

Specific heat of CO₂ near the critical point*

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We describe an experiment to measure the specific heat of CO₂ to an accuracy of 1% along the critical isochore for $4 \times 10^{-5} < |t| < 3 \times 10^{-2}$, where $t = 1 - T/T_c$, giving details of the method and the analysis. After applying a correction term for the effect of gravity on the specific heat of the 1-mm-high sample, we fitted the data with functions of the form $C_v = A|t|^{-\alpha} + B$. With the constraint $\alpha = \alpha'$ the optimum value of the exponent was $\alpha = 0.124 \pm 0.005$. When this constraint was relaxed, we obtained $\alpha = 0.124 \pm 0.014$ and $\alpha' = 0.124 \pm 0.012$. These results are in good agreement with predictions based on renormalization-group analysis and numerical estimates for the three-dimensional Ising lattice. For the ratio A^+/A^- of the coefficients of the divergent term on each side of T_c , we obtained the value 0.54, which is within the range of predictions from scaling and the renormalization-group method, but disagrees with the estimate for the Ising model. We also present the results of measurements of the thermal relaxation time of the sample.

I. INTRODUCTION

Within the past few years there have been considerable advances^{1,2} in the theoretical understanding of the behavior of systems near the critical point. In particular renormalization-group (RG) techniques have been applied and expressions derived for the critical exponents and coefficients as functions of the dimensionality d of the system and the number of degrees of freedom n of the order parameter. Using a variational technique within the RG framework, Kadanoff³ has recently derived values for critical exponents of two- and three-dimensional Ising systems. These and other predictions may be compared with experimental results; here we describe a precise determination of the specific-heat divergence along the critical isochore which allows such comparisons to be made.

The sample material was CO₂, chosen to minimize the gravity effect: under certain assumptions the temperature interval over which the effect is important can be shown to be proportional to $(m/T_c)^{3/5}$, where m is the molecular of the fluid and T_c is its critical temperature. The value of this parameter is less for CO₂ than for any other commonly studied material. By restricting the height of the sample to 1 mm, it was possible to use data obtained for $|t| = |T/T_c - 1|$ as small as 4×10^{-5} in the curve-fitting analysis. This is almost an order of magnitude closer to T_c than has been reported previously^{4,5} for data of similar accuracy, allowing an improved determination of the asymptotic form of the specific-heat divergence at the critical point.

We used a continuous-heating method of mea-

surement, based on observing the power required to change the temperature of the sample at a constant rate. A large amount of precise data was collected comparatively easily, allowing the reliable estimation of the curve-fitting parameters after the application of a small correction for the effect of gravity. We have fitted our results with functions of the class

$$\begin{aligned} C_v/R &= A^+|t|^{-\alpha} + B^+, & T > T_c \\ &= A^-|t|^{-\alpha'} + B^-, & T < T_c, \end{aligned} \quad (1)$$

where A , B , α , and T_c are parameters determined by separately minimizing the squared deviations of the data on each side of the transition. There is good agreement between our estimates of α and α' , the predictions of the RG method^{1,3} and numerical estimates for the three-dimensional Ising model.⁶ Our estimate of the ratio A^+/A^- agrees with the RG prediction⁷ but conflicts with the Ising-model estimate,⁸ possibly due to the low accuracy of the series-expansion method below T_c .

A preliminary report of this experiment has appeared,⁹ and the continuous-heating method has been described in detail.¹⁰ In this paper we present the details of the experiment and the method of analysis, and compare the results with the new theoretical predictions. In Sec. II we describe the calorimeter, the sample preparation and the thermometry, and in Sec. III we discuss the measurements of the thermal relaxation time. Section IV contains a description of the heating-rate dependence of the specific-heat data and a summary of the residual uncertainties in the data. In Sec. V we discuss the effect of gravity on the results and describe a correction term which must be applied.

Section VI is devoted to the details of the data analysis and a comparison of the results with theoretical predictions.

II. EXPERIMENTAL DETAILS

The continuous-heating method we used to measure heat capacity can be described briefly as follows: First the sample is placed in a vacuum-insulated thermal enclosure and its temperature is controlled to equal that of the enclosure. The enclosure is then heated at a constant predetermined rate, and the power required to force the sample to heat at the same rate is measured. With this arrangement the power dissipated in the sample is proportional to its heat capacity, allowing the data to be recorded directly. The thin-parallel-plate calorimeter geometry, dictated by the requirement for small-gravity effects, attenuates the effect of the constant heating rate on the degree of equilibrium within the sample. The residual effects are observed by measuring the heat capacity over a wide range of heating rates.

The calorimeter was a thin, disk-shaped stainless-steel container with lids of thickness 0.015 cm which were internally braced with annular bulkheads. The internal height was 0.10 cm except in the 0.033-cm-diam nickel filling tube which contained less than 0.05% of the sample. The radius of the calorimeter was 1.5 cm. To reduce the effect of the thermal time constant of the calorimeter on the temperature gradients in the specimen and to increase its reflectivity, the calorimeter was plated with a layer of silver 0.002 cm thick. Measurements of the thermal relaxation time of the filled calorimeter made far above T_c were consistent with the calculated value of 5 sec. In this range of temperature the thermal relaxation time of the CO₂ is small, and its heat capacity relatively low, so the calorimeter responded to a heat pulse almost as if it were empty. The measured value of the heat leak between the calorimeter and its surroundings was 0.8 mW/°C. The heat capacity of the empty calorimeter was estimated to be about $\frac{2}{3}$ that of the contents at the critical temperature. Two 415- Ω four-terminal heaters were wound on the periphery of the calorimeter, attached with a thin coating of varnish and covered with a press-fit silver-plated stainless-steel band. To minimize the contamination of the sample, the calorimeter was constructed entirely of type 25-20 stainless steel and nickel, except for the brazing alloy which was a nickel-gold eutectic mixture. Extreme cleanliness was achieved by joining all the components by fluxless vacuum brazing at approximately 800 °C using a rf induction furnace. After removal from the furnace

the calorimeter was sealed for final external machining, and subsequently (for example while measuring its volume) it was filled only with air or CO₂ of the same purity as the final sample. A cross section of the calorimeter is shown in Fig. 1.

