SOVIET PHYSICS JETP VOLUME 24, NUMBER 2 FEBRUARY, 1967

SPECIFIC HEAT C_v OF ARGON AS A FUNCTION OF DENSITY NEAR THE CRITICAL POINT

A. V. VORONEL' and Yu. R. CHASHKIN

Institute of Physico-technical and Radiotechnical Measurements

Submitted to JETP editor February 26, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 394–400 (August, 1966)

The singularity of C_V near the critical point was studied by measuring the specific heat at twelve constant densities lying above and below the critical value. The C_V singularity is approximately symmetrical with respect to density. The specific-heat change ΔC_V as a function of density possesses a slight anomaly near the critical point.

THE singularity of C_V, observed[1-3] near the liquid-vapor critical point, is, of course, a singularity in terms of two variables, T and V. It is therefore of interest to investigate the behavior of the specific heat C_V as a function of the density of the substance near its critical point.

In [4] there was postulated a definite relation between C_V and $v = (V - V_c)/V_c$:

$$C_v = C_v{}^0 + 2\alpha_1 \ln\left[(t + \beta v^2)^2 + \gamma^2 v^4\right], \qquad (1)$$

where C_V^0 is a bounded function. However, the limits of applicability of this analysis are not clear and the interval of smallness of the deviations of the density from the critical value has not been determined.

Measurements of the specific heat of Ar were made for 12 values of the densities, of which six are smaller than critical, five larger than critical, and one equal to critical with accuracy better than 0.5%. The six curves (ρ = 0.225, 0.341, 0.443, 0.521, 0.533, and 0.588 g/cm³) plotted in 1962–1963 have relatively low accuracy [1]. The latest curves (ρ = 0.666, 0.560, 0.549, 0.538, 0.530, and 0.504 g/cm³) were plotted in 1964 with a higher accuracy[5].

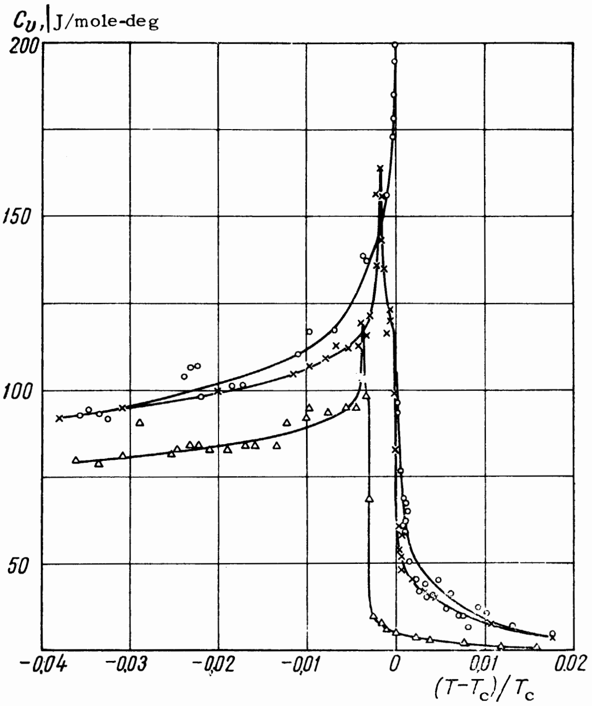

FIG. 1. Specific heat C_v vs. temperature t for the following densities: ○ – ρ = 0.533 g/cm³, × – ρ = 0.504 g/cm³, △ – ρ = 0.666 g/cm³.

The absolute value of T_c determined from the curve for ρ = 0.533 [3] turned out to be lower by 0.02–0.03° than the value obtained for the curves with ρ = 0.530 and 0.538. A thorough analysis has shown that this is caused by impurities, the contents of which are lower in the sample of 1964 than in the sample used in 1962–1963 1). For an accurate estimate of the amount of these impurities it is necessary to carry out for the Ar + impurity system investigations similar to those made in [5] for nitrogen. We have assumed in the present investigation different values of T_c for the first and for the succeeding series of experiments. This is apparently not reflected in the shapes of the curves or in the physical conclusions of the paper. In all the essential cases we use the dimensionless temperature $t = (T - T_c)/T_c$.

The data obtained for several curves are shown in Fig. 1 and in Tables I–IV 2). (Data for the

---

1) The rated purity of both samples of argon was 99.99%.

