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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PENTANE NEAR THE LIQUID-VAPOR CRITICAL POINT

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The thermal equation of state of n-pentane near the critical liquid-vapor point are investigated by experimentally studying the gravitational effect. The form of the top of the coexistence curve, the law governing the variation of the isothermal compressibility, and the shape of the critical isotherm are analyzed. The exponents $\beta = 0.35$ and $\gamma = 1.25$ are determined directly from the experimental data, and the exponent $\delta = 5$ is calculated. It is shown that measurements of the gravitational effect yield the three "critical exponents" needed for the verification of the new theories of the critical state of matter.

THE ideas concerning the nature of the critical state of matter and the behavior of thermodynamic functions in the vicinity of the critical point have recently been greatly altered. A number of investigators believe that the classical theory of critical phenomena is incapable of explaining all the available experimental data[1,2]. In the proposed new phenomenological theories, it is assumed that essential singularities exist in the thermodynamic quantities at the critical point. The character of these singularities should be established experimentally by determining the thermal and caloric equations of state of matter in the immediate vicinity of the critical point[3]. Such data are necessary also for the verification of the new statistical model of the theory of critical phenomena.

In practice, the form of the equations of state is established by using experimentally investigated sections (T = const, ρ = const, etc.) and the characteristic lines on surfaces corresponding to the equations of state. To this end it is possible to use precision data on the temperature dependence of the specific heat, on the shape of the top of the coexistence curve, on the temperature variation of the isothermal compressibility, on the shape of the critical isotherm, etc.

In the aforementioned phenomenological and statistical theories it is customary to describe the behavior of the thermodynamic quantities along characteristic lines on surfaces corresponding to the equations of state, and along their most characteristic sections near the critical point with the aid of power-law equations. The statistical theory gives numerical values for the "critical exponents," and the new phenomenological theory only establishes the connections between them. The presently developed theory of scale transformations proves that there exist only two independent "critical exponents"[4]. Thus, to verify any new theory of critical phenomena it is necessary to have experimental data on the behavior of at least two thermodynamic quantities along two cross sections or characteristic lines as the critical point is approached. The availability of precision data on three or more thermodynamic properties, naturally, makes it possible to carry out not only a more detailed verification of the theory, but to establish the internal consistency of such data.

An analysis of the published experimental data obtained by various authors indicates that each investigation is devoted to some one particular property. Owing to the use of different experimental procedures, these data are not very suitable for our problem. In our opinion, to verify new theories of the critical state of matter it is necessary to have precision investigations of the behavior of at least two or three thermodynamic quantities, carried out in the immediate vicinity of the critical point with the aid of the same experimental apparatus. In our earlier papers we have pointed out that for a simultaneous study of the shape of the binodal, the law governing the isothermal compressibility, and the shape of the critical isotherm, it is convenient to use measurements of the gravitational effect. In general, on the other hand, data on the gravitational effect make it possible to carry out a more complete verification of new theories, since they can be used to establish the entire thermal equation of state of matter near the critical point.

We have previously investigated the form of the binodal and the behavior of the isothermal compressibility of benzene near the critical point[5]. In the present paper we present the results of a study of pentane, obtained with the aid of the same procedure. In the experiments with the pentane we succeeded in coming closer to the temperature of the critical point. In addition, we have extended the number of investigated limiting laws governing the behavior of the thermodynamic functions. Investigations were carried out with normal pentane of brand KhCh (chemically pure).

The procedure consists of three independent but simultaneously employed measurement methods:

1) The Toepler method, which makes it possible to determine the distribution of the gradient of the refractive index along the height of a vessel at each given temperature.

2) The reference-prism method, which gives the absolute value of the refractive index of a substance at two points of a chamber.

3) The method of free microscopic floats, which makes it possible to measure the local values of the density at several points of the vessel.

The foregoing three methods, which supplement one another, ensure elimination of systematic errors and, what is particularly important, make it possible to measure simultaneously and independently both the density of the medium itself and the derivative of the density with respect to the height of the vessel.

