SINGULARITIES IN THE TEMPERATURE DEPENDENCES OF THE SPECIFIC HEAT NEAR THE CRITICAL POINTS

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An analysis is given of some experimental data on the specific heat C_p of liquids near the critical points of the separation of solutions into layers and on the specific heat C_v in the vicinity of the liquid-vapor critical points. The problem is discussed of the presence and form of mathematical singularities in the temperature dependences of the specific heat at these points. It is shown that in the homogeneous region the experimental results for both cases are more consistent with a power-law singularity having a small exponent, but in the heterogeneous region the accuracy of the data near the critical points of the separation into layers is not sufficient to make a choice between logarithmic and power-law singularities.

A problem currently being discussed is that of the presence and nature of mathematical singularities in the temperature dependences of thermodynamic properties, particularly singularities of the special heat, at critical points of liquids and at phase transition points of the second kind. As found by Fairbank, Buckingham, and Kellers[1] for C_p at the λ point of helium and by Voronel' and his colleagues[2-4] for C_v, a logarithmic singularity in the temperature dependence of the specific heat, observed at the critical liquid-vapor points, is evidently of the type

$$C = C^0 - C' \log t, \qquad t = |T - T_c| / T_c, \qquad (1)$$

where C^0 is the normal component of the specific heat, which is different at $T > T_c$ and $T < T_c$, while the constant C' is the same in both cases.

However, at the liquid-vapor critical points the dependence of the type given by Eq. (1) is obeyed somewhat less vigorously than at the λ points of helium. As pointed out by Fisher[5], the results reported in[2] for argon in the homogeneous region ($T > T_c$) are approximated somewhat better by a power-law dependence of the type

$$C_v = C_v{}^0 + \alpha^{-1} C' t^{-\alpha}, \qquad (2)$$

where $\alpha \approx 0.2$; this dependence is equivalent to that given in Eq. (1) when $\alpha \to 0$.

Moldover and Little[6] measured C_v of He^4 and He^3 at the liquid-vapor critical point and also found that although the logarithmic singularity was obeyed well at $T < T_c$, in the homogeneous region the dependence of C_v on $T - T_c$ was stronger. Moreover, a singularity of the type given by Eq. (2) follows also from theoretical estimates of the specific heat at phase transition points of the second kind, obtained by applying the Ising model to three-dimensional lattices.[7,8]

We may expect to observe singularities of the (1) or (2) type for the specific heat C_p near the critical point of the separation of solutions into layers. In order to check this suggestion, we analyzed the results obtained by several workers[9-11] for solutions in the vicinity of these points. It must be pointed out that, in the major-

ity of papers reporting such measurements, the number of experimental points near T_c is insufficient and they have a considerable scatter, which makes it impossible reliably to establish the nature of the temperature dependence. Moreover, the critical temperature itself is known with a low degree of accuracy, and this aspect is particularly important at small values of $T - T_c$.

Among the results known to the present authors, the most detailed and reliable are the data of Skripov and Kostin[10] on the specific heat C_p of triethylamine-water (I) and triethylamine-heavy water (II) solutions. These data were used in our analysis. To determine the nature of the singularity of C_p, Skripov and Kostin's data were plotted in the coordinates C_p-log t (Fig. 1) and $\log (C_p - C_p^0)$-log t (Fig. 2). In plotting graphs in the second figure, the parameter C_p^0 was selected to obtain the best fit of the experimental points to straight lines, and the value of α was determined from the slopes of the obtained lines so obtained. Both figures indicate the errors in the measurements of C_p and the possible shifts of the experimental points
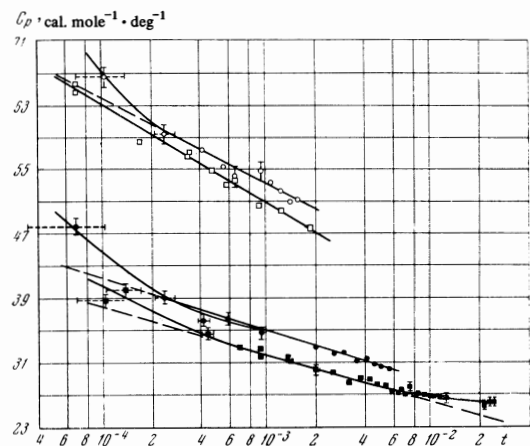

FIG. 1. Dependence of the specific heat C_p of $(C_2H_5)_3N$–H_2O ($\square$,$\blacksquare$) and $(C_2H_5)_3N$–D_2O ($\bigcirc$,$\bullet$) solutions on log t. Open squares and circles denote the range $T > T_c$; the black symbols denote $T < T_c$.

due to an error in the determination of the position of T_C relative to the neighboring points at which the specific heat was measured. This error was estimated to be ± 0.01 deg, because the distance between the nearest points at the C_p peak to the left and right of T_C was 0.05 deg. (The absolute error in the value of T_C could be greater.) The concentration in both solution systems was 6.76 mol.% and the critical temperature was 18.08°C for system I and 14.25°C for system II.

It is evident from Figs. 1 and 2 that at $T > T_C$, i.e., in the heterogeneous region, the points for both systems fitted straight lines (within the limits of the experimental scatter) in dependences of both types, indicating no clear preference for the logarithmic or power-law dependence. However, in the homogeneous region, a logarithmic dependence of the type given by Eq. (2) was obeyed rather than a power law. The semilogarithmic coordinates showed a considerable deviation from the linear dependence but the points fitted the straight lines well when $\log(C_p - C_p^0)$ was plotted as a function of log t.

