

ing conditions are satisfied for all values of B :

$$B - p_{\parallel}' > 0, \quad B + p_{\perp}' > 0. \quad (10)$$

The first condition is always satisfied in the case of interest (magnetic confinement), and the second sets an upper limit of $\frac{1}{2}(B_{\max}^2 - B_{\min}^2)$ on the maximum of p_{\perp} at the center of the well [$p_{\perp\max} = p_{\perp}(B_{\min})$; $p_{\perp}(B_{\max}) = p_{\parallel}(B_{\max}) = 0$]. These are the same as Hastie and Taylor's conclusions, and they are seen to be unaffected by the presence of a nonvanishing \vec{j}_e .

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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PRECISION MEASUREMENT OF THE SPECIFIC HEAT OF CO₂ NEAR THE CRITICAL POINT*

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An experiment is reported in which the specific heat of a 1 mm high sample of CO₂ has been measured to within 12 mdeg of its critical temperature. The results show that the exponent $\alpha = \frac{1}{3}$ both above and below T_c , a value in agreement with the Ising model but inconsistent with scaling law analyses of existing PVT data.

The reliable measurement of the specific heat of a fluid near its critical point presents particular difficulties because of the effects of gravity and the problem of achieving equilibrium in the face of "critical slowing down." Distortion produced by the earth's gravity has been the main limitation on the validity and resolution of attempts reported so far to establish experimentally the form of the specific-heat singularity and in particular the value of α . At the critical density, C_v is assumed to diverge at the critical temperature T_c like $|t|^{-\alpha}$, where α is possibly different for the branches of the expression above and below T_c and where $t = 1 - T/T_c$. The effects of gravity¹ distort the specific heat if the relative temperature difference t is much less than a characteristic value t_h dependent on the height h and the atomic mass m of the fluid sample, where $t_h = (mgh/2kT_c)^{1/\beta\delta}$; $\beta\delta \approx \frac{5}{3}$ (e.g., for Xe with $h = 1$ cm, t_h corresponds to a temperature difference of 0.13 K).

We report here measurements of the specific heat of CO₂ of nominal purity 99.996%, permanently sealed at a density of 0.4660 ± 0.0008 gm cm⁻³ inside a calorimeter of only 1 mm height,

for which t_h corresponds to 17 mdeg. The disk-shaped calorimeter was constructed of high-strength stainless steel with internal reinforcing members to maintain its volume constant while keeping its contribution (about 40% at the specific heat maximum) to the total heat capacity as small as possible. Critical slowing down was evident in the rapid increase (approximately as the inverse $\frac{2}{3}$ power of the temperature interval) in the thermal relaxation time, τ , observed as the temperature was raised towards T_c , the value of τ becoming as large as 1000 sec 2 mdeg below T_c . Precise temperature control of the surroundings of the calorimeter was achieved by the use of a multistage thermal environment combined with a constant-ramp-rate method of measurement, similar to that previously described,¹ but refined by the addition of a further stage of thermal isolation which greatly improved the performance.

At a rate of change of temperature, or ramp rate \dot{T} , of 10^{-6} deg sec⁻¹, for which the signal-to-noise ratio permits a precision of about 1% in the specific heat of the CO₂ specimen, the resolution is limited to about 10^{-2} deg each side of

the critical temperature. Within this interval the increasing thermal time constant τ causes a significant distortion of the measurements. Also the calculated distortion due to gravity for the 1 mm high sample becomes about 1% at this temperature and, while this could be allowed for as in Ref. 1, the necessary information concerning the equation of state so near the critical point is in any case too uncertain to permit a useful extension of the range of measurement. Our reported² results therefore are limited to magnitudes of the relative temperature interval $t > 4 \times 10^{-5}$, corresponding to 12 mdeg. In all, 1100 data points were collected in 35 runs at various ramp rates ranging from 10^{-4} to 3×10^{-7} deg sec⁻¹, each point representing an average of 900 sec of record. Cooling runs were used only for checking purposes. The scatter in the observations ranges from $\frac{1}{4}$ % far from T_c to 1% at the inner limit. This increase is due to the necessary use close to T_c of smaller ramp rates and the consequent lower signal-to-noise ratio. A possible constant error estimated as ± 10 J/mole deg arises from uncertainty in the heat capacity of the empty calorimeter.

