INFLUENCE OF THE HYDROSTATIC EFFECT ON THE SPECIFIC HEAT C_v AT THE CRITICAL POINT IN A PURE SUBSTANCE

Yu. R. CHASHKIN, A. V. VORONEL', V. A. SMIRNOV and V. G. GORBUNOVA

All-union Institute of Physico-technical and Radio Measurements

Submitted to JETP editor, August 29, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 112–117 (January, 1967)

The influence of inhomogeneities due to the hydrostatic effect on specific-heat measurements near the critical point is studied. For this purpose, the specific heat of argon is measured near the critical point in two calorimeters of different height (8 and 2.5 cm) without stirring the substance in the calorimeters. The results of the measurements are compared with those[2] obtained in a high calorimeter with stirring. It is concluded that stirring the material in the calorimeter does not distort the true form of the dependence of the specific heat C_V on the temperature near the critical point. A calculation of the limiting values of the specific heat C_V without stirring is performed at $T \to T_c$ for a homogeneous system. The good agreement between the calculated values and the experimental values seems to indicate that the initial relations and the values of the constants employed are reliable. It is also concluded that, near second-order phase transitions in solids, the temperature dependence of C_p is distorted by the effect of some inhomogeneities which are similar to those produced by the hydrostatic effect at the critical point.

IT is well known that close to the critical point of a pure substance, its compressibility increases sharply. This leads to the appearance of the so-called hydrostatic (gravitational) effect: because of the excess pressure of the upper layers of the material on the lower, a density gradient is established in the vessel in the vertical direction. In the study of the properties of material in the critical state, it is necessary to take special measures to prevent this effect.

In our researches[1-3] for this purpose, the material was mixed at the time of the experiment by means of a magnetic stirrer. It is well known that if such stirring is sufficiently intense, it removes the hydrostatic effect.[4] However, in measurements of the specific heat close to the critical point it is important to wait for the establishment of thermodynamic equilibrium. Equilibrium in the gravitational field presupposes the presence of an inhomogeneity of the material in the direction of the field. It was necessary to establish the fact that the stirring did not lead to any additional departure from equilibrium by eliminating this inhomogeneity and thus turning off, as it were, the gravitational field.

Figure 1 shows the values of the time of equalization (attainment of thermodynamic equilibrium) in a calorimeter of 8 cm height filled with argon, as a function of the departure of the temperature from the critical. As is seen from the drawing, the equilibrium is achieved in systems with and without stirring at approximately the same time. Since this is the longest time in the system, one can think that the mechanism of establishing thermal equilibrium, which has an effect on these results, is the same in both cases. All other processes, particularly the establishment of the inhomogeneity relative to the vertical direction in the calorimeter without stirring, take place more rapidly. We note that the origin of the very large times of establishment of equilibrium in a system with stirring (that is, at distances which are very small in comparison with the dimensions of the vessel) is in itself an interesting problem. This is evidently connected with the fundamental mechanism of the transport phenomena and indicates the presence of a singularity of the kinetic coefficients at the critical point.

In order to establish finally that stirring in no way distorts the true shape of the singularity of the specific heat close to the critical point, the following experiment was carried out.

The specific heat of argon at the critical mean density $\rho = \rho_c = 0.533$ g/cm^3 was measured without stirring in two calorimeters of approximately the same volume, but of different height: 8 cm (the same calorimeter as used in [1-3] and 2.5 cm. The results of the measurements are shown in

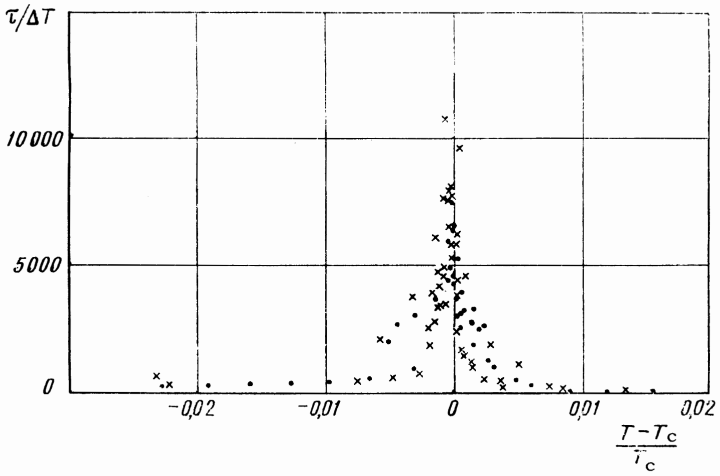

FIG. 1. Equalization time (in min/deg) near the critical point of pure specimen: ×—with stirring of the material ●—without stirring of material.