The internal volume V_i of the calorimeter and its "compressibility," $(1V_i)\partial V_i/\partial P$, were measured by a ratio technique. The calorimeter and a rigid vessel of known volume were connected, filled with high-purity CO₂, and allowed to come into thermal equilibrium. The valves in the connecting tube were then closed, and the vessels separated and weighed. The ratio of the volumes was then equal to the ratio of the weights of the gas filling the two systems. Care was taken to close the valves only when the fluid was in the one-phase region. The volume of the calorimeter at the critical pressure and room temperature was 0.6961 ± 0.0002 cm³ and its compressibility was 1.6×10^{-4} /atm. After the initial filling of the calorimeter with the high-pressure gas, there was no evidence of irreversible volume changes on cycling from 1 to 85 atm. From the above compressibility and the thermal-expansion coefficient of the calorimeter material it can easily be shown that the small deviation of the thermodynamic path followed by the CO₂ sample from the critical isochore has a negligible effect on the values obtained for C_v .

After its volume had been determined the calorimeter was filled with research-grade CO₂ of nominal purity 99.996%. The major impurities were stated¹¹ to be 30 ppm H₂O, and 5 ppm N₂. The filling system was constructed of metal except for two PTFE valve seats, and contained a small bomb for storing pressurized CO₂. After the calorimeter was attached to the filling system and evacuated, the bomb was cooled with liquid nitrogen, and CO₂ condensed in from the storage bottle. The bomb was then opened to a diffusion pump and slowly warmed until an appreciable sublimation rate was achieved. This was gradually increased until the pump throughput saturated. The evacuated calorimeter was then opened to the bomb and the pump valved off. The calorimeter was then cooled until it filled with CO₂ to a density greater

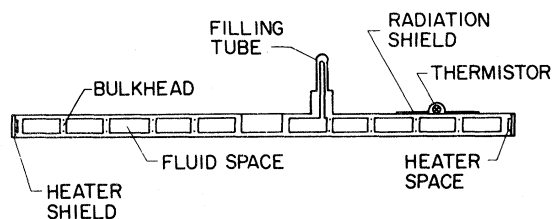


FIG. 1. Vertical cross section of the calorimeter.

than the critical value, when it was sealed off and warmed to room temperature. To reduce the mean density to the critical density, a very slow leak of small internal volume was attached to the all-metal valve on the filling capillary of the calorimeter. By opening the valve for measured time intervals it was possible to adjust the amount of gas inside with a precision of a fraction of a milligram. After the density of the sample has been adjusted, the capillary was clamped shut near the body of the calorimeter, and the unwanted portion cut off. A close-fitting wire was then placed in the open section of the tube, and the hole was welded shut, trapping a very small pocket of gas inside. The increase in the gaseous impurity level in the sample when the clamp was removed was estimated to be well below 1 ppm of the CO_2 , while the change in the mean density of the sample was estimated to be less than 0.01%. The mean density at T_c and the mass of the gas in the calorimeter were $0.466_0 \pm 0.0008 \text{ g/cm}^3$ and $0.3244 \pm 0.0005 \text{ g}$, respectively.

For the specific-heat measurements, we required thermometers with low heat capacity, high resolution, and high stability. Miniature thermistor beads seemed ideal, but little information was available concerning their stability. We therefore monitored the resistance of a number of beads when they were located in water triple point cells cooled to 0.01°C . The equilibrium temperature of these cells is reported¹² to be stable and reproducible to an accuracy of about 10^{-4}°C over long periods of time. We found that for periods of at least 24 h the beads in the cells were stable to the limit of detectability, which was a drift rate of about $10^{-4}^\circ\text{C/day}$. Provided that the beads were adequately protected from any shunting resistances (e.g., moisture) the output signal from the bridge was well behaved, with a noise level of the expected value. Over the course of three weeks testing during which the beads were repeatedly cycled up to room temperature, the triple-point resistance drifted by an amount equivalent to a few millidegrees. These results indicated that the stability of the thermistors significantly exceeded our requirements.

We therefore used thermistor beads of 0.04 cm diam and 100 k Ω nominal resistance at 25°C for all high-resolution temperature measurements. Two thermistors were located on the calorimeter, and others were placed in the thermal enclosure. All were attached with thin films of varnish and covered with aluminum-foil radiation shields. The leads to the thermistors were thermally anchored both to the surface on which they were mounted and to all surrounding thermally controlled surfaces. The resistance R of the thermistors could

be measured with either of two seven-decade transformer-ratio arm bridges, the output signals of which were monitored by a Princeton model HR-8 lock-in amplifier and a Brookdeal model FL355 lock-in. With a 1-sec integration time a temperature change of 10^{-5}°C could easily be detected when dissipating $4 \times 10^{-7} \text{ W}$ in a thermistor. During the specific-heat measurements the resistances of five thermistors were often measured when they were in thermal equilibrium with a platinum resistance thermometer (PRT) located in the thermal environment. This thermometer was previously calibrated to within $\pm 2 \text{ m}^\circ\text{C}$ by the CSIRO National Standards Laboratory. Of these thermistors, four gave readings consistent to within a fraction of a millidegree while the fifth drifted slowly. During a two month period the total drift of the first four, determined by the displacement of the peak of the specific heat of the sample, was found to be approximately $0.3 \text{ m}^\circ\text{C}$. Comparison with the PRT over a six month period showed no drift to within the accuracy of the measurement, which was $\pm 2 \text{ m}^\circ\text{C}$. We calibrated the thermistors against the PRT over an 18°C temperature interval spanning T_c and fitted a three-parameter function to the set of (R, T) points. Values of dT/dR derived from the best-fit function appeared to be accurate to within $\pm 0.2\%$ over the whole range. We expect the variations of any error in dT/dR to be considerably less than 0.1% over the 6°C interval spanning T_c which was of most interest to us.

III. THERMAL RELAXATION TIME

Along the critical isochore in the two-phase region the thermal relaxation time τ of a fluid diverges like $|t|^{-\gamma}$. Dahl and Moldover¹³ obtain $\gamma = 0.97 \pm 0.02$ for ^3He , but Brown and Meyer⁵ find $\gamma = 0.67$ which gives better agreement with our data⁴ for xenon. The effect of this singularity in τ on the accuracy of specific-heat measurements depends on the details of the technique used to obtain the data. With our method of measuring C_v , departures from the equilibrium value of C_v of the order of $\dot{T} \partial \tau / \partial T$ and $(\dot{T} \tau / C_v) \partial C_v / \partial T$ are to be expected at a heating rate \dot{T} . With good calorimeter design, τ can be made quite small, but ultimately it becomes necessary to reduce \dot{T} as $|t|$ becomes very small. In order to predict the region in which these distortions of C_v become important we measured the value of τ as a function of temperature. The results of these measurements are shown in Fig. 2. The data were obtained by applying small pulses of heat to the calorimeter and observing the response of a thermometer on its surface. The solution¹⁴ of the solid-body heat-