The present report is concerned with the asymptotic temperature dependence of the specific heat near the critical temperature. For this purpose we have compared our results with functions of the class

$$C_p/R = A|t|^{-\alpha} + B, \quad (1)$$

where A , B , T_c , and α are separate parameters for the branches of the function above and below T_c , and R is the gas constant.

For any particular test function, the value can be computed of the weighted sum of the squares of the deviations of the data points from that function. The minimum value of this sum as the parameters are varied subject to any constraint imposed on the test function is defined as Σ^2 , which is thus a function of the particular constraints imposed as well as the range of data points included.

The class of functions (1) proves inadequate to describe the data if points too far from T_c are retained. However if the range of $|t|$ is restricted to $|t| < 5 \times 10^{-3}$ no significant reduction in Σ^2 can be obtained by extending the class of functions with the inclusion of further parameters; an additional term, for example one linear in t , can cause a significant improvement if data beyond that limit are included but not otherwise. About 440 of the data points lie within the range

$4 \times 10^{-5} < |t| < 5 \times 10^{-3}$ and further discussion is restricted to this asymptotic region.

For a specified pair of values of α^+ and α^- the value of Σ^2 is by definition minimized with respect to all the other six parameters A^\pm , B^\pm , T_c^\pm . (The superscripts refer to the two branches $T > T_c$ and $T < T_c$, respectively.) The dependence of this Σ^2 on α^+ and α^- is shown in Fig. 1 by the broken line which is the locus of pairs α^+ , α^- for which the value of Σ^2 is one standard deviation greater than the minimum possible value, Σ_0^2 . This contour line thus represents the 68% confidence level, if the data are normally distributed. If any further constraint is imposed on the test function the value of Σ^2 can only increase, but if the constraint is consistent with the data there will remain a significant fraction of the area enclosed by the contour still within one standard deviation of Σ_0^2 . The effect of constraining the value of $T_c^+ - T_c^- = \Delta T_c$ to be zero is to make the one standard deviation contour that shown by the full line in Fig. 1. The area of this contour would be a maximum if the constrained value of ΔT_c were -2 mdeg and would shrink to zero at the limits

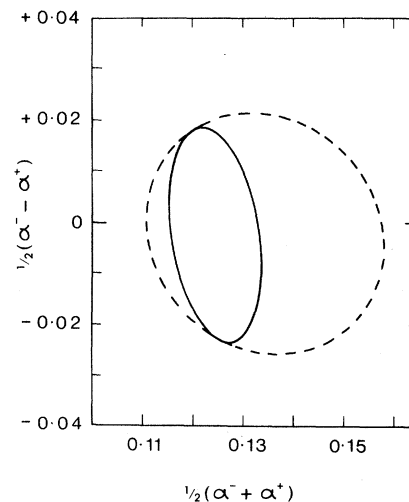


FIG. 1. Showing the goodness of fit of the observed specific heat of CO_2 in the asymptotic region $|T - T_c| < 5 \times 10^{-3} T_c$ by test functions with various values of α^- and α^+ , the critical exponents for the branches below and above T_c , respectively. The curves are contour lines at which the fit is one standard deviation worse than the best possible. The broken curve results when the two branches are considered independently, with possibly different values for T_c ; the full curve when T_c is constrained to be the same for each branch. The figure shows that there is no evidence that it should not be the same. The figure also shows no evidence that the values of α^- and α^+ should differ.