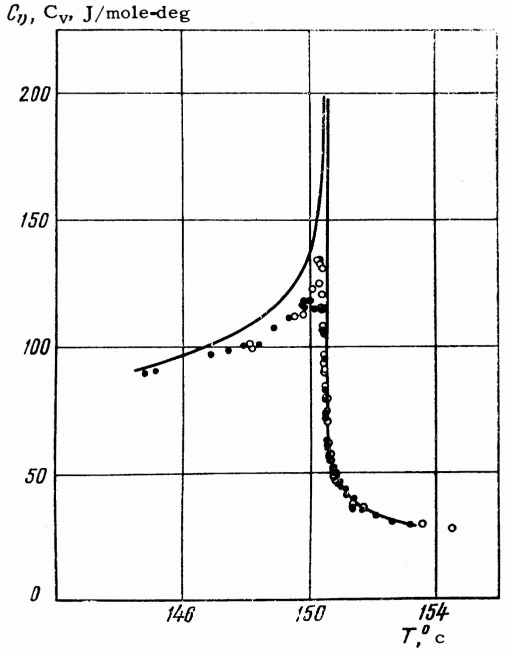

FIG. 2. Dependence of the specific heat on temperature: ●—calorimeter of height 8 cm without stirring, ○—calorimeter of height 2.5 cm without stirring solid curve—from the data of [2] (with stirring).

Figs. 2 and 3. For a comparison, curves from [2] are shown in the drawings; these are for argon of critical density with stirring.

It is evident that in the presence of an inhomogeneous distribution of the density with respect to the vertical direction, the specific heat observed in the experiment will be determined by an integral expression and the true singularity of the specific heat relative to temperature and density is obscured. Actually, it is seen in Fig. 3 that, in the presence of the hydrostatic effect, only a finite maximum of the specific heat is observed at the critical point. With decrease of the height of the vessel, the height of the maximum is increased and thus the results for an infinitely thin layer of medium must approach the curve obtained by means of stirring.

Figure 3 shows the data drawn in a semilogarithmic scale as in [1-3]. It is clearly seen that the singularity is strongly distorted; however, it is also seen that the branch of the specific heat curve corresponding to the homogeneous state of the medium in a calorimeter of height 2.5 cm (the lower curve, open circles) for values $L \equiv \log |(T - T_c)/T_c| \geq -3.65$ is identical with the straight line corresponding to experiments with stirring. Consequently, a logarithmic singularity of the specific heat at the critical point appears in this section. For the 8-cm calorimeter there is no such section of logarithmic dependence. The hydrostatic effect at a height of 8 cm begins

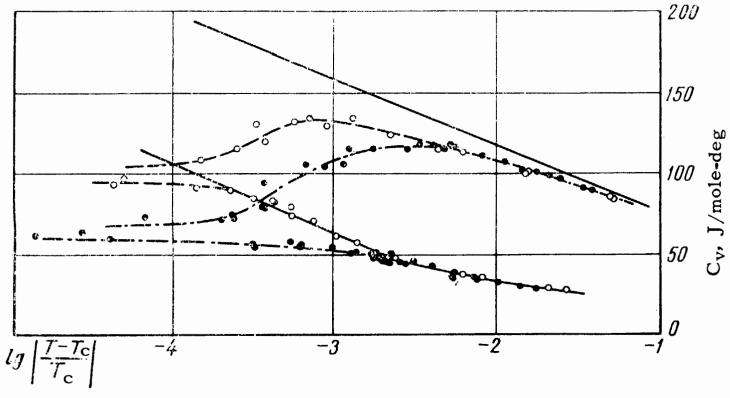

FIG. 3. Dependence of the specific heat C_V on the quantity L. Solid curves—data of [2] obtained with stirring. Dashed and dot-dash curves are drawn through the points whose designation is given in the legend of Fig. 2. The lower branches of the curves correspond to $T > T_c$, the upper to $T < T_c$.