Thus, C_p in the vicinity of the critical point could be represented by the equation

$$C_p^\pm = C_p^{0\pm} + \frac{C'^\pm}{\alpha} t^{-\alpha}. \qquad (3)$$

The plus and minus signs refer to temperatures above and below T_C respectively. The parameters in Eq. (3) are given for both solution systems in the table below (C is in units of cal.mole$^{-1}\cdot$deg^{-1}):

	C_p^{0+}	C_p^{0-}	C'^+	C'^-	α
$(C_2H_5)_3N - H_2O$:	33	18	0.85	0.7	0.2
$(C_2H_5)_3N - D_2O$:	33	20	1.0	0.75	0.2

The values of the exponent α given in the above table correspond to the selected values of $C_p^{0\pm}$, on which this exponent depends very strongly. By varying the values of $C_p^{0\pm}$, we could, without going outside the limits of accuracy of the available data, obtain values of α ranging from 0.1 to 0.25.

It must be stressed that the values of the parameters C_p^{0-}, given in our table, are in agreement with the specific heat of water and heavy water, i.e., they are close to the molar specific heats of the solutions in the

FIG. 2. Dependence of log $(C_p - C_p^0)$ of $(C_2H_5)_3N-D_2O$ ($\square$,$\blacksquare$) and $(C_2H_5)_3N-H_2O$ ($\bigcirc$,$\bullet$) solutions on log t. Open squares and circles denote the range $T > T_C$; the black symbols denote $T < T_C$.

homogeneous region far from the critical point because the molar concentration of triethylamine was low (6.76%). Consequently, C_p^0 is not an arbitrary parameter but represents some normal component of the specific heat. If the parameters C'^+ and C'^- were equal for equal values of α, this would indicate that the specific heat discontinuity ΔC_p is finite at the critical point and is given by the difference between C_p^{0+} and C_p^{0-}. However, C'^+ and C'^- are different (although the difference is not large) and therefore $\Delta C_p \to \infty$ as $t \to 0$. It is at present difficult to decide whether this is due to the experimental errors or represents a general relationship. It must be stressed also that if the results are nevertheless represented approximately by a logarithmic dependence, which is permissible in the range of small values of t, the slopes of the straight lines for $T > T_C$ and $T < T_C$ in Fig. 1 are found to be different, which again indicates an infinite discontinuity ΔC_p.

In addition to the results considered so far, we also analyzed other data on the specific heat of partly miscible mixtures.[9,11] In all these cases, the results indicate a singularity at the critical point of the separation of a solution into layers but it is not possible select either a logarithmic or a power-law dependence because of the large scatter and the limited range of the experimental data.

To determine the nature of the specific heat singularity, particularly on the homogeneous region side, a similar analysis was carried out using some data on the specific heat C_V near the critical liquid-vapor points. As already pointed out, it has been demonstrated for He^4 and He^3 that the dependence of C_V on t should be stronger than logarithmic. However, Moldover and Little[6] also tried a dependence of the type $C_V = At^{-\alpha}$, i.e., they actually assumed that C_V^0 in Eq. (2) was equal to zero, which gave unsatisfactory results. However, when it was assumed that C_V^0 differed from zero, it was possible to select such a value of this quantity that the dependence of Eq. (2) was satisfied by the experimental data within the limits of their accuracy. This dependence was satisfied by He^4 throughout the whole range of values of t for $C_V^0 = 10.5$ J.mole$^{-1}\cdot$deg^{-1}, which was close to the value of C_V for helium at elevated pressures in the same range of temperatures.[12] The value of the exponent α was found to be 0.35, i.e., considerably higher than in the cases analyzed earlier.

We also analyzed the data on C_V for xenon, obtained from the P-V-T relationships by Habgood and Schneider.[13] As in the case of helium, a power-law singularity of the Eq. (2) type was found in the homogeneous region at all temperatures for which the data were available: $10^{-4} < t < 4 \times 10^{-2}$; a logarithmic dependence was satisfied only at $t < 2 \times 10^{-3}$, i.e., for $T - T_C < 0.5$ deg K. The corresponding values of the parameters in Eq. (2) were: $C_V^0 = 3R/2 \approx 3$ cal.mole^{-1}.deg^{-1} and $\alpha = 0.37$. Thus, C_V^0 for xenon was equal to the specific heat of an ideal gas and α was close to the value for helium.

Naturally, these results have not yielded final conclusions on the nature of the singularity in the temperature dependence of the specific heat C_p at the critical point of the separation of solutions into layers, but its
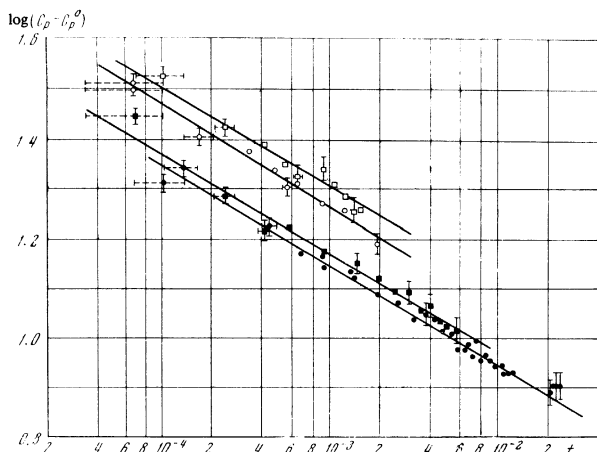
presence, like the presence of the singularity of C_V at the critical liquid-vapor point, has been firmly established. To determine finally the type of singularity for solutions and pure substances, more exact measurements of the specific heat in a wider range of temperatures are required. This applies particularly to the extension of measurements in the range of temperatures close to T_c where $t < 10^{-4}$.

In conclusion, the authors take this opportunity to express their gratitude to V. P. Skripov for supplying tables of numerical values of the specific heat of triethylamine-water solutions, which are not given in the original paper.

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