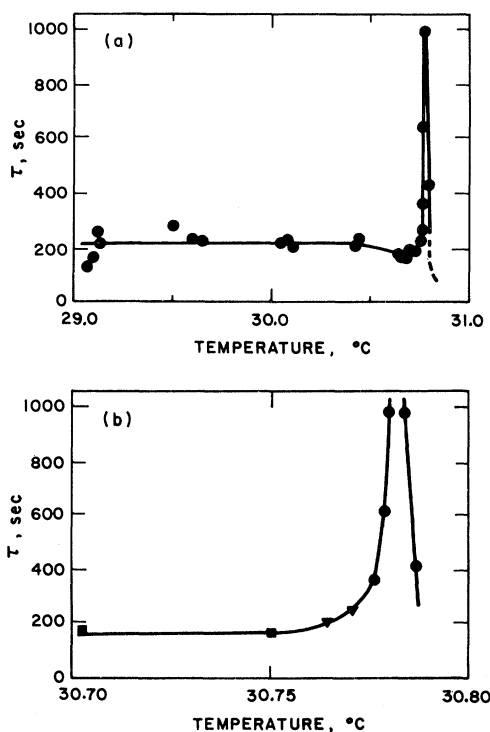


FIG. 2. Temperature dependence of the thermal relaxation time of the sample of CO₂: (a) data obtained over a wide range of temperature; (b) data obtained close to T_c . Heating pulse lengths: ●, 3 m°C; ▼, 6 m°C; ■, 20 m°C.

diffusion equation for this situation predicts that even far from T_c the initial temperature decay should be quite nonexponential, as was observed. However, after a period equal to about one-third the asymptotic relaxation time, a measurement of the interval over which the signal decays by a factor e is predicted to be within 30% of the asymptotic value, τ . With a rough initial estimate of τ , we were able to use this criterion to obtain the asymptotic value from the decay curves by iteration. The accuracy of the measurements was estimated to be $\pm 30\%$, limited primarily by the uncertainty in the final temperature of the calorimeter.

The data in Fig. 2 shows that outside the range 30.75–30.79 °C, $\partial\tau/\partial T$ is less than 100 sec/°C, so for $\dot{T} < 10^{-4}$ °C/sec the error introduced into C_v will be less than 1%. On the other hand, the correction term proportional to $\partial C_v/\partial T$ can approach 10% in the same temperature interval. For this reason, as T_c is approached, we must progressively reduce \dot{T} in order to maintain accuracy in our measurements of C_v .

Very close to T_c , where both τ and $\partial\tau/\partial T$ rise sharply, it might be argued that nonlinear effects

could cause relatively large inaccuracies in the specific-heat data. In similar regions extremely long settling times for density gradients have been reported,¹⁵ which could conceivably affect thermal measurements. However, it is just in this region that we reject data on other grounds: here the corrections applied for the effect of gravity on C_v become uncertain to a degree that would affect our results. We therefore feel confident that the results of the curve-fitting analysis are not significantly affected by long-term relaxation effects. This conclusion is further supported by the results of a previous experiment⁴ in which close agreement was found between specific-heat data obtained with the continuous-heating method and with the more conventional heat-pulse method. In that experiment relaxation times 50% higher were encountered, and heating rates ten times higher were used.

IV. SPECIFIC-HEAT DATA

During the course of the experiment over 300 hours of heat capacity records were obtained. This data was manually averaged over intervals of 900 sec, and then computer corrected as described in Ref. 10. The resulting set of some 1100 data points consisted of measurements made at heating rates in the range 10^{-4} – 3×10^{-7} °C/sec. The dependence of the observed specific heat on heating rates in the range 10^{-4} – 10^{-6} °C/sec is shown as a function of temperature in Fig. 3. Below T_c for small departures from the undistorted curve the fractional deviations are of the order $(\dot{T}\tau/C_v)\partial C_v/\partial T$ as expected, but very close to T_c larger departures are observed possibly due to the correction term $\dot{T}\partial\tau/\partial T$ or higher order terms. Above T_c , the deviations from the undistorted curve are very nonlinear and are better characterized by a settling time, almost independent of the heating rate, with which the sample recovers from the passage through the singularity. This settling time was of the order of 500 sec. In order to check the degree of equilibrium attained within the sample near T_c when heating at 10^{-6} °C/sec, data was also collected while cooling at the same rate. These sets of data are compared in Fig. 4. It can be seen that for $|t| \geq 3.5 \times 10^{-5}$ the two sets of data agree to within approximately 1%. Since in many cases the nonequilibrium effects were not linearly related to the heating rate, we decided to reject the affected data rather than correct it. This reduced our data set to about 800 points¹⁶ for use in the analysis.

There are a number of sources of uncertainty in our data. For the determination of the specific-heat exponents, the most important are in the

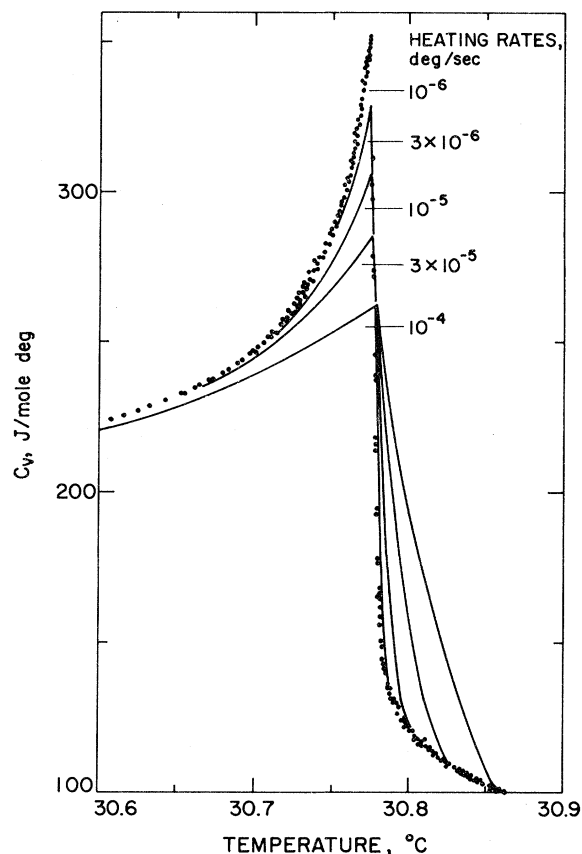


FIG. 3. Dependence of the specific heat of the sample on the heating rate. Points show data used in the analysis, except for the region between 30.763 and 30.787°C, where data obtained at 10^{-6} °C/sec are shown. Solid lines represent discarded data.