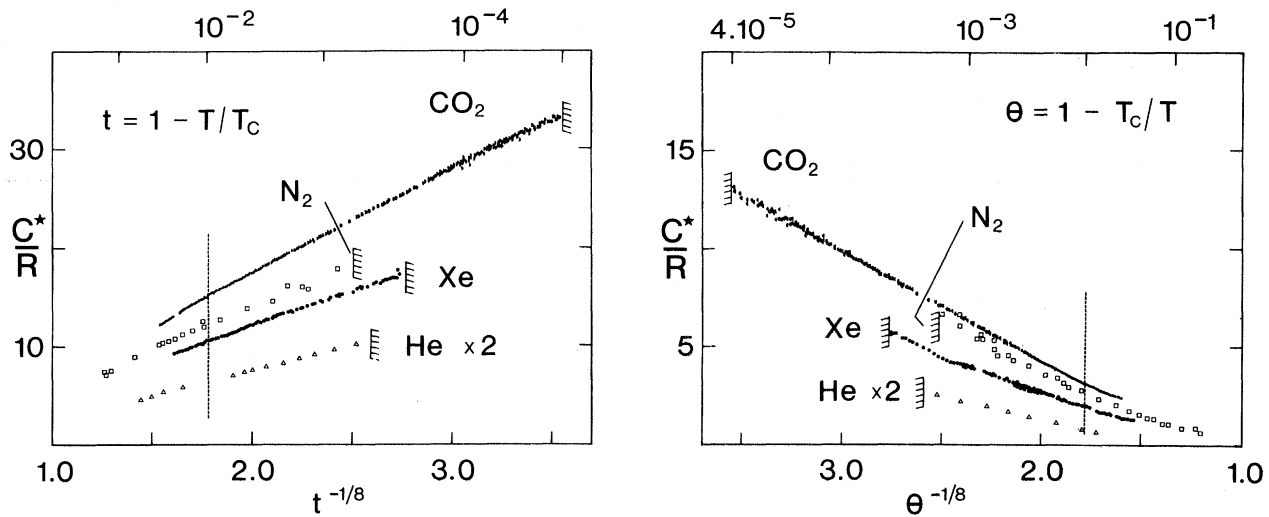


FIG. 2. The upper sets of points show the values observed for the specific heat of CO₂ less its ideal gas value at T_c; C* = C_v - C_{ideal}. (For CO₂, C_{ideal} ≈ 7R/2.) They are plotted against the inverse one-eighth power of the interval from the critical temperature and show the straight line dependence in the asymptotic region (inside the vertical dotted lines) indicating α = 1/8. Nearer to T_c than the cross-hatched markings, measured values are seriously affected by gravity and are not displayed. The other sets of points displays in the same fashion results that have been published for some other fluids. (Note that there is a factor 2 different in the vertical scale of the two parts of the figure; also that C* for He has been multiplied by 2 for clarity.)

of the range

$$T_c^+ - T_c^- = \Delta T_c = -2 \pm 5 \text{ mdeg.}$$

The results are thus fully consistent with the expectation that T_c⁺ = T_c⁻.

Figure 1 also demonstrates that the data require α⁺ and α⁻ to be essentially equal. In fact, taking T_c⁺ = T_c⁻,

$$\frac{1}{2}(\alpha^- - \alpha^+) = 0 \pm 0.02; \quad \frac{1}{2}(\alpha^- + \alpha^+) = 0.125 \pm 0.01.$$

If both T_c and α are constrained to have the same values for each branch we find the best fit function is given by Eq. (1) with α = 1/8 and

$$A = 10.473, B = -0.024, T < T_c;$$

$$A = 5.583, B = -3.457, T > T_c.$$

The observed values for the specific heat of CO₂ are presented in Fig. 2, plotted against the inverse one-eighth power of the interval from the critical temperature. Also shown for comparison are results that have been published for some other fluids: Xe,³ N₂,⁴ and ⁴He.⁵ In each case however the data have been restricted by the hatched markings to the region unaffected by gravity for the appropriate experimental arrangement. Other fluids⁶ show similar features but, for clarity in the figure, are not displayed.

It is apparent that a linear dependence in this diagram, corresponding to α = 1/8, is consistent

will all the measurements within the asymptotic temperature interval up to 1% of T_c, indicated in the figure by the vertical broken line. Thus there is no evidence from direct measurements unaffected by gravity that for any gas the value of α is significantly different from 1/8.

