Experimental investigation of some peculiarities of the equation of state of heptane near the critical point

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Comprehensive measurements of the gravitational effect are carried out by means of optical and microfloat measurements of the density of heptane in thin layers of matter near the critical point. The results are analyzed in terms of the critical exponents. By computer treatment of the experimental data, the critical exponent of the coexistence curve is found to be equal to $\beta = 0.358 \pm 0.009$. The critical exponent and coefficient of isothermal compressibility along the coexistence curve for the liquid branch are found to be $\gamma_1^- = 1.29 \pm 0.06$ and $\Gamma_1^- = (1.24 \pm 0.30) \cdot 10^{-9}\ \mathrm{g^2/erg \cdot cm^3}$. The critical exponent and coefficient of isothermal compressibility along the critical isochore are $\gamma^+ = 1.29 \pm 0.04$ and $\Gamma^+ = (5.00 \pm 0.87) \cdot 10^{-9}\ \mathrm{g^2\,erg \cdot cm^3}$. For $\rho > \rho_{cr}$ the critical exponent of the critical isotherm is $\delta^+ = 5.00 \pm 0.18$ and for $\rho < \rho_{cr}$, $\delta^- = 4.62 \pm 0.16$.

To explain the nature of critical liquid-vapor phenomena and to determine the molecular mechanism of second-order phase transition we need exact data on the equation of state in the vicinities of the corresponding points[1]. We have previously investigated[2,3] the behavior of the thermodynamic properties of pentane and benzene, two organic substances of different classes, near the critical point of vapor formation. In the present paper we reported results on heptane, which is the homolog of pentane. We used standard heptane in the investigations. The investigation procedure was in the main outline the same as in the study of benzene and pentane[2,3]. Comprehensive measurements were made of the gravitational effect produced in matter near the liquid-vapor critical point, using the Toepler optical method supplemented by reference prisms, and a flotation method with free microfloats.

The Toepler method was used to determine directly the distributions of the refractive-index gradient dn/dz over the height of the chamber near the critical point. In the present experiment, we ensured the possibility of registering a much larger range of refractive-index gradients than in our earlier investigations, by measuring dn/dz at two different values of the optical path length in the investigated substance (chamber thicknesses $W_1 = 16$ mm and $W_2 = 3$ mm). Integrating the plots of $-dn/dz = f(z)$ and referring the obtained values of the change Δn of the refractive index as a function of z with the absolute values of n at two points of the chamber, measured with the aid of the reference prisms, we obtained the distributions of the absolute values of the refractive index over the height of the chamber at different temperatures close to the critical temperature. The accuracy with which the refractive index was determined in our investigations was 0.01%.

The flotation method was used to measure individual local values of the density at the locations of the microfloats in the investigated substance. The accuracy of density determination by this method is 0.3%. The use of a large number of floats makes the investigations near the critical point difficult. To study the continuous character of the variation of the density along the height of the chamber we used therefore data on the distribution of the refractive index which were converted into values of the density by the Lorentz-Lorenz formula. Simultaneously, we made a thorough investigation of the refraction of the standard heptane. The results of these investigations, made in a wide range of temperature below the saturation curve and above the critical point, are reported in[4]. The refraction was determined with an accuracy on the order of 0.3%.

In the investigation of heptane we improved the technique of maintaining the temperature constant by introducing double thermostating. The chamber with the investigated substance was placed in a special thermostat, which was a bulky cylindrical oven with two independent heating coils (internal and external), each of 50 Ω resistance. Both heaters were connected to proportional temperature-regulation systems, the operating principle of which is based on phase regulation of the value of the anode current of a thyratron connected to the alternating-current source.

In the double-thermostating circuits, the temperature pickups were platinum resistance thermometers. A 10-Ω thermometer placed in the immediate vicinity of the heater coil was used in the system for the external oven. It was connected to an MO-59 bridge. The null indicator was an M-17/4 galvanometer with a current constant 2×10^{-9} A-m/mm and with internal resistance 35 Ω. The sensitivity of the primary-thermostating circuit was ±0.004°C. The average current through the heater did not exceed 1.5 A. The pickup for the secondary thermostating system was a 100 Ω resistance thermometer connected to an MOD-61 bridge. The null indicator was an M-17/2 galvanometer with a constant 2×10^{-9} A-m/mm and an internal resistance 20 Ω. The sensitivity of the secondary-thermostating circuit was ±0.0001°C. The average current through the internal heater did not exceed 0.1A.