shape of the specific-heat curve rather than in the absolute values. With our apparatus, the major source of systematic error in the measurements was from the thermistor calibration. To obtain accurate values for α and α' it is necessary that the temperature, T^* , calculated from resistance of a thermistor on the calorimeter, be linearly related to the absolute temperature with sufficient precision. It can be shown from Eq. (1) that if dT^*/dT differs from unity by a constant amount, the values obtained for the exponents are unaffected, as long as T_c is assigned correctly. The thermistor calibration described in Sec. II showed that the variation of the ratio dT^*/dT was less than 0.1% over the curve-fitting region. We estimate that this would perturb the apparent exponent values by less than 3%. An independent check on the thermistor calibration and on other aspects of the heat-capacity measurements was made possible by a special feature of the apparatus: we automatically measured the heat capacity of a cop-

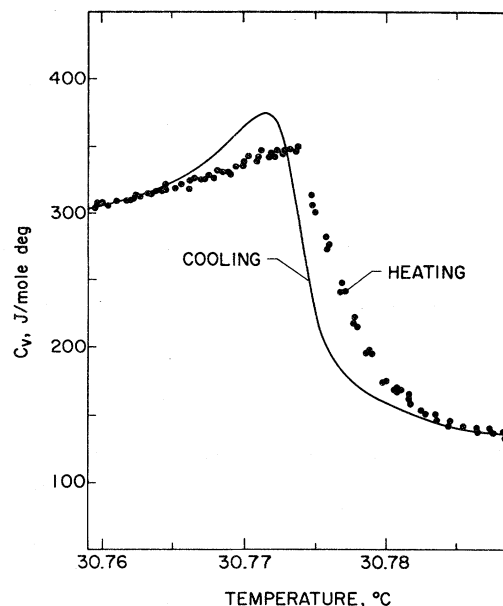


FIG. 4. Comparison of specific heat obtained while heating at 10^{-6} °C/sec with that obtained while cooling at 10^{-6} °C/sec.

per component in the thermal environment during every experimental run. Comparison of this data with tabulated values showed that the total temperature-dependent errors due to the measuring technique were less than ± 0.03 J/mole °C². This is significantly less than the uncertainty in the temperature dependence of the empty calorimeter heat capacity, which was estimated to be equivalent to ± 0.1 J/mole °C². The uncertainty in the calorimeter heat capacity at T_c gives rise to a possible constant error of ± 10 J/mole °C. Far from T_c our results can be compared with those of Michels and Strijland¹⁷: our data appear to be lower by 6 ± 3 J/mole °C. From run to run the measurements were reproducible to within the noise, which was heating rate dependent. At 10^{-6} °C/sec the data was contained within a range of about ± 2 J/mole °C, and this decreased to ± 0.3 J/mole °C at 10^{-4} °C/sec.

V. EFFECT OF GRAVITY ON C_v

The effect of gravity on C_v can be split into two contributions: the first due to the explicit dependence of the free energy on the density gradient in the gravitational field and other terms of a nonlocal character; and the second due to the variation of density with height itself, the free-energy density being the same function of the local density and temperature as in the absence of gravity. We term this latter contribution the *implicit* effect. To our knowledge, no calculation of the

explicit effect of gravity on C_v has yet been made. However, it can be argued¹⁸ that the explicit effect is negligible when $r_c \ll \lambda_\rho$, where r_c is the correlation length and λ_ρ is a characteristic length

$$\lambda_\rho = \left(\rho^{-1} \frac{d\rho}{dz} \right)^{-1}.$$

For CO₂ $r_c/\lambda_\rho < 10^{-4}$ for $|t| \geq 3 \times 10^{-5}$, implying that we can neglect the explicit effect for the present experiment.

On the other hand, the implicit effect of gravity noticeably distorts the singularity in the temperature interval covered by our measurements. A correction term for this effect is derived in the Appendix. The magnitude of the term was calculated from compressibility and coexistence curve data^{19,20} near T_c . In the analysis described below, this correction term was always applied to the data before curve fitting was attempted. Close to T_c the numerical values of the gravity correction are unreliable and it was necessary to reject specific-heat data from the analysis. We chose $|t| = 4 \times 10^{-5}$ as the lower limit for which reliable corrections could be made. Results obtained with the limit set at $|t| = 6.6 \times 10^{-5}$ did not differ significantly.

VI. ANALYSIS AND DISCUSSION

In order to obtain information on the asymptotic form of the specific heat as T_c is approached, we fitted our data with functions of the class in Eq. (1). The range of acceptable values for the parameters was determined by computing χ^2 , the sum of the weighted squared deviations of the data from the function, and comparing it with the minimum obtainable value, χ_0^2 . We accepted only those parameter sets for which

$$\frac{\chi^2 - \chi_0^2}{\chi_0^2} \leq \frac{p}{n-p} [F_{0.05}(p, n-p)], \quad (2)$$

where p parameters are determined by fitting the function to n data points, and $F_{0.05}$ is the 5% F -distribution parameter²¹; that is, there is a 95% probability that the true values of the parameters are within the region of parameter space defined by (2). The parameter $F_{0.05}$ has the limiting values $F_{0.05}(4, \infty) = 2.37$, $F_{0.05}(6, \infty) = 2.10$, and $F_{0.05}(8, \infty) = 1.94$. For $n \geq 180$, our minimum data set, $F_{0.05}$ is within 3% of these limiting values. The weighting function W_i used in calculating χ^2 was determined by estimating the standard deviation of the data as a function of heating rate. We obtained

$$\begin{aligned} W_i &= 8.16(1 + 5/\dot{T}_i)^{-2}, \quad T < T_c \\ &= 12.76(1 + 5/\dot{T}_i)^{-2}, \quad T > T_c \end{aligned}$$

where \dot{T}_i is the heating rate measured in $\mu^\circ\text{C}/\text{sec}$.

Figure 5 shows projections of the four-dimensional constant χ^2 contour defined by Eq. (2) onto the (α, T_c) plane for three different temperature ranges:

- (a) $4 \times 10^{-5} < |t| < 2.5 \times 10^{-3}$,
- (b) $4 \times 10^{-5} < |t| < 5 \times 10^{-3}$,
- (c) $4 \times 10^{-5} < |t| < 10^{-2}$.

