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SPECIFIC HEAT OF NITROGEN NEAR THE CRITICAL POINT

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In connection with the discussion regarding the analytic form of the specific-heat singularity at the critical point,[1, 2] some results of the measurement of the specific heat of nitrogen near the critical point are presented for an extended temperature range to within 0.1° of T_c. The experimental errors do not exceed 5%. The data indicate a logarithmic dependence of the specific heat on the temperature as $T \to T_c$ with the same slope of the curve to the left and to the right (that is, for $T > T_c$ and $T < T_c$) and to the existence of a finite change $\Delta C_V = \lim (C^+ - C_V^-)$ as $|T - T_c| \to 0$, in accord with [13]. Since the value of T_c is important in the interpretation of the results, it has been determined with an accuracy of 0.001° by a method similar to the thermographic one. In this connection, it has been found that by using the results of a previous paper[10] the total amount of impurities in the gas can be determined with greater reliability and with an accuracy to ~0.02%.

FISHER[1, 2] compared our results on the specific heat of nitrogen and oxygen near the critical point[3, 4] with the results of numerical calculations according to the three dimensional Ising model.[5] The supposition was made that our data are better approximated by the formula

$$C_v^* / R = A\alpha^{-1}|t|^{-\alpha} + B \tag{1}$$

above the critical point ($T > T_c$)[1] (where C_V^* is the configurational specific heat ($C_V^* = C_V - iR/2$) of the material at the critical density ($v = v_c$)), than by the logarithmic formula

$$C_v^* / R = -A_{\log} |t| + B. \tag{2}$$

The unsatisfactory agreement of this hypothesis with the more exact experimental data was pointed out previously.[6] However, we considered the problem sufficiently serious to warrant a special investigation.

In the present research, the specific heat of nitrogen has been measured with a temperature interval down to ~0.01°, with a simultaneous reduction of the maximum error to 5%. Such an increase in accuracy has been made possible by the application of automation to maintenance of the adiabatic regime and to a semi-automatic potentiometer R-308 for the temperature measurement. An automatic regulator of the adiabatic regime was constructed in the Radio Engineering Laboratory of our institute on the basis of an improved Kraftmakher circuit;[7] this permitted us to maintain the constancy of the temperature to within better than $\sim 2 \times 10^{-4}$ deg/hour. For such an accuracy of maintenance of the adiabatic regime, the fluctuations of the room temperature become very important and it is necessary to introduce special corrections. The results are shown in the Table.

The fundamental problem is the choice of the temperature T_c. The accuracy of similar experiments is much higher than the accuracy of tabular data, and therefore T_c is converted into a parameter, with the help of which one can somewhat deform the curves on the logarithmic scale. In the best case, the choice of this parameter is limited by the width of one point (or more correctly the distance from the edge of the highest experimental point to the edge of the next after it). This means that the location of the extreme (closest to T_c) points on the logarithmic scale becomes completely indefinite (from $\log 0 = -\infty$ to $\log 0.0001$). A unique form of the graph of the specific heat as a function of the logarithm of $|t|$ is possible only when T_c is determined with an accuracy to an order higher than the width of the calorimetric steps.[2] In the opposite case, by using T_c as an arbitrary parameter, one can get several results

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[1] We shall express the temperature in nondimensional units $T = (T - T_c) / T_c$.

[2] The specific heat is defined experimentally as $\Delta Q/\Delta T$, where ΔQ is the amount of heat communicated to the calorimeter in heating and ΔT is the corresponding change in temperature of the specimen, brought about by the calorimetric step.