To eliminate systematic errors of the measurement of the gravitational effect in pentane we first measured, just as in the case of benzene, the refractive index of pentane in a wide interval of temperatures, including a detailed determination of n in the region of the critical point. Figure 1 shows the results of the measurement of the refractive index of pentane along the coexistence curve. The data near the vertex of the binodal, i.e., under conditions when a noticeable gravitational effect exists in the medium, correspond to layers of the medium locating directly at the meniscus. The numerical values of n at the meniscus were obtained by reconciling the measurements made by the Toepler method with the measurements of the refractive index, performed with the aid of reference prisms[6]. It is interesting to note that the linear-diameter rule holds for the refractive indices of the liquid and vapor pentane actually holds near the critical point, up to the very temperature at which the meniscus vanishes. This fact facilitates the determination of the refractive index in the critical state. The refractive index of pentane in the critical state turned out to be $n_{cr} = 1.1275 \pm 0.005$.

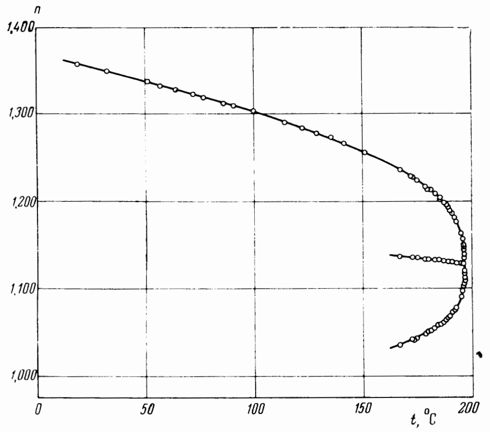

FIG. 1. Temperature dependence of the refractive index of coexisting liquid and vapor n-pentane.

Data on the temperature dependence of the refractive index together with the corresponding tabulated values of the density show that the Lorentz-Lorenz refraction increases monotonically with temperature. The values of the refraction of pentane in states close to critical were determined from simultaneous measurements of the height distribution of the refractive index, carried out by the Toepler method and by the method of reference prisms, and the local values of the density, determined by the microfloat method. In a narrow temperature interval, where an appreciable gravitational effect is observed, the specific Lorentz-Lorenz refraction of pentane turned out to be practically constant at $r_{cr} = 0.357\ \mathrm{cm^3/g}$, whereas for liquid pentane at room temperature its value is $r = 0.350\ \mathrm{cm^3/g}$.

Under conditions close to critical, using the obtained value of the refraction and the refractive index measured directly at the meniscus, we calculated the top of the phase equilibrium curve in terms of the coordinates ρ and t (see the table). It is of interest to note that for the densities of the truly coexisting layers of liquid and gas, the rule of linear diameter turns out to be valid up to the very critical point. The use of this rule together with direct measurements of the density of the investigated substance at different heights and different temperature has made it possible to determine the coordinates of the top of the binodal of pentane: $r_{cr} = 0.232 \pm 0.001\ \mathrm{g/cm^3}$ and $t_{cr} = 196.46 \pm 0.01°\mathrm{C}$.

The vertex of the binodal, constructed in a double-logarithmic scale (Fig. 2), makes it possible to establish its exponent. As can be seen directly from the figure, in a temperature interval $2.0 < -\log(|T - T_{cr}|/T_{cr}) < 4.0$, all 25 experimental points fit well a straight line with a slope $\beta = 0.35 \pm 0.02$. The

Temperature dependence of the refractive indices at densities of the corresponding liquid and gas at the meniscus near the critical point of n-pentane

t, °C	$t-t_{cr}$	n_{liq}	n_g	ρ_{cr}, g/cm³	ρ_g, g/cm³
194,82	—1.64	1.1645	1.0913	0,2972	0.1676
194,91	—1.55	1.1643	1.0914	0,2968	0.1678
195.43	—1.03	1,1594	1,0958	0.2883	0.1757
195,51	—0,95	1,1576	1,0977	0,2852	0,1791
195.76	—0,70	1,1545	1,1009	0,2798	0,1849
195,88	—0,58	1,1533	1.1016	0.2777	0,1861
195,97	—0,49	1.1518	1.1030	0,2750	0.1886
195,99	—0.47	1.1515	1,1036	0,2745	0.1897
196,03	—0.43	1,1499	1,1043	0,2717	0,1909
196,04	—0,42	1,1498	1.1047	0,2715	0.1917
196,05	—0,41	1,1496	1.1049	0.2712	0,1920
196,06	—0.40	1,1495	1.1053	0.2710	0.1927
196.10	—0.36	1.1489	1.1060	0,2700	0.1940
196,12	—0.34	1,1487	1.1062	0.2696	0,1943
196,16	—0.30	1.1481	1,1064	0,2686	0.1947
196.18	—0.28	1,1472	1.1076	0.2670	0.1969
196.25	—0.21	1.1454	1,1093	0.2638	0.1999
196.26	—0.20	1,1450	1.1096	0,2631	0.2004
196.33	—0.13	1.1419	1.1122	0.2577	0.2051
196.35	—0.11	1,1415	1,1138	0,2570	0.2079
196.38	—0.08	1,1402	1,1159	0,2547	0,2117
196,41	—0.05	1,1380	1.1173	0,2508	0,2142
196,44	—0.02	1,1366	1,1184	0.2483	0,2161
196,46	0	1.1275	1.1275	0.2320	0,2320

