[1]R. A. Ferrell, Phys. Rev. 108, 167 (1957).
[2]L. O. Roellig and T. M. Kelly, Phys. Rev. Letters 18, 387 (1967).
[3]J. A. Northby and T. M. Sanders, Jr., Phys. Rev. Letters 18, 1184 (1967).
[4]D. A. L. Paul and R. L. Graham, Phys. Rev. 106, 16 (1957); J. Wackerle and R. Stump, Phys. Rev. 106, 18 (1957); G. E. Manuzio, Nuovo Cimento 43B, 166 (1966).
[5]D. A. L. Paul, Can. J. Phys. 36, 640 (1958).
[6]D. C. Liu and W. K. Roberts, J. Phys. Chem. Solids 23, 1337 (1962), and Phys. Rev. 130, 2322 (1963), and 132, 1633 (1963).
[7]P. P. Fraser, Proc. Phys. Soc. (London) 79, 721 (1961).
[8]R. C. Tolman, J. Chem. Phys. 17, 333 (1949).

SPECIFIC HEAT OF XENON NEAR THE CRITICAL POINT*

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We report measurements of the specific heat of xenon near the critical point. Good accuracy and temperature resolution are achieved with a semiautomatic system permitting direct recording of the heat capacity. From analysis of the results allowing for the effects of gravity, we conclude a value for the exponent α of about 0.08, although a value between 0 and $\frac{1}{8}$ cannot be ruled out. A symmetric logarithm is not consistent with the results.

We have measured the specific heat of xenon at constant critical density in the neighborhood of the critical temperature. Thermodynamic analysis[1] shows that in equilibrium under gravity the specific heat $C_{V,g}$ possesses a high but smooth peak instead of the singularity expected in $C_{V,0}$. Our measurements fully resolve this peak for a sample height of 1 cm.

The xenon (99.94% purity) was sealed at a density of 1.099 ± 0.003 g/cc in a volume consisting of 180 interconnected vertical holes, 1.00 cm high and 0.08 cm in radius, drilled in a copper block wound with two independent heaters and with miniature thermistors mounted in recesses cavities. This calorimeter, silver plated on the outside, was suspended in vacuum inside a massive (5.2 kg) chromium-plated copper cylinder, stage 1, possessing heaters and thermistors. This in turn was supported in a second similar stage equipped in addition with a thermoelectric heat sink, the whole being buried in insulating material (Vermiculite).

The temperature of stage 2 was controlled by a servomechanism having both mean temperature and gradient feedback. The temperature drift rate of stage 1 could thereby be held below 5×10^{-9} deg sec^{-1} for periods of 1 and 2 h without need for manual adjustment. Temperatures were measured with a 21-cps transformer ratio-arm bridge and lock-in amplifier having an rms noise corresponding to 10^{-5} deg with 1-cycle bandwidth. Absolute temperatures were determined to within ±2 mdeg using a platinum resistance thermometer. In the principal mode of operation a constant power is supplied to stage 1 whose temperature rises linearly with time, the temperature of stage 2 being maintained close to that of stage 1 throughout. Constant power is supplied to one of the heaters in the calorimeter, the other receiving the power output of a servomechanism operating to maintain temperature equality with stage 1. Under these conditions the total power supplied to the calorimeter is the product of its heat capacity and the rate of temperature rise; thus the servo power, which is recorded directly, is proportional to the total heat capacity less a constant, and it is therefore possible to record directly the heat capacity of the xenon alone as a function of temperature. The system is very flexible and it is possible to operate with the temperature decreasing with time or to perform more conventional step-by-step measurements. Results obtained by the latter method are shown in Fig. 1 together with measurements of the intrinsic thermal time constant τ of the calorimeter. While we can readily follow transient changes and thus observe the thermal response of the calorimeter, it is difficult to obtain accurate values of τ, particularly where it is changing rapidly with temperature.

Very near the critical temperature the rapid rise in τ results in distortion of the observed heat capacity when $\tau\dot{T}(dC/dT)$ is not small compared with C itself; the lowest convenient value of the ramp rate $\dot{T}$ was 3×10^{-6} deg sec^{-1}.

In this region values obtained during cooling and heating runs differed by as much as 10% as shown in Fig. 1. Away from the inner region our results are accurate to about 1%, but within 20 mdeg from T_c this distortion leads to larger errors. However, the distortion in the shape of the ramping measurements clearly does not affect the integrated area which is the only aspect of the results from the inner region used in the asymptotic analysis below. There is a possible constant error of ±3 J/mole deg in the absolute values quoted due to uncertainty in the heat capacity of the empty calorimeter, which has not been measured separately. It is easily seen that such a constant has no effect on the shape of the specific heat nor on the analysis below.