The effect of gravity shows itself clearly in Fig. 3 which demonstrates that the specific heat

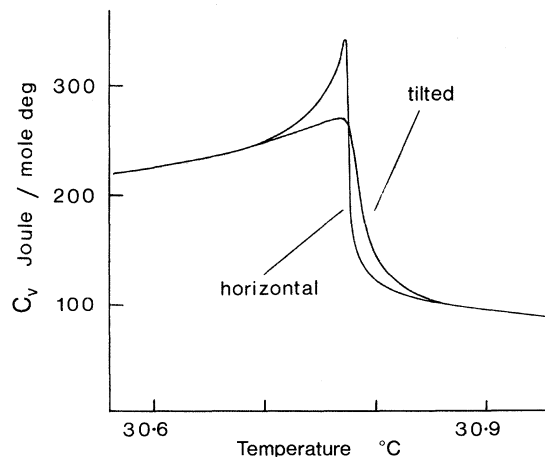


FIG. 3. The measured specific heat of a 1 mm high sample of CO₂ near the critical temperature. The effect of gravity is demonstrated by the curve labeled "tilted" which shows the results measured with the same disk-shaped sample tilted out of the horizontal plane so that its total height is 14 mm.

is grossly distorted in the qualitative way theoretically expected.⁷ From the features shown by this figure it is not hard to see that retention in an asymptotic analysis of results affected by gravity would tend to reduce the apparent value of α for the low-temperature branch while increasing it on the high-temperature side.

It has been noted that in order to reduce the effect of gravity the vertical dimension h must be made small. If it is too small, however, finite-size effects would distort the results. It is reasonable to suppose that so long as the correlation length remains sufficiently small compared with the linear dimensions of the fluid such finite-size effects (and explicit gravity-dependent effects¹) will be negligible. As h is reduced, resolution can be achieved closer to the critical point. However, at that point the correlation length diverges, so that its value at the resolution limit correspondingly increases. There is therefore an optimum height which is a compromise between gravity and finite-size effects. If we adopt the arbitrary criterion that at its largest the correlation length must not be more than $10^{-3}h$ we find that for CO_2 the optimum value for h in the earth's gravity is about 0.3 mm. This value would allow some extension of the range of our C_v measurements—in fact, to the inner edges of the diagrams in Fig. 2, which can in this sense be regarded as the limit of possible measurement in an earth-bound laboratory. It might be thought that an experiment in an orbiting satellite and free of gravity would permit a substantial improvement but this is not so, unless a new and more sensitive type of thermometry becomes available. It is only possible to measure C_v with precision at a resolution about 10^3 times the noise level of temperature measurement. Using thermistors and phase-sensitive detection the latter can be made as low as $10^{-8}T_c$ but much improvement beyond this figure is not yet in sight.

The value $\frac{1}{8}$ found for α is in striking agreement with the value obtained from numerical studies⁸ of the three-dimensional Ising model. On the other hand the value $A^-/A^+ = 1.88$ found for the ratio of the coefficients below and above T_c is much larger than the Ising-model values, e.g., 1.33 found by Gaunt and Domb⁹ for the tetrahedral lattice. This ratio may be expected to depend on more features of a statistical system than does an exponent such as α , however. The exponents are only known for certain to depend on two features of a system with short-range forces. These are the dimensionality d of space

and D of the order parameter. Of three-dimensional fluid systems, $D = 2$ for the λ transition of liquid helium but $D = 1$ for the gas-liquid critical transition, as for the Ising model. Thus if the critical exponents depend on no other property of a system, we could expect a value the same for Ising and gas-liquid systems but different for the helium λ transition. This indeed appears to be the case as far as the specific-heat exponent α is concerned. On this basis one could also expect agreement with the Ising model for the exponents describing the equation of state. For the Ising model¹⁰ $\gamma \approx 5/4$, $\delta \approx 5$, and $\beta \approx 5/16$, where γ , δ , and β are the exponents characterizing the compressibility, critical isotherm, and coexistence curve, respectively. A recent analysis by Vicentini-Missoni, Levelt Sengers, and Green¹¹ of PVT measurements on several fluids including CO_2 , in terms of a scaled equation of state, led to the conclusion that the results were consistent with the scaling laws, with values $\gamma \approx 5/4$, $\delta \approx 4.6$, and $\beta \approx 0.35$. Consistency furthermore required that α was about 0.04, and in any case less than 0.1. The value $\frac{1}{8}$ now found for α suggests a serious inconsistency, if scaling is to be maintained, between the calorimetric and equation-of-state measurements.