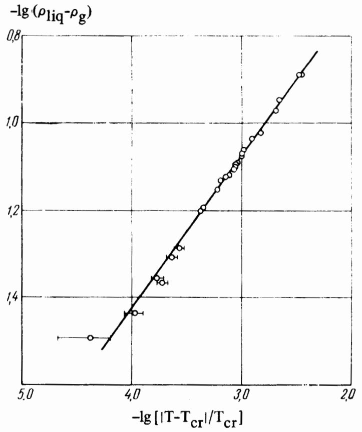

FIG. 2. Top of the coexistence curve of n-pentane, plotted in a log-log scale.

experimental points obtained closer to the critical point are subject to much larger errors in the determination of $(T_{cr} - T)/T_{cr}$; these errors are directly reflected in the plot of Fig. 2. However, even when these errors are taken into account, the obtained experimental points cannot lead to an increase of the slope of the straight line, as would be necessary to obtain agreement with the classical theory[7]. To discuss the remaining results it is therefore logical to use the thermal equations of state, which follow from the new phenomenological theories.

The most perfect is the Widom-Griffiths equation[3], which can be written in the form

$$\frac{\Delta\varphi}{\varphi_{cr}} = |\xi|^{\delta-1}\xi h\left(\frac{\tau}{|\xi|^{1/\beta}}\right), \tag{1}$$

where $\Delta\varphi$ is the difference between the specific Gibbs potential at the arbitrary point $\varphi(\rho, T)$ and its value on the critical isochore $\varphi(\rho_{cr}, T)$, φ_{cr} is the value of the specific Gibbs potential at the critical point, $\xi = (\rho - \rho_{cr})/\rho_{cr}$ is the relative change of the density, and $\tau = (T - T_{cr})/T_{cr}$ is the relative change of the absolute temperature.

This thermal equation makes it possible, in accordance with the experimental data, to vary somewhat the character of the singularities of the thermodynamic quantities at the critical point and to modify the description of the behavior of these quantities in its vicinity. However, a comparison of the Widom-Griffiths equation with the entire aggregate of experimental data on the thermal equation of state is made difficult by the uncertainty of the function $h(\tau/|\xi|^{1/\beta})$.

It seems to us that the following equation

$$\left\{\frac{\partial}{\partial\xi}\left[\frac{\Delta\varphi}{\varphi_{cr}}\right]\right\}_T = a|\tau|^{\gamma-1}\tau + b|\xi|^{\delta-1}, \tag{2}$$

where the notation is the same as in (1), and in addition $a > 0$, $b > 0$, $\gamma \geq 1$, and $\delta > 1$ (γ and δ need not necessarily be integers), while allowing sufficient freedom in the choice of the character of the singularities of the thermodynamic quantities and having sufficient certainty of the functional relations, is the most suitable for the discussion of the experimental data on the thermal equation of state in the region of the critical point[1]. A shortcoming of this equation is the postulate that the singularities occurring in the sections $\rho = \rho_{cr}$ and $T = T_{cr}$ are additive. In this sense, Eq. (2) is a generalization of the equation of Landau and Lifshitz[7].

Equation (2) with $T < T_{cr}$ has an analytic continuation in the metastable and unstable regions. Therefore to find the densities of the coexisting phases at a specified temperature it is necessary to use the conditions that the specific Gibbs potentials and the pressures be equal. The coexistence curve is obtained in the form

$$\xi_i = \pm\{a\delta/b\}^{1/(\delta-1)}\tau^{\gamma/(\delta-1)}, \tag{3}$$

hence the "critical exponent" of the phase-equilibrium curve turns out to be $\beta = \gamma/(\delta - 1)$, in agreement with the conclusions of the theory of Widom and Griffiths[3].