The branches of the data on either side of T_c were treated entirely independently. The variation in the extent of overlapping of the contours with data range gives a quantitative idea of the sensitivity of the final results for α and α' to the outer cut-off point which is the arbitrarily chosen limit of applicability of the function in (1). Since the contour for range (b) falls completely within that for range (a), it is reasonable to consider data for which $|t| < 5 \times 10^{-3}$ as representing the asymptotic form to within the accuracy of the measurements.

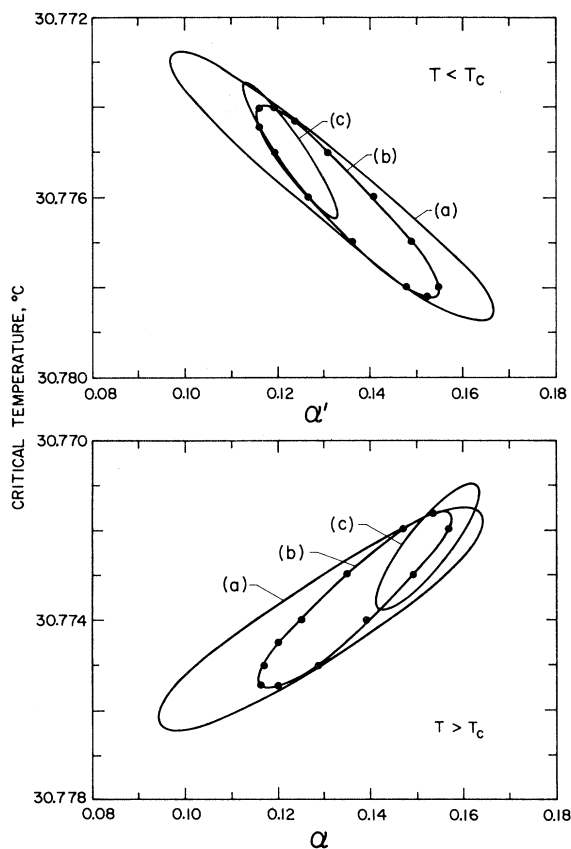


FIG. 5. Projections onto the (α, T_c) plane of the constant χ^2 contours which have 95% probability of including the true values of the parameters. Each branch of the data was treated independently. The three contours in each set correspond to the three fitting regions (a), (b), and (c) described in the text.

We then obtain the results $0.115 < \alpha < 0.157$ and $0.115 < \alpha' < 0.154$ with a 95% confidence level and when no constraints are applied to any of the parameters.

In order to carry the analysis further it is necessary to restrict the class of fitted functions to a subset of those described by Eq. (1). A simple constraint is to require $T_c^+ = T_c^-$ which is consistent with the results shown in Fig. 5 and is to be expected if the density of the sample equals the critical value. For other values of the density, $T_c^+ < T_c^-$, due to the step discontinuity in the specific heat at the coexistence curve. The degree of overlap of the apparent critical temperatures can be estimated from the specific-heat data for ^4He obtained by Moldover²² over a wide range of densities. From this data it is clear that T_c^- is very close to the true value of T_c even for densities differing from ρ_c by up to 10% or 20%. On the other hand, T_c^+ falls rapidly as the density deviates from ρ_c . From Moldover's data we obtain the approximate relation

$$T_c^- - T_c^+ \approx (2.5 \pm 1)(T_c - \hat{T}), \quad (3)$$

where \hat{T} is the temperature at which the coexistence curve is intersected. Using Eq. (3) and coexistence curve data^{19,20} for CO_2 we find that the difference $T_c^- - T_c^+$ is less than 10^{-3} °C even for densities differing from ρ_c by as much as 1%. Since this difference is much less than the ranges of T_c^+ or T_c^- allowed in Fig. 5, and the mean density of our sample is likely to be within 0.5% of ρ_c ,²³ it seems quite conservative to accept the constraint $T_c^+ = T_c^-$ in further analysis of our data. Figure 6 shows the result of applying this con-

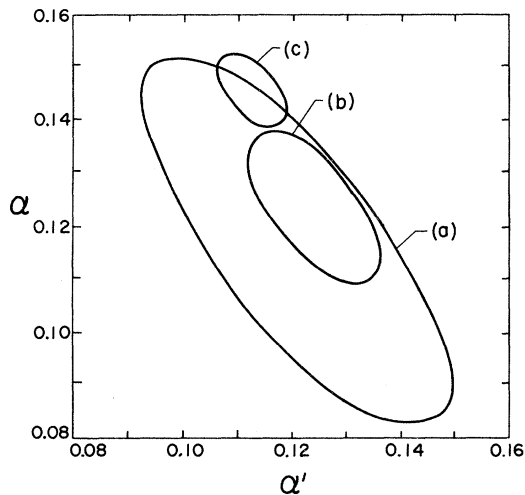


FIG. 6. 95% confidence contours of constant χ^2 projected onto the (α, α') plane for the three fitting regions (a), (b), and (c) described in the text. The function fitted to the data was $C_v/R = A|t|^{-\alpha+B}$, with the constraint $T_c^+ = T_c^-$.

straint and projecting the 95% confidence contours of χ^2 into the (α, α') plane for each of the three data regions (a), (b), and (c). For region (b) we obtain $\alpha = 0.124 \pm 0.014$ and $\alpha' = 0.124 \pm 0.012$. The values obtained for all the parameters are listed in Table I. Of the currently available theoretical predictions for the exponents only the Ising-model numerical estimates do not assume *a priori* that $\alpha = \alpha'$. In three dimensions these estimates⁶ are $\alpha = 0.123 \pm 0.003$ and $0 \leq \alpha' \leq \frac{1}{8}$ which agree very well with our results. Since other theoretical results assume that $\alpha = \alpha'$, and this is consistent with our observations, we applied this equality as a constraint before making further comparisons. We obtained $\alpha = 0.124 \pm 0.005$ with a 95% confidence level. Recent predictions²⁴ obtained by the RG method using an expansion in the parameter $\epsilon = 4 - d$ lie in the range $0.08 \leq \alpha \leq 0.18$. However, for $\epsilon = 1$ convergence is slow at best and the series may only be asymptotic.²⁵ This problem is avoided in the approach of Kadanoff³ which relies instead on generating upper and lower bounds for the recursion relation in the RG method. The resulting estimates of the exponents for two- and three-dimensional Ising models are close to the values obtained by other methods. For $d = 3$, Kadanoff's result $\alpha = 0.113$ is encouragingly close to the value we observe.