2) In all tables, the temperature is given in degrees K and the specific heat in J/mole-deg.

Table I

$\rho = 0.504$ g/cm^3

T	ΔT	C_v	T	ΔT	C_v	T	ΔT	C_v
142,21	1.017	86.2	149.96	0,053	116.4	150,52	0,052	82.7
143.27	0.997	88.2	150.02	0.053	115.6	150,54	0.052	61.0
144.13	0.648	90.9	150.08	0,053	121,6	150.56	0.058	53.9
144,81	0,641	92.0	150.17	0,041	156.4	150,60	0.030	52,1
146.02	0,636	95.0	150.21	0.046	135.3	150,61	0.057	48.1
148,80	0.246	104,5	150.31	0,037	135.1	150,62	0,233	58.6
147.50	0,254	99,7	150.23	0.043	163.7	150.80	0.117	45.6
149.07	0.241	107.0	150.26	0.063	142.9	151.00	0,233	41.8
149,33	0.168	109.0	150.32	0.089	134.7	151.18	0.937	39.9
149.51	0.163	112.7	150.38	0.057	116,3	151,35	0.423	37,0
149,70	0,091	112,1	150.43	0.054	123.1	152.14	1.061	32.4
149.89	0,091	112.5	150,44	0,077	119.8	153.18	1.028	28.8
149.94	0,084	119.3	150.51	0,060	99.0	154,20	1,057	27,2

Table II

$\rho = 0{,}549$ g/cm^3

T	ΔT	C_v	T	ΔT	C_v	T	ΔT	C_v
142.18	0.352	78.6	149.29	0.323	107.0	150,42	0,055	103,0
142.54	0,508	83.3	149.53	0.244	107.4	150.49	0.046	89.7
142.96	0.513	82,4	149.75	0.231	113.8	150,61	0.158	59.1
143.38	0.504	84.6	149.93	0,148	119,6	150,70	0.106	46,6
143.82	0,508	83.7	150.06	0.144	123.0	150.79	0.108	45,3
145.05	0.395	87.7	150.10	0,097	130.4	150,88	0.151	46,2
145.49	0.388	89.5	150,13	0.043	136,1	151.00	0,114	41,9
145,91	0,385	89.6	150.22	0.055	132.1	151,02	0,165	41,0
146.33	0.383	91.0	150.27	0.051	145,8	151.31	0.323	38,2
147,82	0.345	97.0	150.31	0,043	145,2	151,16	0.128	38,7
148.16	0.342	98.5	150.32	0.039	171.0	151,66	0,339	35.2
148.75	0.324	105,3	150.38	0.049	120.7	153,66	0,637	28,1
149.00	0.329	104.5	150.41	0.065	103,6			

Table III

$\rho = 0.560$ g/cm^3

T	ΔT	C_v	T	ΔT	C_v	T	ΔT	C_v
140,77	0,219	111,8	150,09	0,137	122,6	150,39	0,073	117,1
144,98	0,899	87,9	150,11	0,090	116,5	150,45	0,055	121,2
145,77	0,588	89,8	150,19	0,088	121,4	150,50	0,074	84,0
148,59	0,438	102,7	150,21	0,105	125,4	150,51	0,092	63,5
149,08	0,436	102,5	150,22	0,133	125,3	150,57	0,067	57,8
149,34	0,272	103,6	150,27	0,066	132,2	150,61	0,143	59,0
149,36	0,061	106,4	150,30	0,032	139,9	150,75	0,205	56,1
149,64	0,261	108,9	150,33	0,070	122,8	150,82	0,265	46,8
149,70	0,373	107,6	150,33	0,040	105,4	150,88	0,150	47,2
149,92	0,248	115,8	150,35	0,023	122,0	150,83	0,143	43,1
149,96	0,129	112,4	150.38	0,025	113,3	151,03	0,153	39,3
150,01	0,110	120,0						