From (2) we can obtain an equation for the isothermal compressibility of the medium K_T, in the form:

$$\frac{1}{\rho^2 K_T} = \left(\frac{\partial\varphi}{\partial\rho}\right)_T = \frac{\varphi_{cr}}{\rho_{cr}}\left\{\frac{\partial}{\partial\xi}\left[\frac{\Delta\varphi}{\varphi_{cr}}\right]\right\}_T = \frac{\varphi_{cr}}{\rho_{cr}}\{a|\tau|^{\gamma-1}\tau + b|\xi|^{\delta-1}\}. \tag{4}$$

At a fixed temperature, when $T > T_{cr}$, the quantity $\rho^2 K_T$ reaches its maximum value on the critical isochore, but if $T < T_{cr}$ the maximum is reached on the coexistence curve. For $T > T_{cr}$ we obtain the following equation for $\rho^2 K_T$ along the critical isochore:

$$\frac{1}{\rho_{cr}{}^2 K_T} = a\frac{\varphi_{cr}}{\rho_{cr}}|\tau|^{\gamma-1}(-\tau) = a\frac{\varphi_{cr}}{\rho_{cr}}\tau^{\gamma}. \tag{4a}$$

Along the coexistence curve at $T < T_{cr}$, the relation for $\rho^2 K_T$ is of similar form:

$$\frac{1}{\rho^2 K_T} = a\frac{\varphi_{cr}}{\rho_{cr}}(\delta - 1)(-\tau)^{\gamma}. \tag{4b}$$

We emphasize that the obtained form of the laws for the coexistence curve (3) and for the isothermal compressibility (4) is overdefined by the assumption of additivity of the singularities over the cross sections $\rho = \rho_{cr}$ and $T = T_{cr}$, an assumption used in writing down Eq. (2). From the assumption that Eq. (2) is valid, it follows also that the exponents γ and the coefficients a in the equations governing the isothermal compressibility, (4a) and (4b) are equal.

The "critical exponent" γ can be determined from simultaneous measurements of the local values of the density and of the refractive-index-gradient distribution curves. According to the theory of the gravitational effect, $\rho^2 K_T g = -(\partial\rho/\partial z)_T$. The density gradient is determined directly by the Toepler method from the inclination of the rays Δa in the focal plane[9]:

$$\left(\frac{\partial\rho}{\partial z}\right)_T = \frac{6n}{r(n^2+2)^2 Wf}\Delta a; \tag{5}$$

here n is the refractive index, r the specific refraction, f the focal length of the objective of the Toepler optical system, W the horizontal thickness of the investigated layer, and z the vertical coordinate of the layer. The factor $6n/r(n^2 + 2)^2$ varies only 3–4% in a temperature interval on the order of 200°, and in the vicinity of the critical point, where the gravitational effect is ob-

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[1] Eq. (2) is similar to the equation proposed by Alekhin and Chalyĭ [8].

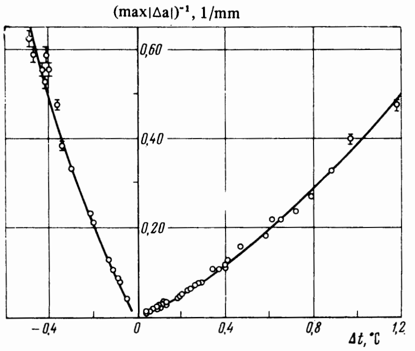

FIG. 3. Temperature dependence of the quantity $(\max|\Delta a|)^{-1}$, which is proportional to the reciprocal of the isothermal derivative $\rho^2 K_T$ of the thermal equation of state.

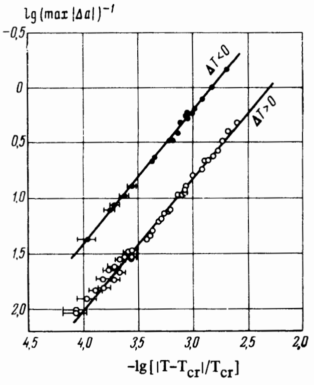

FIG. 4. Temperature dependence of $(\max|\Delta a|)^{-1} \propto \rho^2 K_T$ in a log-log scale.

served, it can be regarded as a constant coefficient. Thus, the quantity $\rho^2 K_T$, which is a derivative of the thermal equation of state, turns out to be proportional to the directly measured inclination Δa in the region of the critical point.