Our results for the whole temperature range measured are shown in Fig. 2. For the purpose of an asymptotic analysis of the results, it is convenient to distinguish three temperature regions: (A) an inner region $|(T-T_c)/T_c|=|t|<3\times10^{-4}$ in which the influence of gravity is large; (B) a region used for analysis, $3\times10^{-4}<|t|<7\times10^{-3}$, in which one may hope that the asymptotic form is an approximation with 1% accuracy, and furthermore in which the gravity corrections are very small (<4%); and (C) an outer region where significant departure from the asymptote may be expected. We thus have available a factor of about 23 in t over which we attempt computed fits to the gravity-corrected results.

Quite apart from any explicit dependence of the thermodynamic functions on density gradient, the effect of gravity is very large on the apparent heat capacity near T_c of a fixed number $N=\rho V$ of atoms in a fixed volume V. An exact thermodynamic analysis of this effect is presented in a separate communication,[1] where comparison is made with some of the results of this experiment in region (A) not used for the present asymptotic analysis. For our purposes here, what is required is the difference between $C_{V,g}(T)$ and $C_{V,0}(T)$ when this difference is small. Consider a volume with cylindrical shape and let π be the pressure difference from the mean pressure $P^*(T)$, defined as the pressure at the level with as many atoms above as below. It can be seen that during a change of temperature the state of an element of the fluid remains at constant π. Thus $T^{-1}C_{V,g}(T)$ is given by the temperature derivative of the mean entropy,

$$S_g(T)=\frac{1}{2\pi_h}\int_{P^*-\pi_h}^{P^*+\pi_h}S(P,T)dP,$$

where $2\pi_h=mgh\rho$. At the critical density ρ_c, but away from T_c, it is valid to expand the

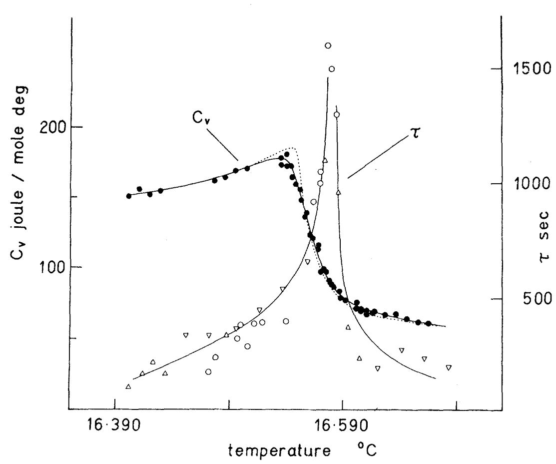

FIG. 1. The full circles show results obtained by conventional step methods in the immediate vicinity of T_c. The full and broken lines represent the average of several ramping measurements at $+10^{-5}$ deg sec^{-1} and a cooling run at -7×10^{-6} deg sec^{-1}, respectively. Open symbols show the result of time-constant measurements taken with 10-mdeg (triangles) and 5-mdeg pulses (open circles).

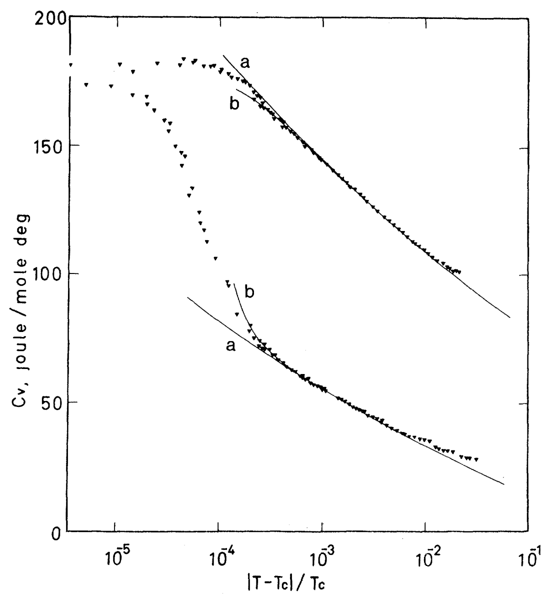

FIG. 2. Measured values of $C_{V,g}$ shown as a function of reduced temperature on a logarithmic scale (T_c =289.697°K). Curves a represent an asymptotic fit with $\alpha=0.065$ to the function: $C^+=101.31t^{-\alpha}-103.41$; $C^-=163.12|t|^{-\alpha}-111.66$. Curves b show the gravity correction applied to curves a.

