Behavior of a disordered system in the tricritical and critical regions. Anomaly of the heat capacity of NH_4Cl at high pressures

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The heat capacity of NH_4Cl at pressures up to 4 kbar is measured by vacuum adiabatic calorimetry in an autonomous high-pressure vessel. The experimental $C_{an}(P, T)$ surface for the anomalous heat capacity as a function of pressure and temperature in the vicinity of the phase-transition curve is plotted. The critical exponents α in the isobaric sections of the surface $C_{an}(P, T)$ are determined by least squares near the tricritical point and at a distance from it. A value $\alpha = 0.45$ is obtained in the range between 0 and 1.8 kbar and for $T < T_c(P)$; at higher pressures α decreases and approaches the value 0.12 corresponding to the transition to the critical region. No transition to the critical region is observed at $T > T_c(P)$. The approximated temperature dependences of the heat capacity and order parameter are compared in the vicinity of the tricritical point with and without allowance for logarithmic corrections within the framework of the molecular-field approximation.

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Landau[1] has treated phenomenologically the singular points at which the second-order phase transition curve goes over continuously into a first-order phase transition curve. This singular point was subsequently called the tricritical point (TCP).[2] By now, TCP have been observed in various systems, the most thoroughly studied of which is the mixture He^3–He^4.[3] Other examples are antiferromagnets, which go over in a magnetic field into a metamagnetic state ($FeCl_2$, Dy–Al-garnet, $Ni(NO_3)_2 \cdot 2H_2O$),[4] as well as substances in which there is a strong dependence of the interaction of the ordered elements on the distance between, e.g., ammonium chloride,[5] and apparently also certain ferroelectrics. In all probability, the existence of TCP can be a rather widespread phenomenon, but so far its studies were mainly theoretical. A new behavior of thermodynamic functions near the TCP, described by an appreciable change in the set of critical exponent on going from the critical to the tricritical region, has been predicted.[6] The interest presently shown in systems with TCP is also connected with attempts at finding a unified description of their behavior in the vicinity of the TCP within the framework of concepts of scale invariance. The lack of experimental data, however, does not make it possible to verify the likelihood of the existing theoretical premises.

It is known that in ammonium chloride the phase transition connected with the disordering of the NH_4^+ tetrahedra can be of either first or second order, depending on the applied pressure.[5] The values of the TCP coordinates given for NH_4Cl in different papers[5,7] are unequal, but all lie in the pressure range 900–1500 bar on the phase curve. Figure 1 shows the phase diagram of NH_4Cl, where the TCP coordinates T_t and P_t are assumed to be 256 °K and 1500 bar, respectively. According to[8], the behavior of the thermodynamic functions of the system is determined by its position in the P–T plane relative to the nearest critical line and tricritical point. In light of these concepts region II on Fig. 1 corresponds to the critical behavior of the system, region III to the tricritical, and region I to first-order transitions, with the boundaries between the regions drawn arbitrarily. Despite the fact that the model system NH_4Cl has been the subject of numerous investigations during the past decades, there are still, unfortunately, no reliable experimental data on the critical behavior of this system along the phase-transition curve. Nor do we know the character of the singularities of the thermodynamic functions near the TCP, or the locations of the region boundaries shown in Fig. 1. We attempt in the present paper to determine, on the basis of data obtained by us on the heat capacity at high pressures, the critical exponent α near the TCP and the character of its variation along the phase-transition curve.

The heat capacity of ammonium chloride was measured in the vicinity of the TCP and far from it, in the temperature interval 220–310 °K and in the pressure range1) 0–4 kbar. We used the ammonium-chloride sample described in[9]. The heat capacity was measured in a vacuum adiabatic calorimeter, the calorimetric vessel being an autonomous high-pressure cell.[10] In the calorimetric experiment we determined the combined heat capacity

$$C = C_c + C_L + C_e,$$

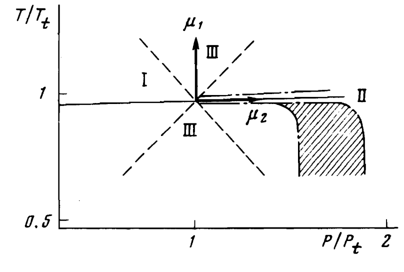

FIG. 1. Phase diagram of NH_4Cl in relative coordinates. Dashed—proposed boundaries of the regions in accordance with[8]; dash dot —region boundaries corresponding to our data. The transition region is shown shaded.