The ratio A^+/A^- of the coefficients of the divergent term in the specific heat is expected to be a universal parameter.⁷ In the present analysis we observed that $A^+/A^- = 0.538$ to within approximately 3% for all sets of parameters which gave acceptable fits to the data. Predictions for the ratio are available from scaling, RG expansions and numerical calculations. Schofield²⁶ has proposed a linearized model for the equation of state in the critical region which is consistent with scaling. For this model the ratio is given²⁷ by

$$\frac{A^+}{A^-} = \frac{1}{4} \left(\frac{\gamma}{\beta} \right)^2 \left(\frac{2\beta}{\gamma} \frac{\gamma-1}{1-2\beta} \right)^{\gamma+2\beta},$$

where β and γ are the exponents defining the asymptotic behavior of the coexistence curve and the

TABLE I. Optimum values of the parameters obtained with the function $C_v/R = A|t|^{-\alpha+B}$ and applying the constraint $T_c^+ = T_c^-$.

| | $T < T_c$ | $T > T_c$ |
|----------|------------------------|-------------------|
| α | 0.124 ± 0.012 | 0.124 ± 0.014 |
| A | 10.6 ± 2.0 | 5.7 ± 1.3 |
| B | -0.1 ± 2.7 | -3.6 ± 1.2 |
| T_c | 30.7748 ± 0.003 °C | |

compressibility. This formula is sensitive to the values used for β and γ . Using the experimental values²⁷ for CO₂: $\beta=0.350$; $\gamma=1.260$, we obtain $A^+/A^- = 0.77$, while the numerical estimates $\beta = 0.312$; $\gamma = 1.250$ for the three-dimensional Ising model yield $A^+/A^- = 0.51$. On the other hand, *direct* estimates⁸ of the ratio from the Ising lattice specific heat give values close to 0.75, varying a few percent from lattice to lattice. It is possible that this last estimate is too high, due to the poor convergence of the low-temperature series expansion of the specific heat. Recently Brézin *et al.*⁷ have developed the RG expansion in the parameter ϵ for the ratio. They obtain

$$A^+/A^- = 2^{\alpha-2}(1+\epsilon)n + O(\epsilon^2).$$

With $\epsilon = n = 1$, substitution of either Kadanoff's value for α or ours gives $A^+/A^- = 0.54$ to first order in ϵ , in very good agreement with our result.

Fisher²⁸ has pointed out that the Ising-model specific heat has no adjustable parameters, so a direct comparison with experiment is possible. The quantity $C^*(T)$ to be compared with the Ising-model values is given by

$$C^*(T) = (\rho_c/\rho_{\max})[C_v(T) - C_{id}],$$

where C_{id} is the ideal gas specific heat and ρ_{\max} is the liquid density extrapolated to zero temperature. In Fig. 7 we plot $C^*(T)$ and the Ising-model values on a semilogarithmic scale. Good agreement exists above T_c , but below T_c the Ising-model values are too low by about 50%. Nevertheless, the gen-

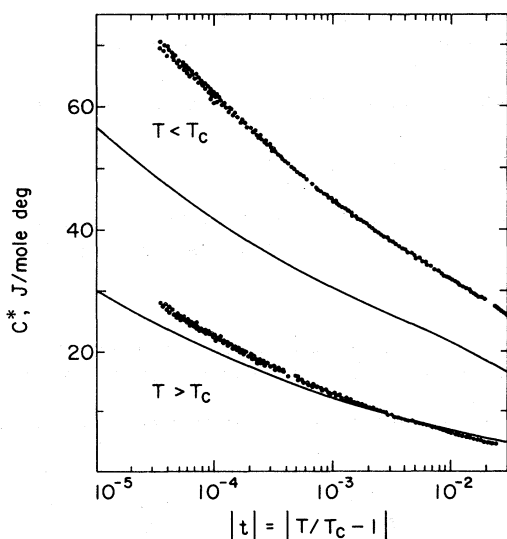


FIG. 7. Comparison of the specific-heat values calculated for the three-dimensional Ising model (solid lines) with the scaled data for CO₂.

eral features of the data are well represented.

In Fig. 8 we show the deviations of the total data set from the best-fit function with $\alpha = \alpha' = 0.12$ and $T_c^+ = T_c^- = 30.775$ °C, using fitting region *b*. It can be seen that the function is a very satisfactory representation of the data over a wide range of temperature. Outside the fitting region, however, systematic deviations occur, which is to be expected with an asymptotic representation of C_v as T_c is approached. In an attempt to extend the temperature range over which the selected function describes the data and to explore the sensitivity of the values of α and α' to the choice of function we considered functions of the form

$$C_v/R = A|t|^{-\alpha} + B + D|t|, \quad (4)$$

where the parameter D can also take on different values for the two branches of the data. The projections onto the (α, α') plane of the 95% confidence contours of χ^2 obtained with this function are shown in Fig. 9 for the data regions (b) and (c) defined above, and a region (d) defined by $4 \times 10^{-5} < |t| < 1.66 \times 10^{-2}$. In this analysis the constraint $T_c^+ = T_c^-$ was applied. Comparison with the results in Fig. 6 using the original function shows that for the region (b) the 95% confidence contours almost completely overlap, indicating that these results are not sensitive to the presence of additional nonasymptotic terms. It can also be seen that the additional undetermined parameter significantly reduces the resolution of the exponents, even when the fitting region is extended as in (d). On the other hand, *consistency* of the exponent values is obtained for all regions, which without the linear term was obtained only for regions (a) and (b). At present we cannot attach much significance to the optimum values of the exponents obtained with the function in (4), since it is possible that other forms of the correction term are more important than

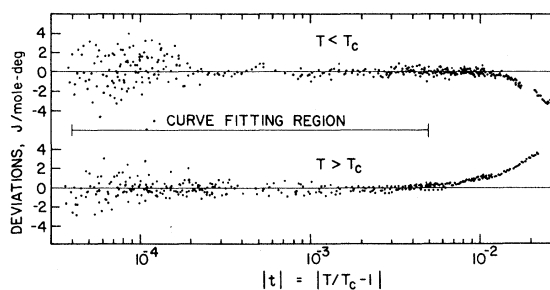


FIG. 8. Deviation of the specific-heat data from the best-fit function having $\alpha = 0.124$ and $T_c = 30.7748$ °C. The function is defined as follows: For $T > T_c$, $C_v = 96.19 \times |T - T_c|^{-\alpha} - 29.88$ J/mole °C; for $T < T_c$, $C_v = 178.79 \times |T_c - T|^{-\alpha} + 0.44$ J/mole °C.