T, °K	ΔT	C_v, J/mole-deg	T, °K	ΔT	C_v, J/mole-deg
105.873	0.3213	83.1	126.243	0,0234	87.9
106.202	0.3296	80.6	126,245	0.0331	79,5 *
109.444	0.4408	84.0	126.258	0,0207	79.7
117.882	0.3557	95.5	126,262	0,0210	84.2
121.908	0.5769	105.6	126.274	0,0347	76.6
122.364	0.4917	106.8	126.283	0.0209	77.8
122.854	0.4853	108.8	126.301	0,0343	75.7
123.342	0,4741	111.5	126,304	0.0224	71.0
123.830	0.4656	114,0	126.346	0.0547	65.3
124,311	0.4538	117,5	126.354	0.0285	67,9
124.756	0,4311	124.9	126,353	0,0479	65.6
124.762	0,4438	120.7	126.396	0,0294	65.0
125.208	0.4280	126.2	126.396	0.0502	61,5
125.641	0.3995	136.6	126,458	0,0777	58.8
125.860	0.0990	142.1	126.409	0,0589	58,8
125.944	0.0707	154.9	126,483	0.0908	56,6
126.001	0.1629	154.1	126.580	0.1218	54,7
126,022	0.0926	153,2	126,738	0.1927	50,5
126.091	0.0306	169.8	126,885	0.1269	49,2
126,127	0.0288	175.8	126.980	0.2896	47.1
126.133	0.0559	168,5	127,068	0.1549	45,8
126.134	0.0584	160.2 *	127.360	0.4640	43,8
126.158	0.0167	180,3	127.924	0.6503	40,4
126.159	0,0224	170,9 *	128.766	1,0184	37,6
126.168	0,0248	190,3	129.807	1.0495	35,7
126,171	0.0112	212,7 *	130.881	1,0761	34.0
126,182	0.0112	209.9	131,987	1,0970	32,8
126.184	0.0137	204.1	133.113	1.1136	31.8
126.205	0,0169	110,3	135,369	0.6974	29.9
126.207	0.0169	105.1	136.351	1.2526	30.0
126,210	0,0179	103.3	142.185	0,7223	28.1
126.219	0.0190	95.7	143.056	1.0370	27,8
126.229	0.0159	94.8	155.652	1.0536	26.4
126.238	0.0194	85.6	156.709	1,0570	26.1
			167.023	1,0418	26,1

*The accuracy of these values is below 5% because the low reliability of the correction introduced for room temperature.

depending on the opinions of the author. For example, the parallelness of the logarithmic branch of the curve obtained by Skalyo and Friedberg[8] and the nonparallelness obtained by Teaney[9] are essentially associated with this circumstance (the authors themselves noted this fact[8]). However, because of the inevitable presence of impurities (see [10]) there is always some diffuseness of the peak, which can even be greater than the width of the single calorimetric step.[11, 8]

In the present experiment, no diffuseness of the singularity has been noted within the limits of width of a point (~0.01°). This means that T_c has been determined with an accuracy to within 0.01°. However, our ordinary accuracy of measurement of the temperature is much higher—approximately 0.0002°, which makes it possible for us to determine T_c more accurately than 0.01°. For this purpose, an experiment was carried out which was similar to the taking of a thermogram, only that the temperature changes were very slow and insignificant in magnitude. Figure 1 shows a graph of one of these experiments (the temperature is plotted along the ordinate in arbitrary units—the readings of the potentiometer). The entire temperature change, which took place in ~6 hours, corresponded to ~0.015°. The graph clearly shows the slowing down of the temperature curve, corresponding to a maximum in the specific heat (T_c'), a break, and then the next increase in the curve corresponding to the jump (T_c'') close to the critical point.

Three such experiments were especially arranged for different rates of heating (incidentally, quite small). The results agreed with an accuracy to ~0.001°. In such a way, we obtained values for these special points which were reproducible with an accuracy to 0.01° ($T_c' = 126.191$° K, $T_c'' = 126.197$° K). In this case it was observed that the maximum and the jump did not coincide, which, as is well known from [10], means the presence of impurities. (The deviation of the density from the critical value leads to a similar result; however, in this case, T_c' would have to be lower than T_c for the pure material. Here, the value of T_c' is larger by 0.03° than the tabular value, which can be explained by the presence of high boiling point impurities.) The results of the experiment mentioned previously[10] permit us to determine the amount of impurities with sufficient accuracy from the shift in the critical point, and in particular from the value of the discrepancy between the maximum and the jump (see Fig. 1). All the estimates lead to the same value for the impurity:

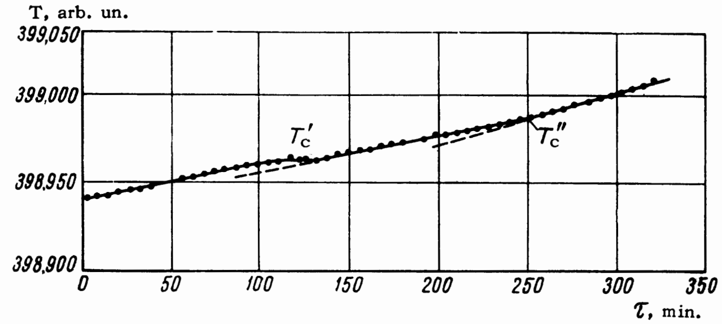

FIG. 1. Dependence of the temperature of the calorimeter on the time. All the change in temperature on the graph – about 0.015° – took ~ 6 hours.