where C_c is the heat capacity of the cell, C_L is the heat capacity of the pressure-transmitting liquid, (polysiloxane), and C_e is the experimentally measured heat capacity of the sample. The heat capacity of the cell was determined in preliminary calibration experiments at normal pressure. Estimates of the influence of the pressure on the heat capacity of the cell have shown that these corrections do not exceed 0.05% of the heat capacity of the sample. In preliminary experiments without the sample we determined the temperature dependences of the heat capacity C_L' of the polysiloxane at various pressures. Since the calorimetric experiment was not performed under isobaric conditions, an additioanl reduction of the experimental data was needed to obtain the heat capacity C_P of the sample at constant pressure.[11] The contribution of the heat capacity of the liquid in experiments with the sample, $C_L(P, T)$, was determined from the relation

$$C_L = C_L' + T\left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{dP}{dT}\right)_e' - \left(\frac{dP}{dT}\right)_e\right],$$

where the quantities $(dP/dT)_e'$ and $(dP/dT)_e$ were determined in experiments without and with the sample, respectively, while $(\partial V/\partial T)_P$ was taken from the published data.[12] The heat capacity of the sample at constant pressure was calculated from the formula

$$C_P = C_e + T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{dP}{dT}\right)_e.$$

The value of $(\partial V/\partial T)_P$ for ammonium chloride was taken from[5]. After the described reduction of the experimental data we obtained the set of curves on the $C_P(P, T)$ surface. Estimates show that the over-all error of the obtained values of the heat capacity does not exceed 2–2.5%.[11] The average scatter of the obtained values is less, ≈0.1%. From the aggregates of the heat-capacity values we separated the regular component in the same manner as in[9]. The data of[13] enabled us to estimate the influence of the high pressure on the various components of the regular part. These corrections turned out to be much less than the experimental errors and were neglected by us in the subsequent reduction. After separating the regular part, we calculated, by three independent methods, the shape of the surface of the anomalous heat capacity $C_{an}(P, T)$ for the region $T < T_c(P)$ (T_c is the transition point corresponding to the given pressure) and its sections are constant P. In the first case the surface $C_{an}(P, T)$ was approximated by two-dimensional spline functions: the entire surface was broken up into 300 cells in accordance with the locations of the experimental points. The function $C_P(P, T)$ was approximated inside each cell by polynomials in P and T, subject to the condition that the functions and their derivatives be equal at boundaries of neighboring cells. The second method consisted of a least-squares approximation of the sections of the surface by functions in the form

$$A(P)+B(P)[X(P)]^{-\alpha(P)}, \tag{1}$$

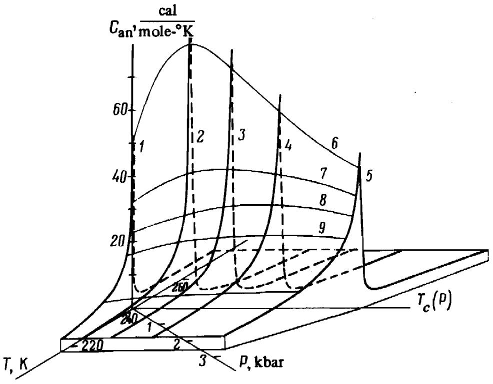

FIG. 2. Over-all form of the $C_{an}(P, T)$ surface.

where A, B, and α are polynomials in P, while $X(P) = T_c(P) - T$. In the third case, C_{an} for a given P was determined by linear interpolation between values taken at different pressures, but at equal distance $T_c(P) - T$ from the phase-transition curve. The region $T > T_c(P)$ was approximated only by spline functions. The surface of the anomalous heat capacity of ammonium chloride as a function of the pressure and temperature is shown in Fig. 2. Curve 1 corresponds to atmospheric pressure,[9] curve 2 is drawn through the experimental points obtained in the pressure interval 0.3–1.5 kbar, curve 3 corresponds to $0.7 < P < 2.2$ kbar, curve 4 to $1.3 < P < 3.0$ kbar, and curve 5 to $2.4 < P < 4.2$ kbar. The temperature dependences obtained by different methods for the anomalous part of the heat capacity in the isobaric sections of the $C_{an}(P, T)$ surface were approximated by least squares to power-law functions of the type

$$C = A + B\tau^{-\alpha}, \tag{2}$$

where $\tau = (T_c - T)/T_c$. It should be noted that all these reductions required an exact description of the phase-transition curve. This equation was obtained by least squares from the results of our measurements of the heat capacity at various pressures, and took the form

$$T_c(P) = 242.9 + 9.891P - 0.629P^2 + 3.22 \cdot 10^{-2} P^3.$$

The analysis of the behavior of the thermodynamic functions in the theoretical papers is usually carried out in the coordinates μ_1 and μ_2 (Fig. 1), which are directed along the normal and the tangent to the phase-transition at the TCP, respectively. In our case the angle between the axes P/P_t and μ_2 is less than three degrees, so that the change to the new coordinate frame should not affect significantly the results of the analysis. Thus, in the isobaric sections the function $C_{an}(T)$ should exhibit a tricritical behavior in the vicinity of the TCP, and its behavior in sections with larger pressures should correspond to second-order phase transitions. The pressure dependence of the critical exponent α at $T < T_c(P)$ is shown in Fig. 3. Different symbols correspond to different methods of constructing the $C_{an}(P, T)$ surface and its sections. It is seen from the figure that all three methods lead to close values of α. The error in the determination of the critical exponent due to the inaccuracies in the construction of the surface $C_{an}(P, T)$