For an experimental determination of the exponent γ^+ in the equation for $(\rho^2 K_T)^{-1}$ in the high-temperature region along the critical isochore, it suffices to establish the law governing the variation of the inverse quantity, $\max|\Delta a|$, *on* approaching the critical temperature. The determination of the analogous exponent γ_1^- reduces to an analysis of the change of $(\max|\Delta a|)^{-1}$ in any of the phases, at temperatures below critical. Figure 3 shows the experimental temperature dependence of the reciprocal quantity $\max|\Delta a|$ for a liquid at $T < T_{cr}$, in the analogous relation for the high-temperature region. The nonlinearity of the discussed laws contradicts the predictions of the classical theory.

To find the exponent in the equations for the temperature dependence of $\rho^2 K_T$, just as in the analysis of the coexistence curve, it is convenient to use a log-log scale. It is seen from Fig. 4 that in the temperature interval $2.5 < -\log(|\Delta T|/T_{cr}) < 4.0$, all the experimental points lie, within the limits of measurement accuracy, on two parallel straight lines with slope $\gamma^+ \approx \gamma^- = 1.25 \pm 0.10$, which is in fair agreement with the predictions of the new statistical theories.

We were unable to measure directly the critical isothermal with the required accuracy, even using our own method, owing to the difficulties in measuring large deflections of the optical rays near the critical point. Therefore, to find the exponent of the critical isotherm we have employed a somewhat indirect method, based on the use of Eq. (2) or, more accurately, of Eqs. (4a) and (4b) that follow from (2). Dividing the second of these equations by the first, we obtain for equal values of $|T - T_{cr}|$

$$\delta - 1 = \frac{(\rho^2 K_T)^{-1}}{(\rho_{cr} K_T)^{-1}} = \frac{(\max|\Delta a|)^{-1}_{\Delta T<0}}{(\max|\Delta a|)^{-1}_{\Delta T\geq 0}} \tag{6}$$

The exponent of the critical isotherm, calculated on the basis of (6), turned out to be close to δ = 5, which differs appreciably from the classical value δ = 3 and coincides with the results of the analysis of the experimental data of some other workers[10]. The error in our method of the determination of the exponent δ was much larger than in the case of the determination of β and γ. Taking into account the average error, we should assume δ = 5.0 ± 0.5.

Thus, from experimental data on the gravitational effect in pentane, we have obtained the exponents of the coexistence curve and of the isothermal compressibility, and also the exponent of the critical isotherm. This raises the question whether these exponents can be regarded as "critical exponents" of the limiting laws. In other words, we can expect changes in the numerical values of these exponents on coming closer to the critical point and when the latter is determined more accurately.

In our opinion, a comparison of the plots of the properties measured at $T < T_{cr}$ with those measured at $T > T_{cr}$ indicates that an increase in the accuracy with which the critical temperature is measured will have no significant influence on the exponents of the investigated laws in the investigated temperature intervals. At the very most, the width of the absolute error may slightly increase. As to the influence of a closer approach to the critical point, we can advance the following argument. In the investigations of pentane we have succeeded in coming closer to the critical temperature point by approximately one order of magnitude than in the case of the investigation of benzene[5]. This had no noticeable effect on the form of the discussed laws. Within the limits of errors, the measured numerical values of the exponents β and γ were the same for both substances. This gives grounds for expecting the obtained exponents to retain the same value also closer to the critical point.

By determining with the aid of identical measurements the two critical exponents β and γ and by calculating the third critical exponent δ, we can verify the relations between them, proposed by Widom, and to calculate the two fundamental critical exponents of the theory of scale transformation[1-4]. Widom's relations

$$\gamma^+ = 2(1-\beta), \quad \gamma_1^- = \beta(\delta - 1) \tag{7}$$

are satisfied in the best manner if, within the limits of errors of our measurements of both pentane and benzene, we assume the following critical exponents: β = 0.33, γ = 1.3, and δ = 5. From the Pokrovskiĭ relation[4]

$$\beta = \frac{3-x}{y}, \quad \gamma = \frac{2x-3}{y}, \quad \delta = \frac{x}{3-x} \tag{8}$$

we get x = 2.49 and y = 1.53.

Using the formulas from Pokrovskiĭ's table, we can calculate the remaining critical exponents. All are close to the results of calculations of the three-dimensional Ising model. It seems to us, however, that there are still no grounds for assuming that the Ising model is fully representative of reality. At the same time, we wish to emphasize that further precision investigations of the gravitational effect can contribute to a solution of this problem.

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