Just as in our earlier investigations, the conditions for the optical measurements were improved by placing the entire cylindrical oven in a steel vacuum jacket[5].

In view of the large number of electric leads, the pressure in the vacuum jacket varied slightly with time. We have therefore developed an additional special circuit to maintain constant vacuum in the oven jacket during the course of prolonged thermostating. The pressure pickup was a mercury manometer with sealed-in electric leads. The actuating particle of the system was an electromagnetic valve connected between the vacuum jacket and a buffer flask.

The improved thermostatic procedure described above has made it possible to maintain the temperature within ± 0.001° C of the critical point. The temperature of the investigated object was determined with the aid of a standard platinum 10-Ω resistance thermometer placed in the vertical channel of the body of the chamber in the immediate vicinity of the investigated substance. The resistivity of the thermometer was measured with a potentiometer circuit built around the R-348 semiautomatic dc potentiometer. The sensitivity of the measuring circuit was ± 0.0003° C. The system for double thermostating in an temperature measurement is shown in Fig. 1.

Owing to the improvement in the procedure, we succeeded in determining directly, from experimental data obtained in the single experiment, a larger number of critical exponents than in the preceding investigations, namely the exponent β of the coexistence curve, the exponents γ^+ and γ_1^- of the temperature dependence of the isothermal compressibility at temperatures above critical along the critical isochore and below critical along the coexistence curve on the liquid side, respectively, and also the exponent δ of the critical isotherm.

The densities obtained from simultaneous optical and flotation measurements at 22 different temperatures near the critical point and at different altitudes reckoned from the meniscus level at $T < T_{cr}$ were from the level with the maximum density gradient at $T > T_{cr}$ are listed in Table I and II.

In the tables containing data on the density at only certain values of the altitude selected from all the investigated continuous vertical distributions of the density. From the data at $T < T_{cr}$ we obtained the densities of the truly coexisting liquid and vapor, i.e., the density of layers located directly at the meniscus. The shape of the heptane coexistence curve measured in this manner is the subject of a separate article[6], in which the critical exponent of the symmetrized coexistence curve is found to be $\beta^* = 0.358 \pm 0.009$, and which gives also the optimal critical parameters obtained by us for heptane:

$$T_{cr} = (539.860 \pm 0.005)^\circ\,\mathrm{K},\ \rho_{cr} = (0.2340 \pm 0.0010)\ \mathrm{g/cm^3}.$$

To discuss the temperature dependence of the isothermal compressibility, and especially the shape of the critical isotherm, it is convenient to represent the data on the gravitational effect in the form of a plot of the difference between the specific Gibbs potential (chemical

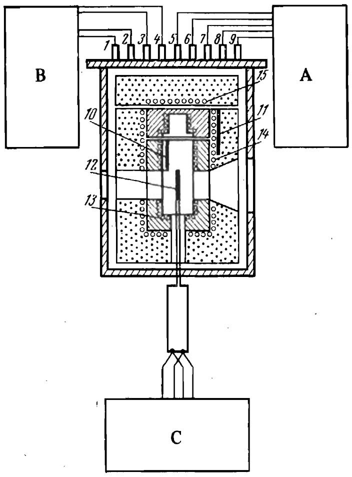

FIG. 1. Diagram of experiment: A – external thermostating block, B – internal thermostating block, C – temperature measurement block. 1, 2 – leads for internal oven, 3, 4 – leads for pickup of the internal thermostating circuit, 5, 6 – leads for pickup of external thermostating circuit, 7, 8 – leads for regulation of current through cover of external oven; 8, 9 – leads feeding the external oven; 10 – pickup of internal thermostating circuit (100-Ω platinum resistance thermometer); 11 – pickup for external thermostating circuit (10-Ω platinum resistance thermometer), 12 – 10-Ω standard platinum thermometer for temperature measurement; 13 – internal oven coil; 14 – external oven winding; 15 – external oven cover winding.