to show up in the results even at values $L \lesssim -2.5$ cm, i.e., far from the critical point, and at a height of 2.5 cm—only for $L < -3.65$, which is much closer. Evidently, further decrease of the height of the vessel would lead to a broadening of the region of coincidence of the results with [2].

We note that for $T < T_c$ the critical specific heat, regardless of the height of the vessel, is not identical with the curve obtained with stirring. This takes place because in a two-phase system in the absence of stirring, regardless of the total volume of the system, there is always a certain inhomogeneity of the conditions (if only a difference in heat emission of the vapor and the liquid), and to obtain equilibrium properties of the material in a heterogeneous state without stirring would be completely impossible.[10]

Thus it is evident to us that the stirring does not distort the true form of the singularity.

Measurements of the specific heat in the hydrostatic effect can be used for verifying the results of [6] on the dependence of C_V on v. Actually, using [5], we can take correctly into account the change of the density with height in the calorimeter:

$$\rho(h) = \frac{\rho_c}{1 - \alpha\rho_c(h - h_0)^{1/3}}. \qquad (1)$$

Here ρ_c is the critical density of the material, h_0 is the height of the level at which the critical conditions are satisfied (if the mean density of the medium is equal to the critical, $h_0 = (\frac{1}{2})H$, where H is the height of the vessel), $\alpha = (6\mu g\rho_c/B)^{1/2}$, g is the acceleration due to gravity, and μ the molecular weight of the material. The value of $B\,(B = (\partial^3 p/\partial V^3)_{T_c})$ for argon was taken in correspondence with [11]:

$$B = -1.5\cdot10^{-4}\ \text{at-mole}^3/\text{cm}^9.$$

The total measured specific heat (in a cylindrical vessel) is determined by the formula1)

$$C_{\text{tot}} = \frac{S}{\mu}\int_0^H C_v(\rho)\rho(h)\,dh, \qquad (2)$$

where S is the cross sectional area of the calorimeter, $\rho(h)$ is the density of the material at the height h, and $C_V(\rho)$ is the specific heat at the density $\rho(h)$.

H, cm	$C_{\text{tot}}^{\text{calc}}$, J/mole-deg	$C_{\text{tot}}^{\text{exp}}$, J/mole-deg
8	62	62 — 65
2.5	100	92 — 98

The integral (2) can be computed if one uses Eq. (1) and the empirical dependence $C_V(\rho)$ from [6]. We obtain, of course, only the limiting value of the specific heat for $T = T_c$ from the $T > T_c$ side. In the table are shown results of such a calculation of the integration (converted to one mole of the substance) in comparison with the experimental data of $C_{\text{tot}}^{\text{exp}}$ for various heights H. The excellent agreement of the experimental data with that computed shows the reliability of the initial dependence of $C_V(v)$ from [6] and the validity of the values of the constant (1).

A smearing of the singularity, which is brought about by the inhomogeneity of the state of the material in the substance, is constantly present in results on studies of second order phase transitions in solids. Although the physical reason for the appearance of these inhomogeneities and their spatial distribution in the specimen are obviously different from the hydrostatic effect, the external characteristics of the smearing in the solids are the same (since the distribution of the inhomogeneities over the specimen $\rho(h)$ enters in the intergrand of (2), the detailed form of the dependence $\rho(h)$ affects weakly the measured specific heat). This situation is illustrated in Fig. 4.

Since the real value of the transition temperature T_c for solids is usually unknown2), the data are processed relative to the temperature of the maximum of specific heat T_{max}. Figure 4 shows the specific heat C_V of argon as a function of L. The dashed and dot-dash lines denote on the specific heat of C_p of two specimens of gadolinium[8,9] of a different degree of purity. The closeness of the form of the curves for liquid (C_V) and solid specimens is evident in the drawing.