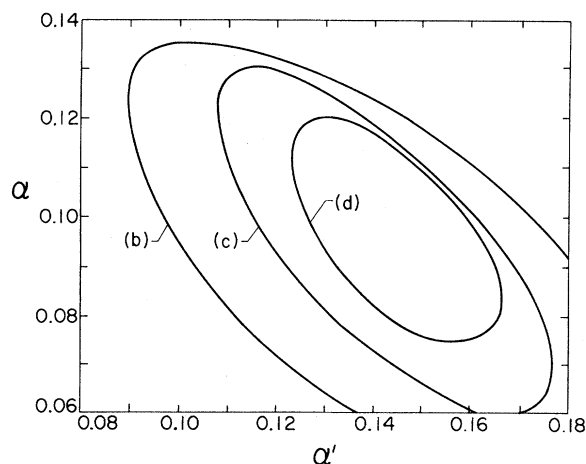


FIG. 9. 95% confidence contours of constant χ^2 projected onto the (α, α') plane for the three fitting regions (b), (c), and (d) described in the text. The function fitted to the data was $C_v = A|t|^{-\alpha + B + D|t|}$, with the constraint $T_c^+ = T_c^-$.

the linear term. For example, thermodynamic and RG arguments²⁹ have led to a correction term to the scaling laws of the form $D|t|^z$, where $z \sim 0.5$, but the magnitude of the coefficient is not yet predicted.

By adding a linear function of $|t|$ to the data we were able to gauge the effect that a possible linear term in the calorimeter heat capacity would have on our estimates of the critical exponents. When a term equal to our maximum estimate of ± 0.1 J/mole $^{\circ}\text{C}^2$ for this uncertainty was added, the exponent values shifted by less than ± 0.004 when no constraints were applied to T_c or α . With the constraint $T_c^+ = T_c^-$ the shift fell to less than ± 0.002 and if we also required $\alpha = \alpha'$, the effect became insignificant.

The critical temperature of our sample was 30.775 ± 0.003 $^{\circ}\text{C}$, which is 0.202 ± 0.005 $^{\circ}\text{C}$ lower than the most recent value obtained²³ from meniscus observations. It is well known¹⁸ that the gravitational distortion of C_v near T_c gives a maximum in C_v somewhat below T_c , but in our case corrections for the effect of gravity were applied before T_c was determined, and in any case this shift would be less than 0.010 $^{\circ}\text{C}$. Another possibility is that the density of the sample differs from ρ_c . If this were the explanation the density error would have to be about 15%. Equation (3) shows that we should then obtain $T_c^- - T_c^+ \approx 0.5 \pm 0.2$ $^{\circ}\text{C}$ when curve fitting is attempted. Clearly this is strongly contradicted by the results in Fig. 5. Similar results obtained without applying the cor-

rections for the effect of gravity do not alter this conclusion. Furthermore, the value of T_c^- should still be very close to the true T_c , which is not observed.

To check our temperature scale, which was derived from a CSIRO calibrated thermometer as described in Sec. II, we independently calibrated a new pair of platinum resistance thermometers to an accuracy of ± 0.020 $^{\circ}\text{C}$. Comparison of the two temperature scales revealed no significant error. As a further check on this point, and on the purity of the gas in our main storage tank, a small quantity of this CO_2 was placed in an insulated cell which allowed visual observation of the meniscus. The maximum temperature of meniscus disappearance was found to be 31.06 $^{\circ}\text{C}$ on the new temperature scale, which confirms that the temperature scale is not low and that the CO_2 was pure originally.

A remaining explanation of the shift of T_c is impurities introduced when the calorimeter was filled. If the sample contains a fixed concentration of impurities, the singularity in C_v would have the form of a cusp, with a renormalized exponent defined³⁰ by $\alpha^* = -\alpha/(1-\alpha)$, where α is the exponent in the absence of impurities. For small concentrations x of impurities and far from T_c , the apparent exponent α^* obtained by curve fitting to a limited range of data is expected to be close to α , while as T_c is approached α^* crosses over³¹ to the value α^+ . This behavior has been observed by Fisher and Scesney³² who numerically analyzed a three-dimensional Ising model exhibiting impurity effects. Their results lead us to expect that

$$\alpha^* \approx \alpha + x(\alpha^+ - \alpha)$$

for specific heat data in the range $10^{-6} < |t| < 10^{-3}$. This indicates that for impurity concentrations of up to a few percent, the results for α and α' will be negligibly perturbed.

The possibility that the apparent exponent value changes sign as T_c is approached can be checked directly by varying the inner limit of $|t|$ at which data is rejected. We performed some analysis with two different values of the inner cut-off point for the data: $|t| = 4 \times 10^{-5}$ and $|t| = 1.3 \times 10^{-4}$. For the latter case the precision of the determination of α was somewhat degraded due to the loss of data, but the 95% confidence limits for α and α' were found to completely span those for the former case.

In conclusion we wish to emphasize two points. Firstly, the thermal relaxation measurements in Fig. 2 together with the heating and cooling data in Fig. 4 show that our results represent the equilibrium specific heat for $|T - T_c| > 0.010$ $^{\circ}\text{C}$. Close to T_c , then, the limit set on our ability to determine the

exponents is due to the implicit effect of gravity. Some improvement can be gained by further reducing the height of the sample, but the gain is slow, and any significant reduction would require careful consideration of both the explicit gravity effect and finite size effects. Secondly, in the region far from T_c the precision of our determination of the exponents is restricted by the limited range of applicability of the asymptotic function fitted to the data. The existence of nonasymptotic terms in the expansion of C_v and T_c introduces error or bias into the value obtained for the exponent. In order to keep the bias less than the statistical uncertainty in the result, the extent of the fitting region must be reduced as the accuracy of the data is improved. This reduction results in an increase in the uncertainty of the determination of the exponents which to a large extent cancels the improvement due to the better data. The full range of the data can be retained if a nonasymptotic term is added to the function fitted to the data, but it is clear from a comparison of Figs. 6 and 9 that this also severely degrades the resolution, due to the additional parameters. It therefore appears that a solution of at least one of these fundamental difficulties is needed to advance our knowledge of the specific-heat singularity at the critical point of fluids.