0.06–0.13%. (We note that the rated purity of the nitrogen used was ~0.01%. However, analyses of argon, which evidently is the chief impurity, are usually very unreliable.) Since this estimate agrees with the estimate of the VNIIKIMASh Physico-technical Laboratory obtained on the basis of chemical analysis, it seems to us that such an investigation itself is not the worst method of obtaining the total amount of impurities.

Although our specimen could be considered pure for a width of the calorimetric step > 0.01°, for a resolution of the problem of the analytic form of the curve of the specific heat in the immediate vicinity of the critical point, it was a matter of concern as to which of the temperatures mentioned above could be regarded as the critical. To eliminate arbitrariness in Fig. 2, the dependences of the specific heat on log $|t'|$ and log $|t''|$ were plotted in Fig. 2, relative to T_c' and T_c'' respectively. The maximum error of measurement falls within the limits of ±5% of the absolute value of the specific heat. It is easy to see that both limiting cases give approximately parallel logarithmic curves both for $T > T_c$ and $T < T_c$. These data agree not only with our previous researches,[3, 4, 6] but also with the recently published work of Moldover and Little[12] on the specific heat of He^3 and He^4, in which the logarithmic curves approach a parallel character. In any case, there is no essential difference in the slopes for $T > T_c$ and $T < T_c$, similar to what was obtained by Teaney,[9] at the critical point of the pure material.

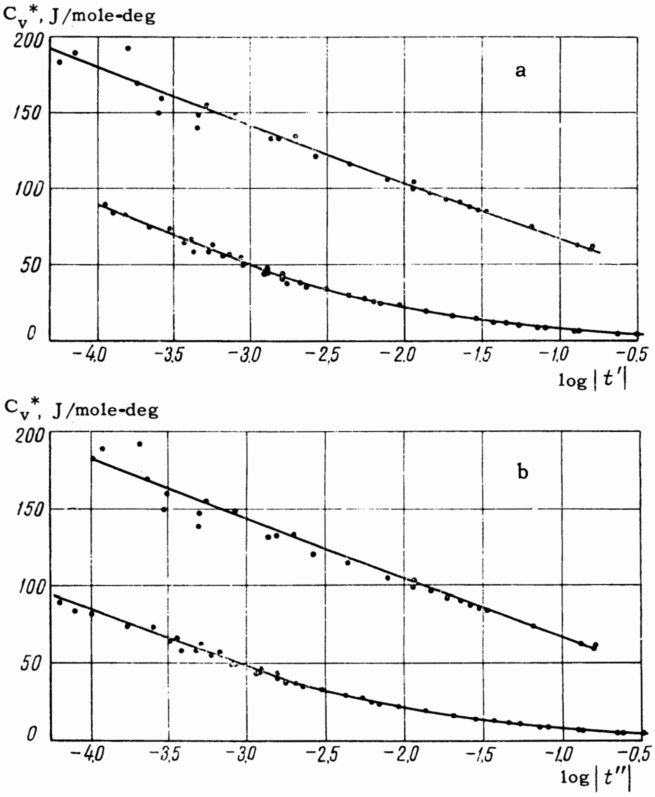

FIG. 2. Dependence of the specific heat C_v^*: a – on log $|t'|$, $T_c' = 126.191$ °K, b – on log $|t''|$, $T_c'' = 126.197$ °K. The upper curve – $T < T_c$, the lower, $T > T_c$.