Table IV

$\rho = 0.666$ g/cm^3

T	ΔT	C_v	T	ΔT	C_v	T	ΔT	C_v
138,51	0,306	69,5	147,03	0,250	84.0	149,97	0,069	103.7
138,86	0,304	70,4	147,17	0.293	84,3	150, 7	0.116	68.2
139,26	0,308	69,2	147,33	0,251	83,1	150,03	0.072	98.2
139,65	0,302	71,1	147,67	0.251	82.9	150,10	0.052	34.5
142,52	0,294	76,5	147,97	0,248	84,3	150.14	0,160	34.4
143,20	0,295	76,8	148,14	0.269	84,2	150,27	0.074	32,4
143,54	0,294	77,3	148,50	0,275	84,1	150.34	0,076	30.8
144,77	0,280	79,5	148,67	0,248	90,6	150,84	0,578	28.5
145,09	0,279	80,0	149,06	0.244	94.6	150,51	0.560	29.7
145,47	0,424	78,9	149,00	0.369	92.0	151,08	0.583	27.8
145,88	0,281	81,1	149,36	0.247	93.5	151.67	0,598	26.8
146,18	0,253	90,3	149,67	0,244	95,0	152,28	0,608	26.1
146,70	0,257	81,7	149,84	0.234	95,1	152,89	0,617	25.5
146,80	0,296	83,1	149,96	0,061	118,6	153.52	0,619	25,5

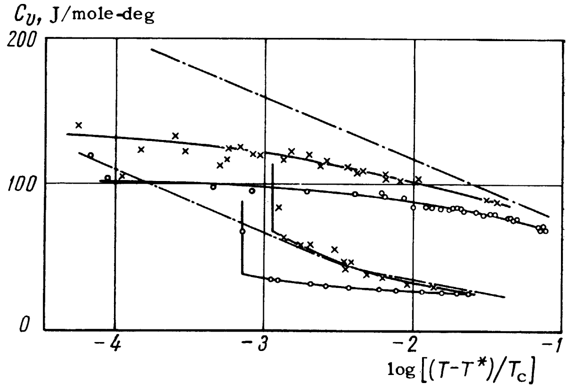

FIG. 2. C_v vs. log $|(T - T^*)/T_c|$ for densities $\rho > \rho_c$: x – ρ = 0.560 g/cm³, o – ρ = 0.666 g/cm³, dash-dot – $\rho = \rho_c$.

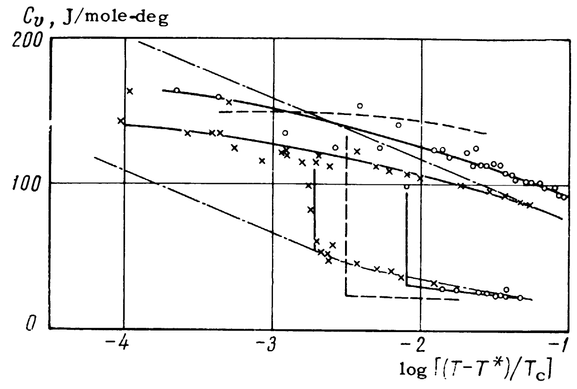

FIG. 3. C_v vs. log $|(T - T^*)/T_c|$ for densities $\rho < \rho_c$: x – ρ = 0.504 g/cm³, o – ρ = 0.341 g/cm³, dashed – ρ = 0.225 g/cm³, dash-dot – $\rho = \rho_c$.

curves for 0.533, 0.530, and 0.538 g/cm³ were given in[3], and those for the curve with ρ = 0.521 g/cm³ were given in[1].) Similar curves are shown in Figs. 2 and 3 in a semilogarithmic scale. The abscissa axis shows log $|(T - T^*)/T_c|$, where T^* is taken to be the temperature of the maximum of the specific-heat curve. Such a representation of the data has many advantages.

Figure 2 shows curves corresponding to $\rho < \rho_c$, and Fig. 3—to $\rho > \rho_c$. In order not to clutter up the figures, not all the available curves were plotted. The figures give a qualitative idea of the character of the deformation of the logarithmic singularity when the density deviates from its critical value. The most characteristic aspect is the unique deformation of the peak of the specific heat upon deviation from critical conditions, wherein the temperature of the maximum becomes different from that of the jump, similar to what occurs when the substance becomes contaminated with impurities[5]. An approximate symmetry in the behavior of the system with $\rho > \rho_c$ and $\rho < \rho_c$ is seen.

The influence of the singularity, which is manifest in a sharp increase in the specific heat (the presence of maxima), disappears quite far from the critical density. However, the picture is made complicated by the fact that in the absence of a singularity, as shown by Krichevskiĭ and Khazanova [8], the specific heat should approach the critical point with an infinite derivative. Because of this, it is impossible to separate the irregular part of the specific heat in pure form. However, certain interesting laws governing the variation of the specific heat with variation of the molar volume can be traced.