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APPENDIX: IMPLICIT EFFECT OF GRAVITY ON C_v

Here we calculate the implicit effect of gravity on C_v for the case in which the cross section of the calorimeter is independent of the height h and when the pressure P is an antisymmetric function of volume V , about the critical isochore for fixed T . The derivation is based on thermodynamics, and the magnitude of the effect is found by expanding in powers of the pressure difference from the mean and evaluating coefficients from equation of state data.

Consider a system of N particles of mass m in a rigid container with $\rho = N/V = \rho_c$, and when the temperature is close to T_c . We wish to calculate the temperature derivative of $S_g(T) - S_0(T)$, where $S_g(T)$ is the value of the entropy of the system in a gravitational field g and $S_0(T)$ is its value in the absence of gravity. Neglecting the explicit effect of gravity, $S_g(T)$ is just the sum of the contributions from the volume elements, each of which contributes as it would in zero gravity, but at the local density. It is useful to take advantage of the following simple property: for a fixed number N

of atoms in a system with cylindrical geometry the distribution of atoms as a function of pressure is a constant, independent of pressure and temperature, regardless of the complexity of their distribution as a function of height. Thus if $P(0)$ is the pressure at the top of the container and n is the number of atoms above a given atom, the pressure at which the latter finds itself $P(n)$ is an amount mgn/A greater than $P(0)$, where A is the cross-sectional area. There are just $(A/mg)dP$ atoms with pressure between P and $P+dP$, if $P(0) < P < P(N)$, and none outside this range. Defining the mean pressure P^* as the pressure at the level at which as many atoms are above as below, we introduce π as the pressure difference from this mean. P^* is a singular function of temperature at $T = T_c$ when $\bar{\rho} = \rho_c$, and is the pressure that would exist throughout the system in zero gravity. In the case of cylindrical geometry the atoms are distributed uniformly in π over the range $-\pi_h < \pi < \pi_h$, where

$$2\pi_h = Nm g/A = \bar{\rho} g h.$$

The entropy in a gravity field is very simply expressible in terms of the function of state π : We have

$$\begin{aligned} S_g(T) &= \frac{1}{2\pi_h} \int_{-\pi_h}^{\pi_h} d\pi S(T, \pi) \\ &= \frac{1}{2\pi_h} \int_{P^* - \pi_h}^{P^* + \pi_h} dP S(T, P). \end{aligned} \quad (A1)$$

The temperature derivative of this entropy gives the heat capacity at constant volume and height. The specific heat is not, as has sometimes been assumed,³³ a certain average of C_v , the specific heat at constant density. We see that it arises from elements following a thermodynamic path not at constant density, but at constant π . By expanding $S(T, \pi)$ away from T_c and performing simple substitutions (A1) can be rewritten in the form

$$S_g(T) - S_0(T) = -\frac{1}{2\pi_h} \int_{-\pi_h}^{\pi_h} d\pi \int_0^\pi d\pi \left(\frac{\partial V}{\partial T} \right)_P. \quad (A2)$$

By using the relation

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_\pi - \frac{dP^*}{dT} \left(\frac{\partial V}{\partial P} \right)_T$$

and expanding $(\partial V/\partial T)_\pi$, the integration in (A2) can be performed and we obtain

$$S_g(T) - S_0(T) = -\frac{\pi_h}{2} \left. \frac{dV}{dT} \right|_{\text{coex}} - \frac{\pi_h^2}{6} \left(\frac{\partial^2 V}{\partial P \partial T} \right)_0 + \dots \quad (A3)$$

the first term vanishing above T_c .

Substituting the asymptotic forms of the coexistence curve and the isothermal compressibility, it is easy to show from (A3) that for $T < T_c$

$$C_{vg}(T) - C_{v0}(T) = A' \pi_h |t|^{\beta-2} + B' \pi_h^2 |t|^{-\gamma'-2} + \dots \quad t \rightarrow 0_-,$$

where A' and B' are constants, while for $T > T_c$

$$C_{vg}(T) - C_{v0}(T) = B'' \pi_h^2 |t|^{-\gamma'-2} + \dots \quad t \rightarrow 0_+.$$

To calculate the magnitude of the correction terms these equations were written in the forms

$$C_{vg}(T) - C_{v0}(T) = \frac{\beta(\beta-1)gh}{4T_c} \left(\frac{\rho_L - \rho_G}{\rho_L + \rho_G} \right) t^{-2} - \frac{\gamma'(\gamma'+1)(\bar{\rho}gh)^2}{24T_c} \frac{\partial V}{\partial P} t^{-2} + \dots \quad T < T_c$$

and

$$C_{vg}(T) - C_{v0}(T) = - \frac{\gamma(\gamma+1)(\bar{\rho}gh)^2}{24T_c} \frac{\partial V}{\partial P} t^{-2} + \dots \quad T > T_c,$$

where ρ_L and ρ_G are the liquid and gas densities.

We evaluated these expressions using the isothermal compressibility and coexistence curve data of Michels *et al.* and Schmidt,¹⁹ and Lorentzen.²⁰ We also made use of the summary of the compressibility data compiled by Heller.³⁴ We found little data for the isothermal compressibility below T_c . From the available data it seemed reasonable to suppose that the isothermal

compressibility at a temperature below T_c was about one-tenth the value at an equal temperature interval above T_c . The precise value of this ratio is not important, as the effect of the total gravity correction on the value of α is not large.

To apply the corrections for the effect of gravity to our data we represented them by the smooth function

$$C_{vg} - C_{v0} = 9.4 \times 10^{-7} (T - T_c)^{-3.30} \text{ J/mole } ^\circ\text{C}, \quad T > T_c + 12 \text{ m } ^\circ\text{C} \\ = -2.04 \times 10^{-3} (T_c - T)^{-1.65} \\ + 9.4 \times 10^{-8} (T_c - T)^{-3.30} \text{ J/mole } ^\circ\text{C}, \quad T < T_c - 12 \text{ m } ^\circ\text{C}.$$

We estimate that the uncertainty in the corrections is about $\pm 20\%$ below T_c and $\pm 50\%$ above T_c , for $4 \times 10^{-5} < |t| < 4 \times 10^{-4}$.

It should be noted that the above analysis can be shown to be approximately valid even in the absence of P - V antisymmetry and also when $\bar{\rho} \neq \rho_c$. Moreover, if as appears likely³⁵ the isotherms $\mu = \mu(\rho)$, where μ is the chemical potential, are more nearly antisymmetric about ρ_c than the corresponding $P = P(V)$ isotherms, then the first-order gravity corrections can be shown to be the same as those derived above, while the second-order terms are not significantly different.

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