In connection with the data of Teaney, we have extended his range of measurements in the direction of higher temperatures in order to estimate the possibility of an approximation of the high temperature branch of the curve by a logarithmic formula with a small slope A. The data show (Fig. 2) that nowhere to the right of log $|t| = -2.5$ is there a constant slope on our curve, and there is observed a gradual approach of the specific heat C_V to its classical value 5/2R. This means that one can separate out a section on the finite interval with an arbitrarily small slope, while for the in-

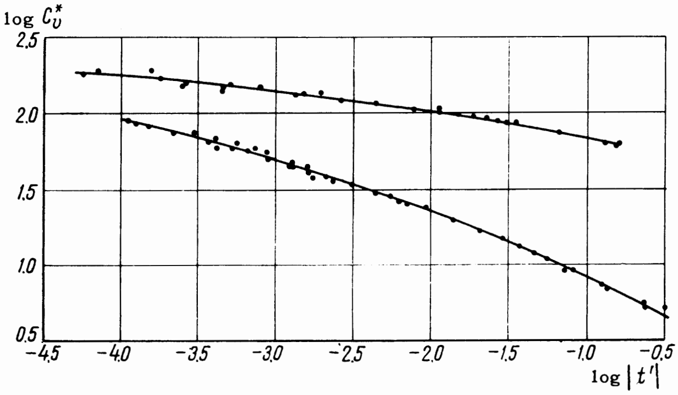

FIG. 3. Dependence of log C_v^* on log $|t'|$, $T_c' = 126.191$ °K.

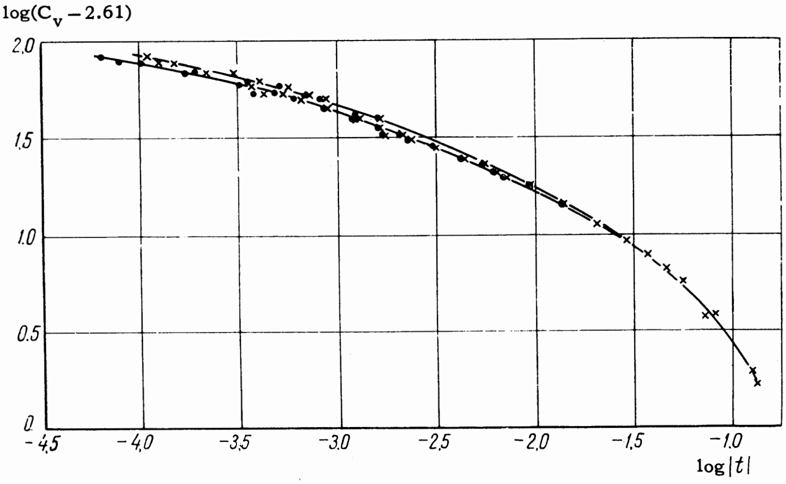

FIG. 4. Dependence of $\log(C_V - 26.1)$ on $\log|t|$: ● – $T_c = 126.191\,°K$, × – $T_c = 126.197\,°K$, $T > T_c$.

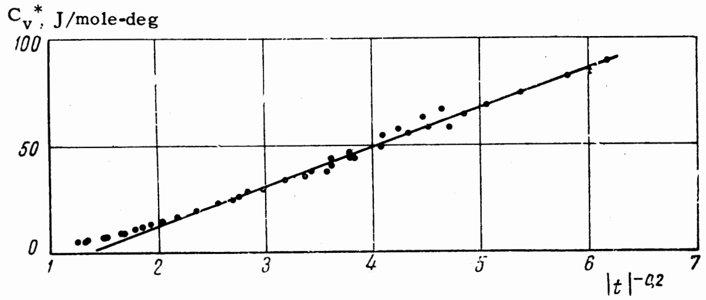

FIG. 5. Dependence of C_V^* on $|t|^{-0.2}$ for $T > T_c$, $T_c = 126.191\,°K$.

terpretation of these data by Eq. (1), one must set $B = 0$.

The same data are shown in Fig. 3 in the coordinates $\log C_V^*$ and $\log|t'|$. In the case of the feasibility of Eq. (1) (for $B = 0$) the branch of the curve corresponding to $T > T_c$ would be a straight line in this scale. The nonlinearity of the curves in Fig. 3 is sufficiently evident.

In Fig. 4, there are plotted the data (only for $T > T_c$) for the maximum possible $B > 0$, equal to 26.1 joule/mole-deg (C_V for $T = 167.023°\,K$ (see the Table)). Such an interpretation is possible if the specific heat approaches not $5R/2$ but some larger value, as $T \to \infty$; however, this value cannot exceed 26 joule/mole-deg. It is obvious that the curvilinearity of the dependences is still on the increase in this case.