entropy about the mean pressure, which in this case is also the pressure the same system would have in the absence of gravity. One then obtains

$$S_g(T)-S_0(T)=-\tfrac{1}{2}\pi_h\left|\frac{dV}{dT}\right|_{\text{coex}}+\tfrac{1}{6}\pi_h^{\,2}\left(-\frac{\partial^2 V}{\partial P\partial T}\right)+\cdots,$$

no linear term arising for $T>T_c$. Assuming that the coexistence curve and the compressibility can be characterized by the usual exponents β and γ, respectively, we can then estimate the gravity contribution to the specific heat from the results of Habgood and Schneider.[2] The dependence on β and γ is only through coefficients $\beta(1-\beta)$ and $\gamma(\gamma+1)$ which were taken as 0.22 and 3.0, respectively. These corrections for gravity, which are significant for the analysis, are shown in Fig. 3. We do not feel confident in extending them to smaller values of t where they would contribute more than 4%, since they do not possess an assured accuracy better than 20%.

We have attempted to fit the gravity corrected results in region (B) to functions of the form

$$A|t|^{-\alpha}+B.$$

Since the value of the entropy far above and far below T_c is unaffected by gravity, the integration of our gravity-affected results should give the correct entropy change also for zero gravity. Allowing for the few tenths of a percent correction from the small tail of the gravity effect beyond the integration region, we can therefore impose conditions on the integrated area of the fitted functions.

A conventional least-squares method of fitting was first used, each side of T_c being independently tested with A, B, α, and T_c as parameters. Demanding that $T_c^{\,+}=T_c^{\,-}$ and that there be agreement within $\frac{1}{2}\%$ with the area integrated over an interval of 2° permitted the calculation of the total rms deviation σ, for each value of α, including the logarithm as the case $\alpha=0$ and in the first instance requiring that $\alpha_+=\alpha_-$. This latter condition (as also the one requiring $T_c^{\,+}=T_c^{\,-}$) led to negligible increase in σ; thus there is no evidence on this score for the value of α not being the same above and below T_c. A plot of values of σ as a function of α reveals a shallow minimum, $\sigma_{\text{min}}=0.60$ J/mole deg, at $\alpha=0.065$ increasing by about 15% at $\alpha=\frac{1}{8}$ and nearly 20% at $\alpha=0$. Deviation plots for the functions with these values of α are shown in Fig. 3. It is clear that systematic deviations are just becoming apparent for $\alpha=0$ and $\frac{1}{8}$. The requirement on the integrated area proves a stringent one, locating the value of T_c, otherwise a free parameter, to within a millidegree for any specific function (the values differing by up to 10 mdeg for various functions however). Different choices of the integration limits should lead to the same results, which they do for $\alpha=0.08\pm0.02$, but outside this range, agreement is only achieved at the expense of a substantial increase in the deviations, amounting to as much as 50% in σ for the logarithm and