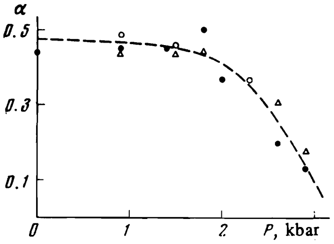

FIG. 3. Dependence of the critical exponent α on the pressure ●—approximation of the $C_{an}(P,T)$ by spline functions, Δ—by polynomials of type (1), o—by linear interpolation in the section τ=const.

is on the average ±0.03. A more complicated task is the determination of the error connected with the separation of the anomalous part of the heat capacity. Besides the lattice part, the total heat capacity of the investigated substance can obtain contributions from parts not accounted for here and connected with the phase transition. Assuming that these contributions are small in comparison with C_{an} near T_c, we can approximate them in first order by a term linear in τ. Then

$$C_{an}=A+B\tau^{-\gamma}+D\tau. \qquad (3)$$

The assumption that $D\tau$ is small is corroborated by the fact that the plot of $\log(dC_{an}/dT)$ against $\log\tau$ is linear in the entire approximation region, apart from a weak deviation from linearity of the experimental points farthest from T_c in some sections. From this deviation we can estimate the value of the term linear in τ in Eq. (3). The error in the determination of the exponent α when the linear term is neglected if our experimental data are approximated by a power-law function, consists of a decrease of the exponent by not more than 0.07. It should be noted that the bending of the plot of $\log(dC_{an}/dT)$ against $\log\tau$ was not observed in all the sections of the $C_{an}(P,T)$ surface. The quantity 0.07 should therefore be regarded as the upper bound of the possible error of the exponent α.

The data of Fig. 3 show that in the pressure interval 0–1.8 kbar the behavior of the system is characterized by an exponent $\alpha=0.45$, which agrees within the limits of experimental error with the molecular-field approximation. In the interval 1.8–3 kbar the value of α approaches gradually the value 0.12 corresponding to second-order phase transitions. In the intermediate region, 1.8–3 kbar, where the transition from the tricritical to the critical behavior occurs, the exponent α in the isobaric sections should vary with increasing distance between the approximation region and the phase-transition curve (see Fig. 1). To determine the position of the boundary between regions III and II, we plotted dC_{an}/dT against T_c-T (in logarithmic scale) for the pressures 2.0 and 2.6 kbar (Fig. 4). It is seen from the figure that in the region $10^{-1}>\tau>2\cdot10^{-3}$ there are no abrupt changes in the behavior at these pressures. This indicates a large width of the transition, in qualitative agreement with the results of[14]. In the constant-τ sections (curves 6–9 on Fig. 2), at small τ, a maximum is observed in the vicinity of the TCP and becomes rapidly smoothed-out with increasing τ.

In the evaluation of the results for the region $T>T_c(P)$ special care must be taken to separate theanomalous part of the heat capacity. It is shown in[9] that when the calculated regular part C_{reg} is subtracted from the total heat capacity C_P the resultant C_{an} does not tend to zero at atmospheric pressure with increasing distance from the transition point. A certain increment ≈2 cal/mole-°K remains and changes little up to 310 °K. The heat capacity C_{an} behaves similarly at high pressures. Since it is difficult to say anything definite at present concerning the causes of this behavior of C_{an}, we have included this increment in the anomalous part of the heat capacity. When the function $C_{an}(T)$ in the isobaric sections is approximated by power-law functions of the type (2), the obtained exponents lie in the interval 0.8–1.1 in the entire range of pressures, 0–3 kbar, with a maximum error $\Delta\alpha=\pm0.15$. Another possible reduction variant consists of graphically separating the anomalous part of C_P. Estimates show that in this case the change of the exponent α is not more than 0.1, since the slopes of the graphically drawn and calculated C_{reg} curves differ insignificantly.