The problem of the introduction of the term $B < 0$ deserves special consideration. In this case, one of the constants of Eq. (1) is not determined exactly by experiment but becomes an arbitrary parameter by means of which we can adjust the data in the formula. In particular, assuming (as has been done by Fisher) that $\alpha = 0.2$,[1] we can obtain a very fair approximation (see Fig. 5) which gives the value $B \approx -3$ for $T > T_c$. However, taking other values for B, we can also obtain other interpolation formulas which represent the experimental data even better. Thus, assuming the value $B \approx -1.68$ for $T > T_c$, we get $\alpha = 0.24$. By changing B, we shall obtain wholly new values for α. Furthermore, it seems that one can also adjust the curve corresponding to $T < T_c$ in such a fashion in Eq. (1) with $B \approx -3$ and $\alpha \approx 0.11$ (see Fig. 6)3) which does not correspond to any theoretical expectation. (By choosing $B \approx +5.7$, we can adjust the part of the curve for $T < T_c$ in Eq. (1) with $\alpha = 0.2$.)

Thus it appears obvious to us that the introduction of an arbitrary parameter permits almost unbounded choice of the class of possible interpolation formulas.

We have tried our best to free the experimental data from arbitrariness and distortion in the interpretation, and have therefore refrained from adjustment in Eq. (1) by choice of $B < 0$. Although such an interpretation is possible in principle, we should observe that there is not sufficient basis for it at the present time.

Thanks to the expanded range of measurement in the direction of lower temperatures, we have also succeeded in noting a small but definite departure from the logarithmic dependence on the upper branch of the curve ($T < T_c$). This depar-

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3) We also note that the logarithmic scale along the ordinates in Figs. 3, 4, 6 conceals the scatter of the points about the curve.

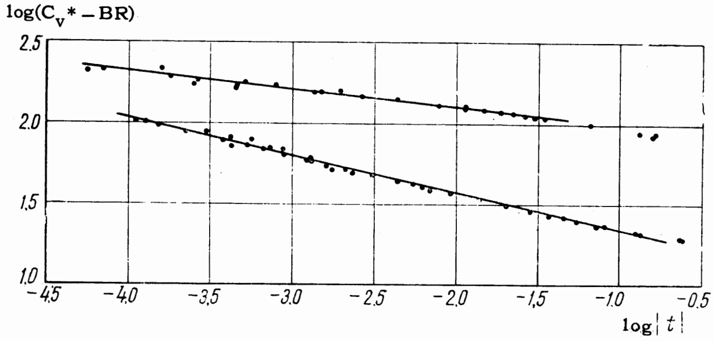

FIG. 6. Dependence of log $(C_V^* - BR)$ on log $|t|$, $T_c = 126.191\,^\circ K$, $B \approx -1.68$ for $T > T_c$, $B \approx -3$ for $T < T_c$.

ture arises an order of magnitude further from T_c than for $T > T_c$ and (in weak fashion) is reflected even in the data for argon.[6] It is obvious for us that the logarithmic law (2) does not describe the behavior of the specific heat of the substance over the entire interval of its existence (as would evidently be the case for a complete correspondence of the investigated system for the Ising model) but gives only the limiting expression for the dependence of the specific heat on the temperature as $T \to T_c$. Evidently, even the concept of specific heat as $\Delta C_V = \lim (C_V^+ - C_V^-)$ as $|T - T_c| \to 0$ can be preserved.

Thus we have as before no basis for giving up the phenomenological formulas of [13], which make it possible to compute the different thermodynamic quantities at the critical point. We note that the recent researches of Sherman[14] and Edwards[15] on the curve of coexistence of He^3 and He^4 also testify to the use of the interpretation given in [13], and the representations associated with it of the form of the critical isotherm (the quantity $(\partial^3 p/\partial v^3)_T$) and the coexistence curve.[16, 17]

The lack of agreement of our researches with the results of Fisher[1, 2] can generally mean (in this case if all the calculations on the Ising model[5] are valid) the inapplicability of the Ising model consequently also of the model of the lattice gas[18] to the study of the critical point of liquid-vapor of pure materials. We note that the same holds true for the λ point of helium.[19]

In conclusion, the authors thank V. Vaks and A. Larkin for discussion of some of the questions studied here.

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