TABLE I. Height dependence of density ρ (in g/cm³) for temperatures below critical.

T, °K	Δz, mm													
	−28.0	−20.0	−15.0	−10.0	−5.0	−2.0	−1.0	+1.0	2.0	5.0	10.0	15.0	20.0	28.0
534.987	0.3328	0.3327	0.3324	0.3324	0.3323	0.3323	0.3322	0.1418	0.1417	0.1416	0.1415	0.1414	0.1412	0.1410
537.010	0.3173	0.3168	0.3164	0.3161	0.3158	0.3157	0.3156	0.1566	0.1564	0.1561	0.1558	0.1554	0.1550	0.1542
537.991	0.3061	0.3058	0.3056	0.3050	0.3046	0.3043	0.3040	0.1670	0.1668	0.1664	0.1658	0.1652	0.1645	0.1633
538.573	0.2976	0 2968	0.2964	0.2959	0.2952	0.2948	0.2946	0.1746	0.1744	0.1736	0.1727	0.1720	0.1712	0.1690
538.987	0.2932	0.2920	0.2910	0.2898	0.2883	0.2875	0.2871	0.1812	0.1808	0.1796	0.1778	0.1762	0.1745	0.1716
539.319	0.2884	0.2866	0.2852	0.2836	0.2816	0.2800	0.2782	0.1888	0.1878	0.1857	0.1828	0.1806	0.1782	0.1745
539.521	0.2838	0.2822	0.2808	0.2790	0.2760	0.2737	0.2726	0.1952	0.1940	0.1910	0.1875	0.1847	0.1822	0.1780
539.737	0.2791	0.2772	0.2755	0.2732	0.2692	0.2652	0.2623	0.2035	0.2008	0.1960	0.1916	0.1884	0.1856	0.1810
539.772	0.2781	0.2765	0.2747	0.2722	0.2682	0.2637	0.2605	0.2057	0.2027	0.1980	0.1930	0.1896	0.1870	0.1822
539.787	0.2780	0.2763	0.2744	0.2718	0.2675	0.2623	0.2588	0.2070	0.2037	0.1982	0.1935	0.1899	0.1872	0.1825
539.827	0.2776	0.2760	0.2742	0.2714	0.2668	0.2610	0.2572	0.2095	0.2056	0.1992	0.1936	0.1898	0.1866	0.1818
539.844	0.2775	0.2757	0.2736	0.2709	0.2660	0.2605	0.2564	0.2095	0.2053	0.1990	0.1935	0.1898	0.1866	0.1820
539.854	0.2776	0.2756	0.2735	0.2703	0.2656	0.2597	0.2558	0.2115	0.2068	0.2000	0.1943	0.1904	0.1870	0.1818

TABLE II. Height dependence of density ρ (in g/cm³) for temperatures above critical.

T, °K	Δz, mm														
	−28.0	−20.0	−15.0	−10.0	−5.0	−2.0	−1.0	0	+1.0	2.0	5.0	10.0	15.0	20.0	28.0
540.030	0.2750	0.2735	0.2714	0.2680	0.2620	0.2540	0.2480	0.2356	0.2225	0.2154	0.2053	0.1982	0.1939	0.1905	0.1855
540.070	0.2742	0.2724	0.2700	0.2665	0.2600	0.2515	0.2453	0.2345	0.2242	0.2177	0.2066	0.1992	0.1946	0.1912	0.1861
540.120	0.2733	0.2718	0.2695	0.2658	0.2590	0.2498	0.2437	0.2345	0.2232	0.2199	0.2086	0.2006	0.1954	0.1916	0.1865
540.164	0.2717	0.2700	0.2675	0.2639	0.2575	0.2481	0.2428	0.2350	0.2274	0.2214	0.2100	0.2016	0.1962	0.1922	0.1868
540.205	0.2715	0.2694	0.2667	0.2626	0.2555	0.2461	0.2411	0.2348	0.2282	0.2228	0.2118	0.2025	0.1972	0.1931	0.1875
540.366	0.2682	0.2662	0.2637	0.2596	0.2522	0.2440	0.2402	0.2359	0.2317	0.2278	0.2177	0.2075	0.2010	0.1964	0.1903
540.441	0.2662	0.2640	0.2611	0.2567	0.2492	0.2418	0.2388	0.2353	0.2317	0.2283	0.2194	0.2090	0.2024	0.1974	0.1910
540.464	0.2655	0.2632	0.2602	0.2557	0.2484	0.2413	0.2382	0.2349	0.2320	0.2288	0.2198	0.2098	0.2032	0.1982	0.1917
540.522	0.2646	0.2620	0.2592	0.2546	0.2474	0.2406	0.2379	0.2351	0.2322	0.2293	0.2213	0.2114	0.2047	0.1996	0.1930