In the molecular-field approximation, near the TCP, above the transition point, there is no anomalous part of the heat capacity.[1] In the critical region the heat capacity should be described by a power law with a small exponent ($\alpha\approx0.1$). The large values of the exponent α obtained at $T>T_c$ correspond more readily to a "smearing" of the heat-capacity jump, which can mask the true singularity in the critical region. To resolve this problem, several approximations each were made in a number of sections and the points closest to T_c were gradually discarded. The exponent α remained in this case within the limit of the indicated scatter even when the interval ≈1–1.3 °K, which includes 90% of the height of the heat-capacity peak, was cut off. It appears that the most probable explanation of the absence of a critical behavior in the region $T>T_c$ is the asymmetrical location of the boundary of the transition from the tricritical to the critical behavior relative to the phase-transition curve. It is possible that this boundary passes at $T>T_c$ very close to the phase-transition curve ($\tau><10^{-3}$).

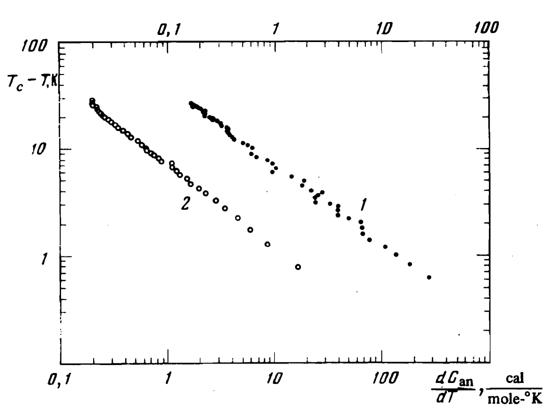

FIG. 4. Dependence of dC_{an}/dT on T_c-T in logarithmic scale for a pressure 2 kbar (curve 1 and upper scale) and 2.6 kbar (curve 2 and lower scale).

TABLE I. Mean squared deviations of σ in the approximation of the data on the order parameter η[15] and on the heat capacity C of ammonium chloride under pressure.

Form of function	σ, rel. un.	Form of function	cal/mole-°K			
			$P=0.9$ kbar	$P=1.2$ kbar	$P=1.5$ kbar	$P=1.8$ kbar
$\psi^2=A\tau^{1/2}$	143.6 $T_c=250{,}49$	$C=A+B\tau^{1/2}$	0,40 $T_c=250.9$	0,27 $T_c=253.6$	0,25 $T_c=256.2$	0.12 $T_c=258.6$
$\psi^2=A\lvert\tau^{-1}\ln\tau\rvert^{1/2}$	24,4 $T_c=250.49$	$C=A+B\left\lvert\frac{\ln\tau}{\tau}\right\rvert^{1/2}$	0,44 $T_c=251.0$	0,35 $T_c=253.7$	0,33 $T_c=256.3$	0,21 $T_c=258.7$

The temperature dependences of the order parameter in deuterated ammonium chloride were investigated in[15] near the TCP and an exponent $\beta=0.18\pm0.01$ was obtained. We have attempted to analyze our data in the vicinity of the TCP jointly with the data of[15]. Using the similarity-theory relations, it is possible, knowing two of the exponents, to determine the remaining ones under the assumption that the thermodynamic functions of NH_4Cl and ND_4Cl have identical singularities. We obtain in this case for the exponent of the anomalous dimensionality a value $\eta=-0.3\pm0.05$, whereas according to the estimates[15] η should not be less than zero. It appears that to describe the singularities of the thermodynamic functions in the vicinity of the TCP it is necessary to take into account the logarithmic corrections to the similarity laws.[17] Stephen *et al.*[18] obtained expressions for the order parameter ψ and for the heat capacity C in the molecular-field approximation:

$$\psi=A\tau^{0.25}(1-D\ln|\tau|)^{0.25}, \tag{4}$$

$$C=A+B\tau^{-0.5}(1-D\ln|\tau|)^{0.5}, \tag{5}$$

with D the same in both equations. Our approximation of the data of[15] with the aid of Eq. (4) has yielded $D\approx16$, so that the unity in the brackets of (4) and (5) can henceforth be discarded.

Table I lists the results of the approximations of the temperature dependences of ψ and C by means of expressions such as (4) and (5) with power-law functions corresponding to the molecular field approximation, namely $C\sim\tau^{-0.5}$ and $\psi\sim\tau^{0.25}$. The approximations were made by least squares, the transition temperature being the varied parameter. It is seen that introduction of the logarithmic corrections improves greatly the description of the behavior of the order parameter in the tricritical region and affects little the description of the behavior of the heat capacity. When C is approximated with and without allowance for the logarithmic corrections, the mean squared deviations lie in both cases near values corresponding to the accuracy with which the surface $C_p(P, T)$ was constructed from the experimental data ($\bar{\sigma}\approx0.27$ cal/mole-°K).

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[1)] We plan to publish tables of the experimental data in Zhurnal fizicheskoĭ khimii (Journal of Physical Chemistry).

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