schneider (Ref. 12) and (b) critical isotherm analysis for thin slab by Habgood and Schneider (Ref. 12).

In a later publication we will present a detailed analysis of the data with attempts at corrections of the gravitational effect using information from *PVT* measurements and from the probable behavior according to scaling laws.

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CYCLIC TEMPERATURE DEPENDENCE OF THE STIMULATED RAMAN EFFECT IN BENZENE*

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The cyclic temperature dependence of two stimulated Raman lines of benzene is reported. These data are inconsistent with the self-focusing theory for the anomalous gain.

We report an unprecedented cyclic temperature dependence of the 1.07-μ and the 8050-Å stimulated Raman lines in benzene. The 1.07-μ is a Stokes line, previously reported,[1] which is created by the interaction of the parallel ruby laser beam with two phonons of 992 cm^{-1}, and one phonon of 3064 cm^{-1}. The 8050-Å is the second Stokes line of the 992-cm^{-1}. Figure 1 shows the characteristic cyclic temperature dependence of the aforementioned lines.

An unfocused beam of a single-mode Q-switched ruby laser was used in these experiments. The laser-beam diameter was 4.2 mm. The 67-cm-long Raman cell was terminated by two optically flat quartz windows. A water jacket, surrounding the cell, enabled the setting of precise and stable temperatures. Sufficient time was allowed to attain temperature uniformity throughout the cell and the laser shots were separated by an interval of 2 min for reproducibility. The lines were separated from the transmitted ruby by a combination of quartz prism and uncoated concave mirror before entering a half-meter monochromator to which the detector was attached.

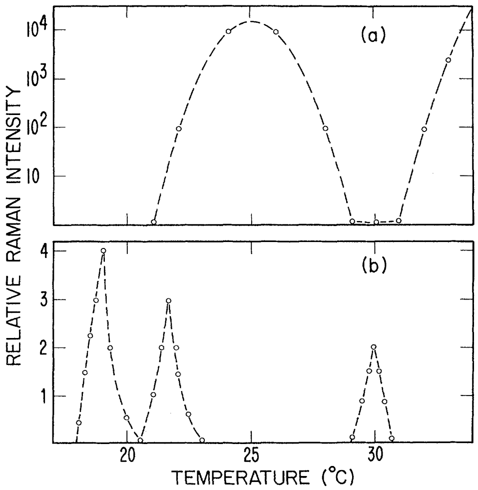

FIG. 1. (a) The relative intensity at 8050 Å as a function of the benzene cell temperature; incident power density at 6943 Å is 70 MW/cm^2. (b) The relative intensity at 1.07 μ as a function of the benzene cell temperature; incident power density at 6943 Å is 140 MW/cm^2.

We summarize here the results for the two lines of benzene mentioned above. The output at 8050 Å shows a maximum between 25 and 26°C and a minimum around 30°C. The intensity change between the maximum and minimum has been measured to be as high as four magnitudes. The data of Fig. 1(a) were taken with a constant laser power density of 70 MW/cm^2. Upon the increase of the laser power density up to 100 MW/cm^2, the position and amplitude of the maximum and minimum of the output remained the same as shown in Fig. 1(a), only the area under the curve increases. Upon the decrease of the laser power to 60 MW/cm^2, the only change is that the area under the curve decreases and the peak becomes sharper, but its position and amplitude remain unchanged.

The temperature behavior of the above line is an indication of a precise molecular mechanism being responsible for the stimulated Raman generation. A careful study of the 1.07-μ line underlines this assertion. Indeed, the 1.07-μ line showed a very specific and different temperature dependence. The data of Fig. 1(b) were taken with a constant laser power density of 140 MW/cm^2, just above the thresh-