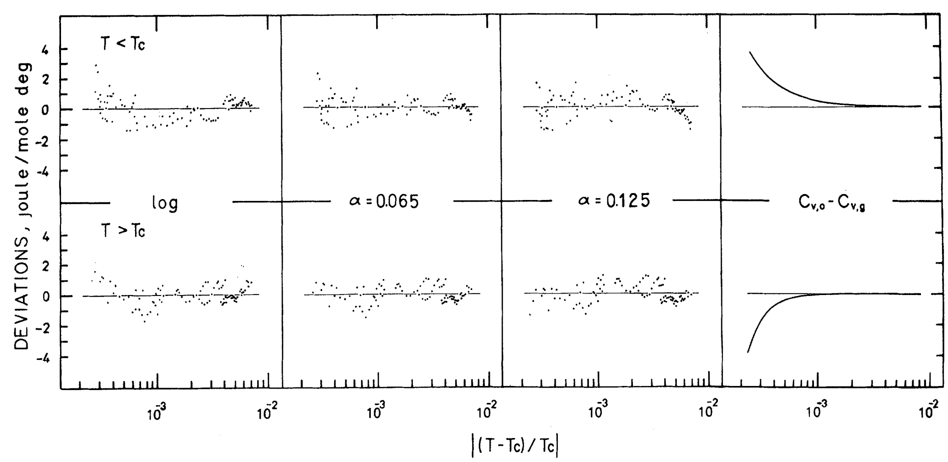

FIG. 3. Deviation plots of the gravity-corrected observed specific heat in the fitting region for three functions. log: $C^+=10.18\ln t^{-1}-14.57$, $C^-=16.13\ln|t|^{-1}+32.89$, $T_c=289.694$°K; $\alpha=0.065$: $C^+=102.22t^{-\alpha}-104.72$, $C^-=162.17|t|^{-\alpha}-110.34$, $T_c=289.695$°K; and $\alpha=0.125$: $C^+=35.87t^{-\alpha}-29.77$, $C^-=56.63|t|^{-\alpha}+8.85$, $T_c=289.695$°K. At the far right-hand side are curves showing the gravity corrections used.

25% for $\alpha = \frac{1}{8}$. In all cases, the ratio $A-/A+$ is within a few percent of 1.6, regardless of α. Attempts to fit a symmetric logarithm (with $A+ = A-$) have been made, but the best solution involves an increase in σ by a factor of more than 4, well outside any experimental uncertainty.

We conclude that our results for xenon favor a value for α of about 0.08, although a value between 0 and $\frac{1}{8}$ cannot be ruled out. The same value of α is indicated for each side of T_c, but the singularity is asymmetric in that the coefficient is 1.6 times as great on the low- as on the high-temperature side. While we do not believe it is justified to expect agreement within 1% of the asymptotic form beyond the value of the temperature difference considered, we note that if one nevertheless does so, these conclusions are not altered.

It is proper to point out a number of difficulties associated with the interpretation of our results. We have no adequate explanation of the difference of about 35 mdeg between the critical temperature and that of the maximum thermal relaxation time shown in Fig. 1. We note that Lorentzen[3] has observed a similar effect near the critical point of carbon dioxide. In this case the time-constant maximum occurred about 30 mdeg above the critical temperature obtained from meniscus observations. Another cause of concern, although perhaps attributable to impurities, is the fact that the critical temperature indicated by the meniscus observations of Habgood and Schneider[2] (16.590°C) is about 45 mdeg higher than that found by us. We can think of no reason to suppose that the density of the xenon in the cell is more than ±0.3% away from the quoted value, although a major error here could account for the temperature differences.

It could be conjectured that in the presence of impurities the establishment of diffusion equilibrium takes even longer than is indicated by our measured values of τ. However, measurements of $C_{V,g}$ made with negative ramp rates give essentially the same results as those for comparable positive rates (distorted slightly as described above). Furthermore, we have held the sample within 1 or 2 mdeg of T_c for periods of 12 h or more before starting a run, and on such occasions no detectable change in C_V has been observed.

We have concluded, as noted above, that a specific-heat singularity which, like that of the two-dimensional Ising problem and the λ transition in liquid helium, is logarithmic with the same coefficient on the high- and low-temperature side, is ruled out for the critical point of xenon by our results. It is not hard to see how the opposite conclusion has been reached[4] in studies of other gases for which the choice of T_c has been less restricted and gravity neglected, particularly in view of the more limited range of asymptotic agreement for $T > T_c$. We do not believe that the measurements themselves are inconsistent with our conclusion. Previous measurements[5,6] that have been reported for xenon are not of sufficient precision to permit a quantitative comparison.

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[1]M. J. Buckingham, C. Edwards, and J. A. Lipa, to be published.

[2]H. W. Habgood and W. G. Schneider, Can. J. Chem. 32, 98 (1954).

[3]H. L. Lorentzen, in Statistical Mechanics of Equilibrium and Nonequilibrium, edited by J. Meixner (North-Holland Publishing Company, Amsterdam, The Netherlands, 1965), p. 262.

[4]A. V. Voronel', V. G. Gorbunova, Yu. R. Chashkin, and V. V. Shchekochikhina, Zh. Eksperim. i Theor. Fiz. 50, 879 (1965) [translation: Soviet Phys.—JETP 23, 597 (1966)].

[5]H. H. Schmidt, J. Opdycke, and C. F. Gay, Phys. Rev. Letters 19, 887 (1967).

[6]A. V. Voronel', Zh. Fiz. Khim. 35, 958 (1961) [translation: Russ. J. Phys. Chem. 35, 471 (1961)].