1. With deviation of the density towards values either higher or lower than critical, the slope of the semilogarithmic curves plotted relative to the temperature of the maximum of specific heat decreases. The absolute value of the specific heat at the maximum also decreases (the values of the specific heat for different curves should be compared only after subtracting from the values pertaining to the heterogeneous part the jump in specific heat ΔC_V, which also depends on the density). The semilogarithmic scale reveals these jumps of specific heat quite clearly; they can be determined (of course, with low accuracy) from the shapes of the curves. Table V gives an idea of these quantitative characteristics of the curves.

2. Although we came within 0.5—4% of the critical density, much closer in the similar measurements reported in the literature [7,8], nevertheless as can be seen from Fig. 4, we have barely reached values of the dimensionless parameter v close to those at which the logarithmic dependence of C_V on t begins (see Fig. 2). Figure 4 shows clearly the increase in the slope of the C_V vs. log v curve on approaching v = 0. The final limit will be determined only if the point v = 0 can be approached closer, within about 0.1%.

3. It is easy to see that our data agree with the notion that the coexistence curve is, in first approximation, a second-degree parabola ($t = -\sigma v^2$).

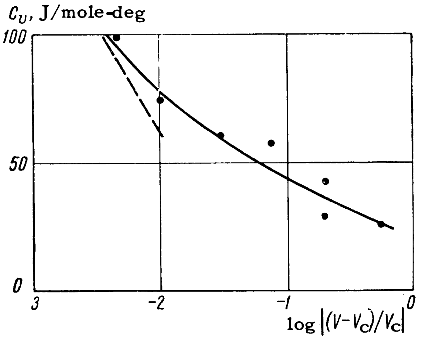

FIG. 4. C_V against log $|(V - V_c)/V_c|$. The dashed curve corresponds to a slope twice as large as $2a_1$ from formula (1).

Table V

ρ	ΔC_v	$C_{v\,max} \pm 10$ J	$\sigma = -\frac{t_{jc}^*}{v^2}$	ρ	ΔC_v	$C_{v\,max} \pm 10$ J	$\sigma = -\frac{t_{jc}^*}{v^2}$
0.225	120--128	20		0.533	90--105	105	
0.341	75--95	80	0,05	0.538	72--80	80	
0,443	65--85	80	0,04	0.549	45--68	90	0,02--0.08
0.504	55--70	80	0,05	0.560	45--60	80	0,03--0,09
0,521	80--90	85		0.588	40--60	75	
0.530	85--95	90		0.666	50--60	45	0.07

---

*$t_{jc} = (T - T_{jc})/T_c$, where T_{jc} is the temperature corresponding to the jump of the specific heat on crossing the coexistence curve.

This notion, which is compatible with the existence of a logarithmic singularity of the specific heat, was advanced in [4] and considered in detail by Giterman [9], who has also shown how the equation for the coexistence curve must be generalized in order to reconcile it with experiment.

The data of the present paper allow us to calculate some parameters of the equation of state in accord with the results of Giterman (see Table V). Of course, we can speak here only of the order of magnitude, since the experimental error in the temperature of the jump near the critical density becomes very large compared with the distance to the critical point.

Several recent papers [10,11] confirm our point of view [4,12] regarding the coexistence curve and consequently regarding the shape of the critical isotherm. The frequently employed cubic formula for the coexistence curve (the Guggenheim formula $t = \sigma |v|^3$) [13] is an empirical formula for a broad temperature interval far from the critical point and is violated precisely in the immediate vicinity of this point. Yet investigations connected with the interpretation of the phenomena at the critical point on the basis of the Ising model make use essentially of the Guggenheim formula [14,15]. If in the future we do not succeed in showing the compatibility of the three-dimensional Ising model with a relation of the type $t = -\sigma v^2$ for the coexistence curve, we may be able to state that this model is not applicable for the study of the liquid-vapor critical point.

4. Interesting information can be obtained by considering the dependence of the jump of C_V on the density of the substance. Let us discuss this question in greater detail.