potential per unit mass) at a given altitude and its value in a layer of critical density, $\Delta\mu = \mu(\rho, T) - \mu(\rho_{cr}, T) = -g(z - z_{cr})$ against the density ρ. At temperatures below critical, the value of the specific Gibbs potential of the medium with critical density was assumed equal to the value of this quantity in the layers located directly at the meniscus, and at temperatures above critical it was assumed to be equal to the value of the specific Gibbs potential in layers with maximum density gradient. The corresponding data are shown in Figs. 2a and 2b.

The behavior of the isothermal compressibility with changing temperature was investigated by comparing the experimental data on the gravitational effect[7,3] with power-law functions of the following type:

$$\left(\frac{\partial\mu}{\partial\rho}\right)^{-1} = \rho_{cr}^2 k_T = -\frac{1}{g}\frac{6n_{cr}}{r_{cr}(n_{cr}^2+2)^2}\frac{1}{Wf}\Delta a = \Gamma^+|\tau|^{-\gamma^+} \quad \text{(1a)}$$

(along the critical isochor) and

$$\left(\frac{\partial\mu}{\partial\rho}\right)^{-1} = \rho^2 k_T = -\frac{1}{g}\frac{6n}{r(n^2+2)^2}\frac{1}{Wf}\Delta a = \Gamma_1^-|\tau|^{-\gamma_1^-} \quad \text{(1b)}$$

(along the coexistence curve, in the liquid phase), where μ is the specific thermodynamic Gibbs potential (the chemical potential per unit mass), k_T is the isothermal compressibility, ρ_{cr}, r_{cr}, and n_{cr} are the density, specific refraction, and the refractive index at the critical point, ρ, r, and n are the density, specific refraction, and refractive index of the liquid phase on the coexistence curve, g is the acceleration due to gravity, W is the horizontal thickness of the investigated layer, f is the focal distance of the lens used in the Toepler optical system, Δa is the deviation of the beam in the focal plane, and $\tau = |(T - T_{cr})/T_{cr}|$.

To find the exponents γ^+ and γ_1^{-1}, we have analyzed the temperature dependences of the deviations $|\Delta a|$ due to layers with critical density at $T > T_{cr}$ or layers of matter at the meniscus on the liquid side at $T < T_{cr}$. At each specified temperature, the deviations of interest to us are maximal, and consequently, it is necessary to analyze the change of the maximum deviations on approaching the critical point with changing temperature[2]. The corresponding experimental data, in the form of plots of the reciprocals of the maximum deviation $|\Delta a|_{max}$ due to the liquid layers located immediately at the meniscus, at $T < T_{cr}$, and the reciprocals of $|\Delta a|_{max}$ for layers with critical density at $T < T_{cr}$, as functions of $\Delta T = T - T_{cr}$, are shown in Fig. 3. The obvious deviation from linearity is evidence that the classical theory of critical phenomena is in error.