The strict requirements of scaling when $\alpha^+ = \alpha^- \neq 0$ imply values of the coefficient A different for the two branches of the function (1) but the same value for B . This is not consistent with the present results: Imposition of the condition $B^+ = B^-$ would lead to an increase in Σ^2 of no less than 9 standard deviations. Extension of the class of function (1) to include nonasymptotic terms in the scaling theory may resolve this problem but such extended analysis of our results is left for another occasion.

The value of T_c for CO_2 found from the present analysis is 303.925 ± 0.005 K (30.775°C) and is significantly lower than the generally accepted value. For example, Michels, Blaisse, and Michels¹² and Lorentzen¹³ find $T_c = (31.04 \pm 0.01)^\circ\text{C}$, although a more recent analysis by Vicentini-Missoni, Levelt Sengers, and Green¹¹ of the former worker's equation of state measurements leads to a value $(30.94 \pm 0.04)^\circ\text{C}$. It is by no means exceptional—indeed it is usual^{6, 14}—for calorimetric measurements to yield smaller values for critical temperatures than PVT or optical measurements. In spite of the great care taken it is difficult to rule out the possible existence of some contamination, perhaps by a small percentage of air which could be expected to shift the

critical temperature (but by less than a part in a thousand) without significantly altering the form of the specific heat singularity.

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The result originally given as $\alpha = 0.08 \pm 0.08$ now becomes 0.14 ± 0.07 .

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EFFECT OF LONGITUDINAL ELECTRIC FIELD ON TOROIDAL DIFFUSION

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The driving toroidal electric field in Tokamaks is shown to lead to a significant pinching effect at low collision frequency. For $\beta_\theta = 8\pi p/B_\theta^2 < 1$, where B_θ is the poloidal field, this pinching is more rapid than outward diffusion in the banana and plateau regimes of toroidal transport theory.

It has been pointed out by Ware¹ that the driving electric field E in plasma confinement devices of the Tokamak type produces for trapped particles a radially inward particle drift of E/B_θ (where B_θ is the poloidal magnetic field), much larger than the usual electric drift $\vec{E} \times \vec{B}/B^2 = EB_\theta/B^2$. This surprising result may be understood by noting that the electric field acts to displace the "banana" orbits of trapped particles leading to an up-down asymmetry due to which the radial magnetic drifts no longer cancel. However, this simple picture is not adequate since the effect of the electric field on untrapped particles is rather complex. More important, the collisional friction between particles perturbs the orbits in a similar way to the electric field. Since the equilibrium field necessary to drive the current must be of the order of the frictional forces, a self-consistent solution of the problem must be sought.

In the present paper self-consistent solutions of the collisional problem are derived in three regimes, namely the "banana," "plateau," and "classical" regimes of transport theory²⁻⁴ in axisymmetric toroidal systems. In each case an inward radial particle flux is found and is shown to be automatically ambipolar. For the smallest collision frequencies (the banana regime) the inward particle flux is found to be $2.8(r/R)^{1/2}nE/B_\theta$, roughly that which would be obtained by multiplying the drift E/B_θ by the density of trapped particles, but in the other regimes the flux is smaller. In both banana and plateau regimes a balance between the inward flux and outward particle diffusion occurs at about $\beta_\theta = 8\pi p/B_\theta^2 \sim 1$, a somewhat larger numerical value pertaining to the plateau regime. However, it must be pointed out that both experimental and thermal diffusion time scales are shorter by an order of magnitude than the time scale for particle diffusion discussed here.

We employ the usual toroidal coordinate system (r, θ, φ) , where θ and φ are angles around the minor