The thermodynamic formula for the calculation of the jump of C_V on crossing the coexistence curve was given by Krichevskiĭ and Khazanova [6]:

$$\Delta C_v = \left[\left(\frac{\partial E'}{\partial v'}\right)_T + \frac{E'' - E'}{v'' - v'}\right]\frac{dv}{dT}\bigg|_{\text{coex}}, \tag{2}$$

where E'' and E' are the internal energy of the liquid and gas phases, respectively. Using the expansions of Landau and Lifshitz [16]

$$-\left(\frac{\partial p}{\partial v}\right)_T = At + Bv^2 + \ldots, \tag{3}$$

$$E'' - E' = \frac{1}{2}\left(\frac{\partial E'}{\partial v'}\right)_T (v' - v'') + \frac{1}{3!}\left(\frac{\partial^2 E'}{\partial v'^2}\right)_T (v' - v'')^2 + \ldots, \tag{4}$$

we can easily obtain the first approximation in the calculation of the jump ΔC_V, which shows no dependence whatever on the density ($\Delta C_V \sim$ const). Adding the next terms of the expansion (3), as was done by Giterman [9], can lead to agreement with the linear dependence of the jump on the molar volume along the coexistence curve, which has been observed in most experiments [7,8] ($\Delta C_V \sim$ const $+ v$).

Our more accurate experiments give a more complicated plot of ΔC_V against v (Fig. 5, Table V), which can be interpreted on the basis of the formulas obtained in [4]. Using (1) and (2) we can readily obtain the finite value of the jump ΔC_V (as a rational function of the parameter t/v^2) at the critical point itself, but an infinite value of its derivative

$$\frac{d\Delta C_v}{dv}\bigg|_{\text{coex}} \sim \frac{1}{v} f\left(\frac{t}{v^2}\right) + \text{const.}$$

Such a peaked dependence corresponds to the experimentally observed picture shown in Fig. 5.

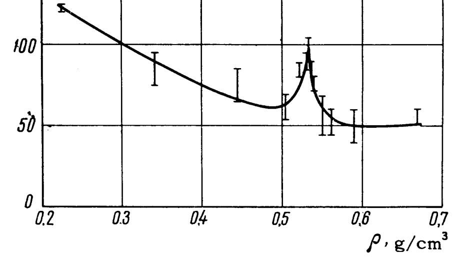

FIG. 5. ΔC_V against the density ρ : $\rho_c = 0.533$ g/cm³.

It must be noted that although certain essential features of the singularity of C_V as a function of t and v are already clear, we can expect very interesting results from a study of the specific heat C_V as a function of v in the interval up to 0.1% of v = 0, which is now being carried out by us.

In conclusion the authors thank V. G. Snigirev, L. A. Snigirev, and G. N. Chernov for help in the laborious measurements and the data reduction, and M. Sh. Giterman for numerous discussions.

---

[1] M. I. Bagatskiĭ, A. V. Voronel', and V. G. Gusak, JETP **43**, 728 (1962), Soviet Phys. JETP **16**, 517 (1963).

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

[3] A. V. Voronel', Yu. R. Chashkin, and V. G. Snigirev, JETP **48**, 981 (1965), Soviet Phys. JETP **21**, 653 (1965).

[4] M. Ya. Azbel', A. V. Voronel', and M. Sh. Giterman, JETP **46**, 673 (1963), Soviet Phys. JETP **19**, 457 (1963).

[5] Yu. R. Chashkin, V. G. Gorbunova, and A. V. Voronel', JETP **49**, 433 (1965), Soviet Phys. JETP **22**, 304 (1966).

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

[7] A. Michels and J. Strijland, Physica **18**, 613 (1952).

[8] Kh. I. Amirkhanov and A. M. Kerimov, Teploenergetika No. 9, 68 (1957).

[9] M. Sh. Giterman, ZhFKh **39**, 989 (1965).

[10] R. H. Sherman, Phys. Rev. Lett. **15**, 141 (1965).

[11] M. H. Edwards, Phys. Rev. Lett. **15**, 348 (1965).

[12] A. V. Voronel', JETP **40**, 1516 (1961), Soviet Phys. JETP **13**, 1062 (1962).

[13] H. Guggenheim, J. Chem. Phys. **7**, 13 (1945).

[14] C. N. Yang and C. P. Yang, Phys. Rev. Lett. **13**, 303 (1964).

[15] M. E. Fisher, J. Math. Phys. **5**, No. 7 (1964).

[16] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Fizmatgiz, 1964.

Translated by J. G. Adashko
44