Thus, the investigation of the hydrostatic effect at the critical point allows us to model definite imperfections in solids, and accordingly to interpret distorted data on second-order phase transitions.

In conclusion, the authors thank M. Sh. Giterman and V. G. Simkin for participation in discussion of the results, and G. N. Chernov for help in

---

1)Sychev and Andrianov [7] took this effect into account by a comparison of the quantity $C_v(v_{av})$ and $C_{v\ av}(v_{av}) = H^{-1}\int_0^H C_v(h)dh$. Inasmuch as the specific heat is a non-additive quantity, this expression does not have physical meaning. The numerical departure, however, of this expression from the correct expression (2) amounts to 5-10% in our case.

2)Liquid specimens had the advantage that the inhomogeneity in them can be removed by simple stirring (and in this case one can determine T_c). The corresponding homogeneization in the solid is brought about by annealing as a result of spontaneous diffusion and is never complete.

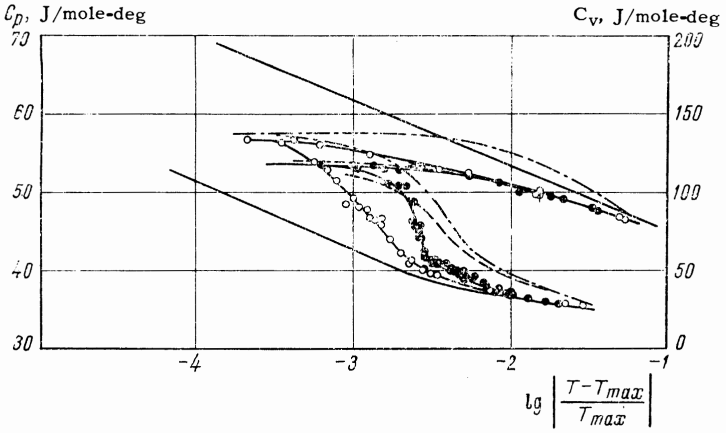

FIG. 4. Dependence of the specific heat C_V on the quantity L. The dashed curves give C_p from the data of[8]; the dot-dash–C_p from the data of [9], the remaining notation the same as in Fig. 2.

the measurements. The authors also use this opportunity to express their gratitude to A. M. Rozen and E. S. Borovik for interest in the research.

---

[1] A. V. Voronel', Yu. R. Chashkin, V. A. Popov and V. G. Simkin, JETP 45, 828 (1963), Soviet Phys. JETP 18, 568 (1964).

[2] A. V. Voronel', V. G. Snigirev and Yu. R. Chaskin, JETP **48**, 98 (1965), Soviet Phys. JETP **21**, 653 (1965).

[3] A. V. Voronel', V. G. Gorbunova, Yu. R. Chashkin and V. V. Shchekochikhina, JETP **50**, 897 (1966), Soviet Phys. JETP **23**, 597 (1966).

[4] M. A. Weinberger and W. G. Schneider, Canad. J. Chem. **30**, 422 (1952).

[5] M. Sh. Giterman and A. V. Voronel', JETP **39**, 1162 (1960), Soviet Phys. JETP **12**, 809 (1961).

[6] A. V. Vornel' and Yu. R. Chashkin, JETP **51**, 394 (1966), Soviet Phys. JETP **24**, 263 (1967).

[7] V. V. Sychev and V. V. Andrianov, Tepolfizika vysokikh temperatur (Thermal Physics of High Temperatures), **1**, 50 (1963).

[8] A. V. Voronel', S. R. Garber, A. P. Simkina an and I. R. Charkina, JETP **49**, 429 (1965), Soviet Phys. JETP **22**, 301 (1966).

[9] M. Griffel, R. E. Skochdopol and F. H. Spedding, Phys. Rev. **93**, 657 (1954).

[10] I. R. Krichevskiĭ and N. E. Khazanova, ZhFKh. **29**, 1087 (1955).

[11] A. V. Voronel', JETP 40, 1516 (1961), Soviet Phys. JETP **13**, 1062 (1961).

Translated by R. T. Beyer
15