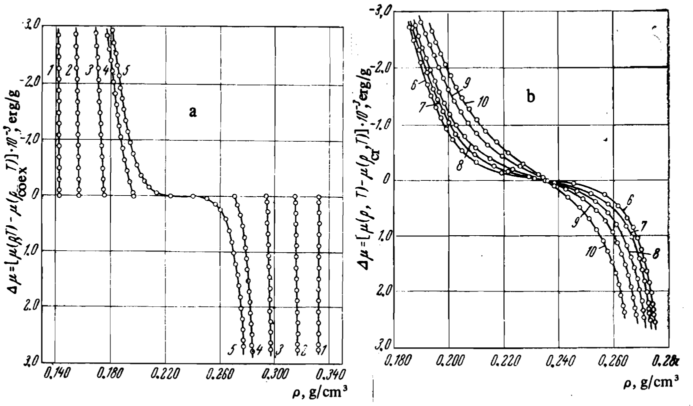

FIG. 2. (a) Chemical potential $\Delta\mu$ against the density of ρ for temperatures below critical ($\Delta T = T - T_{cr}$): 1 – ΔT = –4,873° K, 2 – ΔT = – 2.850° K, 3 – ΔT = – 1.287° K, 4 – ΔT = – 0.339° K, 5 – ΔT = – 0.006° K. The zero ordinate of each curve is chosen to be the location of the meniscus. (b). Chemical potential $\Delta\mu$ vs. the density ρ for temperatures above critical ($\Delta T = T - T_{cr}$): 6 – ΔT = 0.170° K, 7 – ΔT = 0.260° K, 8 – ΔT = 0.345° K, 9 – ΔT = 0.506° K, 10 – ΔT = 0.662° ¹ -The zero ordinate was chosen to be the location of the level with maximum density gradient.

To determine the quantities Γ and γ both above and below the critical temperature, the dependences of the maximal deviations $|\Delta a|_{max}$ on the relative change of temperature $\Delta(T - T_{cr})/T_{cr}$ were plotted in a log-log scale (Fig. 4) and reduced by a computer. For the points close to critical, Fig. 4 shows only the errors connected with the change of the temperature. For all the remaining points, neither the errors of the temperature measurement nor the errors of the measurement of the deviations Δa exceed the dimensions of the points. It is seen directly from Fig. 4 that both series of points fit satisfactorily straight lines with practically identical slopes. By determining the absolute weight of each experimental point and using least squares, we found with the aid of a computer that

$$\gamma^+ = 1.29 \pm 0.04, \; \Gamma^+ = (5.00 \pm 0.87)\cdot 10^{-9} \; \text{g}^2/\text{erg-cm}^3$$

$$\gamma_1^- = 1.29 \pm 0.06, \; \Gamma_1^- = (1.24 \pm 0.30)\cdot 10^{-9} \; \text{g}^2/\text{erg-cm}^3$$

The indicated errors correspond to double the rms deviations, and to 0.95 confidence probability. In view of the difficulty of measuring large beam deviations near the critical state, the experimental points separated from the critical temperature by only ΔT = –0.033, –0.016, and –0.006° K are subject to large errors along the axis of the deviations Δa. It is very difficult, however, to calculate the errors of the deviations Δa. We have therefore calculated γ_1^- also without taking into account the indicated three points. The value $\gamma_1^- = 1.30 \pm 0.06$ obtained in this manner agrees well with the value of the discussed critical exponent determined from all the experimental points. This agreement can be attribu-

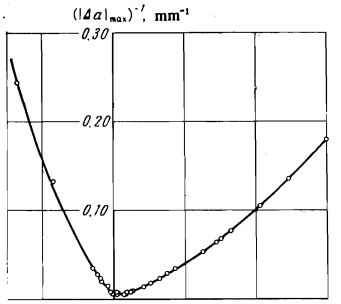

FIG. 3. Temperature dependence of the quantity $(|\Delta a|_{max})^{-1}$, which is proportional to the isothermal derivative of the thermal equation of state and in equal to $(\rho^2 k_T)^{-1}$.

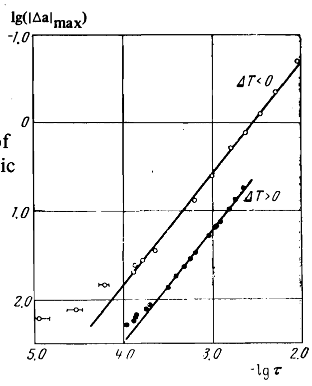

FIG. 4. Temperature dependence of $|\Delta a|_{max} \sim \rho^2 k_T$ in a doubly logarithmic scale.

ted to the small values of the absolute weight of the indicated points.

The exponents γ^+ and γ_1^- of the temperature dependence of the isothermal compressibility, determined in the present paper for heptane, coincide with the values of this exponent obtained earlier for benzene and pentane in our researches[2,3], and also with data obtained by many others for different substances[8]. The experimentally obtained numerical value of γ contradicts the classical theory and agrees satisfactorily with the conclusions of modern statistical theories. We note that according to our data the critical exponents γ^+ and γ_1^- coincide, and the ratio of the coefficients is $\Gamma^+/\Gamma^- = 4$, in accord with the published data on low-temperature substances (see the table in[10]).

In accordance with the equation of state proposed by Widom and Griffiths[10], the limiting law describing the shape of the critical isotherm should be

$$\begin{aligned}\Delta\mu &= \mu(\rho, T) - \mu(\rho_{cr}, T)\\ &= -g(z - z_{cr}) = D\,|\Delta\rho|^{\delta}.\end{aligned} \qquad (2)$$

To analyze the shape of the critical isotherm we can use data not only on the critical isotherm itself, but also resort to sections with isotherms satisfying the condition $|\Delta\rho|/|\tau|^{\beta} \gg 1$[11]. We have analyzed sections of certain isotherms for which $|\Delta\rho|/|\tau|^{\beta} \gg 4$. The corresponding sections of the experimentally obtained isotherms, plotted in coordinates log $|\Delta\mu|$ and log $|\Delta\rho|$, are shown in Fig. 5. It turns out that the points corresponding to densities above critical and corresponding to states of matter with densities below critical lie on different straight lines.

A computer reduction of the presented data with prior weighting of the experimental points and using least squares has made it possible to obtain two exponents γ^+ and γ^- for the critical-isotherm branches, corresponding to densities above and below the critical density

$$\rho > \rho_{cr}, \quad \delta^+ = 5.00 \pm 0.18,$$

$$\rho < \rho_{cr}, \quad \delta^- = 4.62 \pm 0.16,$$

where the errors correspond to double the rms deviations. These data point to a possible absence of complete antisymmetry of the critical isotherm when plotted in coordinates μ and ρ. Both values of δ greatly exceed the classical critical exponent of the isotherm. No difference between δ^+ and δ^- is implied in the Widom-Griffiths equation. The published experimental data on liquids with simple molecules result furthermore in lower values of both δ^+ and δ^-. An attempt to explain the dependence of the exponents of the critical isotherm on the structure of the molecule, on the basis of the drop model of a liquid, is contained in[12]. The same reference cites a calculated value $\delta = 5.206$ for n-heptane, which is close to the experimental $\delta = 5.00$ obtained by us.

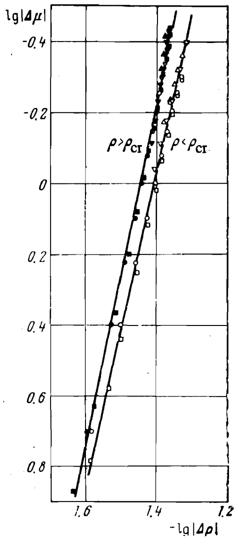

FIG. 5. Dependence of the reduced chemical potential $|\Delta\rho|$ in log-log scale for certain isotherms close to critical (■, □–$\Delta T = -0.006$°K; ●, ○–$\Delta T = 0.012$°K; ▼, ▽–$\Delta T = 0.058$°K; ▲, △–$\Delta T = 0.072$°K).

The difference between δ^+ and δ^- makes it difficult to obtain a generally acceptable check on the mutual agreement between the results on several critical exponents by analyzing the thermodynamic relations. Such a check is formally possible if the exponent of the critical isotherm is taken to be the average of δ^+ and δ^-, which turns out to be $\bar{\delta} = 4.81$. With this choice of the numerical value of $\bar{\delta}$, the isothermal compressibility calculated from the known formula, $\gamma = \beta(\delta - 1) = 0.358 \times (4.81 - 1) = 1.36$, is close to the experimentally obtained $\gamma^+ = \gamma^- = 1.29$. This circumstance indicates that the equations of states in which symmetry (and respectively antisymmetry) of the properties is assumed relative to the critical isochor when plotted in coordinates μ and ρ are more readily a fair but only first approximation to reality.

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